

Bis[(2-pyridyl)(2-pyridylamino)-methanolato]cobalt(III) perchlorate: a consequence of cobalt ion-assisted oxidative deamination of a tris(pyridyl)aminal ligand

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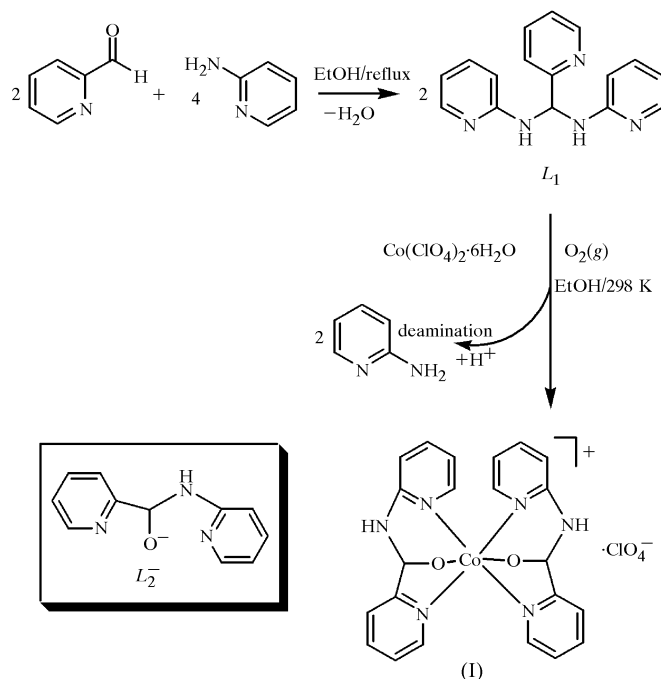
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The title compound, $[\text{Co}(\text{C}_{11}\text{H}_{10}\text{N}_3\text{O})_2]\text{ClO}_4$, designated $[\text{Co}(L_2)_2]\text{ClO}_4$, was synthesized by reaction of Co^{II} with two molar equivalents of (2-pyridyl)bis(2-pyridylamino)methane (L_1) under ambient conditions, whereby the divalent metal ion was oxidized concomitantly with oxygenation and deamination of the aminal polydentate ligand to generate the tridentate ligand anion (2-pyridyl)(2-pyridylamino)methanolate, L_2^- . In the X-ray crystal structure of the complex cation, $[\text{Co}(L_2)_2]^+$, the two L_2^- ligands are coordinated to the central cobalt(III) metal ion in a facial mode to afford a pseudo-octahedral geometry. The four pyridyl N atoms constitute the equatorial plane on which the cobalt(III) ion lies; the methanolate O atoms occupy the axial positions.

Comment

One of the crucial requirements for a metal to act as an electron carrier at biochemical redox centres is the availability of at least two readily accessible stable oxidation states of the metal that differ by one unit. Hence, several of the first-row transition metals play major roles in a diverse range of enzymatic and electron-transfer processes in biological systems. Cobalt is well known for its role in the inorganic biochemistry of the cobalamins, rare examples of naturally occurring organometallic compounds (Cotton *et al.*, 1999). At the centre of the coenzymes of the cobalamins, namely 5'-deoxyadenosylcobalamin (coenzyme B_{12}) and methylcobalamin (MeB_{12}), cobalt participates in catalytic radical-induced 1,2-rearrangement reactions and biomethylations, respectively (Lippard & Berg, 1994; Bertini & Luchinat, 1994; Kaim & Schwederski, 1994). In the catalytic cycles of these processes, cobalt shuttles between the divalent and trivalent states, and in MeB_{12} , the relatively uncommon +1 state is also utilized (Drennan *et al.*, 1994; Kräutler & Kratky, 1996).

