C27—N28*A*	1.351 (13)	Cl3—O4	1.35 (2)
C27—N28*B*	1.347 (13)	Cl3—O1*A*	1.253 (10)
N28*A*—C29*A*	1.49 (2)	Cl3—O2*A*	1.304 (13)
N28*A*—C33*A*	1.48 (2)	Cl3—O3*A*	1.333 (14)
C29*A*—C30*A*	1.51 (2)	Cl3—O4*A*	1.41 (2)
C30*A*—O31*A*	1.48 (5)		
P1—Ni—P2	86.81 (4)	N28*A*—C29*A*—C30*A*	110.0 (9)
P1—Ni—S1	102.69 (4)	O31*A*—C30*A*—C29*A*	109.8 (18)
P2—Ni—S2	93.93 (4)	C32*A*—O31*A*—C30*A*	110 (3)
S1—Ni—S2	79.36 (4)	O31*A*—C32*A*—C33*A*	113.2 (15)
C27—S1—Ni	84.51 (14)	N28*A*—C33*A*—C32*A*	109.4 (10)
C27—S2—Ni	85.21 (14)	C27—N28*B*—C29*B*	122.7 (11)
C3—P1—C9	104.1 (2)	C27—N28*B*—C33*B*	123.7 (10)
C3—P1—C2	105.3 (2)	C33*B*—N28*B*—C29*B*	113.5 (10)
C9—P1—C2	107.1 (2)	N28*B*—C29*B*—C30*B*	109.9 (9)
C3—P1—Ni	104.67 (13)	O31*B*—C30*B*—C29*B*	107.7 (22)
C9—P1—Ni	125.41 (14)	C32*B*—O31*B*—C30*B*	113 (3)
C2—P1—Ni	108.54 (13)	O31*B*—C32*B*—C33*B*	112.0 (20)
C15—P2—C21	107.4 (2)	N28*B*—C33*B*—C32*B*	109.7 (10)
C15—P2—C1	107.8 (2)	Cl1—C34—Cl2	114.6 (4)
C21—P2—C1	107.1 (2)	O1—Cl3—O2	91.8 (13)
C15—P2—Ni	115.30 (13)	O1—Cl3—O3	115.9 (18)
C21—P2—Ni	109.00 (14)	O1—Cl3—O4	124.8 (14)
C1—P2—Ni	109.92 (13)	O2—Cl3—O3	104.9 (14)
N28*B*—C27—S2	123.4 (6)	O2—Cl3—O4	108.5 (17)
N28*A*—C27—S2	122.4 (6)	O3—Cl3—O4	107.8 (19)
N28*B*—C27—S1	123.5 (6)	O1*A*—Cl3—O2*A*	128.8 (14)
N28*A*—C27—S1	123.7 (6)	O1*A*—Cl3—O3*A*	84.5 (15)
S2—C27—S1	110.8 (2)	O1*A*—Cl3—O4*A*	113.6 (14)
C27—N28*A*—C29*A*	123.8 (10)	O2*A*—Cl3—O3*A*	107.2 (17)
C27—N28*A*—C33*A*	122.1 (10)	O2*A*—Cl3—O4*A*	112.5 (16)
C33*A*—N28*A*—C29*A*	112.4 (10)	O3*A*—Cl3—O4*A*	101.0 (11)

