

METAL-ORGANIC COMPOUNDS

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***trans*-Bis(ethylenediamine)dinitrocobalt(III) perchlorate**

KAREN R. MAXCY AND MARK M. TURNBULL

Carlson School of Chemistry and Biochemistry, Clark University, 950 Main St, Worcester, MA 01610, USA. E-mail: mturnbull@clarku.edu

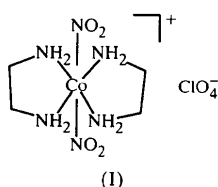
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Abstract

The reaction of cobalt(II) perchlorate with ethylenediamine and sodium nitrite in aqueous solution gave the title Co^{III} compound, $[\text{Co}(\text{NO}_2)_2(\text{C}_2\text{H}_8\text{N}_2)_2]\text{ClO}_4$, as yellow crystals. The complex crystallizes in three different conformations in the asymmetric unit, two on centers with $\bar{1}$ symmetry and one in a general position. Numerous hydrogen bonds occur between molecules, but most are quite weak. The ethylenediamine N atoms occupy the equatorial sites with the NO_2 ions bonded in axial positions. The NO_2 moieties nearly eclipse a pair of *trans* amine-N atoms in one independent molecule [$\text{O}-\text{N}-\text{Co}-\text{N}$ angles range from $-1.4(6)$ to $4.3(5)^\circ$], while they bisect the $\text{N}-\text{Co}-\text{N}$ angle in the other two [$\text{O}-\text{N}-\text{Co}-\text{N}$ angles range from $-44.8(6)$ to $52.1(5)^\circ$].

Comment

We are interested in the synthesis of compounds of the general formula $[\text{M}(\text{en})_2(\text{NO}_2)]\text{X}$, where M is a transition metal in the 2+ oxidation state, en is ethylenediamine and X is a non-coordinated anion, for study of the Haldane gap (Haldane, 1983). The structure of the parent compound in this family ($\text{M} = \text{Ni}$, $\text{X} = \text{ClO}_4$) was reported by Meyer *et al.* (1982) and exists as a coordination polymer with the $\text{Ni}(\text{en})_2$ units bridged by nitrite ions. While compounds in this family with half-integer spins, such as those containing Co^{II} , will not exhibit a gap in their low-temperature magnetization, they may provide useful information regarding the broader field of one-dimensional magnetic chains. Thus, we attempted the preparation of $[\text{Co}(\text{en})_2(\text{NO}_2)]\text{ClO}_4$ (I).



Reaction of $[\text{Co}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$, $[\text{Co}(\text{en})_3](\text{ClO}_4)_2$ and NaNO_2 in water under argon resulted in a variety of products, including a yellow crystalline material which proved to be the oxidized product $[\text{Co}(\text{en})_2(\text{NO}_2)_2]\text{ClO}_4$. Crystals suitable for diffraction grew from the reaction mixture over the course of a few days under a stream of argon and proved to be triclinic, $P\bar{1}$. The asymmetric unit (see Fig. 1) contains three independent Co^{III} ions, one each at the $0,0,0$ and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ inversion centers and the third in a general position. This particular mode of packing is unusual. Slightly less than 9% of $P\bar{1}$ structures have $Z = 4$ (Brock & Dunitz, 1994). In addition, Padmaja *et al.* (1990) have looked at incidence of two half molecules in the asymmetric unit being located on symmetry elements to generate $Z' = 1$ (Z' is the number of molecules in the asymmetric unit). Neglecting polymers and those systems with only solvent molecules or disordered water molecules on the inversion center, they found only 134 examples of structures with two half molecules in the space group $P\bar{1}$ (this space group represents nearly 50% of all such structures). The current