The importance of low-spin cobalt(III) revolves around the kinetic inertness of its compounds, which has facilitated mechanistic studies in coordination chemistry. Virtually all octahedral cobalt(III) complexes are diamagnetic (configuration t_{2g}^6), with the exception of $[\text{CoF}_6]^{3-}$ and $[\text{CoF}_3(\text{H}_2\text{O})_3]$ (Cotton *et al.*, 1999). Generally, in coordination chemistry, Co^{III} is obtained from Co^{II} by atmospheric or chemical oxidation (using oxidants such as H_2O_2). The title compound, (I), was synthesized by reaction of $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ with two molar equivalents of (2-pyridyl)bis(2-pyridylamino)methane (L_1) (Galvez *et al.*, 1986; Arulsamy & Hodgson, 1994) in EtOH in the presence of molecular oxygen at room temperature (see scheme below). Compound (I) was also obtained from the template reaction of stoichiometric amounts of pyridine-2-carbaldehyde, 2-aminopyridine and $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in refluxing ethanol. Microanalyses (C, H and N) of a crystalline sample of (I) are consistent with the suggested chemical formulation of (I). The IR spectrum of this compound exhibits a sharp absorption at 3356 cm^{-1} , confirming the presence of NH (secondary amine) in the L_2^- ligand synthesized *in situ*. The aliphatic and aromatic $\nu(\text{C}-\text{H})$ absorptions occur at 2875 and 3080 cm^{-1} , respectively. The pyridyl ring vibrations are indicated by the stretching frequencies in the range $1400\text{--}1620\text{ cm}^{-1}$. The uncoordinated perchlorate ion is characterized by an intense and broad absorption centred around 1090 cm^{-1} and a moderate and sharp band at 625 cm^{-1} (Nakamoto, 1997; Srinivasan *et al.*, 2005).



As observed previously for other octahedral Co^{III} complexes with $S = 0$ (e.g. Mak *et al.*, 1991; Emseis *et al.*, 2004), the ^1H NMR spectrum of $[\text{Co}(L_2)_2]\text{ClO}_4$ in $\text{DMSO}-d_6$ exhibits sharp resonances, showing that (I) is indeed diamagnetic. A signal corresponding to the secondary amine H atom is observed at 5.52 p.p.m., and several multiplets in the chemical shift range 6.22–8.85 p.p.m. are associated with the pyridyl H atoms. Further evidence for the singlet ground state of

compound (I) is provided by UV–visible spectroscopy. The electronic spectrum of (I) (Fig. 1) displays a shoulder at 398 nm [partially obscured by an intense intraligand $\pi \rightarrow \pi^*$ band at 315 nm ($\epsilon = 19500 M^{-1} \text{ cm}^{-1}$)] and a weak band at 514 nm ($\epsilon = 80 M^{-1} \text{ cm}^{-1}$), typical of low-spin Co^{III} complexes. Owing to the common chromophore $\text{Co}^{\text{III}}\text{N}_4\text{O}_2$, regardless of the differences in the other moieties present, the related Co^{III} compounds carbonatobis[2-(2-pyridylamino)-5,6-dihydro-4H-1,3-thiazine]cobalt(III) chloride (Barros-García *et al.*, 2004), (4,11-diacetato-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane)cobalt(III) hexafluorophosphate (Lichty *et al.*, 2004) and *trans*-bis(1,3-diamino-2-propanolato)-cobalt(III) perchlorate (Bruce, 2003) have electronic spectra that resemble that of compound (I), with two cobalt-based absorptions in each case at 395 (shoulder) and 532 nm, 355 and 494 nm, and 394 and 498 nm, respectively. For all these aforementioned compounds, including (I), the two absorptions are attributable to ligand–field transitions; the higher-energy absorption represents the $^1A_{1g} \rightarrow ^1T_{2g}$ transition, whereas the other is ascribed to the $^1A_{1g} \rightarrow ^1T_{1g}$ transition. Commonly, the higher-energy *d–d* band is masked by intra-

ligand $\pi \rightarrow \pi^*$ or LMCT bands (Djebbar-Sid *et al.*, 2001; Tiliakos *et al.*, 2001; Shongwe, Al-Hatmi *et al.*, 2002; Saha *et al.*, 2003; Barros-García *et al.*, 2004). The pink–red colour of (I) is consistent with the electronic absorptions (Fig. 1).

