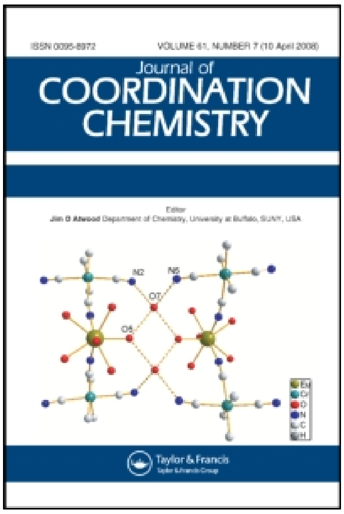

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Synthesis, characterization, electrochemical and crystal structure investigation of bis(2-((2-aminoethylimino)methyl)-6-methoxyphenolato) cobalt(III)

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Synthesis, characterization, electrochemical and crystal structure investigation of bis(2-((2-aminoethylimino) methyl)-6-methoxyphenolato) cobalt(III)

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The mononuclear cobalt(III) complex $[Co(L)_2]Cl \cdot H_2O$ (1) (where L is $H_2N(CH_2)_2N{=}CC_6H_3(OMe)(O^-)$) has been prepared and characterized by IR, UV-Vis spectroscopy, conductivity measurements, elemental analysis, TGA, cyclic voltammetry and an X-ray structure determination. The cobalt(III) coordination sphere in [Co(L)2] is *cis*-CoN_4O_2 with the NNO ligands. Electrochemical studies of **1** using cyclic voltammetry indicate an irreversible cathodic peak (E_{pc}, ca -0.60 V) corresponding to reduction of cobalt(III) to cobalt(II).

Keywords: Cobalt(III) complex; Schiff base; Electrochemistry; Crystal structure

1. Introduction

Research on design and synthesis of mono- and polynuclear coordination compounds of cobalt in its varied oxidation levels continues unabated [1]. In bioinorganic chemistry, cobalt Schiff-base complexes are synthetic models for investigation of similar sites in metallo-proteins and metallo-enzymes [2]. Exploiting the various coordination environments around the metal center, different geometries may be accessed using varied organic blockers and bridging units. Cobalt permits a wide range of symmetries and coordination numbers in its cobalt(III) complexes and exhibits higher antiviral and antimicrobial activities in biological systems [3].

Bis-NNO-chelate complexes of tridentate Schiff bases with Co(II) were first prepared by Sacconi *et al.* [4], and cationic complexes of Co(III) and Fe(III) derived from an o-hydroxyarylketone and diamine were synthesized by a template method [5]. Co(II) complexes are oxidized to Co(III) derivatives depending on the compartmental ligand; in some cases simple air oxidation is sufficient to convert Co(II) halides into Co(III)

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complexes [6]. The Fe(III) complexes exhibited spin-crossover behavior. Kinetically inert Co(III) compounds can be converted into kinetically labile Co(II) derivatives in reducing biological environments and providing the means for delivery of NNO-donor ligands, *e.g.* some cytotoxins, to specific locations [7].

Here we report the synthesis, characterization, crystal structure, electrochemical and spectroscopic studies of a bis-NNO-chelate cobalt complex. We have successfully isolated the cobalt(III) mononuclear complex prepared by stirring a mixture of mono Schiff-base ligand and cobalt chloride in absolute ethanol.

2. Experimental

All chemicals were reagent grade and used as received if not otherwise indicated. Ethylenediamine and $CoCl_2 \cdot 6H_2O$ were obtained from Aldrich. Solvents were purified by standard methods [8].

2.1. *Physical measurements and methods*

Elemental analyses (carbon, hydrogen and nitrogen) were performed on a Carlo-Erba model DP 200 instrument.

FT-IR spectra were recorded using KBr discs (4000–400 cm^{-1}) on Bruker Tensor 27 instruments. Electronic spectra in the 200–900 nm range were obtained on a Shimadzu UV-265 FW spectrophotometer and quartz cells of 1.00 cm path length, using 1×10^{-5} M solutions in ethanol. Thermogravimetric analyses were obtained with a STA 409 PC analyzer in air and a heating rate of 10°C/min. The molar conductance in 10^{-3} $mol \cdot dm^{-3}$ ethanol solution was measured using a Global DCM-900 digital conductivity meter. Melting points were taken using a X-4 apparatus without correction.

