Regularities of Magnetocaloric Effect and Determination of Some Thermodynamic Parameters for (Octaethylporphynato)chloromanganese(III)

Victor V. Korolev, Marija E. Klyueva, Igorj M. Arefyev, Anna G. Ramazanova, Tatyana N. Lomova, and Anatolij G. Zakharov

Introduction

The high spin state of the central manganese atom in complexes with cyclic tetrapyrole ligands is reliably confirmed by measurements of the magnetic susceptibility for their solid samples or solutions. Effective magnetic moment ($\mu_{eff}$) value is equal $5.9 \pm 6.6 \mu_B$ for porphyrin complexes of manganese(II) and $4.8 \pm 5.0 \mu_B$ for the complexes of manganese(III) – the most stable form in the aromatic macrocyclic complexes.

Paramagnetic properties are used when studying and elaborating the building blocks of molecular magnets on the base of manganese porphyrins and their tetraazaanlogs – phthalocyanines. Complex macrocyclic core in these materials is a cation in the composition of a charge transfer complex or a free radical with unpaired electron on the base of manganeseporphyrins and their tetraazaanalogs – the most stable form in the aromatic macrocyclic complexes.

Experimental

The measurements of MCE and specific heat capacity of water suspension of the manganese complex were made with the use of automatic microcalorimeter with isothermal cover. The microcalorimeter cell with the isothermal cover was placed into the interpoles clearance of the electromagnet (60 mm) (Figure 1). It allowed measurements of MCE and specific heat capacity values in magnetic fields from 0 to 0.7 T at temperatures 283-315 K. Temperature changing was registered by the high accuracy voltmeter connected with a computer. Specially elaborated program allowed the online presentation of the temperature resistance in dependence of time and storage of the data to file for further analysis.

Heat capacity values were calculated according to equation (1):

$$C_p = \frac{Q_C}{\Delta T} - W,$$

where $Q_C$ – quantity of heat (in J) introduced into the calorimetric vessel by calibrated heater, $\Delta T$ – the change of the temperature in the calorimeter per joule of the introduced heat with account for heat exchange in initial and final periods; $W$ – the calorimeter constant.

Sensitivity of the apparatus was $2 \times 10^{-5} ^\circ C$, errors in the measurements of MCE and of the specific heat capacity were ± 0.1% and ± 1%, respectively.

(2,3,7,8,12,13,17,18-octaethylporphynato)chloro-manganese(III) (Cl)MnOEP was synthesized by Adler method and purified by chromatography on Al$_2$O$_3$. The measurements of MCE and of the specific heat capacity were ± 0.1% and ± 1%, respectively.

Magnetocaloric effect (MCE) and specific heat capacity of (2,3,7,8,12,13,17,18-octaethylporphynato)chloromanganese(III) (6% suspension in water) were measured by microcalorimetric method in the dependence of temperature (298-353 K) and magnetic field (0-0.7 T). It is found that the MCE has positive value which increases with growth of the magnetic field induction at all the temperatures and decreases with the temperature growth at all the magnetic fields. Breaking the magnetic field leads to adiabatic demagnetizing. The dependence of specific heat capacity of the studied system from the value of magnetic field induction has maximum at 0.2-0.3 T at all the temperatures. When the induction value is higher than 0.6 T the specific heat capacity value is less than that in zero field. The temperature growth leads to the increase of the specific heat capacity in all the magnetic fields. On the base of the experimental data on the magnetocaloric effect and specific heat capacity of the manganese complex the dependencies of enthalpy, of the magnetic components of molar heat capacity and entropy from the temperature and magnetic induction are calculated.
Results and Discussions

Previous systematic study of spectral characteristics of meso-tetraphenylporphyrin complexes of transition metals in connection with the structure and stability of the coordination spheres showed specificity of the manganese complexes in metalloporphyrin series \[11\]. Ratio of ionization potentials Mn$^{3+}$/Mn$^{2+}$ equal 33.69/15.64 provides stability of the isolated Mn$^{2+}$ cation. In complexes with tetrypyrrole macrocyclic ligands – porphyrins a formal charge of manganese cation may be equal +2, +3, +4 or +5. Reaction of manganese(II) salts with porphyrins (H$_2$P) in solution leads to formation of highly stable acidoporphyrin complexes of manganese(III). For example, redox potential of Mn$^{III}$TPP/Mn$^{II}$TPP (TPP – meso-tetraphenylporphyrin dianion) pair is equal –0.22 V \[12\]. Stabilization of manganese oxidation state +3 is achieved due to action of the cyclic π-system of the organic ligand increasing the thermodynamic stability of the coordination bonds and the kinetic effects of the central metal screening as well.

As it is established by physical-chemical methods an absolute majority of manganese porphyrins are high spin compounds. This fully applies to manganese(III) complexes with 3$d^4$ electron configuration. Presence in Mn$^{III}$ of half-filled $d_z^2$ and antibonding low energy $d_{x^2-y^2}$ orbitals promotes formation of π-bonds in the molecule in stationary and exited states along with coordination σ-bonds. Specificity of the electronic structure of manganese porphyrins is reflected in particular in revealing the magnetocaloric effect of (Cl)MnOEP suspension in water.

Magnetocaloric effect takes place when magnetic field is applied to a substance having magnetic properties (magnetics, paramagnetic salts, rare-earth elements alloys). As a result of the action the heat is developed or absorbed due to the changing of the substance magnetic state and therefore its inner energy. In conditions of adiabatic heat isolation the temperature increase or decrease can be registered.

Heat capacity measurements are very important in the study of molecular magnetics, since the analysis of the temperature dependencies of the heat capacity in magnetic fields provides useful information about magnetic regulation of magneto active substances. It should be noted that MCE and heat capacity of macroheterocyclic complexes in magnetic fields were not studied earlier.

Figures 2-5 show experimental results of study of MCE and heat capacity of the 6% water suspension of the manganese complex. The observed MCE values are positive. They increase non-linearly with growth of the magnetic field induction and decrease with growth of the temperature in the studied ranges of magnetic induction and temperature (Figure 2, 3). The slopes of polytherms rise when the field increases.
Figure 4. Specific heat capacity of (Cl)MnOEP particles as a function of applied magnetic field. $T$, K: 1 – 298, 2 – 313, 3 – 328, 4 – 343.

Figure 5. Specific heat of (Cl)MnOEP particles as a function of temperature in various applied magnetic fields. $B$, T: 1 – 0, 2 – 0.15, 3 – 0.32, 4 – 0.65.

induction are of the extreme character and have maxima at 0.25 T. Heat capacity values at induction higher than 0.5-0.6 T become less than in zero field. Tendency of the heat capacity values to decrease in the fields higher than 0.5 T evidences about changing of the complex magnetic structure. The presence of the heat capacity maximum is connected with magnetic structure of the particles. Earlier we have observed similar maxima for high disperse particles with ferrimagnetic and ferromagnetic structures. It is difficult to give an interpretation of the maximum at the present stage of the study.

Specific heat capacity increases with the temperature growth at all values of the magnetic field (Figure 5).

With the use of the calorimetric equipment described above change of the enthalpy for the manganese complex particles in water suspension at applied magnetic field was determined by comparison of the temperature dependence of MCE and heat of the calibrated heater; heat exchange error in the calorimetric experiment was taken into account. Dependencies of the enthalpy from magnetic induction and temperature are analogous to MCE dependencies and are not shown here.

Figure 6. Changes of the magnetic part of the molar heat capacity for (Cl)MnOEP particles as a function of applied magnetic field. $T$, K: 1 – 298, 2 – 313, 3 – 328, 4 – 343.

Figure 7. Changes of the magnetic part of the molar heat capacity for (Cl)MnOEP particles as a function of temperature in various applied magnetic fields. $B$, T: 1 – 0.15, 2 – 0.32, 3 – 0.65.

Only heat capacity of magnetic phase of water suspension, i.e. the manganese complex particle, undergoes changes at applied magnetic field. By subtraction of the heat capacity value in zero field from the value of specific heat capacity in current field the change of magnetic part of specific or molar heat capacity, in respect to 1 mole of the complex at constant induction and temperature, i.e. $\Delta C_{m}(H,T)$, may be obtained. Induction and temperature dependencies of $\Delta C_{m}(H,T)$ are shown in Figures 6 and 7. Their values are necessary for calculation of the dependencies of the magnetic part of entropy $\Delta S_{m}(H,T)$ at applied magnetic field. The $\Delta S_{m}(H,T)$ values were found according to thermodynamic equation (2): \[ \Delta S_{m}(H,T) = \Delta T \Delta C_{m}(H,T) / T, \] where $\Delta T$ – magnetocaloric effect.

Dependencies of the obtained $\Delta S_{m}(H,T)$ values from the applied magnetic field and temperature are shown in Figures 8 and 9.

Isotherms of the $\Delta S_{m}(H,T)$ dependence from magnetic field induction have an extreme character with the maxima
at induction equal 0.3±0.4 T (Figure 8). The maximum height decreases when the temperature increase. The ∆S_m(H,T) values decrease with the temperature growth and become negative when induction is equal 0.65 T (Figure 9).

Figure 8. Changes of the magnetic part of molar entropy for (Cl)MnOEP particles as a function of applied magnetic field. T, K: 1 – 298, 2 – 313, 3 – 328, 4 – 343.

Figure 9. Changes of the magnetic part of the molar heat entropy for (Cl)MnOEP particles as a function of temperature in various applied magnetic fields. B, T: 1 – 0.15, 2 – 0.32, 3 – 0.65.

Conclusions

It is found that (2,3,7,8,12,13,17,18-octaethyl-porphynato)chloromanganese(III) in aqua suspension reveals noticeable magnitocaloric effect which decreases with temperature increase.

For the first time specific heat capacity of solid particles of manganese porphyrin complex in magnetic field and its dependence from magnetic stream density are determined. Dependence of specific heat from applied magnetic field shows a maximum in medium fields.

Change of the magnetic part of the molar entropy for the manganese complex particles ∆S_m(H,T) as a function of applied magnetic field has maximum at 0.3±0.4 T, the maximum height decreasing with temperature increase.

Thus, the method used allowed to obtain the thermodynamic characteristics of macroheterocyclic complex for the first time. For the further developing magnetochemistry of macroheterocyclic complexes it is necessary to study a series of the compounds having related structure.

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References


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Effect of pH on Formation of Metalloporphyrins

Vladimir B. Sheinin, a,b Olga R. Simonova, a and Ekaterina L. Ratkova b

 aInstitute of Solution Chemistry of Russian Academy of Science, Ivanovo, 153045, Russia.
 bIvanovo State University of Chemistry and Technology, Ivanovo, 153000, Russia.
 Corresponding author E-mail: vbs@isc-ras.ru

Although complexation reactions of porphyrins with metal salts in organic solvents have a long research history, the influence of pH on these processes was not studied. The main reason is complications connected with the pH measurements in nonaqueous solutions. To solve this problem the special instrumentation was created for application of the spectropotentiometric method (spectroscopy + pH-metry with glass electrode) in nonaqueous solutions. Using this method it became possible to investigate complexation reactions at different pH values using electronic absorption spectroscopy. The pH control of reaction systems allows us to explain the peculiarities of metalloporphyrins formation without invoking the Fleischer’s idea of SAT-complexes.

Introduction

Substituted derivatives of 21H,23H-porphine (H2P) are named porphyrins (H3L). Due to the presence in the coordination cavity of the porphyrin macrocycle of two types of activity centers (acidic imino-groups and basic aza-atoms) porphyrins are amphoteric and can produce in the protolytic reactions four types of ionic species L 2–, HL –, H2L + and H3L2+ according to Equilibria (1)-(4) which are correct for polar solvents (S):

\[
H_3L \rightleftharpoons K_{a1} HL^- + H^+ \quad (1)
\]
\[
HL^- \rightleftharpoons K_{a2} L^{2-} + H^+ \quad (2)
\]
\[
H_3L + H^+ \rightleftharpoons K_{b1} H_2L^+ \quad (3)
\]
\[
H_2L^+ + H^+ \rightleftharpoons K_{b1} H_2L^{2+} \quad (4)
\]

Due to the double positive charge and presence of four endocyclic NH-groups which are hydrogen bonds donors, the dication H2L2+ in contrast to H3L and H2L + exhibits properties of the anion-molecular receptor. In solutions H2L2+ exists only in the form of supramolecular homogeneous and heterogeneous complexes with solvent molecules and background anions - H2L2+S2, H2L2+S(X) + and H2L2+(X)2.