Definitive evidence for the cobalt ion-assisted transformation of (2-pyridyl)bis(2-pyridylamino)methane (L_1) to (2-pyridyl)bis(2-pyridylamino)methanolate (L_2^-) *in situ* was provided by single-crystal X-ray crystallography. Compound (I) was isolated at room temperature as pink–red block-shaped crystals; it crystallized in the orthorhombic space group $Pca2_1$. The crystal structure of (I) comprises a complex cation, $[\text{Co}(L_2)_2]^+$, and a disordered perchlorate counter-anion (Fig. 2). The arrangement of the discrete mononuclear complex cations and counter-ions is shown in Fig. 3. Selected bond distances and angles are given in Table 1. The crystal structure of the complex cation shows two tridentate (2-pyridyl)bis(2-pyridylamino)methanolate ligands coordinated facially to the cobalt(III) ion to form a distorted octahedral geometry. The distortion, evidenced by deviations from idealized O_h angles of 90° and differences in bond distances in the coordination sphere, is a consequence of ligand constraints. The cobalt(III) ion resides on a pseudo-twofold axis of symmetry and on an equatorial plane formed by the pyridyl N atoms of the two ligands. The methanolate O atoms, in the axial positions [$\text{O1}–\text{Co1}–\text{O2} = 172.61 (19)^\circ$], have stronger interactions with the central metal atom [$\text{Co}^{\text{III}}–\text{O}_{\text{methanolate}} = 1.893 (4)$ and $1.894 (4) \text{ \AA}$] than do the pyridyl N atoms (Table 1). The $\text{Co}^{\text{III}}–\text{O}_{\text{methanolate}}$ distances compare favourably with the $\text{Co}^{\text{III}}–\text{O}_{\text{propanolate}}$ [$1.867 (6)$ and $1.921 (5) \text{ \AA}$; Bruce, 2003], $\text{Co}^{\text{III}}–\text{O}_{\text{carboxylate}}$ [$1.882 (6)$ and $1.916 (3) \text{ \AA}$; Shongwe, Al-Juma & Fernandes, 2002; Lichty *et al.*, 2004], $\text{Co}^{\text{III}}–\text{O}_{\text{naphtholate}}$ [$1.886 (4)–1.9139 (17) \text{ \AA}$; Kurahashi, 1976;

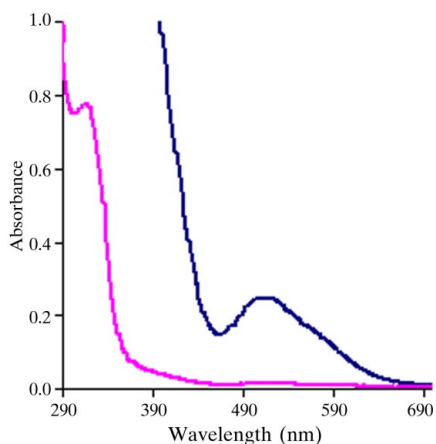


Figure 1
The electronic absorption spectrum of (I) in dimethyl sulfoxide (DMSO): 0.10 mM (lower line) and 3.0 mM (higher line).

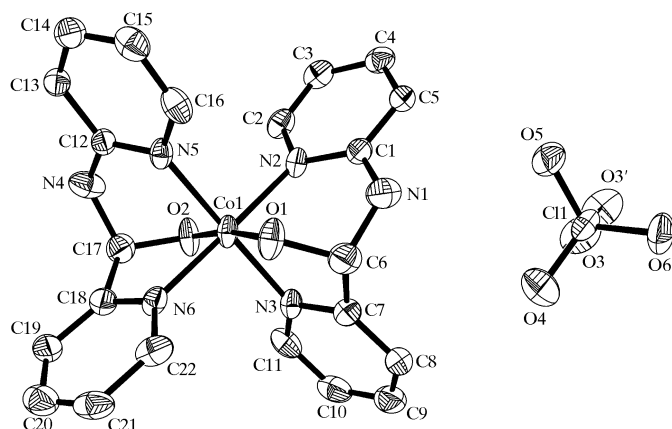


Figure 2
The crystal structure of (I), showing the mononuclear complex cation and the disordered perchlorate counter-ion.

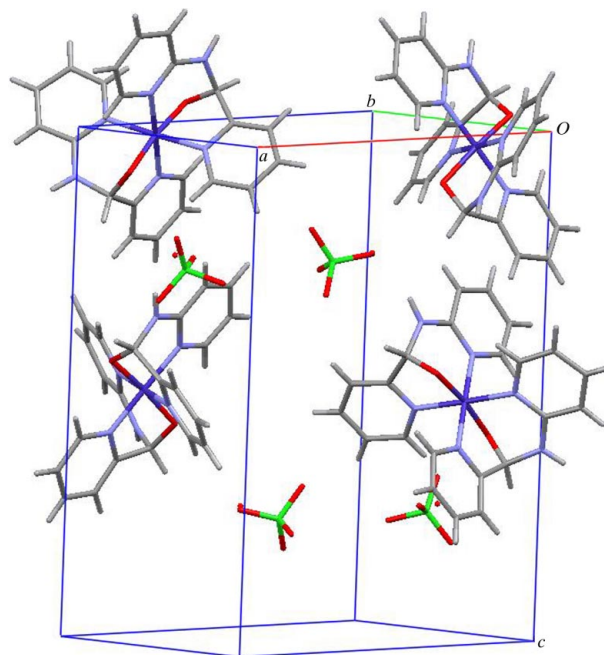


Figure 3
The packing of (I).