Cyclic voltammograms were performed on 1×10^{-3} M solutions in ethanol using an CHI660B. All solutions were deoxygenated by passing a stream of N_2 (99.9% pure) into the solution for at least 10 min prior to recording the voltammogram. All potentials reported herein were measured at room temperature and referenced to the saturated Ag/AgCl electrode as an internal standard. A platinum disc with a diameter of 3 mm was used as the working electrode and a platinum wire was used as counter electrode. Before each experiment the working electrode was rinsed thoroughly with distilled water and acetone. TEAP (tetraethylammonium-perchlorate, 0.1 M solution in ethanol) was used as the supporting electrolyte. Scan speeds of 50–350 $mV\,s^{-1}$ were employed.

2.2. *Synthesis of Schiff-base ligand*

Schiff-base ligand HL was prepared similar to the literature [9], as the following general method: To the vigorously stirred and cooled dilute solution ($T = 10°C$) of ethylenediamine (20 mmol) in absolute ethanol (100 mL) was added dropwise a cooled solution of o-vanilline (15 mmol) in absolute ethanol (80 mL). After the addition was complete, the mixture was stirred for 10 min and then refluxed for 2 h. The resulting solution was evaporated under vacuum to remove most of the solvent. The precipitated

Schiff base was filtered and recrystallized from hot ethanol. Yield: 40%, color: yellow, m.p. 60°C. Elemental Anal. found (%, calc.) for $C_{10}H_{14}N_2O_2$ (HL): C 61.63 (61.84), H 7.53 (7.47), N 14.37 (14.42).

FT-IR (KBr, cm^{-1}): 3441 [m (OH)], 2932 [w (CH_3)], 2848 [w (CH_2)], 2662 [m (O–H–N)], 1632 [s (CH=N)], 1295 [w (C–OH)], 792(s), (out-of-plane C–H (phenyl) deformation).

UV-Vis (max/nm, EtOH as solvent): 423, 331, 299, 263, 231.

2.3. *Synthesis of the complex*

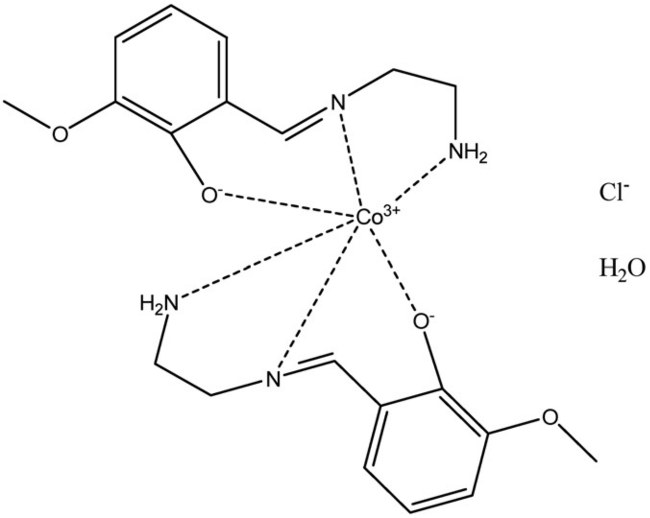
The cobalt complex shown in scheme 1 was synthesized as follows: $Co(Cl)_2 \cdot 6H_2O$ (1 mmol, 132 mg) and the Schiff base HL (3 mmol, 584 mg) were dissolved in absolute ethanol, then the mixture was refluxed for 1 h with stirring. The resulting clear yellow solution was kept in a desiccator and after slow evaporation of the solvent over a period of two weeks, brown crystals of **1** were formed, isolated, washed three times with ethanol and dried in a vacuum desiccator using anhydrous $CaCl_2$ (yield = 38%). The complex decomposes at 398°C. Elemental Anal, found (%, Calcd) for $C_{20}H_{28}ClCoN_4O_5$: C 47.62 (47.96), N 11.11 (11.03), H 5.79 (5.92).

