

A dinuclear complex of cobalt(II) with 2,2'-(1,4-butanediyl)dibenzimidazole

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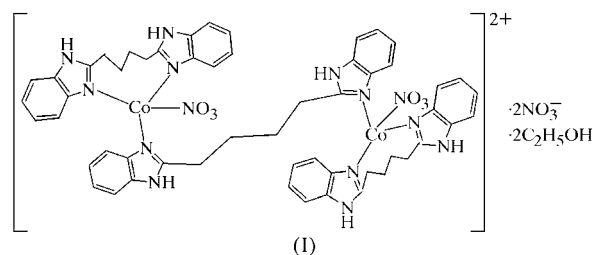
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The title complex, $[\mu\text{-}2,2'\text{-(1,4-butanediyl)di-1H-benzimidazole-}\kappa^2\text{N}^3:\text{N}^3']\text{bis}\{[2,2'\text{-(1,4-butanediyl)di-1H-benzimidazole-}\kappa^2\text{N}^3,\text{N}^3'](\text{nitrate-}\kappa\text{O})\text{cobalt(II)}\}$ dinitrate ethanol disolvate, $[\text{Co}_2(\text{NO}_3)_2(\text{C}_{18}\text{H}_{18}\text{N}_4)_3](\text{NO}_3)_2 \cdot 2\text{C}_2\text{H}_6\text{O}$, was obtained from self-assembly of cobalt(II) nitrate with 2,2'-(1,4-butanediyl)dibenzimidazole (*L*). The complex molecule lies about

an inversion centre and the flexible *L* ligands act in both bridging and chelating modes to form a dinuclear complex with unanticipated nine-membered chelate rings. The unique uncoordinated nitrate anion is linked to the cation by pairs of $\text{N-H}\cdots\text{O}$ hydrogen bonds, which determine the overall cation conformation. Cation–anion sets are then linked by a further $\text{N-H}\cdots\text{O}$ hydrogen bond to generate a chain along [010]. Chains are linked by $\text{C-H}\cdots\text{O}$ hydrogen bonds to form sheets in the (100) plane.

Comment

The role of coordination bonds in crystal engineering is currently of great interest because of their use in constructing novel compounds with special properties, such as electrical



conductivity, magnetism, host–guest chemistry and catalysis (Fujita *et al.*, 1994; Inoue *et al.*, 1996). So far, much of the work

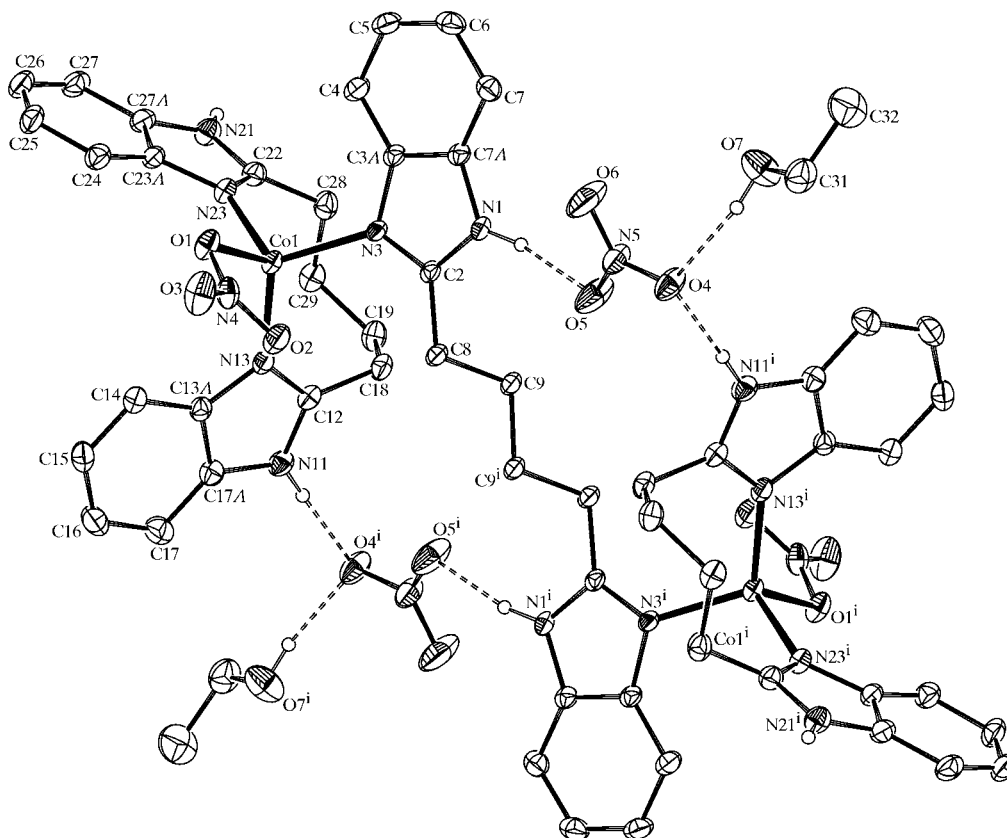


Figure 1

A view of the structure of (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 20% probability level. [Symmetry code: (i) $1 - x, 1 - y, 1 - z$.]