Data collection, cell refinement and data reduction were performed using *XSCANS* (Siemens, 1991). The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1990*a*) and refined using *SHELXL*93 (Sheldrick, 1993). Atoms in the morpholine ring showed very high disorder with unreliable C—C bond lengths (1.12 Å). Moreover, the displacement ellipsoids for all the atoms in the ring were oriented in the same direction, *i.e.* perpendicular to the mean plane of the ring. Hence, it was decided to consider the morpholine ring as two entities with opposite orientations (*A* and *B*) and the occupancies of *A* and *B* were initially refined and then fixed at 0.5. The atoms in *A* and *B* were refined anisotropically with the same U_{ij} values being assigned to the same atom species (N28*A* ≡ N28*B*, O31*A* ≡ O31*B*, C*nA* ≡ C*nB*). The O atoms of the disordered perchlorate group were divided into two sets, each having 0.5 occupancy, and refined anisotropically. The H atoms were fixed geometrically and not refined, but were allowed to ride on those atoms to which they are attached. *SHELXTL/PC* (Sheldrick, 1990*b*) software was used for the molecular graphics and *PARST* (Nardelli, 1983) was used for all other geometrical calculations.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: LI1125). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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fac-$[Co(C_5H_4NOS)_3].H_2O.\frac{1}{2}CH_3OH$ and *fac*-$[Co(C_5H_4NOS)_3].\frac{1}{3}CH_3OH$

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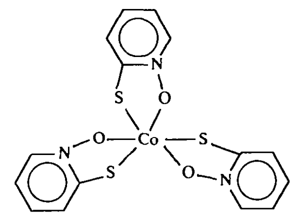
Abstract

Crystals of tris(2-mercaptopyridine *N*-oxido)cobalt(III) monohydrate hemimethanol solvate, *fac*-$[Co(C_5H_4NOS)_3].H_2O.\frac{1}{2}CH_3OH$ (1), contain *fac*-$[Co(III)(mpo)_3]$ (Hmpo = 2-mercaptopyridine *N*-oxide), H_2O and MeOH molecules linked by hydrogen bonds. The asymmetric unit consists of two molecules of the cobalt complex, two water and one methanol molecule. The asymmetric unit of the closely related complex tris(2-mercaptopyridine *N*-oxido)cobalt(III) $\frac{1}{3}$-methanol solvate, *fac*-$[Co(C_5H_4NOS)_3].\frac{1}{3}CH_3OH$ (2), contains three discrete $Co(mpo)_3$ molecules and one MeOH molecule which is linked to one of the $Co(mpo)_3$ units *via* a hydrogen bond. The Co^{III} complex molecules in (1) and (2) do not differ significantly. Each Co atom is coordinated by an O_3S_3 donor set which defines a distorted *facial* octahedron. Three mpo ligands are chelated to each Co atom, the average O—Co—S

bite angle is 87.5 (2) for (1) and 87.4 (2)° for (2). The average Co—S and Co—O distances are 2.205 (3) and 1.942 (2) Å, respectively, for (1), and 2.205 (3) and 1.951 (5) Å, respectively, for (2).

Comment

Both compounds (1) and (2) were synthesized as part of our investigation of transition metal complexes with bidentate sulfur–oxygen ligands (Kang, Weng, Wu, Wang, Guo, Huang, Huang & Liu, 1988; Chen, Hu, Weng, Xu, Wu & Kang, 1991). Seven chelating modes for the ligand *o*-mercaptophenol (H_2mp) have been observed in a series of mixed *O*,*S*-ligated transition metal complexes (Kang, Weng, Liu, Wu, Huang, Lu, Cai, Chen & Lu, 1990; Kang, Peng, Hong, Wu, Chen, Weng, Lei & Liu, 1991; Kang, Hu, Weng, Wu, Chen & Xu, 1992). We have now extended our research to the ligand 2-mercapto-pyridine *N*-oxide (Hmpo).



The structures of the Co(mpo)$_3$ units of both compounds are quite similar to those reported earlier for *fac*-[Co(mpo)$_3$].MeCN (Hu, Weng, Huang, Chen, Wu & Kang, 1991) although the average Co—S, Co—O and S—C distances in (1) and (2) are all lengthened slightly (by nearly 0.01 Å) as a result of the presence of hydrogen bonds and also of differences in the molecular packing. The average O—N distances are within the range found for other mpo-ligated complexes (Kang, Xu, Peng, Wu, Chen, Hu, Hong & Lu, 1993). In compound (1), the ligand atoms O(4) and O(6) are connected to H_2O(*w*) and the atom O(5) to H_2O(*ww*) *via* weak hydrogen bonds, while the latter water molecule [H_2O(*ww*)] is also hydrogen bonded to H_2O(*w*) and MeO(1*m*)H. The mean chelate angles Co—S—C and Co—O—N [96.4 (2) and 115.8 (2)°, respectively, for (1), and 97.1 (2) and 115.8 (2)°, respectively, for (2)] and the mean bite angle of 87.5 (2) in (1) and 87.4 (2)° in (2) are very close to those reported by Kang, Xu, Peng,