FT-IR (KBr, cm^{-1}): 3606 (w, br, O(water)–H), 3380 and 3168 (w, br, N–H), 3095 (w, aromatic C–H), 1652 (s, C=N), 1599 (m, phenyl), 1544 (m, br, phenol C–O), 737 (s), (out-of-plane C–H (phenyl) deformation).

UV-Vis (max/nm, EtOH as solvent): 400, 250.

2.4. *X-ray structural determination*

Brown crystals of $[(C_{10}H_3N_2O_2)_2Co]Cl \cdot H_2O$ were grown by slow evaporation from ethanol.



Scheme 1. Chemical structure of $[Co^{III}(L)_2]Cl \cdot H_2O$.

Diffraction data were collected at 298 K on a Bruker diffractometer using Mo-Kα radiation (0.71069 Å) monochromatized from graphite. The radiation source was fine-focus sealed tube and the scan type was ω scans.

The structure solution and refinements were by SHELXL-97 [10] as incorporated in the package WINGX. Absorption corrections were made by MULTISCAN. Non-hydrogen atoms were anisotropic and hydrogen atom positions were included in riding mode. Further details are given in table 1.

3. Results and discussion

3.1. *Synthesis and properties*

The condensation of o-vanillin with ethylenediamine gave a 1 : 1 mono Schiff-base product HL, ($H_2N(CH_2)_2N{=}CC_6H_3(OMe)(OH)$), in both phenol and ketone configurations. The mono Schiff-base ligand with $CoCl_2 \cdot 6H_2O$ in ethanol yields a brown complex of composition $[Co(L)_2]Cl{\cdot}H_2O$ (**1**). Presumably an initially formed Co(II) complex is oxidized by accidentally admitted air. The molar conductance value in EtOH suggests that $[Co^{III}(L)_2Cl \cdot H_2O]$ is a 1 : 1 electrolyte [11]. Elemental analysis is found to be in good agreement with this formulation.

Table 1. Crystal data and structure refinement for **1**.

Empirical formula	$C_{20}H_{28}ClCoN_4O_5$
Formula weight	498.83
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic,
Space group	*Pbca*
Unit cell dimensions (Å,°)	
a	10.208(2)
b	13.541(3)
c	32.299(7)
Volume (A^3)	4464.7(15)
Z	8
D_{Calcd} ($mg \cdot m^{-3}$)	1.484
Absorption coefficient (mm^{-1})	0.928
F(000)	2080
Crystal size (mm^3)	$0.44 \times 0.36 \times 0.22$
θ range for data collection (°)	2.36–25.00
Index ranges	$-7 \leq h \leq 12$, $-16 \leq k \leq 16$, $-37 \leq l < \leq 38$
Reflections collected	18,052
Independent reflections	3840 [$R(int) = 0.0764$]
Completeness to $\theta = 25.00$	97.8%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.815 and 0.676
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3840/0/299
Goodness-of-fit on F^2	0.899
Final *R* indices ($I > 2\sigma(I)$)	$R_1 = 0.0488$, $wR_2 = 0.0909$
R indices (all data)	$R_1 = 0.0772$, $wR_2 = 0.1008$
Largest diff. peak and hole ($e \cdot A^{-3}$)	0.481 and −0.302

3.2. *Thermal study*

$[Co^{III}(L)_2]Cl \cdot H_2O$ was studied by thermogravimetric analysis (TGA) under a dynamic air atmosphere in the temperature region 30–690°C at a heating rate of $10°C\,min^{-1}$. The presence of chloride and a molecule of water outside the coordination sphere is confirmed. Complex **1** is stable to 133°C. From 133 to 160°C a mass loss of 9.1% is attributed to the combined loss of water and chloride (theoretical value 10.8%). After 390°C the complex starts to decompose and a mass loss of 38.6% at 398°C corresponds to the loss of one ligand (theoretical value 41.5%). The total mass loss up to 561°C is found to be 81.4%, which shows the formation of cobalt oxide. The high mass of the residue (theoretical value 15.0%) is attributed to carbonaceous matter. Thus the decomposition pattern confirms the proposed formulation of the complex.