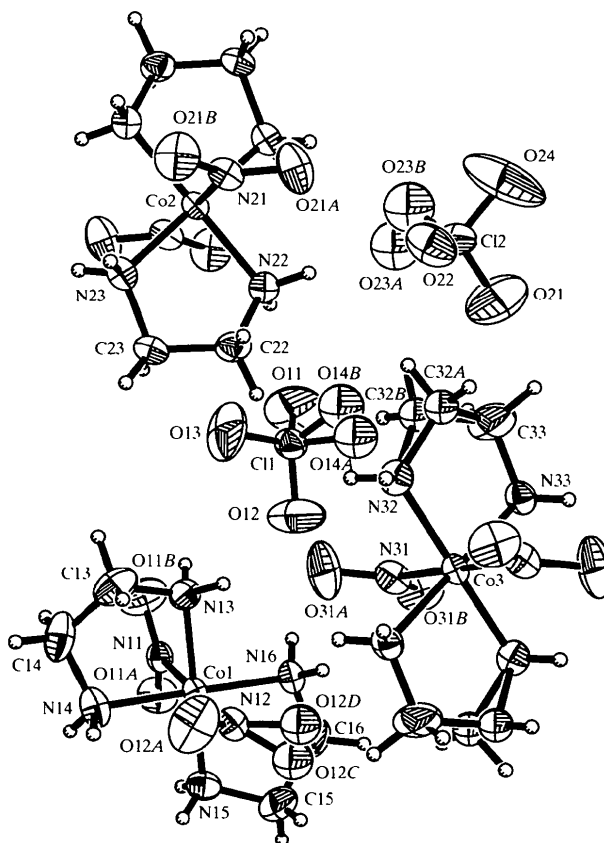


Fig. 1. The structure of $[\text{Co}(\text{en})_2(\text{NO}_2)_2]\text{ClO}_4$ shown with 50% probability displacement ellipsoids. Only atoms in the asymmetric unit are labeled.

situation with two half molecules on inversion centers and one molecule in a general position must be similarly rare.

The molecule containing Co1 sits in a general position near $\frac{1}{4}, \frac{3}{4}, \frac{1}{4}$. One of the O atoms on one of the nitrite ions is disordered with 50% occupancy at each O12C and O12D. Co1 and the four ethylenediamine N atoms are nearly coplanar with a mean deviation of 0.0036 Å. The two en rings both show the δ conformation (and thus the inversion-related molecule has a λ, λ conformation). The non-disordered nitrite ion is oriented such that it eclipses a pair of *trans* amine-N atoms [O11A—N11—Co1—N15 = -4.3 (5) and O11B—N11—Co1—N13 = -1.4 (6)°]. The disordered nitrite ion is positioned such that O12A and the average position of O12C and O12D each lie over one of the en rings [O12A—N12—Co1—N14 = -20.6 (6), O12C—N12—Co1—N16 = -34.3 (12) and O12D—N12—Co1—N16 = 2.4 (12)°].

The Co2 atom is located at the cell origin. The conformation of the en rings are thus δ and λ , unlike those in Co1. The plane of the nitrite ion nearly bisects the N—Co—N angle between en rings [O21A—N21—Co2—N22 = 49.2 (5) and O21B—N21—Co2—N23 = -46.9 (5)°]. No disorder is observed in the Co2 molecule.

The Co3 atom is also located on an inversion center, *i.e.* $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. The conformation of the nitrite ion is similar in this molecule to Co2 with respect to the en rings [O31A—N31—Co3—N32 = -44.8 (6) and O31B—N31—Co3—N33 = 52.1 (5)°]. One C atom lies nearly in the en ring [mean deviation of Co3, N32, N33 and C33 from planarity is 0.017 (4) Å], while the second C atom is disordered (C32A/C32B 0.48:0.52 occupancies) above and below that plane. The overall effect is that of the four molecules in the unit cell, two form an enantiomer pair, one is *meso* and one is disordered.

The bond lengths and angles about the Co ions do not vary greatly between molecules. The Co—N bonds to the amine-N atoms all lie in the range 1.945 (5)–1.957 (5) Å, while those to the nitrite-N atoms have a broader range of 1.924 (5)–1.975 (5) Å. The chelating N—Co—N angles for the en ligands are also all similar with an average value of 85.9 (2)°. The nitrite ions lie near the ideal axial sites with an average angle of 87.7 (3)° between the nitrite nitrogen and the mean plane of the amine-N atoms. These bond lengths and angles are all in good agreement with those observed for similar *trans*-[Co(en)₂(NO₂)₂]X complexes, such as the iodide and isothiocyanate (Bernal & Cetrullo, 1986) and nitrate (Bortin, 1976) complexes, and the related *cis*-salts, such as the chloride (Bernal, 1985), iodide (Bernal *et al.*, 1993) and nitrite (Marsh, 1997).