has been focused on coordination compounds with rigid ligands such as 4,4'-bipyridine and pyrazine (Carlucci *et al.*, 1994; Robinson & Zaworotko, 1995; Gable *et al.*, 1990). We are interested in utilizing substituted benzimidazole or imidazole ligands to construct new coordination compounds (Yang *et al.*, 2003). Our previous investigation of cobalt(II) complexes with the flexible ligand 1,1'-(1,4-butanediyl)dibenzimidazole (*L*) gave one- and two-dimensional coordination polymers (Ma *et al.*, 2000). In the present work, the assembly of 2,2'-(1,4-butanediyl)dibenzimidazole (*L*) with cobalt(II) nitrate resulted in the dinuclear complex $[\text{Co}_2\text{L}_3(\text{NO}_3)_2]^{2+} \cdot 2\text{NO}_3^- \cdot 2\text{C}_2\text{H}_5\text{OH}$, (I). The structure of the free ligand *L* has been reported (Chen *et al.*, 2002) and that of a copper complex, *catena*-[bis-(azido- κ N)copper(II)- μ -1,4-bis(2-benzimidazolyl)butane], is known (van Albada *et al.*, 2000); in both cases, ligand *L* lies about an inversion centre.

The $[\text{Co}_2\text{L}_3(\text{NO}_3)_2]^{2+}$ cation in complex (I) (Fig. 1) lies about an inversion centre [chosen for convenience to be $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$]. The unique cobalt(II) ion is in a distorted tetrahedral coordination environment, with three N atoms from two *L* ligands and one O atom from a nitrate anion (see Table 1 for selected geometric parameters). The *L* ligands in (I) display two different coordination modes; one *L* ligand lies about an inversion centre and bridges two cobalt(II) ions, while the other *L* ligand chelates the cobalt(II) ion, leading to a complex with two unanticipated nine-membered chelate rings. The Co—N distances (Table 1) are shorter than those found in other related cobalt(II) complexes (2.132 and 2.159 Å; Ma *et al.*, 2000). The distance between Co1 and Co1ⁱ [symmetry code: (i) 1 - x, 1 - y, 1 - z] is 10.420 (2) Å. We have previously reported two related complexes, namely $[\text{CoL}'_2(\text{H}_2\text{O})_2]^{2+} \cdot 2\text{NO}_3^- \cdot 8\text{H}_2\text{O}$ with a (4,4)-network and $[\text{CoL}'(\text{H}_2\text{O})_2(\text{CH}_3\text{CO}_2)_2] \cdot \text{H}_2\text{O}$ with an infinite chain structure, where *L'* is 1,1'-(1,4-butanediyl)dibenzimidazole (Ma *et al.*, 2000).

The uncoordinated nitrate moiety plays the role of counter-anion and determines the cation complex conformation by acting as an acceptor for pairs of N—H...O hydrogen bonds (Table 2) from the N1—H1 and N11ⁱ—H11ⁱ groups. The

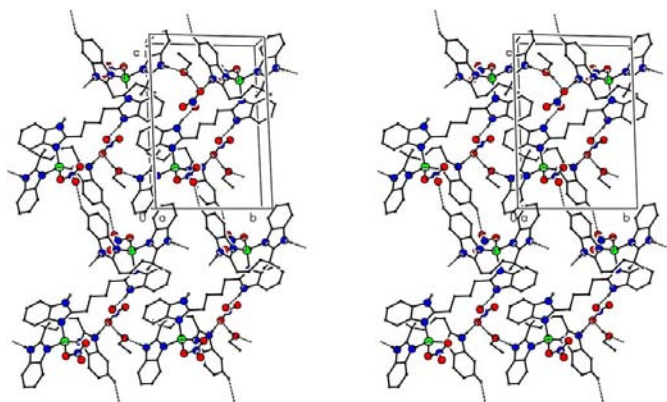


Figure 2
A stereoview of part of the hydrogen-bonded (100) sheet of (I).