Equilibria (1)-(4) cover a wide pH range. Deuteroporphyrin IX dimethyl ester (H2DP) is the only porphyrin for which both acid and base ionization constants have been reliably determined in one solvent (DMSO). The difference between \( K_{a1} \) and \( K_{b1} \) exceeds 24 orders of magnitude. Constants of the Equilibria (1)-(4) for H2DP and some other porphyrins are presented in Table 1.

Substitution of two endocyclic hydrogen atoms in porphyrins by a metal cation leads to metalloporphyrins. In these complexes, e.g. M2P, porphyrins can be considered as dianionic tetradeinate ligands. The reactivity of the ionic forms of porphyrins in complexation with metal cations decreases in the order \( L^{2-} > HL^- > H_2L > H_2L^+ > H_2L2+ > H_2L2+S(Hal^-) > H_2L2+(Hal^-) \). Therefore acid-base properties of porphyrins and pH of the medium should have a strong influence on the mechanism of metalloporphyrin formation.

Complexes of Cd2+ with “acidic” porphyrizine, H2PA, and its derivatives are formed in System (5) as a result of interaction between the metal ion and the most reactive form of ligand (L2–) according to Equilibrium (6):

\[
\text{Cd(Ac)$_2$} + \text{H}_2\text{L} + \text{HClO}_4 + \text{DMSO} \quad (5)
\]
\[
L^{2-} + \text{Cd}^{2+} \rightleftharpoons K_{st} \quad (6)
\]
\[
\text{H}_2\text{DP (R= H)}
\]
\[
\text{H}_2\text{MP (R= C}_2\text{H}_4)
\]
\[
\text{H}_2\text{PP (R= CH=CH$_2$)}
\]
\[
\text{H}_3\text{PA}
\]
Table 1. Constants of Equilibria (1)-(4) measured by spectropotentiometric method at 298 K.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>ε</th>
<th>DN</th>
<th>$K_1$</th>
<th>$H_2PA$</th>
<th>$H_2P$</th>
<th>$H_2DP$</th>
<th>$H_2MP$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethyl-sulfoxide</td>
<td>46.68</td>
<td>29.8</td>
<td>$pK_{a1}$</td>
<td>11.94 ± 0.04</td>
<td>22.35 ± 0.02</td>
<td>25.30</td>
<td></td>
</tr>
<tr>
<td>(DMSO)</td>
<td></td>
<td></td>
<td>$pK_{a2}$</td>
<td>13.45 ± 0.08</td>
<td>0.87 ± 0.03</td>
<td>1.48 ± 0.03</td>
<td>2.15 ± 0.03</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>36.02</td>
<td>14.1</td>
<td>$lgK_{a1}$</td>
<td>6.38 ± 0.03</td>
<td>8.71 ± 0.03</td>
<td>11.95 ± 0.05</td>
<td></td>
</tr>
<tr>
<td>(AN)</td>
<td></td>
<td></td>
<td>$lgK_{a2}$</td>
<td>6.20 ± 0.15</td>
<td>5.80 ± 0.03</td>
<td>7.51 ± 0.05</td>
<td></td>
</tr>
</tbody>
</table>

The $H_2PA$ molecules are ionized partly even in pure DMSO ($pH \approx 10$) – the quota of $[H^+PA^+]$ and $[PA^2+]$ is 1.14 and $4 \times 10^{-4}$ %, respectively. As a result Equilibrium (6) is completely displaced to the right side and the complexes of porphyrines are formed instantaneously upon mixing of reagents. Equilibrium (6) can be observed only in acidified solutions of DMSO when only $H_2L$ and CDL are seen in the electronic absorption spectra of System (5) and Equilibrium (7) can be studied. The stability constant $K_{11}$ can be derived from Equation (8).

\[
H_2L + Cd^{2+} \rightleftharpoons Ke \rightarrow CdL + 2H^+ \tag{7}
\]

\[
Ke = K_{a1}K_{a2}K_{a1} \tag{8}
\]

Figure 1 shows equilibrium composition for System (5) at 298 K.

Figure 1 shows equilibrium composition for System (5) in the case of $H_2PA$. In the point of half-conversion the equilibrium concentration of $[PA^2+]$ is only $6.38 \times 10^{-25}$ M and its quota is $6.38 \times 10^{-18}$ %. Nevertheless, Equilibrium (7) in System (5) is achieved very quickly and has the rates comparable with that usual for protolytic processes. The constants of true and formal kinetic Equations (9) and (10) describing formation of CDL are connected by Equation (11).

\[
V = k [M^{2+}[L^2-] \tag{9}
\]

\[
V = k' [M^{2+}][H_2L] \tag{10}
\]

\[
k' = kK_{a1}K_{a2}[H^+]^2 \tag{11}
\]

Common porphyrins ($H_2P$ and its derivatives obtained by substitution of exocyclic hydrogen atoms), have much weaker acidic properties than porphyrines - the difference in the $K_{a1}$ values is more than 11 orders of magnitude. In this case the neutral form $H_2L$ was postulated as the reactive particle in the complex formation. In neutral DMSO at overall concentration of $H_2L$ $1 \times 10^{-5}$ M the equilibrium concentration of $[L^{2-}]$ is not exceeded $10^{-23}$ M. In addition, the mechanisms and conditions of formation and dissociation of common porphyrins complexes are different. Because of that compexation reaction of common porphyrins (12) proceeds slowly and irreversibly:

\[
H_2L + M^{2+} \rightarrow Ke \rightarrow ML + 2H^+ \tag{12}
\]

It is assumed that positively charged protonated forms of common porphyrins $H_2L^+$ and $H_2L^{2+}$ can not be coordinated by metal cations. It should be noted that information about structure and reactivity of solvato-complexes of metal ions in nonaqueous solutions at different acidity is absent.

Though Reaction (12) is pH-dependent, the influence of the solution acidity on the complexation kinetics of porphyrins has never been previously studied. The main reason is complication of pH measurements in nonaqueous solutions. To solve this problem we have elaborated the equipment for spectropotentiometric titration (spectroscopy + pH-metre with glass electrode) in nonaqueous solutions. This enables the investigation of the pH influence on complexation equilibrium using electronic absorption spectroscopy. Results of the spectropotentiometric investigation of the influence of solution acidity on Reaction (12) between the neutral form of porphyrins and metal ions in Systems (13) and (14) are reported in this paper.

\[
H_2MP – Cu(NO_3)_{2} \cdot 3H_2O – DMSO \tag{13}
\]

\[
H_2MP – Cu(NO_3)_{2} \cdot 3H_2O – HClO_4 – DMSO \tag{14}
\]

Experimental

Reagents

Mesoporphyrin IX dimethyl ether ($H_2MP$) was prepared according to the known method and purified by column chromatography on alumina (II degree of activity by Brockmann, eluent – chloroform). Purity of the product was controlled by electronic absorption spectra.

Chemically pure DMSO was kept over NaOH for 24 hours and distilled in vacuum (2-3 mmHg). Residual amount of water was 0.2267%. Chemically pure HClO$_4$·3H$_2$O was used without additional purification. Analytically pure Cu(NO$_3$)$_2$·3H$_2$O was prepared as described elsewhere. Pure Et$_4$NCl was recrystallized twice from dry acetonitrile and dried during 24 hours under vacuum (0.01 mmHg) at room temperature. Et$_4$NClO$_4$...
Effect of pH on Formation of Metalloporphyrins

was prepared by precipitation as result of mixing chemically pure HClO₄·3H₂O with purified Et₄NCl. After that it was recrystallized from glacial distilled water and dried 24 hours under vacuum (0.01 mmHg) at room temperature.

**Measurements**

Measurements were pursued with the specially designed spectrophotometric cell (Figure 2).

![Figure 2. Spectrophotometric cell (1 - rabble; 2 - mercury thermometer; 3 - microsyringe with titrant; 4 - gas feed capillary; 5 - thermostat; 6 - optical cell; 7 - work solution; 8 - reference electrode; 9 - glass electrode; 10 - electrolytic bridge)](image)

Electronic absorption spectra were measured with spectrophotometer Agilent 8453. Potentiometric measurements (accuracy 1 mV) were carried out with Element (15), using p

meter OP 211, glass electrode EGL-43-07 (GE) and silver chloride electrode; 9 - glass electrode; 10 - electrolytic bridge)

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Electronic absorption spectra were measured with spectrophotometer Agilent 8453. Potentiometric measurements (accuracy 1 mV) were carried out with Element (15), using pH-meter OP 211, glass electrode EGL-43-07 (GE) and silver chloride reference electrode filled with Et₄NCl in DMSO.

![Figure 2. Spectrophotometric cell (1 - rabbles; 2 - mercury thermometer; 3 - microsyringe with titrant; 4 - gas feed capillary; 5 - thermostat; 6 - optical cell; 7 - work solution; 8 - reference electrode; 9 - glass electrode; 10 - electrolytic bridge)](image)

$\text{AgCl} \quad \text{saturated solution of Et}_4\text{NCl in DMSO} \quad 0.01 \text{ M solution Et}_4\text{NClO}_4 \quad \text{System (13) or (14) GE} \quad \text{Ag}$

To separate the investigated solution from chloride ions the reference electrode was supplied by the electrolytic bridge filled with 0.01 M solution of Et₄NCl in DMSO. The glass electrode was kept in water. It was washed with DMSO and drained with filter paper before each measurement. The temperature of the solution was maintained with accuracy $\pm 0.1^\circ\text{C}$ using liquid thermostat.

**Graduation of the Element for pH Measurements in DMSO.**

Graduation of the glass electrode was carried out with buffer solutions in DMSO (Table 2.).

**Table 2.** The pH values of buffer solutions in DMSO in the temperature range 298 – 318 K

<table>
<thead>
<tr>
<th>$\text{Composition (1:1)}$</th>
<th>$C, \text{ M}$</th>
<th>$\text{pH}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>picric acid + it’s lithium salt</td>
<td>0.05</td>
<td>1.10 – 0.005($T$ – 298)</td>
</tr>
<tr>
<td>salicylic acid + it’s sodium salt</td>
<td>0.05</td>
<td>6.05 – 0.010($T$ – 298)</td>
</tr>
<tr>
<td>2- nitrobenzoic acid + it’s sodium salt</td>
<td>0.05</td>
<td>7.16 – 0.001($T$ – 298)</td>
</tr>
<tr>
<td>benzoic acid + it’s sodium salt</td>
<td>0.05</td>
<td>9.60 – 0.003($T$ – 298)</td>
</tr>
</tbody>
</table>

**Kinetic Experiment**

Reaction (12) was investigated in systems I, II, III, IV, V and VI (Table 3). To 75 ml of the pH-neutral or acidified H₂MP solution 3 ml of the concentrated solution of Cu(NO₃)₂·3H₂O was added and following changes of pH and electronic absorption spectra were registered.

**Calculations**

Values of [CuMP] and [H₂MP] were calculated using Equations (16)-(18).

$C_{\text{HMP}} = [\text{CuMP}] + [\text{H₂MP}] + [\text{H₂MP}^+] + [\text{H₂MP}^{2+} (\text{DMSO})_2] \quad (16)$

$A_T = \frac{C_{\text{HMP}} - [\text{CuMP}]}{1 + K_{b1}a_{\text{H}^+} + K_{b2}a_{\text{H}^+}^2 \times \left[ e_{\text{CuMP}} + K_{b1}a_{\text{H}^+} e_{\text{H₂MP}}^+ + K_{b2}a_{\text{H}^+}^2 e_{\text{H₂MP}}^{2+} \right]} \quad (17)$

$[\text{H₂MP}] = \frac{C_{\text{H₂MP}} - [\text{CuMP}]}{1 + K_{b1}a_{\text{H}^+} + K_{b2}a_{\text{H}^+}^2} \quad (18)$

where $C_{\text{HMP}}$ - general concentration of porphyrin, M; $A_T$ - current value of optical density; $e_i$ - molar absorption coefficient at analytical wave-length; $a_{\text{H}^+} = 10^{-pH}$; $K_{b1}$ and $K_{b2}$ - constants of Reactions (3) and (4); $l$ - thickness of absorbent layer, cm.

**Table 3. Initial conditions of kinetic experiments for reaction systems I-VI at 318K.**

<table>
<thead>
<tr>
<th>System</th>
<th>(13)</th>
<th>(14)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH₀</td>
<td>9.99</td>
<td>9.99</td>
</tr>
<tr>
<td>$C_{\text{HMP}}$</td>
<td>$3.38 \times 10^{-5}$</td>
<td>$2.78 \times 10^{-5}$</td>
</tr>
<tr>
<td>$C_{\text{Cu(NO}_3)_2 \cdot 3\text{H}_2\text{O}}$</td>
<td>$2.90 \times 10^{-2}$</td>
<td>$1.45 \times 10^{-2}$</td>
</tr>
</tbody>
</table>

* - analytical concentration in M at 298K
Results and Discussions

Solvolysis of Cu(NO₃)₂·3H₂O in DMSO

Addition of Cu(NO₃)₂·3H₂O in pH-neutral DMSO leads to drastic decrease of pH (Figure 3).

