Polyhedron 33 (2012) 410–416

Contents lists available at SciVerse ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Synthesis of cobalt(III) complexes with new oxime-containing Schiff base ligands and metal–ligand coordination in solution

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ARTICLE INFO

Article history:
Received 17 October 2011
Accepted 2 December 2011
Available online 21 December 2011

Keywords:
Oxime-containing Schiff base ligands
Cobalt(III) complexes
Synthesis
Cobalt(II)
Solution equilibria

ABSTRACT

Cobalt(III) complexes with new oxime-containing Schiff base ligands: 2-hydroxyimino-*N*′-[1-(2-pyridyl)ethylidene]propanohydrazone (Hpop) and 2-hydroxyimino-*N*′-[(pyridine-2-yl)methylidene]propanohydrazone (Hpoa) have been investigated. The crystal and the molecular structure of 2[Co(pop)$_2$]Br·3CH$_3$OH·0.5H$_2$O (**1**) has been determined using single-crystal X-ray diffraction methods. Electrospray ionization mass spectrometry confirmed the presence of polynuclear complexes with Co(II). The potentiometric and spectrophotometric results in 10/90 (v/v) DMSO/water solution reveal that both of the oxime-containing Schiff base ligands show a very high efficacy in the coordination of Co(II) ions. As it has been indicated, the difference between the two ligands in their complexing ability may be attributed to the presence of the methyl group in Hpop and by the steric interaction during chelate formation. The experiments in solution were carried out under an inert atmosphere since in both cases the complexes are capable of dioxygen uptake, followed by irreversible oxidation to Co(III) complexes.

1. Introduction

The interest in oxime-containing Schiff base compounds (Scheme 1) is still increasing due to their implication in self-assembled polymetallic grid structures with Cu(II), Ni(II) and Mn(II) [1,2]. The relatively easy-to-prepare non-symmetric ligand strand provides two distinct donor compartments: a tridentate {N$_2$O} site and a bidentate {NO} site.

It was shown in the previously reported molecular grids with Ni(II), Mn(II) and Cu(II) that the presence of labile sites in the ligands, such as the pyridine nitrogen, hydrazone N atom and oxime O atom, brings about unique features of the coordination sphere [3,4]. In addition, for the Cu(II) molecular grids, significant ferromagnetic coupling has been observed [5,6].

In the present work we report the synthesis, structure and investigation of a Co(III) complex with one of the two oxime-containing Schiff base ligands (Hpop) along with potentiometric and spectrophotometric studies of complex formation in mixed DMSO/water solution under an inert atmosphere for both ligands (Hpop and Hpoa). The presence of labile coordination sites in these ligands may potentially be used to obtain Co(III) complexes of higher nuclearity.

2. Experimental

2.1. Materials and general procedures

All reagents and solvents were purchased from commercial sources and were used as received. Both the Hpop and Hpoa ligands were synthesized according to a published procedure [7] and [8], respectively.

2.2. Preparation, mass spectrometric and spectroscopic characterization of the complex

CoBr$_2$·6H$_2$O (0.0163 g, 0.5 mmol) was dissolved in 5 ml of methanol and added to Hpop (0.022 g, 1 mmol, dissolved in 10 ml of methanol). The obtained mixture was stirred at 50 °C for 30 min. Subsequently the clear brown solution was filtered off and set aside for crystallization at room temperature. Dark red single crystals of 2[Co(pop)$_2$]Br·3CH$_3$OH·0.5H$_2$O were obtained in 72 h. Yield: 65%. *Anal.* Calc. for CoC$_{22}$N$_8$O$_6$H$_{30}$Br: C, 41.20; H, 4.71; N, 17.47; Co, 9.19. Found: C, 41.28; H, 4.83; N, 17.34; Co, 9.12%. ESI-MS, *m*/*z* (%): 497.0450 (100), $\{[Co(pop)_2]\}^+$; 831.09 (100), $\{[Co_3(pop)_3] + 2e^-\}^+$. IR (cm^{-1}): 1590 ν(C═O, amide I), 1040, 900 ν(N–O, oxime).

