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Bis(diethylenetriamine)cobalt(III) hexacyanocobaltate(III) dihydrate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
R factor = 0.032
wR factor = 0.095
Data-to-parameter ratio = 17.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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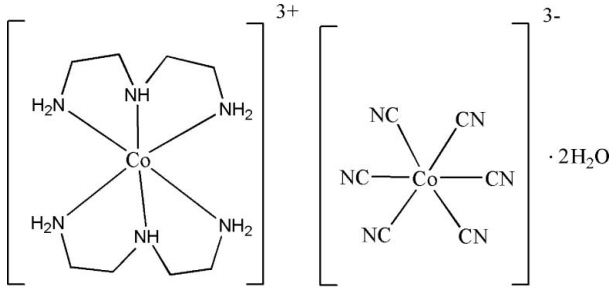
The title compound, $[Co(C_4H_{13}N_3)_2][Co(CN)_6]\cdot 2H_2O$, comprises one $[Co(dien)_2]^{3+}$ cation (dien is diethylenetriamine), one $[Co(CN)_6]^{3-}$ anion and two water molecules. The Co^{3+} atom of the $[Co(dien)_2]^{3+}$ cation is six-coordinated by six N atoms from two diethylenetriamine groups. The Co^{3+} atom of the $[Co(CN)_6]^{3-}$ anion is six-coordinated by six C atoms from six cyanide ions. Neighboring cations and anions are connected by hydrogen bonds to each other and to the water molecules. The metal atoms lie on inversion sites.

Comment

There is a possibility of fine-tuning the magnetic properties of bimetallic assemblies based upon hexacyanometallate building blocks, $[M(CN)_6]^{3-}$ (M = Fe, Cr, Mn or Co), by modifying the chelating ligand. A large number of two-dimensional (Ohba *et al.*, 2002; Miyasaka *et al.*, 2003) and one-dimensional (Fu *et al.*, 1997) structures of the formula $[M'(L)_n]_y[M(CN)_6]_x$ have been obtained (M' = Cu and L = diethylenetriamine or ethylenediaminemonoacetate). Diethylenetriamine (dien) has been used as the ligand L to prepare the title Co^{3+} complex, (I), in our laboratory.



(I)

The asymmetric unit of (I) consists of one $[Co(dien)_2]^{3+}$ cation, one $[Co(CN)_6]^{3-}$ anion and two water solvent molecules. The Co^{3+} atom of the $[Co(dien)_2]^{3+}$ cation is six-coordinated by six N atoms from two dien groups. The Co^{3+} atom of the $[Co(CN)_6]^{3-}$ anion is six-coordinated by six C atoms from six cyanide groups (Fig. 1). The metal atoms lie on inversion sites.

Neighbouring cations and anions are connected by hydrogen bonds to the water molecules and to each other, to form sheets (Table 2, Fig. 2).

Experimental

KCN (1.302 g, 20 mmol) in H_2O (10 ml) and diethylenetriamine (0.710 g, 5.8 mmol) in CH_3OH (10 ml) were added dropwise to a

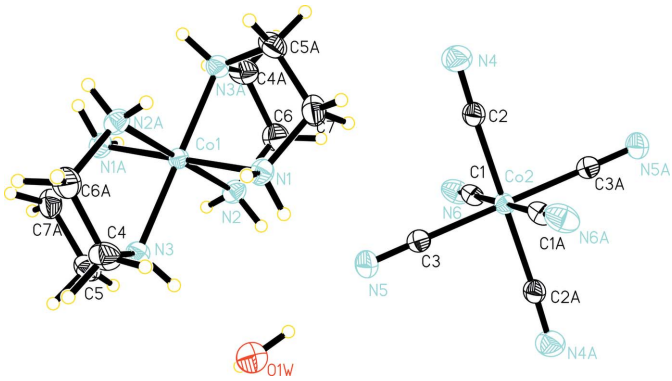


Figure 1
The structure of (I), showing 30% probability displacement ellipsoids.