The structure is stabilized by hydrogen bonding. The strongest of these are nearly linear (160–170°) and between amine groups and nitrites of adjacent molecules [N13—H13A···O31A = 2.973 (7) and N14—

H14A···O21A($x, y + 1, z$) = 3.037 (8) Å], and between amine groups and one of the perchlorate ions [N15—H15A···O24 = 2.97 (1) Å]. Numerous other weaker hydrogen bonds are also found (~3.05–3.30 Å and 120–155°). The bond lengths and angles within the perchlorate ions are generally unremarkable and there is mild disorder in the perchlorate-O atoms that are not involved in significant hydrogen bonds. The disordered O atoms were refined isotropically.

Finally, in an attempt to prevent the oxidation which we guessed might be due to the perchlorate ions, we attempted to synthesize the desired salt as the BF₄ complex. The results were nearly identical to the perchlorate reaction with several products resulting. Yellow crystals with similar morphology proved to be the analogous material [Co(en)₂(NO₂)₂]BF₄. This suggests that NO₂⁻ must be the oxidizing agent as the Co(BF₄)₂ solution is stable indefinitely under argon in the presence of en. The crystals were of poor quality and so full refinement was not possible. The unit-cell parameters [$a = 6.694$ (1), $b = 13.414$ (1), $c = 15.618$ (1) Å, $\alpha = 114.150$ (2), $\beta = 94.818$ (5) and $\gamma = 95.736$ (5)°] are in good agreement with the perchlorate salt and the solution is isostructural (the coordinates have been deposited at the Cambridge Crystallographic Data Centre for general access; reference code CCDC #129259).

Work to identify the other components of the product mixture is in progress.

Experimental

[Co(H₂O)₆](ClO₄)₂ (2.33 mmol), [Co(en)₃](ClO₄)₂ (4.67 mmol) and NaNO₂ (7.00 mmol) were dissolved in degassed water (15 ml) under argon resulting in a dark red/orange solution. A green/brown precipitate formed over the next 3 h. The mixture was filtered and the filtrate left under a stream of argon. Yellow crystals which formed over the course of several days were collected by filtration, dried in air and separated by hand from numerous other crystals which formed in the mixture. The crystals were isolated in only 5.4% yield, with a green/brown powder being the major product.

Crystal data

[Co(NO₂)₂(C₂H₈N₂)₂]ClO₄

$M_r = 370.61$

Triclinic

$P\bar{1}$

$a = 6.718$ (1) Å

$b = 13.595$ (1) Å

$c = 15.637$ (1) Å

$\alpha = 114.015$ (4)°

$\beta = 95.196$ (3)°

$\gamma = 94.984$ (3)°

$V = 1287$ (2) Å³

$Z = 4$

$D_x = 1.913$ Mg m⁻³

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 16 reflections

$\theta = 11.85$ – 20.78 °

$\mu = 1.592$ mm⁻¹

$T = 293$ (2) K

Chunk

$0.45 \times 0.40 \times 0.35$ mm

Yellow

Data collection

CAD-4 diffractometer $\theta_{\max} = 28.46^\circ$
 $\theta-2\theta$ scans $h = 0 \rightarrow 8$
 Absorption correction: $k = -18 \rightarrow 18$
 ψ scan (Fair, 1990) $l = -20 \rightarrow 20$
 $T_{\min} = 0.529, T_{\max} = 0.573$ 3 standard reflections
 6468 measured reflections frequency: 420 min
 6468 independent reflections intensity decay: 0.7%
 4849 reflections with $I > 2\sigma(I)$

Refinement

Refinement on F^2 $(\Delta/\sigma)_{\max} = 0.018$
 $R[F^2 > 2\sigma(F^2)] = 0.063$ $\Delta\rho_{\max} = 0.97 \text{ e } \text{\AA}^{-3}$
 $wR(F^2) = 0.204$ $\Delta\rho_{\min} = -0.64 \text{ e } \text{\AA}^{-3}$
 $S = 1.207$ Extinction correction: none
 6468 reflections Scattering factors from
 363 parameters *International Tables for*
 H atoms constrained *Crystallography* (Vol. C)
 $w = 1/[\sigma^2(F_o^2) + (0.0516P)^2 + 8.8786P]$
 where $P = (F_o^2 + 2F_c^2)/3$