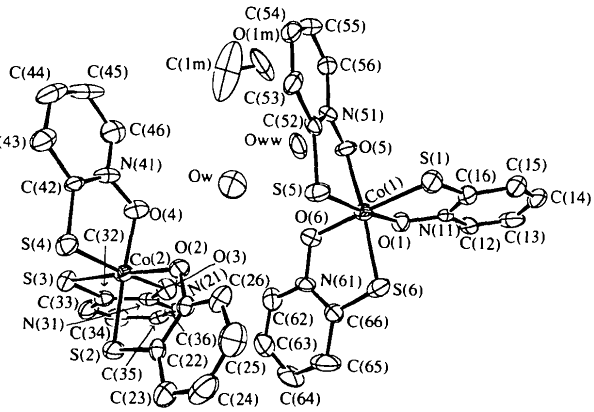


Fig. 1. Structure and atomic labelling of (1) with displacement ellipsoids drawn at the 40% probability level (*ORTEP*II; Johnson, 1976).

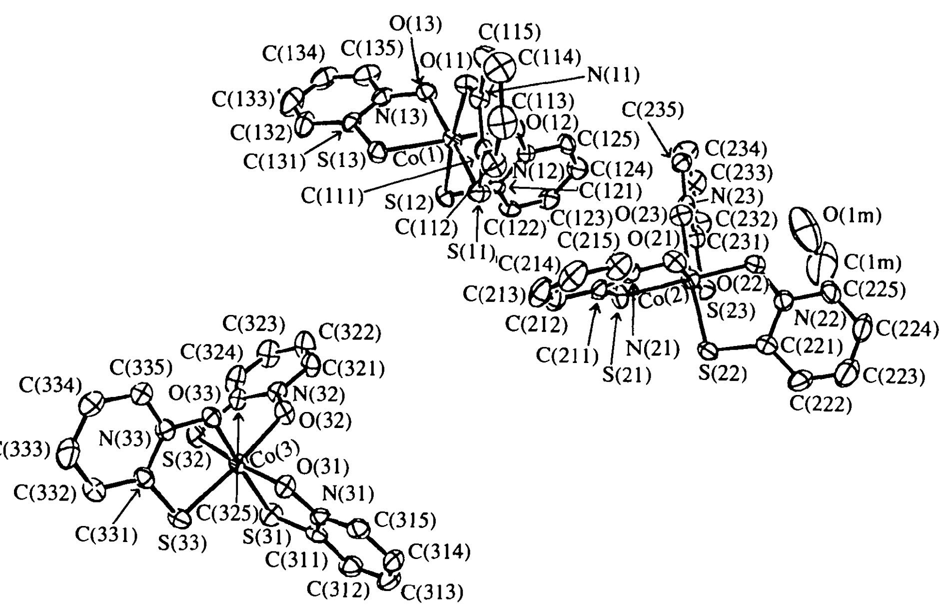


Fig. 2. Structure and atomic labelling of (2) with displacement ellipsoids drawn at the 40% probability level (*ORTEP*II; Johnson, 1976).

Wu, Chen, Hu, Hong & Lu (1993), and correspond well to the previous interpretation of bonding orbitals. The packing of the molecules of (2) in the unit cell is interesting, consisting of two sets of staircase-like stripes made up of parallel and independent triangular units of three $Co(mpo)_3$ groups with one MeOH tail (*via* a hydrogen bond). This type of arrangement of molecular units may lead to interesting physical properties which are still under investigation. Figs. 1 and 2 show the asymmetric units of (1) and (2), respectively.

