



Synthesis, characterization and crystal structure of dinuclear cobalt(II) macrocyclic complexes, containing thiocyanate and azide groups



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ABSTRACT

Dinuclear cobalt(II) complexes with II–II oxidation state of 20-membered N₄, binucleating macrocycle derived by a cyclic [2 + 2] condensation of isophthaldialdehyde with 1,3-diaminopropane have been synthesised and characterised by analytical, spectroscopic and X-ray diffraction methods. The solid and solution states investigations show that overall structures and geometries of the complexes are very similar. The molecular structure of [Co₂L(OMe)(NCS)₃], which has been determined by single crystal X-ray diffraction, indicate that the cobalt(II) ions have a distorted trigonal bipyramidal environment, with methoxy bridge in an equatorial positions and N-bound thiocyanate ion in axial positions to metals. Also, the structure of [Co₂L(OMe)(NCS)₃] complex was optimized using density functional theory for all of the possible spin states of the complex. The results indicated that septet spin state is the most stable form of the complex.

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1. Introduction

Transition dinuclear metal complexes and macrocyclic ligands capable of yielding them are the subject of very extensive investigations due to the broad range of their structural and magnetic properties [1–8]. This type of compounds have been widely explored as structural models to understand the reactivity changes caused by the proximity of the two metals, and also to understand the reactivity of metalloenzymes which require two metal centres located at specific distances to accomplish their biological function [9–15]. Also dinuclear macrocyclic complexes have been used successfully for the recognition and assembly of external species of different natures, such as inorganic or organic substrates [16–22]. Recently, we have added isophthaldialdehyde to the 1,3-diaminopropane used in Schiff-base and polyaza macrocyclic chemistry [23–25] and, as a consequence, dicopper and dicobalt complexes with special electronic properties have been reported. The halide and hydroxyl moieties bridge the metal ions in these macrocyclic complexes and are well known to control metal...metal centers, thus these complexes can possess diverse magnetic and biological properties. The pseudo-halides N₃[−] and NCS[−] are also known to coordinate to metals as bridging ligands and link a pair of metal

centres in either an end-on (μ-1,1) or a side-on (μ-1,3) bonded fashion [26,27].

In recent years density functional theory (DFT) methods have been widely used to study the structural and electronic properties of di-nuclear complexes due to its reliable results with reasonable computational cost in comparison with higher level ab initio methods [28–30]. Martinho et al. studied reaction of ([Fe^{III}(μ-O)(μ-O₂H₃)(L₂)]³⁺, L = tris(3,5-dimethyl-4-methoxyppyridil-2-methyl) amine) with H₂O₂ to form a diiron(IV) intermediate using Mößbauer spectroscopy and DFT. Their results exhibited that two Fe^{IV} sites are ferromagnetically coupled [28]. Kal et al. reported synthesis of Mn₂LAc⁺, and Zn₂LAc⁺ complexes where L is a tetrakis-Schiff base macrocycle with an N₆O₂ coordination structure. Also, they used DFT calculations to confirm their experimental results and observed a weak anti-ferromagnetic coupling between Mn²⁺ ions [29]. Maxwell et al. studied cleavage of three dinuclear Zn^{II} complexes as models of DNA and RNA chains by DFT method and found their results in good agreement with experimental data [30].

As a part of our ongoing research on the design and synthesis of new dinuclear cobalt(II) complexes, incorporating the pseudo-halides N₃[−] and NCS[−] into macrocycle in this way is a significant step forward in the development of new binuclear cobalt(II) complexes. Moreover, density functional theory (DFT) method will be used in order to review of experimental results.

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2. Experimental

2.1. Materials

Solvents were dried and purified before being used according to the usual methods [31]. Co_2 salt was synthesized according to published procedures [32]. Other reagents used in these studies were obtained from commercial sources and were used as received.

2.2. Physical measurements

Elemental analyses were carried out using an Elementar Vario EL III instrument. IR spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer. Electronic spectra were recorded on a Shimadzu, UV-1650 PC spectrophotometer from solutions in acetonitrile. Conductivity data were measured in acetonitrile on a Metrohem 712 conductometer instrument.

2.3. X-ray crystallography

Single crystals of $[\text{Co}_2\text{L}(\text{OMe})(\text{NCS})_3]$ complex were obtained from acetonitrile/methanol (1:2) solution by slow evaporation. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares procedures using the SHELXL97 program package [33]. Data were reduced and corrected for absorption using SADABS [34].

The data set was collected on a CCD detector Smart6000 diffractometer with graphite-monochromated Mo $K\alpha$ (0.71073 Å) at 140 (2) K: Molecular formula $\text{C}_{26}\text{H}_{35}\text{Co}_2\text{N}_7\text{OS}_3$, M 675.65, orthorhombic, space group $Pbca$, $a = 16.4072(4)$ Å, $b = 15.2770(4)$ Å, $c = 23.7810(6)$ Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, $V = 5960.8(3)$ Å³, $Z = 8$, $D_{\text{calc}} = 1.506$ Mg/m³, absorption coefficient $\mu = 1.356$ mm⁻¹, crystal dimensions: $0.20 \times 0.19 \times 0.10$ (mm), $F(000)$: 2800, θ range for data collection: $1.71\text{--}33.58$ ($^\circ$), index ranges: $-25 \leq h \leq 25$, $-22 \leq k \leq 23$, $-35 \leq l \leq 35$, reflections collected/unique: 88434, independent reflections: 11201 [$R_{\text{int}} = 0.0296$], refinement method: Full-matrix least-squares on F^2 , Data/parameters/restraints: 11201/0/492, goodness-of-fit on F^2 : 1.048, final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0396$, $wR_2 = 0.0945$, R indices (all data): $R_1 = 0.0512$, $wR_2 = 0.0997$, weighting scheme: $w = 1/[(\sigma F_o)^2 + (0.0419 * P)^2 + 3.1902 * P]$ where $P = (F_o^2 + 2F_c^2)/3$, largest difference peak and hole ($e/\text{Å}^3$): 0.855 and -0.902 .

