Homotrinuclear Complexes of [30]Trithiadodecaaza-hexaphyrine with Transition Metals: Ni(II), Cu(II) and Mn(II)

Evgeny N. Ivanov, a Olga N. Trukhina, b Oskar I. Koifman, a Mikhail K. Islyaikina®

Dedicated to Professor Tomas Torres Cebada on the occasion of his 65th birthday

*International Research Laboratory on Nanomaterials, Research Institute of Macroheterocycles, Ivanovo State University of Chemistry and Technology, 153000 Ivanovo, Russian Federation

b Depart. de Química Orgánica (C-I), Universidad Autónoma de Madrid, Cantoblanco, 28049 Madrid, Spain

® Corresponding author E-mail: islyaikin@isuct.ru

Homotrinuclear complexes were synthesized by reaction of [30]trithiadodecaaza-hexaphyrine (hemihexaphyrazine) with nickel(II), copper(II) or manganese(II) acetates in phenol. The compounds were characterized by UV-Vis, IR spectroscopy, mass-spectrometry and elemental analysis. Study of thermal behavior of manganese complex has shown high thermal stability. The structure of a cationic copper complex observed in mass-spectrum was elucidated by quantum chemistry calculations at the DFT level.

Keywords: Homotrinuclear complexes, expanded porphyrinoids, [30]trithiadodecaaza-hexaphyrine, hemihexaphyrazine.
Introduction

Since the beginning of this millennium considerable efforts have been devoted to the synthesis, structure elucidation and study of the properties of new macroheterocyclic compounds (Mc’s) with enlarged coordination cavities.[1-6] A principal aspect derived from structures of these compounds is aromaticity of central core and capability of Hückel’s rule to describe its electronic structure.[7-9] Among compounds is aromaticity of central core and applicability of Hückel’s rule to describe its electronic structure. [7-9] Among transition metal complexes based on the unsubstituted macroheterocyclic compounds, Mc’s of ABABAB-type (hemihexaphyrine, H3Hhp) containing six consecutively interlinked 1,3,4-thiadiazole (A) and isindole (B) subunits bridged by nitrogen atoms[10,11] induce a particular interest. Indeed, various substituted macroheterocyclic compounds of this type were synthesized to date[12-18] and their structures were confirmed by gas electron diffraction (GED)[19,20] and single crystal X-ray diffraction[21] methods. It was established that compounds of this type have a nonaromatic macrocyclic backbone containing 30 carbon and nitrogen atoms which form an expanded coordination cavity compared to that of porphyrins and phthalocyanines.

This extended macrocyclic system is able to bind up to three transition metal atoms.[10,11,22] Since nonsubstituted H3Hhp is only slightly soluble in organic solvents,[23] information on the metal complexes of these compounds was limited by synthesis of metal complexes of substituted hemihexaphyrines. Therefore, the aim of this work is the synthesis of transition metal complexes based on the unsubstituted H3Hhp.

Experimental

MALDI-TOF spectra of metal complexes were performed on a Bruker Reflex III instrument in Universidad Autónoma de Madrid, Spain and MALDI-TOF spectra of metal free H3Hhp on Axima Confidence, Shimadzu (Ivanovo State University of Chemistry and Technology). UV-vis spectra were recorded by a HELIOS ZETA Technology). UV-vis spectra were recorded by a HELIOS ZETA spectrophotometer (ISUCT).

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out on STA 449 F1 “Jupiter” (Netzsch, Germany) unit at a heating rate of 5 °C.min⁻¹ under atmosphere of argon-oxygen.

Quantum Chemistry Details

Quantum chemistry calculations have been carried out by the density functional theory method (DFT, B3LYP functional) with the use of 6-31G(d,p) basis set for describing the electron shells of C, N, O, S, and H atoms and an effective core pseudopotential LANL2DZ[24] for Cu atoms. Since this cationic complex is an open shell system, a formalism of UHF has been applied. The results of second derivatives calculations showed no imaginary frequencies. All calculations were carried out using the Firefly QC package,[25] which is partially based on the GAMESS (US)[26] source code. ChemCraft software[27] was applied for preparation of input data file, as well as for processing and visualization of the computed results.

Synthesis of H3Hhp (1)

A solution of phthalonitrile (0.64 g, 5.0 mmol) and 2,5-diamino-1,3,4-thiadiazole (0.58 g, 5.0 mmol) in ethylene glycol (150 ml) was stirred at reflux for 24 h. After cooling to room temperature, the reaction mixture was poured into water (100 ml). The precipitate was filtered, triturated repeatedly with hot solvents: DMF, water, methanol, acetone and hexane. Yield 23 %. IR (KBr) v cm⁻¹: 3420, 2969, 2926, 2843, 2228, 1624, 1467, 1404, 1307, 1217, 1092, 1041, 852, 804, 701. UV-Vis (CH3Cl): ε = 0.369·10⁴ mol/l λ max nm (λ, u.abs.): 391 (0.35), 411 (0.32), 464 (0.086), 501 (0.06). MS (MALDI-TOF, α-cyano-4-hydroxycinnamic acid) m/z: 681.8 [M+H]+. Calcd for [C16_H16_N6_S3]+: EM=681.7. Found, %: C, 52.85; H, 2.22; N, 30.82; S, 14.11. Calcd. for [C16_H16_N6_S3]+, %: C, 52.13; H, 2.29; N, 31.17; S, 13.92.