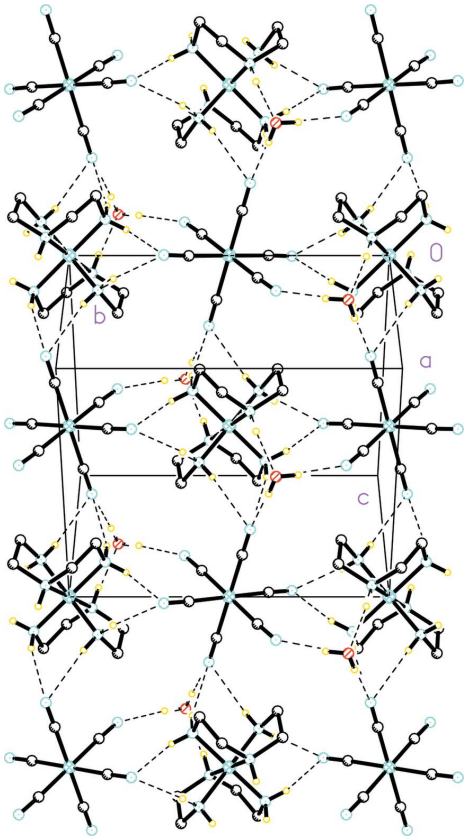


Figure 2
A view along [10$\bar{1}$], showing a single layer of (I), with hydrogen bonds indicated by dashed lines.

solution of $CoCl_2{\cdot}6H_2O$ (0.700 g, 2.9 mmol) in H_2O (10 ml). The mixture was stirred for 30 min, filtered, and left to stand at room temperature. Yellow crystals of (I) formed after several weeks (yield 50%).

Crystal data

$[Co(C_4H_{13}N_3)_2][Co(CN)_6]{\cdot}2H_2O$
M_r = 516.36
Monoclinic, $P2_1/n$
a = 8.148 (3) Å
b = 12.217 (4) Å
c = 10.935 (4) Å
β = 94.973 (7)°
V = 1084.3 (6) Å^3
Z = 2
D_x = 1.582 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 1.57 mm^{-1}
T = 293 (2) K
Block, yellow
0.48 × 0.31 × 0.13 mm

Data collection

Bruker APEX area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.520, T_{max} = 0.822
6186 measured reflections
2375 independent reflections
1473 reflections with $I > 2\sigma(I)$
R_{int} = 0.023
θ_{max} = 27.2°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.095
S = 1.04
2375 reflections
139 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0501P)^2 + 0.0602P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.45 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Co1—N3	1.960 (2)	Co2—C2	1.900 (3)
Co1—N1	1.965 (2)	Co2—C3	1.903 (3)
Co1—N2	1.971 (2)	Co2—C1	1.903 (3)
N3—Co1—N3^{i}	180	N3—Co1—N2	94.05 (9)
N3—Co1—N1^{i}	86.83 (9)	N1^{i}—Co1—N2	90.12 (9)

Symmetry code: (i) $-x, -y, -z$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2A···N5	0.90	2.27	3.083 (3)	149
N2—H2B···N6^{ii}	0.90	2.30	3.082 (3)	146
O1W—H1D···N4^{iii}	0.86	2.04	2.886 (3)	168
N3—H3A···O1W	0.91	2.05	2.955 (3)	174
N1—H1A···N6^{iv}	0.90	2.15	2.990 (3)	154
O1W—H1C···N5	0.86	2.02	2.879 (3)	175

Symmetry codes: (ii) $x-\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$; (iii) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (iv) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$.

H atoms were visible in difference maps and were subsequently treated as riding atoms with distances C—H = 0.97 Å (CH_2), and N—H = 0.90 (NH_2) and 0.91 Å (NH). H atoms attached to water O atoms were located in difference Fourier maps and constrained to ride on their carrier atoms, with O—H = 0.86 Å, and U_{iso} (H) = 1.5U_{eq}(O).

Data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1999); software used to prepare material for publication: *SHELXTL*.

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