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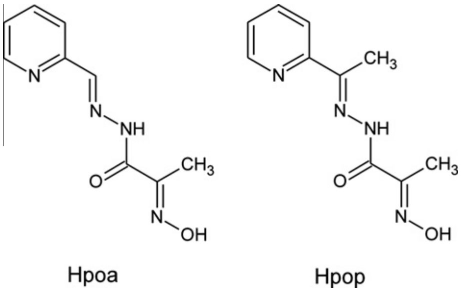
doi:10.1016/j.poly.2011.12.011



Scheme 1. Structure of the ligands used.

2.3. Solid-state X-ray studies

Single crystals of 2[Co(pop)$_2$]Br·3CH$_3$OH·0.5H$_2$O suitable for X-ray crystallography were grown by slow evaporation of a methanol solution at room temperature. Diffraction data for a single red crystal (0.22 × 0.17 × 0.09 mm) were collected at 100(2) K on a Bruker KAPPA APEX II DUO CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Triclinic, space group $P\bar{1}$, a = 11.5517(3) Å, b = 14.5163(4) Å, c = 16.0027(4) Å, α = 93.0890(10)°, β = 97.6010(10)°, γ = 92.2300(10)°, V = 2653.14(12) Å^3, Z = 2, F(000) = 1286. Experimental data sets were collected by the ω–φ-scans method with κ-offsets and covered the full Ewald sphere, $\theta_{\min}$ = 1.78° and $\theta_{\max}$ = 28.28°, 54490 measured reflections of which 13177 were unique, 694 parameters, R_1 = 0.0519, wR_2 = 0.0747, GOF = 1.016. Maximum/minimum residual electron density 0.76/−0.63 e/Å^3. Initial intensities were integrated and corrected for Lorentz and polarization effects with the SAINT program [9]. Absorption corrections were made semi-empirically with the SADABS program [10]. The structure was solved by direct methods using SHELXS-97 [11] and refined by full-matrix least squares on F^2 using the SHELXL-97 software [12].

One of the hydrogen atoms of the water molecule was located on an inversion center. The oxygen atom and the second hydrogen atom were disordered over two sites with equal occupancies. The H$_2$O and OH hydrogen atoms were located from the difference Fourier map but constrained to ride on their parent atom, with U_{iso} = 1.5 U_{eq} (parent atom). Other hydrogen atoms were positioned geometrically and were also constrained to ride on their parent atoms, with C–H = 0.95–0.98 Å, and U_{iso} = 1.2–1.5 U_{eq} (parent atom). The highest peak is located 0.76 Å from the atom Br2 and the deepest hole is located 0.63 Å from atom Br2.

2.4. Measurement procedures in solution

Potentiometric equilibria studies were carried out with a Molspin automatic titration kit with a combined microelectrode Russell CMAWL/4/5/S7. All the experiments were carried out at a constant temperature of 25.0 ± 0.1 °C. The ligand (insoluble in water) was initially dissolved in DMSO (10% v/v) and then a 10 ml flask was filled up with an aqueous solution containing HNO$_3$ in excess, KNO$_3$ and in the titrations in the presence of the metal also with Co(NO$_3$)$_2$. Then the ionic strength of the final solution was 0.1 (KNO$_3$). The protonation and formation constants were determined by pH-metric titrations of 4.0 cm^3 samples. Alkali (0.1 M NaOH carbonate-free, Malinckrodt Baker B.V.) was added from a 0.500 cm^3 calibrated micro syringe The measurement cell was daily calibrated with 0.1 M NaOH in the −log [H$^+$] scale by titration of 0.005 M HNO$_3$ in 10/90 (v/v) DMSO/water solution (containing KNO$_3$ up to I = 0.1). Overall concentration formation constants: $\beta_{\mathrm{mlh}} = [\mathrm{M_mL_lH_h}]/[\mathrm{M}]^m[\mathrm{L}]^l[\mathrm{H}]^h$ were calculated from at least three titration files by SUPERQUAD [13] and then HYPERQUAD 2008 [14]. The total concentration of the ligand in each sample amounted to 2.0 × 10^{-3} M. The metal–ligand interaction was studied at ligand-to-metal ratios of 1:1, 2:1 and 4:1. Co(NO$_3$)$_2$ p.a. of POCh Gliwice was used – the standard solution was titrated with the disodium salt of EDTA in the presence of murexide.