Experimental

Crystals of (1) were obtained from the reaction of $CoCl_2$ with mpoNa (1:2 ratio) in MeOH solvent (AR, 0.5% water) at room temperature, while those of (2) came from the reaction of $CoCl_2$ with mpoNa (1:2 ratio) in anhydrous MeOH (dried vigorously before use) at room temperature.

Compound (1)

Crystal data

$[Co(C_5H_4NOS)_3].H_2O.\frac{1}{2}CH_4O$
$M_r = 471.44$
Triclinic
$P\bar{1}$
$a = 12.679$ (6) Å
$b = 14.794$ (10) Å
$c = 12.653$ (7) Å
$\alpha = 114.16$ (5)°
$\beta = 117.54$ (4)°
$\gamma = 75.97$ (6)°
$V = 1915.9$ Å^3
$Z = 4$
$D_x = 1.63$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 20 reflections
$\theta = 9$–12°
$\mu = 1.24$ mm^{-1}
$T = 293$ K
Cube
0.30 × 0.25 × 0.20 mm
Black

Data collection

Rigaku AFC-5*R* diffractometer
ω–2θ scans
Absorption correction: empirical
$T_{min} = 0.901$, $T_{max} = 0.996$
7088 measured reflections
6944 independent reflections
2728 observed reflections [$I > 2\sigma(I)$]
$R_{int} = 0.082$
$\theta_{max} = 25°$
$h = 0 \rightarrow 15$
$k = -17 \rightarrow 17$
$l = -15 \rightarrow 13$
3 standard reflections monitored every 250 reflections intensity decay: 0.8%

Refinement

Refinement on F
$R = 0.062$
$wR = 0.064$
$S = 1.36$
2584 reflections
487 parameters
H-atom parameters not refined
$w = 4F_o^2/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{max} = 0.42$
$\Delta\rho_{max} = 0.65$ e Å^{-3}
$\Delta\rho_{min} = -0.52$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from Cromer & Waber (1974)

Compound (2)

Crystal data

$[Co(C_5H_4NOS)_3].\frac{1}{3}CH_4O$
$M_r = 448.08$
Monoclinic
$P2_1/n$
$a = 21.997$ (11) Å
$b = 9.094$ (5) Å
$c = 27.594$ (9) Å
$\beta = 95.87$ (4)°
$V = 5490.8$ Å^3
$Z = 12$
$D_x = 1.63$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 20 reflections
$\theta = 9$–12°
$\mu = 1.24$ mm^{-1}
$T = 296$ (1) K
Cubes
0.41 × 0.33 × 0.24 mm
Black

Data collection

Rigaku AFC-5*R* diffractometer
ω–2θ scans
Absorption correction: empirical
$T_{min} = 0.810$, $T_{max} = 1.00$
10 629 measured reflections
10 614 independent reflections
5535 observed reflections [$I > 3\sigma(I)$]
$R_{int} = 0.046$
$\theta_{max} = 25°$
$h = 0 \rightarrow 26$
$k = 0 \rightarrow 10$
$l = -32 \rightarrow 32$
3 standard reflections monitored every 250 reflections intensity decay: 0.4%

Refinement

Refinement on F
$R = 0.052$
$wR = 0.062$
$S = 1.38$
5523 reflections
694 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.010F_o)^2 + 1]$
$(\Delta/\sigma)_{max} = 0.03$
$\Delta\rho_{max} = 0.44$ e Å^{-3}
$\Delta\rho_{min} = -0.57$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from Cromer & Waber (1974)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (1)