unique ethanol molecule is also linked to the counter-anion by an O—H...O hydrogen bond (Table 2). In the crystal structure, the $[\text{Co}_2\text{L}_3(\text{NO}_3)_2]^{2+} \cdot 2\text{NO}_3^- \cdot 2\text{C}_2\text{H}_5\text{OH}$ units are linked to form chains in the [010] direction by an N—H...O hydrogen bond involving the N21—H21 group and the adjacent ethanol O atom (see Table 2). Chains are linked to form sheets in the (100) plane by C—H...O hydrogen bonds (Table 2) between aromatic group C16—H16 and nitro atom O3 of a symmetry-related cation (Fig. 2)

Experimental

Ligand *L* was synthesized according to the method reported by Berends & Stephan (1984). A mixture of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.291 g, 1 mmol) and *L* (0.435 g, 1.5 mmol) in ethanol (20 ml) was refluxed for 30 min, and a purple solution was obtained. Purple crystals were obtained after leaving the solution to stand at room temperature for several days. The same product, (I), was isolated using different cobalt(II)/*L* molar ratios of 1:1, 1:1.5 and 1:2; this result may be caused by the low solubility of complex (I) (yield 64% based on Co). Analysis calculated for $\text{C}_{58}\text{H}_{66}\text{Co}_2\text{N}_{16}\text{O}_{14}$: C 52.41, H 5.00, N 16.86%; found: C 52.35, H 4.92, N 16.41%. IR (cm^{-1} , KBr): 3436 (s), 3121 (w), 2943 (w), 2340 (w), 1641 (w), 1529 (m), 1458 (s), 1382 (vs), 1240 (w), 1103 (s), 1038 (w), 948 (w), 837 (w), 757 (w), 622 (m).

Crystal data

$[\text{Co}_2(\text{NO}_3)_2(\text{C}_{18}\text{H}_{18}\text{N}_4)_3] \cdot (\text{NO}_3)_2 \cdot 2\text{C}_2\text{H}_6\text{O}$	$Z = 1$
$M_r = 1329.13$	$D_x = 1.427 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 8.7260$ (17) Å	Cell parameters from 7174 reflections
$b = 11.295$ (2) Å	$\theta = 2.3\text{--}27.5^\circ$
$c = 16.284$ (3) Å	$\mu = 0.61 \text{ mm}^{-1}$
$\alpha = 90.16$ (3)°	$T = 193$ (2) K
$\beta = 96.76$ (3)°	Block, purple
$\gamma = 103.85$ (3)°	$0.51 \times 0.44 \times 0.23 \text{ mm}$
$V = 1546.6$ (5) Å ³	

Data collection

Rigaku R-Axis RAPID diffractometer	6778 independent reflections
ω scans	4638 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	$R_{\text{int}} = 0.032$
$T_{\text{min}} = 0.725, T_{\text{max}} = 0.867$	$\theta_{\text{max}} = 27.5^\circ$
13 292 measured reflections	$h = 0 \rightarrow 11$
	$k = -14 \rightarrow 13$
	$l = -21 \rightarrow 20$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.040$	$w = 1/[\sigma^2(F_o^2) + (0.0475P)^2]$
$wR(F^2) = 0.089$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.91$	$(\Delta/\sigma)_{\text{max}} < 0.001$
6778 reflections	$\Delta\rho_{\text{max}} = 0.50 \text{ e \AA}^{-3}$
408 parameters	$\Delta\rho_{\text{min}} = -0.38 \text{ e \AA}^{-3}$

Table 1
Selected geometric parameters (Å, °).

Co1—O1	1.9980 (15)	Co1—N3	2.0233 (17)
Co1—N13	2.0125 (17)	Co1—N23	2.0303 (18)
O1—Co1—N13	117.59 (7)	N13—Co1—N23	102.62 (7)
O1—Co1—N3	105.64 (7)	N3—Co1—N23	112.74 (7)
N13—Co1—N3	116.37 (7)	N4—O1—Co1	105.64 (12)
O1—Co1—N23	100.93 (7)		

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 \cdots O5	0.88	1.91	2.777 (3)	168
N11—H11 \cdots O4 ⁱ	0.88	1.99	2.869 (2)	178
N21—H21 \cdots O7 ⁱⁱ	0.88	1.89	2.747 (3)	163
O7—H7 \cdots O4	0.84	2.01	2.817 (3)	162
C16—H16 \cdots O3 ⁱⁱⁱ	0.95	2.57	3.358 (3)	140

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

All H atoms were visible in difference maps and were allowed for in the refinement as riding atoms, with C—H distances of 0.95–0.99 Å, N—H distances of 0.88 Å and an O—H distance of 0.84 Å, and with $U_{\text{iso}}(\text{H})$ values of 1.2–1.5 times $U_{\text{eq}}(\text{C,N,O})$.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *PROCESS-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997) in *WinGX* (Farrugia, 1999); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1805). Services for accessing these data are described at the back of the journal.

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