Shongwe, Al-Juma & Fernandes, 2002], $\text{Co}^{\text{III}}-\text{O}_{\text{phenolate}}$ [1.862 (6)–1.928 (2) Å; Nassimbeni *et al.*, 1976; Chen *et al.*, 1991; Shongwe, Al-Hatmi *et al.*, 2002] and $\text{Co}^{\text{III}}-\text{O}_{\text{carbonate}}$ distances [1.907 (2) and 1.919 (2) Å; Barros-García *et al.*, 2004]. Likewise, the $\text{Co}^{\text{III}}-\text{N}_{\text{pyridyl}}$ distances of (I) [1.917 (4)–1.962 (4) Å] are normal (Tiliakos *et al.*, 2001; Ghiladi *et al.*, 2003; Barros-García *et al.*, 2004; Stamatatos *et al.*, 2005). Owing to steric constraints, the two $\text{Co}^{\text{III}}-\text{N}_{\text{pyridyl}}$ distances (for each L_2^- ligand) in (I) are significantly different (by 0.044 Å). Similar behaviour has been demonstrated by the Co^{III} complex of deprotonated N,N' -bis(2-pyridyl)urea (Tiliakos *et al.*, 2001).

The metal ion-assisted conversion of L_1 to L_2^- has been demonstrated previously (Arulsamy & Hodgson, 1994) using manganese(II) and iron(II) to form the M^{III} complexes $[\text{Mn}(L_2)_2]\text{ClO}_4$ and $[\text{Fe}(L_2)_2]\text{ClO}_4$, respectively, which are chemically isostructural with (I). It is noteworthy that in the case of the high-spin ($t_{2g}^3 e_g^1$) Mn^{III} analogue, the equatorial bonds ($\text{Mn}-\text{N}_{\text{pyridyl}}$) appear elongated in accordance with the Jahn–Teller effect (evident axial compression). In the reaction of M^{II} ($M = \text{Mn}, \text{Fe}$ or Co) with L_1 in air, oxygen is inserted into the ligand at the aliphatic C atom, causing deamination, as shown in the scheme. Cytochrome P450-dependent incorporation of O atoms from freely available molecular oxygen into organic chemical substrates occurs extensively in nature (Kaim & Schwederski, 1994). In our system, we and others (Arulsamy & Hodgson, 1994) have shown that a crucial requirement for the oxidative degradation of the aminal ligand L_1 is accessibility of a stable M^{III} oxidation state. Oxygenation of the ligand occurs in conjunction with oxidation of the M^{II} ions. In the case of Ni^{2+} (Arulsamy & Hodgson, 1994) and Cu^{2+} , the ligand L_1 remains intact during the reaction.

Experimental

L_1 was synthesized following literature procedures (Galvez *et al.*, 1986; Arulsamy & Hodgson, 1994). A solution of 2-aminopyridine (4.7152 g, 0.050 mol) in ethanol (20 ml) was mixed with a solution of pyridine-2-carbaldehyde (2.6780 g, 0.025 mol) in ethanol (20 ml) to give a light-yellow–brown solution. This solution was heated under reflux for 10 h, during which time its colour remained essentially the same. Slow evaporation of the solution at room temperature over a period of 5 d gave colourless block-shaped crystals, which were washed several times with ice-cold ethanol and dried in air (yield 6.1012 g, 88.0%; m.p. 389–391 K). Microanalysis found: C 69.40, H 5.47, N 25.15%; calculated for $\text{C}_{16}\text{H}_{15}\text{N}_5$ ($M_r = 277.328$): C 69.30, H 5.45, N 25.25%; IR (KBr, cm^{-1}): 3290, 3245 (N–H); UV–vis (DMSO, nm): 260 ($\epsilon = 15500 \text{ M}^{-1} \text{ cm}^{-1}$), 300 ($\epsilon = 9540 \text{ M}^{-1} \text{ cm}^{-1}$). For the preparation of (I), $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.1464 g, 0.40 mmol) was added to a solution of L_1 (0.2219 g, 0.80 mmol) in ethanol (20 ml); an orange solution formed immediately and progressively darkened over time with continuous stirring at room temperature. After 5 min of stirring, the pink–red solution was filtered and kept at room temperature. After three days of slow evaporation, bright pink–red block-shaped crystals were deposited. After one week, the crystals had grown larger and become dark red. The crystals were washed with ice-cold ethanol and dried in air (yield 0.1375 g, 61.5%). $[\text{Co}(L_2)_2]\text{ClO}_4$ was also obtained in higher yield (75%) from the template reaction of stoichiometric amounts (0.20 mmol scale based on the