Synthesis of [30]Trithiadodecaazahexaphyrine Complexes (2-4)

General procedure: The corresponding metal acetate (0.6 mmol) was added to a solution of H3Hhp (0.14 mmol) in phenol (5 g) at 45 °C. Then the reaction mixture was stirred for 5 h at 100 °C and after that was poured into 150 ml of hot water. A precipitate was filtered and vigorously washed with hot water, DMF, acetone, hexane and dried under vacuum at 60 °C for 4 h. 2-4 are dark brown powders which are insoluble in common organic solvents, very low soluble in DMF and pyridine, soluble in phenol.

2. Cu-complex, was obtained following the general procedure using 0.139 g (0.55 mmol) of Cu(CH3COO)2·4H2O and 0.1 g (0.14 mmol) of H3Hhp. Yield 42 %. UV-Vis (phenol-methanol 1:1 v/v, ε=0.678·10⁴ mol/l) λ max nm (A, u.abs.): 386 (0.37), 421 (0.39), 452 (0.97). IR (KBr) ν cm⁻¹: 3435, 2920, 1591, 1510, 1430, 1290, 1190, 1100, 819, 498. MS (MALDI-TOF, dithranol) m/z: 869.9 calc. for [C30_H24_Cu_N15_S3]+: EM=868.8 [H3Hhp+3Cu]+; 884.9, calc. for [C30_H24_{Cu}_N15_S3]+: EM=884.3 [H3Hhp+3Cu]+; Found, %: C, 48.33; H, 1.98; N, 24.27; S, 10.05. Calcd. for C30_H24 Cu_N15 S3, %: C, 41.45; H, 1.39; N, 24.17; S, 11.06.

3. Ni-complex, was obtained following the general procedure using 0.136 g (0.55 mmol) of Ni(CH3COO)2·4H2O and 0.1 g (0.14 mmol) of H3Hhp. Yield 61 %. IR (KBr) ν cm⁻¹: 3431, 2922, 2853, 1619, 1537, 1430, 1060, 781 UV-Vis (phenol-methanol 1:1 v/v, ε=0.690·10⁴ mol/l) λ max nm (A, u.abs.): 364 (0.58), 450 (0.97), 524 (0.39). MS (MALDI-TOF, dithranol) m/z: 853.9, calc. for [C30_H24_{Ni}_N15_S3]+: EM=853.9 [H3Hhp+3Ni]+; 869.9, calc. for [C30_H24_{Ni}_N15_S3]+: EM=869.9 [H3Hhp+Ni]+; Found, %: C, 48.33; H, 1.89; N, 24.27; S, 11.05. Calcd. for C30_H24 Cu_N15 S3, %: C, 42.15; H, 1.42; N, 24.58; S, 11.25.

4. Mn-complex, was obtained following the general procedure using 0.162 g (0.7 mmol) of Mn(CH3COO)2·4H2O and 0.15 g (0.22 mmol) of H3Hhp. Yield 20 %. IR (KBr) ν cm⁻¹: 3448, 3287, 2914, 1628, 1515, 1500, 1468, 1406, 1319, 1300, 1219, 1041, 852, 780, 732, 703, 636, 486, 437. UV-Vis (phenol-methanol 1:1 v/v, ε=0.369·10⁴ mol/l) λ max nm (A, u.abs.): 416 (0.39), 433 (0.38), 540 (0.21). MS (MALDI-TOF, dithranol) m/z: 842.0. Calcd. for [C30_H24_{Mn}_N15_S3]+: EM=842.9 [H3Hhp+3Mn]+. Found, %: C, 43.20; H, 1.93; N, 24.82; S, 10.87. Calcd. for C30_H24_{Mn}_N15_S3, %: C, 42.72; H, 1.43; N, 24.91; S, 11.40.

Results and Discussion

One of the most prevalent synthetic methods to gain access to macroheterocyclic compounds is reaction of substituted phthalonitriles or their functional derivatives with aromatic diamines in appropriate solvents. As usual, the reaction of 1,3-diamines in the condensation results in four membered macroheterocyclic compounds of ABAB-type formation.[24] However, utilization of 2,5-diamino-1,3,4-thiadiazole as starting material led to a new class of macroheterocyclic compounds of ABAB-type formation.[10,11] Herein, a nonsubstituted H3Hhp was obtained by condensation of phthalonitrile and 2,5-diamino-1,3,4-thiadiazole in

Homotrinuclear Complexes of [30]Trithiadodecaazahexaphyrine with Transition Metals
phenol.\textsuperscript{[23]} To avoid the use of this highly toxic solvent, we have established a new synthetic protocol, employing ethylene glycol as a reaction medium (Scheme 1). Thus, we found out that compound $\text{H}_3\text{Hhp}$ can be obtained in 23\% yield in refluxing ethylene glycol in 26 h.\textsuperscript{[23]} The product obtained was characterized by MALDI TOF, IR, UV-Vis spectroscopy, and elemental analysis, and its spectroscopic parameters agree well with those reported elsewhere.\textsuperscript{[21,23]}

However, efficient metallation of 1 could be only achieved in phenol as a solvent, employing acetates of copper(II), nickel(II) and manganese(II) in homogenous medium (Scheme 1), where reagents are present in sufficiently high concentrations. Following the same procedure, metal complexes 2–4 were prepared. During synthesis, the characteristic color change of the reaction solution took place, with color turning from orange to brown. It has been found that complexes formation was finished within 4 hours in all cases.