3.3. *IR and UV-Vis spectra*

$[Co^{III}(L)_2]Cl \cdot H_2O]$ has a v(C=N) at $1652\,cm^{-1}$ which shifts $20\,cm^{-1}$ compared to the ligand indicating imine N coordinates to Co. Bands at 3380 and $3168\,cm^{-1}$ are assigned to v(N–H); the low value of v(N–H) is attributed to coordination of the NH_2 group. The band at $1544\,cm^{-1}$ has been assigned to the v(C–O) of the phenol [12] as a consequence of the delocalization of the double bond in the chelate ring, increasing the bond order of the phenolic C–O. This is confirmed by the crystal structure determination. A broad band at $3606\,cm^{-1}$ is due to v(OH) in water molecules occluded in the lattice.

The UV-Vis spectra show that the ligand has five bands at 423, 331, 299, 263 and 231 nm which are of the phenol configuration and ketone configuration. Diamagnetic **1** has two bands at 400 and 250 nm with the d-d band expected for the $^1A1_g \rightarrow {}^1T1_g$ transition in a distorted octahedral geometry [13] masked by the intense ligand to metal charge transfer (LMCT) band at 400 nm. The other bands observed are assigned to intra-ligand transition. The spectral pattern supports six-coordinate distorted octahedral symmetry around cobalt.

3.4. *Crystal structure of[$Co^{III}(L)_2$]$Cl \cdot H_2O$*

The structure of **1** is shown in figure 1 and some selected bond lengths and angles are presented in table 2. Complex **1** is composed of the $[Co^{III}(L)2]^+$ cation, Cl^- and the water molecule. The Schiff-base ligand, 2-((2-aminoethylimino)methyl)-6-methoxyphenol with a formal charge of −1, being deprotonated at the phenol O atom, acts as a tridentate ligand through one phenolate oxygen, one imine nitrogen and one amine nitrogen. The central Co(III) is six-coordinate and the coordination geometry can be described as slightly distorted octahedral, coordinated by two Schiff-base ligands.

The axial positions are occupied by two imine N atoms of two different Schiff-base ions and the other two amine N atoms and two O atoms of Schiff-base ligands occupy the planar position (within 0.0035 Å).

The two Co–O bonds are 1.894(3) and 1.919(3) Å, the two Co–N(imino) distances are 1.888(4) and 1.899(3) Å, and the Co–N(amino) average distance is 1.956(3) Å. The bond

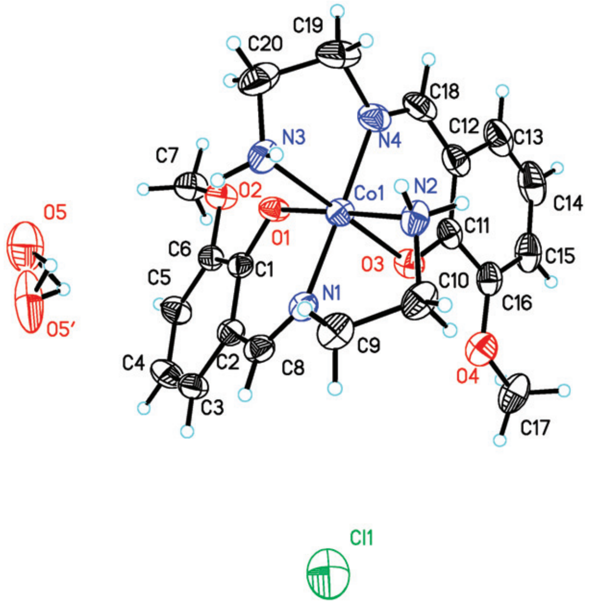


Figure 1. The molecular structure of $[Co^{III}(L)_2]Cl\text{-}H_2O$ showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $-x$, y, $-z+1/2$].

Table 2. Bond lengths (Å) and angles (°) for **1**.