Table 1. Selected geometric parameters (\AA , $^\circ$)

Co1—N12	1.945 (6)	Co2—N23	1.947 (5)
Co1—N13	1.945 (5)	Co2—N22	1.949 (5)
Co1—N15	1.946 (5)	N21—O21A	1.224 (7)
Co1—N14	1.957 (5)	N21—O21B	1.230 (7)
Co1—N16	1.960 (5)	Co3—N31	1.924 (5)
Co1—N11	1.975 (5)	Co3—N32	1.950 (5)
N11—O11B	1.229 (7)	Co3—N33	1.953 (5)
N11—O11A	1.232 (7)	N31—O31B	1.229 (7)
N12—O12A	1.205 (8)	N31—O31A	1.233 (8)
Co2—N21	1.932 (5)		
N12—Co1—N13	89.1 (2)	N16—Co1—N11	89.1 (2)
N12—Co1—N15	90.8 (2)	O11B—N11—O11A	117.4 (5)
N13—Co1—N15	179.6 (2)	O11B—N11—Co1	121.7 (4)
N12—Co1—N14	90.3 (2)	O11A—N11—Co1	120.8 (4)
N13—Co1—N14	86.0 (2)	O12A—N12—Co1	120.4 (5)
N15—Co1—N14	93.6 (2)	N21—Co2—N23	90.6 (2)
N12—Co1—N16	90.1 (2)	N21—Co2—N22	89.8 (2)
N13—Co1—N16	94.9 (2)	N23—Co2—N22	86.0 (2)
N15—Co1—N16	85.5 (2)	O21A—N21—O21B	119.5 (5)
N14—Co1—N16	179.0 (2)	O21A—N21—Co2	120.1 (4)
N12—Co1—N11	178.1 (2)	O21B—N21—Co2	120.4 (4)
N13—Co1—N11	89.3 (2)	N31—Co3—N32	89.6 (2)
N15—Co1—N11	90.8 (2)	N31—Co3—N33	90.6 (2)
N14—Co1—N11	90.6 (2)	N32—Co3—N33	85.8 (2)

Table 2. Hydrogen-bonding geometry (\AA , $^\circ$)

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N13—H13A \cdots O31A	0.90	2.08	2.973 (7)	170
N14—H14A \cdots O21A ⁱ	0.90	2.17	3.037 (8)	161
N15—H15A \cdots O24 ⁱⁱ	0.90	2.09	2.969 (10)	164

Symmetry codes: (i) $x, 1+y, z$; (ii) $1+x, 1+y, z$.

H atoms were included as a riding model with C—H = 0.97 \AA and N—H = 0.90 \AA .

Data collection: *CAD-4 EXPRESS* (Straver, 1992). Cell refinement: *CAD-4 EXPRESS*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990). Program(s) used to refine structure: *SHELX97* (Sheldrick, 1997). Software used to prepare material for publication: *SHELX97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1228). Services for accessing these data are described at the back of the journal.

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A redetermination of bis(ethylenediamine-*N,N'*)bis(perchlorato-*O*)copper(II)

KAREN R. MAXCY AND MARK M. TURNBULL

Carlson School of Chemistry and Biochemistry, Clark University, 950 Main Street, Worcester, MA 01610, USA.
E-mail: mturnbull@clarku.edu

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Abstract

Reaction of copper(II) perchlorate with excess ethylenediamine (en) in aqueous solution gave the title complex, [Cu(ClO₄)₂(C₂H₈N₂)₂]. The cation is centrosymmetric with a mean Cu—N distance of 2.016 (2) \AA . There are semi-coordinate bonds to the perchlorate ions with a Cu—O distance of 2.579 (4) \AA . The N—Cu—N angle is 84.69 (9)°, as expected for chelating en. The structure is stabilized by hydrogen bonds from three of the perchlorate O atoms to amino H atoms within each molecule and between molecules, linking them into chains.