Figure 3. Changes of pH in systems I-VI at 318 K.

Figure 4 shows the pH dependence from concentrations of Cu(NO₃)₂·3H₂O and HClO₄ which was used to determine acidity of Cu(NO₃)₂·3H₂O in DMSO. Both dependencies belong to one straight line which obeys Equation (19) with the correlation factor 0.9997.

\[ p\text{H} = -1.241 \cdot \log C + 2.91; \quad N=56 \] (19)

Under such experimental conditions the Cu(NO₃)₂·3H₂O is strong one-basic acid. The complex Cu²⁺(OH)₃(DMSO)₃ is a product of the salt solvolysis.[24] Moreover, in the case of non-hydrated copper(II) salt the complex Cu²⁺(OH)(DMSO)₅ might be a product of interactions with residual water.

Protonation of H₂MP in DMSO

Protonation of H₂MP according to Equilibria (3) and (4) was investigated in System (20) at 298-318 K.[8]

\[ \text{H}_2\text{MP} - \text{HClO}_4 - \text{DMSO} \quad \text{(20)} \]

As it has been shown, the porphyrinum dication H₄MP²⁺(DMSO)₂ exhibits properties of the anion molecular receptors.[1-3] In the system (20) the equilibrium (21) is completely displaced to the right side while formation of complexes with H₂O, ClO₄⁻ and NO₃⁻ are suppressed with excess of solvent.

\[ \text{H}_4\text{MP}^{2+} + 2\text{DMSO} \rightleftharpoons \text{H}_2\text{MP}^{2+}(\text{DMSO})_2 \] (21)

It has been shown[6] that increase of stability of the porphyrin solvatocomplex leads to levelling of \( K_{b1} \) and \( K_{b2} \) values. The value of \( \log(\text{H}_2\text{MP}/\text{H}_4\text{MP}) \) is equal to 0.83 for H₂MP in DMSO and to 4.44 in acetonitrile under the same conditions (at 298 K). Generally, both Equilibria (3) and (4) are overlapped at \( \log(\text{H}_2\text{MP}/\text{H}_4\text{MP}) < 4 \).[25] The constants of acid dissociation of H₂MP in DMSO are unknown. Value of \( p\text{K}_a1 \) for H₂MP in DMSO should be higher than that for H₂DP (\( p\text{K}_a1=25.30 \) in DMSO at 298 K[9,10]) in which two ethyl radicals are absent. Equilibrium structure of the System (17) was calculated using Equations (22)-(25) at the \( p\text{H} \) range from 2.5 to 4.0 (Figure 5) ignoring the equilibrium concentrations of HMP⁻ and MP²⁻.

Figure 5. Dependences of equilibrium concentrations from \( p\text{H} \) in System (20)

\[ C_{\text{H}_2\text{MP}} = [\text{H}_2\text{MP}] + [\text{H}_3\text{MP}^+] + [\text{H}_4\text{MP}^{2+}(\text{DMSO})_2] \] (22)

\[ [\text{H}_2\text{MP}] = \frac{100\%}{1 + K_{b1} \cdot a_{H^+} + K_{b1} \cdot K_{b2} \cdot a_{H^+}^2} \] (23)

\[ [\text{H}_3\text{MP}^+] = K_{b1} \cdot a_{H^+} \cdot [\text{H}_2\text{MP}] \] (24)

\[ [\text{H}_4\text{MP}^{2+}(\text{DMSO})_2] = K_{b1} \cdot K_{b2} \cdot a_{H^+}^2 \cdot [\text{H}_2\text{MP}] \] (25)

In Figure 5 it is possible to allocate areas corresponding individual step of Equilibria (3) at \( p\text{H} > 1.7 \) and Equilibria (4) at \( p\text{H} < 1.5 \), while at 1.7 > \( p\text{H} > 1.5 \) both Equilibria (3) and (4) are overlapped. In the electronic
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absorption spectra (Figure 6) the equilibria between pairs of light-absorbing species $H_2MP$, $H_3MP^+$ and $H_4MP^{3+}$; $H_4MP^{3+}(\text{DMSO}_2)$ correspond to individual series of isosbestic points at 462; 512; 612 and 537; 558; 609 nm, respectively. The isobestic points are not observed in the area of the triple equilibrium between $H_2MP$, $H_3MP^+$ and $H_4MP^{3+}(\text{DMSO}_2)$.

![Figure 6. Changes of electronic absorption spectra in System (20) in the pH range from -2.5 to 4.0 at 318 K; (→) $H_2MP$; (←) $H_4MP^{3+}(\text{DMSO}_2)$.

Kinetics of Complex Formation in Reaction Systems I - VI

Solvolysis of $\text{Cu(NO}_3\text{)}_2\cdot3\text{H}_2\text{O}$ in DMSO leads to acidification of solution (26):

$$\text{Cu(NO}_3\text{)}_2\cdot3\text{H}_2\text{O} + 3\text{DMSO} \rightarrow$$

$$\text{Cu}^{2+} (\text{OH}^-) (\text{DMSO})_3 + 2\text{H}_2\text{O} + 2\text{NO}_3^- + \text{H}^+ \quad (26)$$

Parameters of the investigated kinetic systems with allowance made for solvolysis are presented in Table 4.

Self acidification observed in systems I - III does not lead to protonation of $H_2MP$, which occurs only at lower values of pH. Therefore the porphyrin exists only in the molecular form and all changes of the electronic absorption spectra are caused only by changes of concentrations of $H_2MP$ and CuMP (Figure 7). One series of isobestic points at 510 and 576 nm is in agreement with them. In these isobestic points Equation (27) is fulfilled.

$$A = \varepsilon_i \cdot ([H_2MP] + [\text{CuMP}]) \quad (27)$$

![Figure 7. Changes of electronic absorption spectra in Systems I - IV (Table 4): (→) $H_2MP$ at pH 9.99; (←) CuMP at pH 4.00 - 2.71.

The presence of the isobestic points indicates the absence of other light-absorbing forms of porphyrin, such as sitting-atop (SAT) complexes. The formation of CuMP was studied at the constant concentration of $H_2MP$ and various excesses of $\text{Cu(NO}_3\text{)}_2\cdot3\text{H}_2\text{O}$ in systems I - IV. The reaction obeys the linear kinetic Equation (28) and is characterized by the pseudo-first order rate law in $H_2MP$.

$$\ln ([H_2MP]_0/[H_2MP]) = k_{ef} \cdot \tau \quad (28)$$

The parameters of the kinetic dependence (28) are presented in Table 4 and Figure 8.

![Figure 8. Kinetic dependences of Reaction (12) in systems I - VI.

Table 4. Parameters of reaction systems I - VI with regard to solvolysis of $\text{Cu(NO}_3\text{)}_2\cdot3\text{H}_2\text{O}$ and protonation of $H_2MP$

<table>
<thead>
<tr>
<th>System</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
<th>VI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Range of pH</td>
<td>9.99 - 3.87</td>
<td>9.99 - 3.87</td>
<td>9.99 - 4.00</td>
<td>3.01 - 2.71</td>
<td>1.31 - 1.23</td>
<td>0.61 - 0.60</td>
</tr>
<tr>
<td>$[H_2MP]_0$</td>
<td>3.38 - 10^{-5}</td>
<td>2.78 - 10^{-5}</td>
<td>2.98 - 10^{-5}</td>
<td>2.89 - 10^{-5}</td>
<td>1.93 - 10^{-5}</td>
<td>0.69 - 10^{-5}</td>
</tr>
<tr>
<td>( % of $H_2MP$ )</td>
<td>(100)</td>
<td>(100)</td>
<td>(100)</td>
<td>(98.91)</td>
<td>(64.01)</td>
<td>(22.75)</td>
</tr>
<tr>
<td>$C_{\text{Cu}(\text{DMSO})_3(\text{OH})}$</td>
<td>2.90 - 10^{-2}</td>
<td>1.45 - 10^{-2}</td>
<td>2.90 - 10^{-3}</td>
<td>2.98 - 10^{-3}</td>
<td>2.98 - 10^{-3}</td>
<td>2.98 - 10^{-3}</td>
</tr>
<tr>
<td>$R$ (Figure 5)</td>
<td>0.999</td>
<td>0.999</td>
<td>0.999</td>
<td>0.999</td>
<td>0.999</td>
<td>0.997</td>
</tr>
<tr>
<td>lg $k_{ef}$ (318 K)</td>
<td>-3.12</td>
<td>-3.36</td>
<td>-3.86</td>
<td>-3.86</td>
<td>-4.01</td>
<td>-4.17</td>
</tr>
<tr>
<td>lg $k_c$ (318 K)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.95 ± 0.04</td>
<td></td>
</tr>
</tbody>
</table>

*equilibrium concentration, M (at 298 K).
The system IV was investigated at initial pH = 3 (beginning of protonation of H₂MP) when total equilibrium content of H₂MP⁺ and H₂MP²⁺(DMSO)₂ is 1% and the results of kinetic measurements can not be influenced. This value of pH was only one unit less than that at the end of Cu(NO₃)₂·3H₂O solvolysis. The acidification sharply narrows the interval of pH change to 0.3 units (Figure 5). As has been shown above the salt Cu²⁺H₂O(DMSO)₃ is a strong one-basic acid in DMSO. This conclusion was proved by full coincidence of kinetic dependences for systems III and IV.

Spectral changes in the system VI are shown in Figure 9. The equilibrium mixtures of H₂MP, H₂MP⁺ and H₂MP²⁺(DMSO)₂ (Figure 5) were investigated under initial conditions (Table 4). The pH changes in systems V and VI are very small.

![Figure 9](image)

Figure 9. Changes of electronic absorption spectra of system VI (Table 4). (→) H₂MP at pH 9.95; (→→) initial equilibrium mixture H₃MP, H₂MP⁺, H₂MP²⁺(DMSO)₂ at pH 0.61; (→→→) CuMP at pH 0.60.

At the constant value of pH the ratio of components in the equilibrium mixture H₂MP, H₂MP⁺ and H₂MP²⁺(DMSO)₂ is constant (Figure 5). The electronic absorption spectra of such mixtures can be similar to that of individual substances. The formation of CuMP is characterized by the same isobestic points at 510 and 576 nm (Figure 9) in systems I – VI. The only reactive form of the ligand is H₂MP. In systems I – III the formation of CuMP was studied at various excesses of salt and constant H₂MP concentration. In systems IV, V and VI it was studied at constant concentration of Cu(NO₃)₂·3H₂O taken in excess and various concentrations of the porphyrin ligand.

In all these systems the reaction obeys linear kinetic Equation (28) and it is characterized by pseudo-first order rate law in H₂MP. The dependences of effective constant of Reaction (29) from the concentration of the salt Cu(NO₃)₂·3H₂O (in Systems I-IV) and on the concentration of H₂MP (in Systems IV-VI) were obtained. In the case of the first order in salt, effective kₑ and true kₑ constants can be connected by linear Equation (30). It was experimentally confirmed that this equation is correct for all investigated Systems I-VI.

\[
\text{Cu}^{2+}(\text{OH}^+)(\text{DMSO})₃ + \text{H}_₂\text{MP} \rightarrow \text{CuMP} + \text{H}_₂\text{O} + \text{H}^+ + 5\text{DMSO} \quad (29)
\]

\[
kₑ = kₑ \times [\text{H}_₂\text{MP}][\text{Cu}^{2+}(\text{OH})(\text{DMSO})₃] \quad (30)
\]

The experimental dependence of kₑ from [H₂MP][Cu²⁺(OH)(DMSO)₃] (Equation (31)) have the correlation coefficient R = 0.9998 (Figure 10).

\[
kₑ = (884.66 \pm 9.47)[\text{H}_₂\text{MP}][\text{Cu}^{2+}(\text{OH})(\text{DMSO})₃] \quad (31)
\]

The value of kₑ in Equation (30) is equal 884.66 ± 9.47 at 318 K (lg kₑ = 2.95±0.04).