Co^{II} salt) of 2-aminopyridine, pyridine-2-carbaldehyde and $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (m.p. 514–515 K). Microanalysis found: C 47.20, H 3.62, N 14.94%; calculated for $\text{C}_{22}\text{H}_{20}\text{ClCoN}_6\text{O}_6$ ($M_r = 558.82$): C 47.29, H 3.61, N 15.04%; IR (KBr, cm^{-1}): 3356 (N–H), 1090, 625 (ClO_4^-); UV–vis (DMSO, nm): 263 ($\epsilon = 19500 \text{ M}^{-1} \text{ cm}^{-1}$), 315 ($\epsilon = 7800 \text{ M}^{-1} \text{ cm}^{-1}$), 398 (shoulder), 514 ($\epsilon = 80 \text{ M}^{-1} \text{ cm}^{-1}$); ^1H NMR (DMSO- d_6 , p.p.m.): δ 5.52 (*d*), 6.22–8.85 (*m*).

Crystal data

$[\text{Co}(\text{C}_{11}\text{H}_{10}\text{N}_3\text{O}_2)_2]\text{ClO}_4$
 $M_r = 558.82$
 Orthorhombic, $Pca2_1$
 $a = 14.802$ (3) Å
 $b = 8.6144$ (18) Å
 $c = 17.832$ (4) Å
 $V = 2273.8$ (8) Å³
 $Z = 4$
 $D_x = 1.632$ Mg m^{−3}

Mo $K\alpha$ radiation
 Cell parameters from 1903 reflections
 $\theta = 2.3$ – 27.6°
 $\mu = 0.93$ mm^{−1}
 $T = 150$ (2) K
 Block, red
 $0.32 \times 0.12 \times 0.12$ mm

Data collection

Bruker SMART 1000 diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 1997)
 $T_{\text{min}} = 0.756$, $T_{\text{max}} = 0.897$
 23722 measured reflections

5164 independent reflections
 4598 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.065$
 $\theta_{\text{max}} = 27.6^\circ$
 $h = -19 \rightarrow 18$
 $k = -10 \rightarrow 11$
 $l = -23 \rightarrow 22$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.060$
 $wR(F^2) = 0.159$
 $S = 1.12$
 5164 reflections
 336 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0829P)^2 + 2.318P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 1.33 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.46 \text{ e \AA}^{-3}$
 Absolute structure: Flack (1983), 2431 Friedel pairs
 Flack parameter: 0.11 (2)

Table 1

Selected geometric parameters (Å, °).

Co1–O1	1.893 (4)	Co1–N6	1.930 (4)
Co1–O2	1.894 (4)	Co1–N2	1.959 (4)
Co1–N3	1.917 (4)	Co1–N5	1.962 (4)
O1–Co1–O2	172.61 (19)	N3–Co1–N2	90.19 (16)
O1–Co1–N3	83.59 (16)	N6–Co1–N2	178.32 (16)
O2–Co1–N3	90.82 (17)	O1–Co1–N5	94.80 (16)
O1–Co1–N6	91.29 (16)	O2–Co1–N5	90.84 (17)
O2–Co1–N6	83.94 (15)	N3–Co1–N5	178.29 (17)
N3–Co1–N6	90.73 (16)	N6–Co1–N5	89.86 (15)
O1–Co1–N2	90.21 (16)	N2–Co1–N5	89.27 (16)
O2–Co1–N2	94.64 (15)		

Attempts to solve the structure in space group $Pcam$ with the central Co atom on a crystallographic twofold axis proved to be unsuccessful. Refinement and full convergence of the structure was achieved in the space group $Pca2_1$. H atoms were positioned geometrically and refined with a riding model, with C–H distances of 0.95–1.00 Å, N–H distances of 0.88 Å, and $U_{\text{iso}}(\text{H})$ values constrained to be 1.2 times U_{eq} of the carrier atom. The maximum residual electron density is 1.05 Å from atom O2.

Data collection: SMART (Bruker, 1997); cell refinement: SMART; data reduction: SAINT (Bruker, 1997); program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 1997); software used to prepare material for publication: SHELXTL.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA1161). Services for accessing these data are described at the back of the journal.

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