Co(1)–N(4)	1.892(3)
Co(1)–O(3)	1.894(2)
Co(1)–N(1)	1.898(3)
Co(1)–O(1)	1.920(2)
Co(1)–N(3)	1.955(3)
Co(1)–N(2)	1.959(3)
N(4)–Co(1)–O(3)	94.79(12)
N(4)–Co(1)–N(1)	175.12(12)
N(4)–Co(1)–N(2)	92.09(13)
O(3)–Co(1)–N(2)	87.01(11)
O(1)–Co(1)–N(2)	177.96(11)
N(3)–Co(1)–N(2)	93.80(12)

lengths and angles of Co–O and Co–N (table 1) are within the expected ranges [14] and significantly shorter than Co(II)–N and Co(II)–O bond lengths, 2.12–2.14 and 2.07–2.15 Å, respectively.

In the ligand, C=N bonds range from 1.267(5) to 1.294(6) Å, longer than the ordinary C=N bond. The C=N bond has a *trans* configuration and the C9–N1–C8–C2, C19–N4–C18–C12 torsion angles are 177.7(4) and 177.5(4)°, respectively. The C2–C8 and C12–C18 [1.445(6), 1.419(7) Å] and N1–C9 and N4–C19 [1.476(5), 1.484(6) Å] distances confirm π-electron delocalization from benzene rings, and the anion can be regarded as a partially delocalized π-electron system. Shortening of N–C, C(sp2)-C(ar) and the lengthening of N=C(sp2) observed in **1** is common [15] and other bond lengths and angles are within the expected ranges [16].

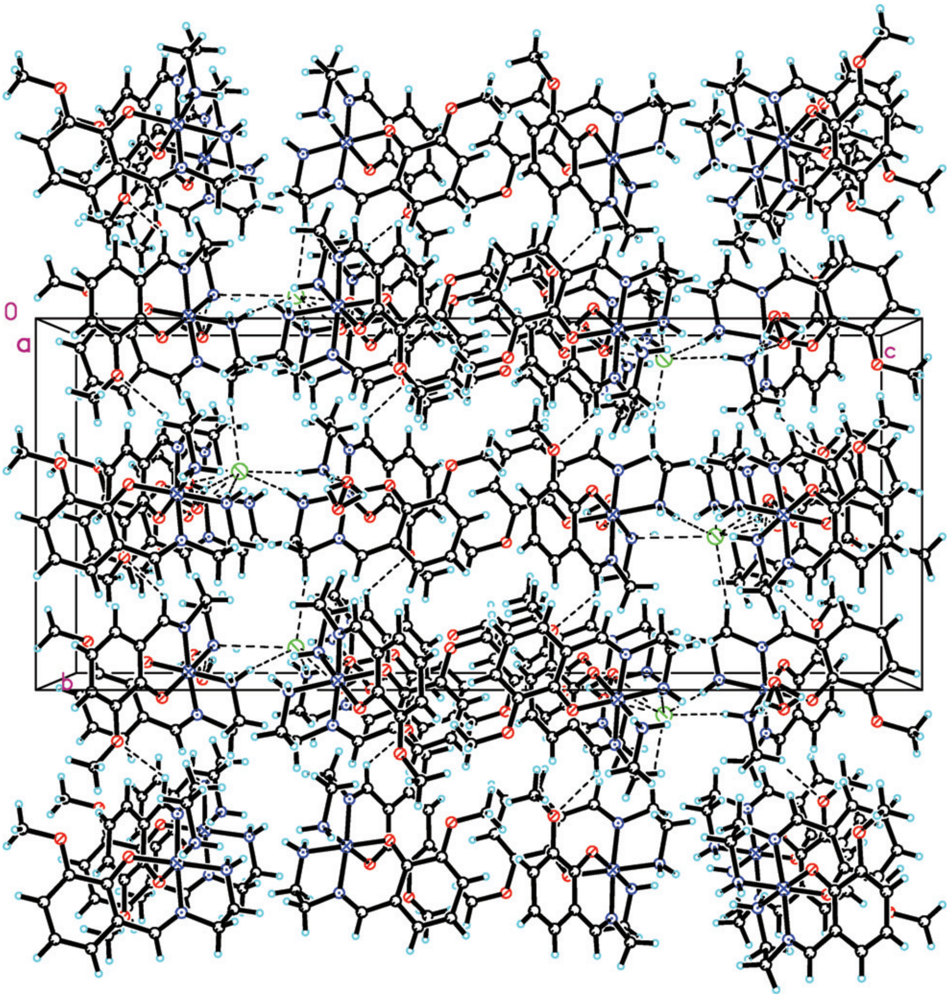


Figure 2. The crystal packing of **1** viewed along the *a* axis. Hydrogen-bonding interactions are shown as dashed lines.