Fleischer’s SAT-complex

The porphyrinium dications H₄L²⁺ have properties of pH-dependent anion-molecular receptors. They are formed due to sequential protonation coordination cavity of porphyrin macrocycle by two proton. The second proton activates porphyrin receptor H₄L²⁺ and starts up self-assembling of anion-molecular complexes H₄L²⁺S₂, H₄L²⁺SB and H₄L²⁺B₂ (B – molecular or anion substrate). The composition and stability of these complexes are determined by each reaction system.

\[
\text{H}_₄\text{L}^{2+}S₂ + B \xrightleftharpoons[K_d1]{K_d2}\text{H}_₄\text{L}^{2+}\text{SB} + S \quad (32)
\]

\[
\text{H}_₄\text{L}^{2+}\text{SB} + B \xrightarrow[K_d2]{K_d1}\text{H}_₄\text{L}^{2+}\text{B}_₂ + S \quad (33)
\]

Generally, values of K_d1, K_d2, K_d3, K_d4 exhibit antibatic dependencies from basicity (DN) and polarity (ε) of solvents In highly basic and polar DMSO (reaction System (14)) the dication H₄MP²⁺ exists as molecular complex H₄MP²⁺(DMSO)₂. Because of small values of K_d1 and K_d2 (Table 1), large excess of acid is necessary for formation of H₄MP²⁺ in DMSO. The values of K_d3 and K_d4 are increased by ten and seven of orders magnitude in going from DMSO to moderately basic and polar acetonitrile (AN). The dication H₄MP²⁺ is characterized by high selectivity to halide-ions. As it can be seen (Table 5), the complexes H₄MP²⁺(AN)(Hal⁻) and H₄MP²⁺(Cl⁻) are very stable. Due to the formation of H₄MP²⁺(Cl⁻) in acetonitrile the energy of stabilization of H₄MP²⁺ achieves 54.4 kJ/mol.
Effect of pH on Formation of Metalloporphyrins

<table>
<thead>
<tr>
<th>lgK</th>
<th>Substrate (B)</th>
<th>H_2MP – HClO_4 – B – acetonitrile at 298 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>ClO_4</td>
<td>H_2O</td>
<td>I^-</td>
</tr>
<tr>
<td>lgK_{a1}</td>
<td>&lt;&lt;1</td>
<td>0.93±0.08</td>
</tr>
<tr>
<td>lgK_{a2}</td>
<td>&lt;&lt;1</td>
<td>0.52±0.05</td>
</tr>
</tbody>
</table>

*SCN^−, NO_3^−, HSO_4^−, IO_3^−, CH_3COO^−*

Complexes H_2MP^2+(AN)(Hal^-), H_2MP^2+(Hal^-)_2 and H_2MP^2+(AN)_2 have very similar electronic absorption spectra.

Solvents with weak polarity (for example chloroform) are characterized by smaller DN and ε values in comparison with acetonitrile. Obviously, the stability of the complexes of porphyrin dications with halogens will be higher in such solvents. This fact allows us to interpret the data obtained in System (34) by Fleischer in a new way.

H_2PP – FeCl_3 – CHCl_3  

In this system instead of the Fe^{III} complex CIFe^{III}PP a stable species is formed which was named the SAT-complex. It is characterized by electronic absorption spectrum which strongly resembles the spectrum of H_2PP^2+.

Addition of such bases as pyridine and ethanol destroys the SAT-complex with appearance of the molecular form H_2PP. This SAT-complex was considered as a mixed complex FeCl_3–H_2PP. This conclusion did not take into account self-acidification in System (34). Hydrogen chloride which is responsible for acidification appears due to hydrolysis of FeCl_3 by residual water and oxidation of chloroform by air oxygen. Therefore Fleischer’s SAT-complexes are in fact the chloride complexes of protoporphyrinium dichloride H_2PP^2+(Cl)_2 and not sitting-a-top FeCl_3–H_2PP species. These conclusions may be extended to other analogous systems in solvents of low polarity.

Conclusions

Porphyrins are amphoteric complexes. That is why reactions of metalloporphyrins complex formation are pH-dependent. Depending on the pH of solutions they form four types of ionic species HL^+, L^2+, H_2L^+ and H_2L^2+ which differ in their reactivity in metal complex formation. The porphyrins acid-basic properties are changed widely and differ in their reactivity in metal complex formation. The metalloporphyrins formation peculiarities without idea of Fleischer’s SAT-complex formation.

References

The Ferric–Oxo Moiety in Porphyrin Complexes – a Ferryl in Disguise?

Radu Silaghi-Dumitrescu

“Babes-Bolyai” University, Department of Chemistry, Cluj-Napoca RO-40028, Romania
E-mail: rsilaghi@chem.ubbcluj.ro

Mononuclear ferric-oxo moieties are known in non-heme environments, and have been proposed as reaction intermediates in some hemoproteins. Recently, such hemoprotein adducts have been detected spectroscopically via low-temperature cryoradiolytic reduction of their Fe$IV$-oxo counterparts. Here computational results (UBP86/6-31G**) are shown indicating that the electronic structures of such adducts are well described as $S=1$ Fe$IV$-oxo coupled to a porphyrin radical, as opposed to the clean ferric state predicted at the same level of theory (and demonstrated experimentally) for the non-heme systems.

Introduction

Mononuclear ferryl species, formally Fe$IV$-oxo, are known to play central roles in catalysis within several classes of hemoproteins, and have consequently received much attention.$^1$-$^5$ Mononuclear ferric-oxo moieties are particularly reactive, and their recent characterization in a non-heme environment has required some remarkable synthetic efforts$^6$ in order to protect/stabilize the oxo ligand with sterics and especially with hydrogen bonding. In such adducts, the ferric moiety is $S=5/2$ and features an Fe-O bond distinctly longer (~0.15 Å) than typical Fe$IV$-oxo counterparts.$^6$-$^9$ Heme ferric-oxo adducts have been discussed as possible reaction intermediates in proteins,$^{10}$ and have very recently been detected spectroscopically via low-temperature cryoradiolytic reduction of their Fe$IV$-oxo counterparts, with some interesting connotations to an ongoing debate about the protonation state of the latter.$^{11}$ Here, a computational description is provided for models of the ferric-oxo moieties in histidine- and cysteine-ligated hemoproteins, unexpectedly finding that ferryl descriptions, rather than ferric, are better suited for such species.

Experimental

Geometries for models shown in Figure 1 (formally ferric oxo, with an imidazole or methylthiolate ligand, respectively, and an unsubstituted porphyrin) were optimized for $S=1/2$, $S=3/2$ and $S=5/2$ spin states, respectively, with the BP86 functional, which uses the gradient-corrected exchange functional proposed by Becke (1988)$^{12}$ the correlation functional by Perdew (1986)$^{13}$ and the DN** numerical basis set (comparable in size to 6-31G**), as implemented in Spartan.$^{14}$ For the SCF calculations, a fine grid was used, and the convergence criteria were set to $10^{-6}$ (for the root-mean square of electron density) and $10^{-8}$ (energy), respectively. For geometry optimization, convergence criteria were set to 0.001 au (maximum gradient criterion) and 0.0003 (maximum displacement criterion). Charges and spin densities were derived from Mulliken population analyses after DFT geometry optimization. Energies for selected models were also computed with an SCRF procedure within the Gaussian 98$^{15}$ software package, using the UBP86/6-31G** functional and the CPCM$^{15}$ model with the default solvent number 13 (dielectric constant 4.335, mimicking the interior of a protein). A convergence criterion of $10^{-8}$ hartree was set for these calculations.

Results and Discussions

Table 1 lists relative energies for the ferric-oxo models of Figure 1.

For both the thiolate- and imidazole-ligated models, the $S=1/2$ and $S=3/2$ states are essentially degenerate, with the $S=5/2$ somewhat higher in energy; considering the known propensity of non-hybrid functionals to favour lower-spin states,$^{16}$ it cannot be ruled out based on our results that in reality the $S=3/2$ and $S=5/2$ are also accessible. On the other hand, Davydov et al. do find that the $S=1/2$ form of the ferric oxo adduct is observable experimentally at low temperature.$^{11}$

<table>
<thead>
<tr>
<th>Spin state/model</th>
<th>thiolate</th>
<th>imidazole</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S=1/2$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$S=3/2$</td>
<td>1.1</td>
<td>2.6</td>
</tr>
<tr>
<td>$S=5/2$</td>
<td>15.4</td>
<td>22.5</td>
</tr>
</tbody>
</table>

Figure 1. Ferric oxo models examined in the present study.
The Ferric-Oxo Moiety in Porphyrin Complexes

Table 2. Iron-axial ligand distances and average iron-porphyrin (Å) in imidazole (“N”) and methylthiolate (S) –ligated ferric oxo models.

<table>
<thead>
<tr>
<th>model</th>
<th>Fe-O</th>
<th>Fe-N/S</th>
<th>Fe-N(porphyrin)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S=1/2,N</td>
<td>1.68</td>
<td>2.19</td>
<td>2.030</td>
</tr>
<tr>
<td>S=3/2,N</td>
<td>1.67</td>
<td>2.18</td>
<td>2.041</td>
</tr>
<tr>
<td>S=5/2,N</td>
<td>1.68</td>
<td>2.30</td>
<td>2.115</td>
</tr>
<tr>
<td>S=1/2,S</td>
<td>1.71</td>
<td>2.48</td>
<td>2.045</td>
</tr>
<tr>
<td>S=3/2,S</td>
<td>1.70</td>
<td>2.46</td>
<td>2.045</td>
</tr>
<tr>
<td>S=5/2,S</td>
<td>1.70</td>
<td>2.48</td>
<td>2.115</td>
</tr>
</tbody>
</table>

The data in Table 2 show that the iron-oxygen distance remains constant regardless of spin state, which suggests that the electronic structure of the [FeO] moiety remains essentially constant in all models; this value is less than 0.05 Å different from that seen in the related ferryl (formally FeIV states) examined with similar methodology,[2,4] and, even in the S=5/2 model, remain more than 0.1 Å shorter compared to non-heme S=5/2 ferric-oxo adducts.[6,8] Likewise, the iron-thiolate and iron-imidazole distances do not show the variations seen in other iron complexes when examining different spin states,[5,17] suggesting again that certain elements of the electronic structure at the iron remain similar in all spin states of the ferric-oxo heme models.

Figure 2 shows spin densities computed for S=1/2 and S=5/2 imidazole-ligated models; while delocalization of spin density onto the porphyrin would not be unexpected for S=3/2 or S=5/2 ferric complexes, the significant negative spin density on the porphyrin in the S=1/2 models cannot be reconciled with a ferric-oxo description, and can only be explained in terms of an FeII-oxo moiety coupled to a porphyrin cation radical, or an FeIV-oxo moiety coupled to a porphyrin anion radical. Neither FeIII,oxo nor FeIV + porphyrin anion radical states have to our knowledge been previously described in any heme complexes.

Table 3 shows d-orbital populations for all spin states of the ferric-oxo models examined here. In the S=1/2 imidazole model, the iron dxy, dxy and dz2,xy orbitals must both be formally empty (indeed, as expected, LUMOs are found with distinct dxz,dyz and dz2 contributions for all S=1/2 models – data not shown); the total of 0.96 and 1.29 electrons, respectively, that are found in these two orbitals come from covalent mixing (and may also partly be a manifestation of often invoked[18] shortcomings of unsophisticated population analyses such as Mulliken). On the other hand, in the same model, dxz, which features 1.37 electrons, is formally doubly-occupied. These observations, together with the 1.5 electrons found in the dxz and dyz orbitals, respectively, and together with a total spin density on the Fe-O moiety of 1.84 (1.03 on Fe, 0.81 on O), lead us to a description of the Fe-O bonding as a classical S=1 ferryl moiety, in no way different from other ferryls previously characterized. Such [FeO]5+ groups are indeed typically characterized by 4 electrons clearly placed in iron d orbitals (dx2-y2, dyz, dz2, xz), with an additional two electrons shared equally between iron and oxygen within the two Fe-O π* orbitals.[2,5,19] This ferryl in our formally ferric-oxo models must then be antiferromagnetically coupled to a porphyrin anion radical. The S=3/2 imidazole model has an electronic structure almost identical to that of the S=1/2 counterpart, except that the S=1 ferryl and S=1/2 porphyrin are now ferromagnetically coupled. Similarly, the S=5/2 counterpart is described as S=2 ferryl + S=1/2 porphyrin radical. Table 3 also shows that the thiolate-ligated ferric-oxo models feature exactly the same electronic descriptions as their imidazole-ligated counterparts – i.e. ferryls coupled to porphyrin radicals.

To test whether the conclusions drawn from Table 3 and related data are dependent on the computational model chosen, the electronic structure of the S=1/2 imidazole model was also examined using a different approach, which included solvation as well as a non-hybrid functional (cf. Experimental). In this case as well, the sum of spin densities on the Fe-O moiety was essentially 2, even though a slight polarization was noticed compared to the gas-phase (Fe-1.34, O-0.64, compared to values listed above for gas-phase).