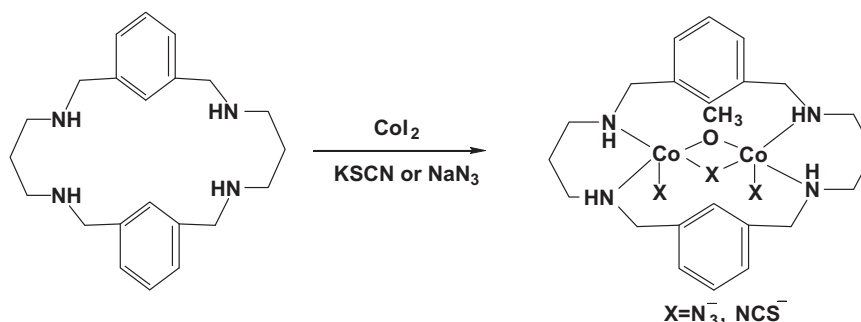
$$R_1 = [\sum ||F_o| - |F_c||] / \sum |F_o| \text{ (based on } F)$$

$$wR_2 = [(\sum w(|F_o^2 - F_c^2|)^2) / (\sum w(F_o^2)^2)]^{1/2} \text{ (based on } F^2)$$

2.4. Syntheses

2.4.1. Macrocycle (L)

The macrocycle was prepared in a way similar to the reported method [25] using isophthaldialdehyde and 1,3-diaminopropane.



Scheme 1. Synthesis and structure representation of compounds **1** and **2**.

2.4.2. $[\text{Co}_2\text{L}(\text{OMe})(\text{NCS})_3]$ (**1**)

2 equiv. of Co_2 (1 mmol, 0.3127 g) dissolved in methanol (10 cm^3) were added to a solution of macrocycle L (0.5 mmol, 0.1765 g) in methanol (10 cm^3) and left stirring overnight. A solution of potassium thiocyanate (3 mmol, 0.2949 g) in acetonitrile (40 cm^3) was added to the stirred solution. The mixture was stirred for 2 h at room temperature to give a blue solution. The blue crystalline product was separated by slow evaporation.

Yield: 15%. Selected FT-IR data, ν (cm^{-1}): 3237s, 3025w, 2927m, 2878w, 2850w, 2072s, 2013s, 1646s, 1459s. Anal. Calc. for $\text{C}_{26}\text{H}_{35}\text{Co}_2\text{N}_7\text{OS}_3$: C, 46.22; H, 5.22; N, 14.51. Found: C, 46.43; H, 5.24; N, 14.58%. Electronic spectra in CH_3CN solution (λ , nm) (ϵ , $\text{M}^{-1} \text{ cm}^{-1}$): 558(138), 589(565), 626(982), 910(106). Electronic spectra in solid state (λ , nm): 575, 768, 830, 882, 909, 937, 984, 1049. Molar conductivity (CH_3CN solution): $\Lambda_m = 146 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

2.4.3. $[\text{Co}_2\text{L}(\text{OMe})(\text{N}_3)_3]$ (**2**)

This complex was prepared by a similar method to that of $[\text{Co}_2\text{L}(\text{OMe})(\text{NCS})_3]$ using macrocycle L (0.5 mmol, 0.1765 g), Co_2 (1 mmol, 0.3127 g) and sodium azide (3 mmol, 0.1990 g). In this case, a dark blue solution was evaporated at room temperature to give dark blue crystalline product, unfortunately all attempts to prepare suitable single crystal for X-ray diffraction analysis failed. Yield: 10%. Selected FT-IR data, ν (cm^{-1}): 3231m, 3038w, 2950m, 2930m, 2867m, 2365m, 2117s, 2052s, 1627m, 1470m. Anal. Calc. for $\text{C}_{26}\text{H}_{35}\text{Co}_2\text{N}_{10}\text{O}$: C, 50.37; H, 5.78; N, 22.57. Found: C, 50.25; H, 5.68; N, 22.54%. Electronic spectra in CH_3CN solution (λ , nm) (ϵ , $\text{M}^{-1} \text{ cm}^{-1}$): 512(127), 546(586), 594(933), 863(109). Electronic spectra in solid state (λ , nm): 570, 777, 648, 833, 891, 905, 943, 983, 1037. Molar conductivity (CH_3CN solution): $\Lambda_m = 137 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

2.5. Computational method

The gas phase geometry of the $[\text{Co}_2\text{L}(\text{OMe})(\text{NCS})_3]$ complex was optimized by B3LYP hybrid-DFT functional and LANL2DZ basis set containing effective core potentials (ECPs) for cobalt and sulfur atoms which lead to lower computational cost of the calculations [35–37]. All of the calculations were performed by Firefly quantum chemistry program which is partially based on GAMESS (US) source code [38,39]. The spin multiplicities of 1, 3, 5, and 7 were considered in optimization calculations.

3. Results and discussion

3.1. Synthesis and characterization

The macrocyclic complexes $[\text{Co}_2\text{L}(\text{OMe})(\text{NCS})_3]$ and $[\text{Co}_2\text{L}(\text{OMe})(\text{N}_3)_3]$ have been prepared in poor yields by direct reaction of the macrocycle with a stoichiometric amount of Co_2 and subsequent reaction with an excess solution of potassium thiocyanate or

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