In the crystal structure, the water is disordered; the water in the complex and Cl^- form intermolecular hydrogen bonds (table 2) with the amino of anionic ligands. Those hydrogen bonds bind the molecules to form a one-dimensional supramolecular structure along *a*. The hydrogen bond chains are parallel to each other and extended into a three-dimensional network. There are only ordinary, weaker, van der Waals interactions in the *b* and *c* directions (figure 2).

3.5. *Cyclic voltammetry*

The electroactivity of **1** was examined in EtOH using cyclic voltammetry (CV) at a platinum-working electrode. A representative voltammogram is shown in figure 3.

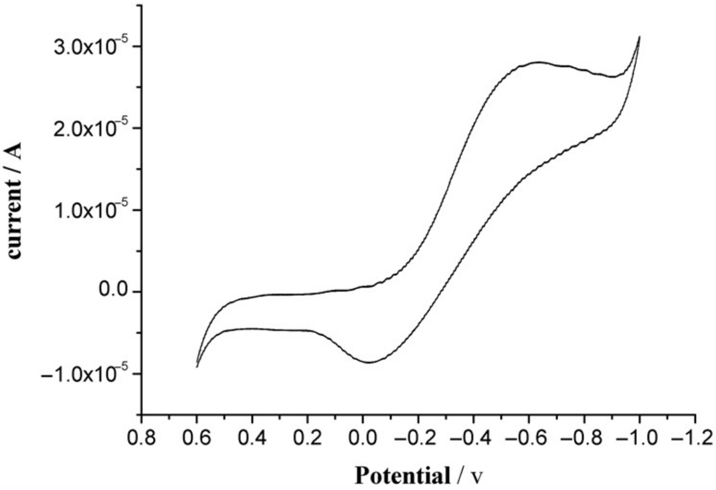


Figure 3. Cyclic voltammogram of **1** (0.1 mM) in EtOH at 200 mV/s.

Table 3. Hydrogen bond for **1**.

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
N(3)–H(3B)···Cl(1)#1	0.90	2.42	3.290(3)	163.8
N(3)–H(3A)···Cl(1)#2	0.90	2.41	3.299(3)	170.9
N(2)–H(2B)···Cl(1)#1	0.90	2.34	3.222(3)	166.9
N(2)–H(2A)···O(5)#3	0.90	2.22	3.101(12)	164.5
N(2)–H(2A)···O(5')#3	0.90	1.95	2.822(12)	163.6
O(5')–H(5A)···Cl(1)#2	1.02(6)	2.20(6)	3.111(13)	147(5)

Symmetry transformations used to generate equivalent atoms: #1$-x, y+1/2, -z+1/2$ #2$-x+1/2, y+1/2, z$ #3$x-1, y, z$.

The cyclic voltammogram shows one irreversible wave at $E_{pc} = -0.46$ to -0.69 V versus Ag/AgCl, with 50–350 mV s^{-1} scan rates, attributed to Co(III) to Co(II) reduction [17]. No anodic peak could be observed even after applying a 350 mV s^{-1} scan rate indicating the irreversible nature of the electrode process. The linear plot of the cathodic peak current (Ipc) versus the square root of the scan rate ($v^{1/2}$) passes close to the origin, indicating that the electrode reaction is mainly diffusion controlled. An irreversible anodic peak at $E_{pa} = 0.18$ to -0.21 V could be assigned to oxidation of the ligand on the electrode surface.

Supplementary material

CCDC 647486 contains the supplementary crystallographic data for **1**. The data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44) 1223–336–033 or E-mail: deposit@ccdc.cam.ac.uk).

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