Ferric-oxo complexes in non-heme environments have been extensively characterized experimentally and computationally (including, with the same computational methodology as applied in the present work), and all available data indeed supports a ferric-oxo description.[6-9]

By contrast, the porphyrin counterparts examined in the present work all seem to prefer a ferryl description, with a porphyrin anion radical. Non-heme ferric-oxo complexes have been shown experimentally to be relatively weak oxygen atom transfer agents, with no observed propensity towards reductive activity – as opposed to ferryl species and especially to ferryl species bearing a porphyrin cation...
radical on the porphyrin (the so-called Compound I), which are at the same time strong oxidizing agents and good oxygen transfer agents.\[7\]

We propose that the strong ligand field of the porphyrin, together with the four short iron-nitrogen(porphyrin) bonds energetically disfavour the high-spin ferric-oxo state in favour of the ferryl state, to the extent where the latter becomes preferred. To partially support our assertion, a simpler version of the imidazole-ligated \(S=1/2\) model, where all nitrogenous ligands are replaced by ammonia and the geometry of the system is subsequently fully optimized, shows a clear ferric-oxo description, as opposed to the ferryl one seen in the porphyrin model. Thus, in this non-heme model the Fe-O elongates to 1.77 Å, and the spin densities are 0.67 on the iron and 0.39 on the oxygen, i.e. essentially equivalent to the sole unpaired electron expected of a \(S=1/2\) \(\text{Fe}^{III}\) center.

The gas-phase proton affinities of the ferric-oxo moieties are computed to be very high. For the imidazole model this value is 362 kcal/mol, \(i.e.\) very similar to the 340-410 kcal/mol computed for models of similar charge, size, and chemical composition, such as thiolate-ligated ferryl or imidazole-ligated ferric-peroxo, with the same computational approach.\[3\] For both of these latter better-characterized species, the non-protonated form appears to be undetectable at room temperature. For heme ferric-peroxo species (overall charge identical to ferric-oxo, and with very similar stoichiometry), the non-protonated form is only detectable at low temperature, and in some hemoproteins it appears to undergo protonation even at liquid nitrogen temperature.\[3,11,20,21\] The very similar proton affinities found here for ferric-oxo compared to ferric-peroxo are well paralleled by the similar behaviour of the two classes of species in cryoradiolytic EPR (electron paramagnetic resonance experiments).\[11\] thus, our computations are consistent with, and provide support for, the recent\[11\] experimental observation of heme ferric-oxo species in proteins.

Conclusions

A ferryl+porphyrin radical electronic structure description is found using density functional theory methods for formally ferric-oxo heme models. These results support to some extent and are likely to help further explore the significance of the recently described ferric-oxo moieties in hemoproteins.\[11\]

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Conversion of 1,2,5-Selenadiazoloporphyrazine to Diformamidoporphyrazine

Anwar Ul-Haq and Pavel A. Stuzhin

Department of Organic Chemistry, Ivanovo State University of Chemical Technology, RF-153000 Ivanovo, Russia
Corresponding author E-mail: stuzhin@isuct.ru

Introduction

It is known that reductive opening of the 1,2,5-selenadiazole ring leads to the vicinal dianiminospecies [1] and H₂S has been reported [2,3] as a convenient reducing agent. This reaction has been used for the peripheral modification of porphyrazines with annulated 1,2,5-selenadiazole rings [4-6]. In a common procedure H₂S was bubbled through the pyridine solution of 1,2,5-selenadiazoloporphyrazines until the characteristic colour change and following treatment of the reaction mixture with α-diketones led to pyrazinoporphyrazines [4,5]. When aromatic aldehydes were used the Schiff-base porphyrazines were obtained [6]. The in situ formation of the intermediate vicinal aminoporphyrazine species was postulated. Recently, investigating the reaction products obtained by treatment of the Fe⁺ complex of hexaphenyl substituted 1,2,5-selenadiazoloporphyrazine [Py₆Fe⁺[SeNₓ]PAPh₆] with H₂S in chloroform in the presence of 1-2% pyridine we have observed the direct substitution of Se atom by S atom with formation of the 1,2,5-thiadiazole analogue [Py₆Fe⁺[SNₓ]PAPh₆] [7]. According to the mass-spectral and UV-vis data under these reaction conditions the annulated 1,2,5-selenadiazole ring is first converted to the S,Se-bridged 6- or 7-membered heterocycle which can be either aromatized with expulsion of Se and excessive S atoms to 1,2,5-thiadiazoloporphyrazine or further reduced to vicinal dianimoporphyrazine. Due to instability of N-S and N-Se bonds in the intermediate S,Se-substituted diazine and diazepine species in acidic media, they should give similar products in reaction with electrophiles, e.g. with carbonyl compounds, as vicinal dianimoporphyrazine. It was attractive to use these reactive species for peripheral modification of porphyrazines.

Aromatic ortho-diamines react readily with carboxylic acids, e.g. with formic acid, with formation of imidazo derivatives. Thus, 4,5-diaminophthalodinitrile reacted with RCOOH (R=H, Me, Pr) to give 5,6-dicyanobenzimidazoles which were then converted to tetra(5,6-benzimidazo)porphyrazines by usual template condensation procedure in the presence of metal salts [8,9]. However, commercially available 4,5-dicyanoimidazole failed to form corresponding tetra(imidazo)porphyrazine in analogous template tetramerization procedure [10]. It was reported that only its N-alkylated derivatives can react in mixed co-condensation with substituted phthalodinitriles affording low symmetry (N-alkylimidazo)tribenzimidazoles [11]. In present work we have made an attempt to obtain imidazo annulated porphyrazine [H₂[1H]PAPh₆] (4) by deselenation of 1,2,5-selenadiazoloporphyrazine [H₂[SeNₓ]PAPh₆] (1) under action of H₂S followed by treatment of the resulting reaction mixture containing dianimoporphyrazine [H₂PA[NHₓ]PPh₆] (2) with formic acid (Scheme 1). However instead of the expected imidazoporphyrazine 4 we have observed the formation of diformamidoporphyrazine [H₂PA[NHCOH]PPh₆] (3).

Scheme 1.
Experimental

UV-vis spectra were recorded using Hitachi U-2000 spectrophotometer. MALDI-TOF spectra were measured on Ultraflex Brucker Daltonics mass-spectrometer without matrix or with CCA matrix.

Reagents and solvents for synthesis, chromatography and spectroscopic characterization of compounds were pure chemicals (Fluka, Aldrich). 4,5-Dicyanomimidazole was prepared following the known procedure[12] and was identical with the commercial product (Aldrich). 7,8,12,13,17,18-Hexaphenyl[1,2,5]selenadiazolo[3,4-b]porphyrazine, [H₂{SeN₆}PAPh₆] (1) was prepared as described in our recent works[7,13].

2,3-Diformamido-7,8,12,13,17,18-hexaphenylporphyrazine, [H₂PA{NHCOH}PAPh₆] (3): H₂S was bubbled through solution of [H₂{SeN₆}PAPh₆] (1) (20 mg, 0.023 mmol) in pyridine-chloroform mixture (1:4, 5 ml) for 1 min until colour was changed from green to dark blue. Then formic acid (20 ml) was added and solution was refluxed for 1 hour. After vacuum distillation of solvents residue was dissolved in chloroform and chromatographed on silica gel. The first fraction was collected and after evaporation of the solvent 15.7 mg (81 %) of 3 was obtained.

MS (MALDI-TOF): m/z = 858 (100 %)[M+H]⁺, calc m/z = 857. UV-vis λ_{max} (CHCl₃) nm (ε/μM cm): 361(1.00), 448(0.51), 589(0.51), 671(0.88).

Results and Discussions

We have attempted to prepare imidazoporphyrazine [H₂{ImH}PAPh₆] (4) using two approaches - (i) by direct synthesis from two dinitrile precursors and (ii) by peripheral modification of porphyrazine macrocycle. Mixed co-cycloctetramerization (i) of diphenylhumarodinitrile taken in excess with 4,5-dicyanomimidazole (4:1 molar ratio) in the presence of Mg²⁺ butoxide in n-butanol under reflux led exclusively to Mg²⁺ complex of symmetrical octaphenylporphyrazine [MgPAPh₆] and no formation of 4 or other low-symmetry imidazo-annulated porphyrazines was observed. This is in contrast with successful use of this procedure for preparation of Mg²⁺ complexes of 1,2,5-thiadiazolo- and benzannulated β-phenylsubstituted porphyrazymes from diphenylhumarodinitrile and corresponding heterocyclic dinitrile or phthalodinitrile.[13,15]

For peripheral modification (ii) we have chosen [H₂{SeN₆}PAPh₆] (1) and studied first its behaviour in the presence of H₂S. Bubbling of H₂S into the solution of [H₂{SeN₆}PAPh₆] (1) in pure chloroform did not produce any changes in the UV-vis spectra. However, in the presence of pyridine additions (10-20%) the colour of the solution saturated with H₂S was rapidly changed from green to dark blue. In the UV-vis spectra two characteristic Q-bands (576 and 694 nm) of the initial 1,2,5-selenadiazoloporphyrine 1 disappeared and the broad absorption band with maximum at 578 nm appeared (Figure 1, spectra a and b). Such broad Q-band is characteristic feature of the UV-vis spectra of aminosubstituted porphyrazines.[14] In the MALDI-TOF spectra of the reaction probe the peak corresponding to the molecular ion [M+H]⁺ of dianimoporphyrine [H₂PA{NH₂}₂Ph₆] (2) was observed at m/z = 801. The mass-spectrum contains also the peak at m/z = 827 which can be assigned to 1,2,5-thiadiazoloporphyrine [H₂{SN₆}PAPh₆]. However, in the UV-vis spectrum of the reaction mixture no indication can be seen about presence of [H₂{SN₆}PAPh₆] which have Q-bands at 574 and 679 nm.[13] Taking into account previous observations made for the Fe²⁺ complex [Py₂Fe²⁺{SeN₆}PAPh₆],[7] we can conclude that also in the case of the free base [H₂{SeN₆}PAPh₆] the reaction mixture after treatment with H₂S contains along with dianimoporphyrine [H₂PA{NH₂}₂Ph₆] (2) some amount of its precursors with the S,Se-substituted diazine and diazepine rings [H₂{((NH₂)₂}X)PAPh₆] (X = SSe, S₂, S). One can suppose that upon evaporation of the solvent before and/or during mass-spectral measurements these species are transformed to the more stable 1,2,5-thiadiazole derivative [H₂{SN₆}PAPh₆] (3).

We have tried to convert [H₂PA{NH₂}₂Ph₆] (2) and its precursors [H₂{(NH₂)₂}X)PAPh₆] (X = SSe, S₂, S) into imidazoporphyrazine [H₂{ImH}PAPh₆] (4) by treatment of the reaction mixture with formic acid. The UV-vis spectrum of the reaction product obtained after chromatography is shown in Figure 1 (c). It contains two narrow Q-bands in the visible region which is typical for porphyrazine having C₂ᵥ symmetry of the π-chromophore. The maxima of the long-wave Q₁-component is shifted hypochromically and Q₂-component bathochromically and the splitting of the Q-band is reduced from 2950 cm⁻¹ to 2075 cm⁻¹ as compared with the initial [H₂{SeN₆}PAPh₆]. Such spectrum might be characteristic for imidazoporphyrazine 4. However in the MALDI-TOF mass-spectrum of this species (Figure 2) no peak which can be assigned to the molecular ion of imidazo derivative [H₂{ImH}PAPh₆] (calculated m/z = 811 for [M⁺]) is present. Instead the spectrum contains the intense peak at m/z=858 which shows no defragmentation but is accompanied by two less intense peaks at 1061 and 1264 having the difference of 203 mass units. The presence of these peaks evidences that under the used reaction conditions formic acid is not condensed with two vicinal amino groups of [H₂PA{NH₂}₂Ph₆] (2) with closure of imidazole ring, but formylate them with formation of formamidoporphyrine (3). The peak at m/z=858 corresponds to [M+H⁺]¹ and at 1061 and 1264 to the daughter ions [M+H+203]² and [M+H+203]³.
Deselenation of 1,2,5-Selenadiazoloporphyrazine

Figure 2. MALDI-TOF mass spectrum of 3.

Unsuccessful efforts of synthesis of imidazoporphyrazine both by direct template cyclotetramerization of two dinitrile precursors and by peripheral modification of vicinal dianinoporphyrazine can be understood if one takes into account that in both cases formation of imidazoporphyrazine involves closure of 5-membered ring fused to another 5-membered ring (pyrrole to imidazole or imidazoporphyrazine involves closure of 5-membered ring into account that in both cases formation of dinitrile precursors and by peripheral modification of porphyrazine both by direct template cyclotetramerization or deselenation of 1,2,5-selenadiazoloporphyrazine and reaction of intermediate “diaminoporphyrazines” with formic acid. The closure of imidazole ring is hindered by steric strain and did not occur under condition used. Instead new diformamidoporphyrazine was obtained and characterized by mass-spectrometry and UV-vis data.