Then hot dark brown mass was poured into water and vigorously washed with hot water to eliminate phenol. After that the precipitates were carefully washed by hot solvents: DMF, acetone, hexane and the precipitates were dried under vacuum. The yields of 2–4 are in range of 20–61\% which may be explained by loss of products during phenol elimination and their different solubility in DMF.

Metallocomplexes 2–4 were characterized by MS (MALDI-TOF), UV-vis, IR data and elemental analysis. Mass spectrum of Cu-complex 2 displays a low intensity peak at 868.9 Da which corresponds to $[\text{Hhp+3Cu}]^+$ and major peak at 884.9 Da of $[\text{Hhp+3Cu+O}]^+$ (Figure 1). Isotope distributions of the signals are in good agreement with those derived from theoretical calculations. It’s worthy to note that

Scheme 1. Synthesis of hemihexaphyrazine 1 and its homotrinuclear complexes with Cu(II) 2, Ni(II) 3, Mn(II) 4: \textit{i} – ethylene glycol, reflux, 26 h; \textit{ii} – phenol, 5 h at 100 °C.

Figure 1. MALDI-TOF spectrum (dithranol) of 2. Insets: isotopic distributions of the main peak at 884.9 Da (above); calculated isotopic pattern for $[\text{Hhp+3Cu+O}]^+$ (below).

no signals corresponding to metal free H₃Hhp or complexes of 1:1 or 2:1 structures were detected in the spectrum.

The formation of the [Hhp+3Cu+O]⁺ detected in the MS may occur during both synthesis and MALDI-TOF experiment. This phenomenon is not clear yet and will be under consideration in the future. Since this cationic complex was found to be stable in gas phase, theoretical method was used to elucidate its structure. It was assumed that oxygen atom can be located in the center of molecule. Full geometry optimization carried out at DFT level led to a plane structure corresponding to the minimum of potential energy surface with symmetry near to D₃h point group (Figure 2).

Since 2–4 are very insoluble in common organic solvents, their UV-Vis spectra were recorded in phenol–methanol mixture (1:1 v/v) (Figure 3). The spectra of metal complexes are significantly different from that of the metal-free 1. Broadened absorption bands of different intensity appear at 350–550 nm and can be attributed to electron transfers transitions with participation of p-orbitals of ligand and d-electronic shells of metal. It’s worthy to note that there is a strong influence of metal upon electronic structure as reflected in UV-vis spectra of these complexes. The bathochromic shifts of absorption are increased in row Cu, Mn, Ni, what is just opposite to those observed in corresponding complexes of phthiocyanine. [20-32]

A signal at 3220 cm⁻¹ corresponding to vibrations of inner N-H bonds in IR spectrum of metal-free compound 1 disappears upon complexation (Figure 4). The vibrations of -C=N-bonds, which appear as strong bands at 1624 cm⁻¹ in spectrum of 1, are shifted in lower field to 1510 cm⁻¹ during complexation.

**TG and DSC Analysis**

Thermal behavior of the obtained complexes were studied via investigation of the manganese complex 4 in argon-oxygen atmosphere. The TG analysis of 4 shows a two-step degradation process (Figure 5). After initial loss of the moisture at 70–100 °C, the pyrolysis of the complex with a loss of weight of 49.5 % takes place in the range of 386–501 °C. An intense elimination of H₂O, CO, CO₂, NO, NO₂, SO₂ synchronously detected by mass-spectrometer shows that a profound oxidation of macrocyclic core takes place in this temperature range. Early it was communicated [23] that metal-free 1 is decomposed at 460 to 510 °C. Hence introduction of three atoms of manganese into coordination cavity of 1 led to decrease in its thermostability.

**Conclusion**

Homotrinuclear complexes of [30]trithiadodecaaza-hexaphyrine (2–4) were synthesized by interaction of H₃Hhp with nickel(II), copper(II) or manganese(II) acetates in phenol. All compounds were characterized by UV-Vis, IR spectroscopy, mass-spectrometry and elemental analysis. A complex of the formula [Hhp+3Cu+O]⁺ was detected in the mass-spectrum and elucidated by quantum chemistry calculations at DFT level. TG and DSC analysis of manganese complex 4 showed its high thermal stability.
Acknowledgements. This work was financially supported by Russian Science Foundation (project № 14-23-00204).

References


Received 30.09.2016
Accepted 16.10.2016

Figure 5. TG and DSC curves for 4 with heating rate of 5 °C·min⁻¹ in argon–oxygen atmosphere.