The UV–Vis absorption spectra under an oxygen-free atmosphere (argon) were recorded on a Cary 50 Bio spectrophotometer, slit width 1.5 nm, equipped with a fiber-optic device. Thanks to this device it was possible to investigate the equilibrium systems spectrophotometrically, simultaneously with the potentiometric measurements. The fiber-optic probe of 5 mm (which corresponds to a pathlength of 1 cm) was dipped directly into the titration vessel (initial volume 25.0 cm^3, total cobalt concentration 5.0 × 10^{-5} or 1.0 × 10^{-4} M and owing to optimum absorbance measurements, ligand:metal ratio 2:1, temperature 25.0 ± 0.1 °C). Because of the highly disturbing absorption of the nitrate ion at ca. 300 nm, the UV experiments were carried out mainly in perchlorate medium (electrolyte NaClO$_4$). The ionic strength in the aqueous phase was 0.5, i.e. higher than in the solely potentiometric measurements, so as to avoid the undesired dilution of samples during titration with 0.1 M NaOH. The used alkali (0.5 M NaOH carbonate-free, Malinckrodt Baker B.V.) was added from a 0.250 cm^3 calibrated micro syringe. After each base addition, the pH and EMF were controlled by the Molspin titrator with a combined InLab Semi-Micro (METTLER TOLEDO) electrode. A time delay was given to equilibrate the system. After each point or set of points, a pause was made and the spectrum was recorded at a slow scan rate (300 nm/min). After the collection of each curve, new aliquots of base were added and the procedure repeated. It was therefore possible to collect a spectrum at each titration point or at each chosen pH. The molar absorbances of species have been calculated after deconvolution by HypSpec (part of the Hyperquad 2008 suite, Protonic Software).

Caution! Perchlorate salts are potentially explosive and were handled only in small quantities with care.

2.5. Computational details

The optimized geometries of the ligands and their mononuclear unprotonated and monoprotonated complexes with cobalt were calculated at the DFT level using the M06-2X functional [17] expressed in the 6-311+G(d,p) basis set [18], as implemented in the GAUSSIAN09 package.[19] Default convergence criteria were used. Vibrational analysis was performed to confirm that the optimized structures correspond to stationary points (3n−6 real vibrations) and to calculate the Gibbs free energies (at 298.16 K). A zero-point energy correction was included.

3. Results and discussion

3.1. Description of the structure

The unit cell in the reported structure contains two crystallographically independent complex cations, [Co(pop)$_2$]$^+$, two Br$^-$ anions, solvate methanol and water molecules, which form an extensive system of H-bonds linking the elements of the structure together. A view of the molecule and the numbering scheme for 2[Co(pop)$_2$]Br·3CH$_3$OH·0.5H$_2$O is shown in Fig. 1 and selected bond lengths and angles are given in Table 1. The complex adopts a slightly distorted octahedral geometry. The central Co atom is coordinated by four nitrogen atoms of two pyridine cycles and two azomethine groups, and by two oxygen atoms of the hydrazone groups. The ligands are ionized to the anionic form due to deprotonation of the hydrazone H-atom, and are coordinated in a tridentate {N,N′,O}-bis(chelate) fashion, thus forming two five-membered chelate rings. The Co–N (1.850(2)–1.925(2) Å) and