Acknowledgements. This work have received the partial financial support from Russian Foundation of Basic Research (Grant No 06-03-81022).

References

10. Stuzhin P.A., Ercolani C. Porphyrines with Annulated 5-membered heterocycles consisting of only the 2p elements (C,N,O) are practically unknown.

Evidently formation of the system with two fused 5-member rings, when possible, requires more severe conditions than that used in our experiments. In our case since the closure of the imidazole ring was hindered by steric strain, formylation of vicinal amino groups has occurred. Semiempirical AM1 calculations demonstrate that the obtained structure of bisformamide derivative 3 can be additionally stabilized by formation of hydrogen bonds, and formylamino groups adopt conformation which is close to planarity (Figure 3). This enables their conjugation with porphyrazine chromophore and agrees with the character of UV-vis spectra.

Conclusion

In summary, we have investigated the reaction of deselenation of 1,2,5-selenadiazoloporphyrazine and reaction of intermediate “diaminoporphyrazines” with formic acid. The closure of imidazole ring is hindered by steric strain and did not occur under condition used. Instead new diformamidoporphyrazine was obtained and characterized by mass-spectrometry and UV-vis data.

Figure 3. The AM1 optimized structure of 3.
The Peculiarities of the Reaction of Benzo- and Dibenzocrown Ethers with N-Halogenosuccinimides

Sergei A. Kotlyar and Sergei M. Pluzhnik-Gladyr

The aromatic halogenation of benzo- and dibenzocrown ethers by N-halogenosuccinimides in solid phase, water or organic medium was researched for the first time. Under mechanochemical activation depending on stoichiometry of the process, benzocrown ethers smoothly and selectively transform into corresponding mono or dihalogeno derivatives. Addition of solid N-halogenosuccinimides to benzocrown ethers’ water solutions with high yields leads to mono halogenation products. At that, the process proceeds under the action of hypohalogenous acids, i.e. inside hydrolysis products. However, only 4,5-dibromo- or -diodobenzocrown ethers were selectively obtained in 20% solutions of sulphuric acid. In similar conditions, dibenzocrown ethers in solid phase form mixtures of products and do not react with N-halogenosuccinimides in water solutions. In the boiling chloroform medium, the reactivity of investigated macrocycles is vastly varying. If bromination of benzo- and dibenzocrown ethers proceeds easily and with good yields, then under chlorination similar products form with low yields during significantly longer period of time. Only benzocrown ethers out of researched compounds undergo mono iodination at the influence of N-iodosuccinimide.

Introduction

Bromo- and iodosubstituted benzo- (BCE) and dibenzocrown ethers (DBCE) easily transform into either hardly obtainable or unavailable by other methods acetylenic, vinyl, n-alkyl, n-hydroxyalkyl phosphorus containing derivatives, and also crown heterocycles, bis-benzocrown ethers, etc. Synthesis and properties of corresponding chloroanalogues are almost not researched.

Chlorination of BCE and DBCE by molecular chlorine is not selective and leads exceptionally to the products of aromatic perchlorination. Molecular bromine, rarely - N-bromosuccinimide commonly employed for the bromination, and as for iodination, oxidants are necessary. Therefore, it is carried out in the systems: I₂–HIO₃–H₂SO₄, I₂–CF₃COOAg, I₂(HI)–H₂O₄ or trimethylbenzylammonium iodide dichloride–ZnCl₂–CH₃COOH.

Intensification of substance transformation relates to one of the main problems of contemporary organic chemistry. Aiming at development of the obtaining methods and enhancing of the “family” of these compounds, continuing the search for new ligands, extragants and biologically active molecules, we have researched for the first time the interaction of some BCE and DBCE with N-chloro- (NCS), N-bromo-, (NBS) and N-iodosuccinimides (NIS) in solid, water and organic phases. Here we report the main results of recently carried out researches.

Experimental

Macrocycles 1–5 (Schemes 1 and 2) were purified by crystallization to the 98% purity (GLC). Due to the fact, that N-halogenosuccinimides (NHS) at standing liberate and sorb halogens, we subjected them to additional purification and used only fresh ones. Commercially available NCS and NBS (Acros Organics) were purified to m. p. 144–150 °C and 175–178 °C, correspondingly, by crystallization from benzene (NCS) and water (NBS). NIS (m. p. 200–201 °C) was synthesized and purified similarly. Used NHS represented white crystals with purity not less than 98–99% (titrimetrically). H₂SO₄ (Aldrich Chemical Co) contained no more than 2% of water.

Solid phase synthesis was performed in electromechanic hermetical vibratory pounder «KM–1» (Germany). ¹H NMR spectra were recorded in CDC₁₉ (99.8%) on the 299.95 MHz Varian WXP 300 instrument using Me₄Si as internal standard. Mass spectra were obtained with a MX 1321 spectrometer equipped with a direct inlet; ionization voltage 70 eV and ionization chamber temperature 200 °C. The thin layer chromatographic control of the substances purity was performed on Silufol UV 254 plates using halogenated BCE and DBCE, synthesized (see Introduction) according to well–known methods, as reference compounds.

In a series of cases (for example, method B), the necessity to purify the products by crystallization was no longer relevant. The products 6–26 were obtained as stable white crystals. Interval of temperature values of melting is provided for all methods A–D, and data on elemental analysis is introduced for one of them.

Method A. General Procedure. The mixture of 5 mmol of BCE 1–3, 5 (or 10) mmol of NHS and equimolar amount of p-toluene sulphuric acid (PTSA) monohydrate was mechanochemically pondered for 1 h (amplitude 14). After that, reaction mixture was thoroughly washed with 2x5 ml of cold water. The precipitate was filtered and dried at lowered (40–60 mm Hg) pressure to constant mass, and, if necessary, was crystallized from n-hexane or n-heptane. Dichlorides 15–17 were isolated with fractional crystallization.

Method B. Well-graunted NHS (5 mmol) was added in small portions to the BCE solution (5 mmol in 50 ml of distilled water). The mixture was stirred for 2 h at room temperature and cooled to 10 °C. The solution was neutralized by NaHCO₃ till pH 7. Precipitated crystals were filtered, thoroughly washed with water (3x5 ml, 10 °C) and treated as described for method A.

Method C. Concentrated H₂SO₄ (~5 ml) was added to the solution of 5 mmol of BCE 1–3 in 50 ml of distilled water while stirring and cooling. Well-grounded NHS or NBS (10 mmol) was...
Reaction of Benzo crown Ethers with N-Halogenosuccinimides

added by small portions (during 15-20 min) to the obtained solution at intensive stirring. The mixture was stirred for 2 h at 20 °C. After that 10 ml of 3% Na2SO4 solution was added and the reaction mixture was stirred for ~15 min until decolorization. The solution was neutralized by 10% NaHCO3 water solution till pH 7. The precipitate was filtered, washed with 3x10 ml of warm water and dried to constant mass. According to solid NCS (20–40 ml of CHCl3) was dissolved in chloroform (25 ml), heated to 50 °C, and the mixture of cis- and trans-isomers was added. The precipitate obtained was filtered and washed with 10 ml of 3% Na2SO4 solution of hot water and dried to constant mass. According to 1H NMR and mass spectroscopy data, the obtained compound 24 contained impurities of mono- and trichlorides. The impure product was suspended in 150 ml of n-hexane and refluxed for 1 h. Then the mixture was filtered. The precipitation of the product 24 was dried and crystallized from 1.4-dioxane (yield 2.82 g, 82%). m. p. 177–184 °C. Found: C 55.92, H 0.8, Cl 16.47 %. C17H14Cl2O4 requires C 55.96, H 5.17, Cl 16.52. m/z (ESI) (%) 428 (21), 430 (14) [M]+, 214 (6) [1/2M]+, 170 (100), 171 (34), 172 (34). δ6 (CDCl3, 298 K) 7.15–6.71 (6H, m, Ar), 4.29–4.21, 4.19–4.06, 4.00 (16H, m, OCH2CH2O).

Method D. 4,4′,6,6′-Dibromo[3,3]dibenzo-18-crown-6, mixture of cis- and trans-isomers (25). Method D. 4,4′,6,6′-Dichloro[3,3]dibenzo-18-crown-6, mixture of cis- and trans-isomers (24). Macrocycle 4 (3.0 g, 8 mmol) was dissolved in chloroform (25 ml), heated to 50 °C. The precipitate obtained was filtered. The reaction mixture was re-refluxed at 10 h and cooled. The obtained precipitate was washed with 10 ml of 3% Na2SO4 solution of hot water and dried to constant mass. According to 1H NMR and mass spectroscopy data, the obtained compound 24 contained impurities of mono- and trichlorides. The impure product was suspended in 150 ml of n-hexane and refluxed for 1 h. Then the mixture was filtered. The precipitation of the product 24 was dried and crystallized from 1.4-dioxane (yield 2.82 g, 82%). m. p. 177–184 °C. Found: C 55.92, H 0.8, Cl 16.47 %. C17H14Cl2O4 requires C 55.96, H 5.17, Cl 16.52. m/z (ESI) (%) 428 (21), 430 (14) [M]+, 214 (6) [1/2M]+, 170 (100), 171 (34), 172 (34). δ6 (CDCl3, 298 K) 7.15–6.71 (6H, m, Ar), 4.29–4.21, 4.19–4.06, 4.00 (16H, m, OCH2CH2O).

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Results and Discussions

The replacement of fluid technologies on “dry” ones, which are not requiring usage of various solvents and their following removal and regeneration, is relevant in fine organic synthesis. Previously, mechanochemical activation of solid reagents at the absence of solvent was not employed in preparing of crown ethers. Their interaction with N-halogenosuccinimides (NHS) was performed by us in electromechanical hermetrical vibratory agatic pounder under fixed time and intensity of ball’s amplitude of oscillation.

It was discovered, that benzo-12-crown-4 (1), benzo-15-crown-5 (2), benzo-18-crown-6 (3), [3.3]dibenzo-18-crown-6 (4) and [4.4]dibenzo-24-crown-8 (5) halogenation with any ratios of reagents leads only to the mixture of products. At the same time, in the presence of p-toluene sulfonic acid monohydrate (TSA), it is significant, that it was already used in solid-phase synthesis[34], BCE 1–3 quickly (1 h) and selectively react with either NBS or NIS, depending on the stoichiometry of the reaction (BCE:NHS = 1:1 or 1:2), forming the products of 4', 9–14 or 4',5'-substitution (18–23), correspondingly (Method A, Scheme 1). These compounds are isolated with 83–95% yields after simple purification.

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Scheme 1. Method A: solid phase, in presence of TSA; method B: water solution; method C: 20% H2SO4 solution; method D: boiling CHCl3 medium.

4',5'-Diodobenzo-18-crown-6 (23). Method–yield, %: A 93, C 94, m. p. 91–93 °C. Found: C 33.00, H 3.73, I 44.91 %. C16H14O2I6 requires C 34.06, H 3.86, I 44.99 %. m/z (ESI) (%) 564 (55) [M]+; 388 (100), 389 (11), [(M–(CH3CH2O)3)2]+ δ9 (CDCl3, 298 K) 7.26 (2H, s, Ar), 4.11–4.09 (4H, t, J=5.6 Hz, CH2O), 3.90–3.87 (4H, t, J=5.6 Hz, CH2O), 3.75–3.70 (8H, m, J=4.7 Hz, OCH2CH2O).

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Methods A, B, D

Methods A, C (X=Br, D) (X=Cl, Br)

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Methods A, B, D

Methods A, C (X=Br, D) (X=Cl, Br)
Selective chlorination of polyethers 1–3 to monochlorides 6–8 (yields 71–80%) was realized for the first time and passes smoothly only at equimolar ratio of reagents. The increase of BCE:NCS ratio up to 1:2, unlike NBS and NIS, yields in the mixture of chlorinated macrocycles. Therefore, we could isolate dichlorides 15–17 with low yields of 16–31% only under fractional crystallization.

However it is impossible to isolate in the same way the halogenation products of DBCE 4 and 5 in pure form. Analysis of resulting mixtures points at significantly larger reactivity of polyether 5 comparing to 4.

The examples of CE halogenation in their water solutions, not containing organic solvents as addition agents, are not known to us. Compounds 1-3 form ~3–5% water solutions, which allowed to carry out this process in homogeneous conditions. It was discovered, that addition of equimolar quantities of solid NBS or NIS to water solution of macrocycles 1–3 at room temperature and intensive stirring quickly and selectively leads (Method B, Scheme 1) exceptionally to corresponding 4'-substituted BCE 9–14 with 76–81% yields. These products crystallize from water solution and are isolated by simple filtration. Their little solubility in water is the reason of observed selectivity. Such conclusion (1H NMR spectroscopy, mass spectrometry, TLC) is proved by the absence of corresponding 4,5,5-dioidoBCE in the reaction mixture and products.

Unlike its analogues, NCS does not react at room temperature with compounds 1–3, and such transformation is observed only into 4'-chloro derivatives 6–8 with 75–83% yields at 55–60°C (Scheme 1).

Obviously, the route of reaction includes quick NHS hydrolysis to corresponding hypohalogenous acids HXO (X = Cl, Br, I) and following oxidizing halogenation of the BCE.

The addition of catalytic quantities (1 drop) of concentrated H₂SO₄ insignificantly accelerates the process, not influencing the selectivity and the yield of compounds 9–14. Under interaction of polyethers 1-3 with equimolar quantities of NIS in 10–20% H₂SO₄ water solutions, we obtained corresponding mono- and diiodo derivatives with prevailing of the first ones.

However, bromination and iodination of BCE 1–3 in ~20% H₂SO₄ water solutions (BCE:NHS = 1:2, 20 °C) allows selective synthesis of 4,5,5-disubstituted BCE 18–23 with 90–94% yields (Method C, Scheme 1). It is possible to make a certain assumption, that intermediates 9–14 as oxonium ion adducts dissolve in strong-acid water medium, and this fact provides their smooth homogeneous halogenation to the finishing products 18–23. It is important to mention, that in these conditions NCS doesn’t react with compounds 1–3, i.e. at room temperature semi-products 6–8 do not form even in acid solution. Resinification of the reaction mixture starts when heating.

In all cases, while conveying the process in water solutions, macrocycles 4 and 5 almost do not react with NHS.

Considerable differences in crown compounds reactivity exhibit at halogenation in the halogenohydrocarbon medium (Method D, Scheme 2), from which CHCl₃ seems to be optimal.

It was found, that addition of stoichiometric quantity of solid NBS to polymer 4 suspension in CHCl₃ (20 °C) leads to quick (5–15 min) warming of reaction mixture and extensive precipitation of dibromide 25 (mixture of cis- and trans-isomers), which was obtained with 90% yield (Scheme 2).

At the same time, for DBCE 5 such effect is less noticeable and additional short boiling of reaction mixture is necessary for obtaining corresponding dibromide 27. Even smaller reactivity is observed for [2.3]dibenzo-15-crown-5. It is possible to exclude that in the case of 18-member macrocycle 4, the DBCE:NBS complex is formed most easily, which provide to significant polarization of the N–Br bond. This assumption is proved by the fact that, under similar bromination of DBCE containing biphenyl and diphenyl oxide fragments, the speed of reaction is in 5–30 times higher, than for model non-cyclic biphenyls and diphenyl oxides and also depends on the size of macrocycle. Synthesis and properties of these bromo compounds will be considered by us in a separate paper.

Interaction of polyethers 1–3 with NBS smoothly and quickly (30 min–1 h) proceeds in boiling CHCl₃, what (depending on the reagents ratio) allows preparing of derivatives 9–11 or 18–20 (Scheme 1) with 69–90% yields.
We should mention, that by-products which are connected with the participation of solvent were not found even in the traces.

Absolutely opposite results were obtained for NIS. Incomplete conversion was fixed for all BCE, and due to this, products 12–14 were obtained with yields not higher than 20% but diiodides 21–23 do not form at all. Conversion is even lower under iodination of DBCE 4 and 5, so it is impossible to separate mono and diiodo derivatives.

At the same time, long-lasting (8-10 h) boiling is necessary for chlorination of compounds 1-3, what also leads to the formation of impurities. Thus, the obtained chlorides 6–8 contain impurities of the substrate and corresponding dichloro-derivatives and were isolated in pure form only with 23–41% yields after fractional crystallization. Products 15–17, yields of which do not exceed 50%, were purified by the similar method. Nevertheless, durational chlorination of DBCE 4, as for NBS, allowed preparing dichloride 24 with 82% yield.

The structure of synthesized compounds 6–26 was defined by 1H NMR spectroscopy, mass spectrometry and the composition was determined by elemental analysis. Individuality of the products was controlled by TLC using crown compounds synthesized by common methods (see Introduction) as the standards. Melting points and other physicochemical characteristics of the prepared macrocycles agreed with that described in literature.

Conclusions

Consequently, using reagents of the same type, namely NHS, we for the first time carried out selective chlorination, bromination and iodination of BCE and partially, DBCE and compared their reactivity. Developed methods of BCE halogenation in solid state and water are simple and, from our view, they offer an obvious advantage to the known ones.

It is worthwhile of mentioning, that in the conditions of B and C methods, NHS actually are the only sources of halogen because of being easily hydrolyzed, what is proved by additional experiments. At the same time, hypohalogenous acids proved themselves as efficient halogenating agents for BCE.

The macrocycles studied often demonstrate noticeable differences in reactivity, which not always may be explained now and needs in performance of additional experiments.

Some of reported results put an idea to investigate the possibility of preparing crown ether “host-guest” complexes with ionic compounds or neutral organic molecules in solid phase under mechanochemical activation.

References

Template Synthesis into Gelatin–Immobilized Matrix as Perspective Method of Obtaining Supramolecular Macroheterocyclic Compounds

Oleg V. Mikhailov, a@ Marina A. Kazymova, b and Denis V. Chachkovb

aKazan State Technological University, 420015 Kazan, Russia
bKazan State University, 420015 Kazan, Russia
Corresponding author E-mail: ovm@kstu.ru

Template synthesis processes proceeding for MII ion – ligand synthon I – ligand synthon II triple systems (M=Co, Ni, Cu) into solutions and gelatin-immobilized matrix, have been obtained and analyzed. It has been shown that final results of these processes are distinguished extremely considerably. The distinction predicted has been displayed by examples of template synthesis for some MII – (N,S)-/(N,O,S)-amidinate ligand synthon – (C=O)-containing ligand synthon in water-ethanol solutions and metalhexacyanoferate gelatin-immobilized matrix implantates. The quantum-chemical calculation of structures of macrocyclic coordination compounds formed as a result of template processes, has been carried out with using DFT B3LYP method.

Introduction

Template synthesis is known to be one of extremely important synthetic methods of modern coordination and supramolecular chemistry. In this method, metal ion having specific stereochemistry of coordination environment and electronic structure, is a peculiar “pattern” and ensures a formation of such specific metallocomplexes, the synthesis of which under other conditions either has been very difficult or cannot be realized at all. In principle, template synthesis enables to obtain metallomacrocyclic and supramolecular coordination compounds, including even having very complex structure (for example, coordination compounds of various metal ions with phthalocyanines and porphirines) from comparatively simple starting chemical compounds (what are known as ligand synthons). However, such a synthetic method leads to formation of chemical compounds which are of far more complex composition and structure compared with metal ions with phthalocyanines and porphirines) from comparatively simple starting chemical compounds (what are known as ligand synthons). However, such a synthetic method leads to formation of chemical compounds which are of far more complex composition and structure compared with

Theoretical consideration

One of possible ways to decision of given problem, preliminary “regulation” of reactionary system (and, namely, “compulsory” decrease of entropy in it) which, as it is easily noticed, leads to that tangent of angle of slope of linear ΔG(T) dependence to abscissa axes decreases, may be. Indeed, because entropy is additive value, and, in the case of availability of such a preliminary “regulation”, general equation ΔS = ΔS'' + ΔS''', where ΔS is a change of entropy of reaction in an absence of “regulation” indicated, ΔS' is a change of entropy of reaction in an availability of it, ΔS''' is a change of entropy in the course of the very “regulation”, will takes place. As a result, the equation of ΔG(T) dependence in the system where “compulsory” decrease of entropy indicated takes place, is described as

$$\Delta G'' = \Delta H - T(\Delta S - \Delta S''')$$

and, because ΔS''' is negative value, ΔS > 0, hence, $$|\Delta S' - \Delta S'''| < |\Delta S|$$. According to this, the range of temperature values in which given template process is thermodynamically possible, increases. This circumstance is illustrated by Figure 1.

![Figure 1. ΔG(T) dependences (1,2,3) and ΔG(T) ones (1,2,3) for three various variants of template process: 1, 1 and 2 – for such template processes having ΔH > 0 which, in principle, can be realized in the metal ion – ligand synthon I – ligand synthon II triple systems without “compulsory” decrease of entropy indicated, 3, 3 – for template process having ΔH > 0 which may be realized only in the case of “compulsory” decrease of entropy. Lower slope of straight lines of ΔG(T) and ΔG(T) dependences to abscissa axe has been clearly seen.](image-url)
One of examples of reactionary mediums where such preliminary “regulation” of reactionary system and “compulsory” decrease of entropy occurs, are biopolymer-immobilized matrix (for example, thin-layer implantate on some film) containing immobilized coordination compound. The most suitable biopolymer for creation of matrix indicated is gelatin which very easily forms thin transparent layers. A length of gelatin molecule is ~ 285000 pm whereas its diameter only 1400 pm; this molecule is sharply asymmetric. A typical fragment of structure of the given polymer is shown in the Figure 2.

![Figure 2](image)

Figure 2. Three polypeptide α-chains form a triple-helix of gelatin. Gelatin is stabilized by the formation of covalent cross-links, both within the gelatin triple helix and between gelatin helices.[3]

Such a structure is potentially very suitable for the formation of polymer-immobilized matrix materials; it permits the formation of no kind of rigid crystalline blocks and furthermore, contains a fairly large number of cells for the reception and subsequent fixation of the molecules of the immobilized substance. When filled with the molecules of corresponding compound, these cells retain a certain freedom of migration in space. With a polymer of such a structure, it may be, in principle, to obtain immobilized matrix systems characterized by a fairly uniform distribution of the metal-containing chemical compounds in some part of the polymer massif. In addition, such immobilized matrices are sterically accessible for the occurrence of diverse chemical processes in particular chemical processes and, among their number, template synthesis reactions. Gelatin has an extremely high surface area and an extensive system of micropores, so that when it comes into contact with any kind of aqueous solution, the permeation of both the solvent molecules and of the solute into polymer massif is a rule ensured comparatively readily.[8,9] In this connection, polymer layers on the basis of gelatin exhibits isotropic physical and mechanical parameters and is transparent, hydrophilic, and plastic.

One of most suitable immobilized substances are hexacyanoferrates(II) of various transition metals having general formula \[ M_n[Fe(CN)_6] \] where \( M = VO, Mn, Co, Ni, Cu, Zn, Cd \) et al. According to experimental data, such thin-layer gelatin-immobilized matrix implantates containing these coordination compounds (further MHF-GIM) are transparent as regards to electron flow, and, hence, have nano-structured level of organization of immobilized substance. On the other hand, the overwhelming majority of template reaction found is known to be a variant of Shiff’s condensation accompanied with intra-molecular formation of water at the expense of mobile hydrogen atoms of one ligand synthon and oxygen atoms of another ligand synthon.[5] A probability of any such a template reaction is the higher, the more mobile hydrogen atoms in corresponding ligand synthon, that, in its turn, is connected with proton-donor ability of this chemical compound. Because gelatin molecules, as ampholyte and polyelectrolyte, acquire in alkaline medium the negative charge, proton-donor ability of any chemical compound immobilized in this polymer mass, becomes more considerable in comparison with proton-donor ability of this compound in water solution. Hence, template synthesis into MHF-GIM, in principle, must proceed more effectively than in solution or solid phase. It should be noted in this connection that as a result of template synthesis in MHF-GIM, supramolecular metalheterocyclic coordination compounds in which template complex (“core”) is connected with gelatin molecules by intermolecular forces, are formed.

It was noted in reviews[9,10] that character of template synthesis into MHF-GIM for a number of systems (metal ion – ligand synthones) differs considerably from character for template synthesis in conditions what is known as «traditional» (that is to say in solution and solid phase). In this connection, the given paper is short review of basic results of template reactions in the \( M^{II}-(N,S)-(N,O,S) \)-ambidentate ligand synthon – (C=O)-containing ligand synthon triple systems proceeding into MHF-GIM and collation of them with results of template reactions in the same systems in water-ethanol solutions.

### Results and Discussions

As suitable objects to give possibility more clearly to reveal such distinctions, are ambidentate ligand synthones. They have in its composition three or more number of donor centers and capable to coordinate to metal ion by various way in dependence of conditions of realization of complexing process. As ambidentate ligand synthon I, such \((N,S)-\) and \((N,O,S)-\)donoratomic organic compounds as ethanedithioamide-1,2, thiocarbamoylmethaneamide, hydrazinomethanethiohydrazide, propandithioamide-1,3, capable to coordinate to metal ion through nitrogen, sulfur and oxygen atoms, may be used:

\[
\begin{align*}
\text{H}_2\text{N-C-C-NH}_2 & \quad \text{H}_2\text{N-C-C-NH}_2 \\
\text{H}_2\text{N-HN-C-NH-NH}_2 & \quad \text{H}_2\text{N-C-CH}_2\text{-C-NH}_2 \\
\text{Hydrazinomethanethiohydrazide} & \quad \text{Propandithioamide-1,3}
\end{align*}
\]

The possible variants of coordination of these compounds to metal ion are presented in the Table 1.
Table 1. The variants of coordination of ethanedithioamide-1,2, thiocarbamoylmethaneamide, hydrazinomethane-thiohydrazide and propandithioamide-1,3 to metal ions.

<table>
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<tr>
<th>Coordination</th>
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<td>( \text{H}_2\text{N-C-C-NH}_2 )</td>
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</table>

As ligand synthon II ensuring template “stitching” of metallochelate cycles in common closed contour, chemical compounds having carbonyl group C=O, for example methanal, ethanal, propanone, ethanedial, buthanedione-2,3 and penthanedione-2,4, may be used.

The data concerning the final products of template synthesis in triple systems containing some of ligand synthones indicated, is presented in the Table 2.

<table>
<thead>
<tr>
<th>Components of triple system</th>
<th>Products of complexing processes</th>
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<tr>
<td>In solution or solid phase</td>
<td>In gelatin-immobilized matrix</td>
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Table 2. The products of complexing processes proceeding in the \( M^{II} \)-\( (N,S) \)-containing ligand synthon - \( O \)-containing ligand synthon in the solutions or solid phase and in the \( M_2[Fe(CN)_6] \)-gelatin-immobilized matrix.

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<th>Components of triple system</th>
<th>Products of complexing processes</th>
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<td>In solution or solid phase</td>
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\( M^{II} \) ethanedithioamide-1,2 methanal (\( M = \text{Co} \))
Table 2 (continuation)

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<td>1</td>
<td>M\textsuperscript{II} \ ethanedithioamide-1,2 \ propanone (M= Co)</td>
<td><img src="image1" alt="Diagram" /></td>
<td><img src="image2" alt="Diagram" /></td>
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<td>2</td>
<td>M\textsuperscript{II} \ ethanedithioamide-1,2 \ ethanedial (M= Co)</td>
<td><img src="image3" alt="Diagram" /></td>
<td><img src="image4" alt="Diagram" /></td>
</tr>
<tr>
<td>3</td>
<td>M\textsuperscript{II} \ ethanedithioamide-1,2 \ methanal (M= Ni, Cu)</td>
<td><img src="image5" alt="Diagram" /></td>
<td><img src="image6" alt="Diagram" /></td>
</tr>
<tr>
<td>4</td>
<td>M\textsuperscript{II} \ ethanedithioamide-1,2 \ ethanedial (M= Ni, Cu)</td>
<td><img src="image7" alt="Diagram" /></td>
<td><img src="image8" alt="Diagram" /></td>
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<tr>
<td>5</td>
<td>M\textsuperscript{II} \ ethanedithioamide-1,2 \ ethanal (M= Ni, Cu)</td>
<td><img src="image9" alt="Diagram" /></td>
<td><img src="image10" alt="Diagram" /></td>
</tr>
<tr>
<td>6</td>
<td>M\textsuperscript{II} \ ethanedithioamide-1,2 \ propanone (M= Ni, Cu)</td>
<td><img src="image11" alt="Diagram" /></td>
<td><img src="image12" alt="Diagram" /></td>
</tr>
<tr>
<td>7</td>
<td>M\textsuperscript{II} \ ethanedithioamide-1,2 \ butanedione-2,3 (M= Ni, Cu)</td>
<td><img src="image13" alt="Diagram" /></td>
<td><img src="image14" alt="Diagram" /></td>
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<tr>
<td>8</td>
<td>M\textsuperscript{II} \ propanedithioamide-1,3 \ methanal (M= Ni, Cu)</td>
<td><img src="image15" alt="Diagram" /></td>
<td><img src="image16" alt="Diagram" /></td>
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According to theoretical views indicated above, it may be expected that assortment of processes of template synthesis in a separately taken \( \text{M}^{II} \) – (N,S)-containing ligand synthon – carbonyl-containing ligand synthon triple system in organizing reactionary medium with preliminary entropy decrease (and, among their number, into MHF-GIM) will be more considerable than assortment of template processes in «traditional» conditions where the aforesaid decrease of \( S \) values does not take place. It should be expected correspondingly to the above that a number of metalcomplexes formed as a result of realization of template processes in organizing medium must be more considerable than a number of metallocomplexes in «non-organizing» one. The data presented in the Table 2 as it may be easily seen, are in full agreement with such a forecast, in the last resort, for triple systems containing Cu\(^{II} \) as a “template” metal ion; besides, in an availability in it of hydrazinomethanethiohydrazide, template synthesis in water-ethanol solution leads to formation of only one metallochelate whereas template synthesis into MHF-GIM leads to two or even more their number; in an availability in it of ethanedithioamide-1,2 or propanedithioamide-1,3, template synthesis in water-ethanol solution does not occur (only bis-chelate copper(II) complexes with ligand synthons indicated) whereas template synthesis into MHF-GIM takes place.\(^{11-15}\)

At the present time, quantum-chemical calculations of template complexes formed in the \( \text{M}^{II} \) – ethanedithioamide-1,2 – methanal, \( \text{M}^{II} \) – ethanedithioamide-1,2 – propanone and \( \text{M}^{II} \) – hydrazinomethanethiohydrazide – propanone (\( \text{M} = \text{Co, Ni, Cu} \)) triple systems, were carried out by us. For this purpose, B3LYP 6-31G(d) method, which is hybrid DFT method using Becke function (1988) including Slater exchange, by beginning with amendment including density gradient, and correlation function of Lee, Yang and Parr, which includes
local and non-local therms.\textsuperscript{[16]} was used by us for calculations. The energy values \( E \) were calculated according to equation (2)

\[
E = V + \langle hP \rangle + \frac{1}{2} \langle PJ(P) \rangle + \text{EX}[P] + \text{EC}[P]
\]  

(2)

where \( V \) is nuclearic energy of repulsion, \( \langle hP \rangle \) – one-electronic (kinetic + potential) energy, \( \frac{1}{2} \langle PJ(P) \rangle \) – energy of electrons repulsion, \( \text{EX}[P] \) – exchange function; \( \text{EC}[P] \) – correlation function. 6-31G(d) basic set where each inner atom orbital (AO) is described by six functions of Gauss type (GTO), valence 2s AO by three GTO, valence p-AO by one GTO, with addition of polarization d-GTO to each p-function, was used. All calculations were made with using Gaussian 98 program.\textsuperscript{[17]} Time of quantum-chemical calculations of complexes studied was from 3 to 15 months. According to experimental data presented in Table 2, (N,N,S,S)-coordination of donor centers of chelate ligand to M\textsuperscript{III} occurs in the complexes arising as a result of template synthesis in the systems indicated. Such coordination does not contradict a conception of “hard” and “soft” Pearson’s acids and bases.\textsuperscript{[18]} Among their number, for M\textsuperscript{III} – ethanedithioamide-1,2 – propanone systems, template process is described with general equation (3):

\[
\text{M}_2\text{[Fe(CN)]}_4 + 4\text{H}_2\text{N-C-CH}_3 + 4\text{OH}^- \rightarrow \text{M}_2\text{[Fe(CN)]}_4 \text{NH}_2 + 4\text{H}_2\text{N-C-CH}_3 + 4\text{OH}^- + 8\text{H}_2\text{O}
\]  

(3)

A numbering of atoms in these complexes is shown in the Figure 3; the space structures of given template complexes obtained as a result of quantum-chemical calculations, are presented in the Figures 4-6. As may be seen from the data presented, coplanar coordination of donor centers of ligand related metal ion is more preferable for Ni\textsuperscript{II} and Cu\textsuperscript{II} complexes under examination, with \( M_5 \) of basic state equal to 1 and 2, respectively. This circumstance is in a full harmony with experimental data published in\textsuperscript{[19,20]} according to which, planar structure seems most probable for given Ni\textsuperscript{II} and Cu\textsuperscript{II} complexes. For Co\textsuperscript{II} complex, however, is more preferable quasi-tetrahedral coordination with \( M_5 = 4 \). The distinctions between energies of structures having \( M_5 \) value differ from \( M_5 \) of basic state [doublet in the case of Co\textsuperscript{II}, triplet in the case of Ni\textsuperscript{II} and quartet in the case of Cu\textsuperscript{II}] are 10.2, 25.6 and 65.7 kJ/mole, respectively. The average M–N and M–S bond lengths in planar Ni\textsuperscript{II} and Cu\textsuperscript{II} complexes are 187.7 and 219.9 pm in the case of Ni\textsuperscript{II}, 203.0 and 227.5 pm in the case of Cu\textsuperscript{II}. In the Co\textsuperscript{II} complex having quasi-tetrahedral coordination, these bonds are longer than in planar complexes indicated (214.9 and 228.0 pm, respectively).

Figure 4. The space structure of cobalt(II) complex with (N,N,S,S)-coordination of donor centers of “template” ligand to M\textsuperscript{II} formed in the Co\textsuperscript{II} - ethanedithioamide-1,2 – propanone triple system: “open”, front view (A) and “shielded”, view from the side (B).
Figure 5. The space structure of nickel(II) complex with (N,N,S,S)-coordination of donor centers of “template” ligand to M\textsuperscript{II} formed in the Ni\textsuperscript{II} – ethanedithioamide-1,2 – propanone triple system: “open”, front view (A) and “shielded”, view from the side (B).

Figure 6. The space structure of copper(II) complex with (N,N,S,S)-coordination of donor centers of “template” ligand to M\textsuperscript{II} formed in the Cu\textsuperscript{II} – ethanedithioamide-1,2 – propanone triple system: “open”, front view (A) and “shielded”, view from the side (B).

It should be noted in this connection that according to data of given quantum-chemical calculations of other macrocyclic complexes containing plane N\textsubscript{2}S\textsubscript{2} chelate grouping and six-numbered additional cycles, the six-numbered cycles indicated are extremely sharply inclined to flatness of N\textsubscript{2}S\textsubscript{2} chelate groupings, too.

Conclusions

As can be seen from foregoing, template synthesis in the MHF-GIM is specific phenomenon in coordination chemistry of transition metals. It should be noted especially that at the template synthesis under such unusual conditions which take place in gelatin-immobilized matrix systems, supramolecular coordination compounds which were not been obtained up to now at template synthesis either in solution or solid phase, can be formed. Most sharply this distinction is in that case when if only one of participants of template reaction is ambidentate ligand synthon, for example, some of (N,S)-ligand synthons considered in this article. Besides, as a rule, at the template synthesis in the MHF-GIM there is formed more considerable number of coordination compounds that at complexing under “traditional” conditions. Undoubtedly, template synthesis in the MHF-GIM merits of close attention of chemists working in this specific field of chemical science. That is why, new researches need in given field to understand the nature of this phenomenon, to forecast of compositions of metalcomplexes formed and to learn to guide with it.

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The monograph is devoted to porphyrinpolymers - the unique compounds sharing properties of porphyrins and polymers. Synthesis, properties of polyporphyrins, immobilized porphyrins and coordination porphyrinpolymers and and their applications in macromolecular chemistry are considered.

Berezin B. D., Lomova T. N.  
**Dissociation Reactions of Complex Compounds.**  
Moscow: Nauka, 2007. 278 p. (in Russ.)  
ISBN 5-02-035607-7

The monograph considers the dissociation processes of complex compounds: classification, regularities and mechanisms. Special attention is given to complexes of aromatic macrocycles - porphyrins and their analogues.
Ivanovo State University of Chemical Technology invites you to take part in the VIIIth International Young Scientists School on Chemistry of Porphyrins and Related Compounds which will be held in 2009 in Ivanovo, located in the center of the Golden Ring of Russia formed by ancient Russian cities Suzdal, Vladimir, Rostov, Yaroslavl', Kostroma and Plyos on Volga. Please direct your inquiries and suggestions to the organizer of the School Prof. Oleg Golubchikov (golubch@isuct.ru) and to the secretary Dr. Tatyana Ageeva (tageeva@isuct.ru).