$B_{eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}
Co(1)	0.4826 (1)	0.7273 (1)	0.3470 (1)	2.61 (4)
Co(2)	0.1697 (1)	0.7858 (1)	0.7138 (1)	2.74 (4)
S(1)	0.5732 (3)	0.7724 (2)	0.2659 (3)	3.80 (9)
S(2)	0.3152 (3)	0.7950 (2)	0.9017 (3)	3.54 (8)
S(3)	0.0415 (3)	0.7515 (2)	0.7621 (3)	3.50 (9)
S(4)	0.1180 (3)	0.9463 (2)	0.7803 (3)	3.43 (9)
S(5)	0.4449 (3)	0.8838 (2)	0.4484 (3)	3.45 (9)
S(6)	0.6502 (3)	0.7203 (2)	0.5128 (3)	3.64 (9)
O(*w*)	0.1568 (9)	0.7169 (8)	0.3644 (9)	7.9 (4)
O(*ww*)	0.139 (2)	0.606 (2)	0.129 (2)	14 (1)
O(1)	0.5089 (6)	0.5907 (5)	0.2463 (6)	3.2 (2)
O(1*m*)	−0.089 (2)	0.665 (3)	−0.0221 (2)	19 (1)
O(2)	0.2870 (6)	0.8087 (5)	0.6705 (6)	3.2 (2)
C(2*m*)	−0.097 (3)	0.736 (3)	0.084 (4)	15 (2)
O(3)	0.1984 (6)	0.6444 (5)	0.6393 (6)	3.5 (2)
O(4)	0.0516 (7)	0.7803 (5)	0.5447 (6)	3.9 (2)
O(5)	0.3275 (6)	0.7341 (5)	0.2097 (6)	3.4 (2)
O(6)	0.4054 (6)	0.6767 (5)	0.4114 (6)	3.6 (2)

N(11)	0.5769 (7)	0.5755 (6)	0.1848 (7)	2.8 (2)
N(21)	0.3919 (7)	0.8373 (6)	0.7669 (7)	2.5 (2)
N(31)	0.1438 (8)	0.5842 (6)	0.6491 (7)	2.8 (3)
N(41)	−0.0180 (8)	0.8649 (6)	0.5381 (7)	3.4 (3)
N(51)	0.2823 (7)	0.8296 (6)	0.2151 (7)	2.9 (2)
N(61)	0.4782 (8)	0.6535 (6)	0.5174 (7)	2.9 (3)
C(12)	0.6061 (10)	0.4797 (8)	0.1227 (9)	3.4 (3)
C(13)	0.6724 (10)	0.4593 (9)	0.0594 (10)	4.9 (4)
C(14)	0.7066 (10)	0.5374 (10)	0.0488 (10)	6.1 (5)
C(15)	0.6796 (10)	0.6345 (9)	0.1121 (10)	3.9 (4)
C(16)	0.6121 (9)	0.6534 (8)	0.1810 (9)	3.6 (3)
C(22)	0.4200 (9)	0.8334 (7)	0.8815 (9)	2.5 (3)
C(23)	0.5323 (10)	0.8622 (9)	0.9797 (10)	4.2 (4)
C(24)	0.6064 (10)	0.8965 (10)	0.9544 (10)	5.7 (5)
C(25)	0.5733 (10)	0.9038 (10)	0.8361 (10)	5.6 (4)
C(26)	0.4633 (10)	0.8735 (9)	0.7440 (10)	3.8 (4)
C(32)	0.0689 (9)	0.6233 (8)	0.7083 (9)	2.8 (3)
C(33)	0.0138 (10)	0.5586 (9)	0.7190 (10)	4.1 (4)
C(34)	0.0338 (10)	0.4578 (9)	0.6664 (10)	4.5 (4)
C(35)	0.1095 (10)	0.4221 (8)	0.6047 (10)	3.5 (3)
C(36)	0.1661 (10)	0.4859 (7)	0.6004 (9)	2.9 (3)
C(42)	0.0041 (9)	0.9469 (8)	0.6362 (9)	2.8 (3)
C(43)	−0.0691 (10)	1.0359 (9)	0.6189 (10)	4.2 (4)
C(44)	−0.1576 (10)	1.0294 (9)	0.5034 (10)	5.3 (4)
C(45)	−0.1831 (10)	0.9396 (9)	0.4043 (10)	5.8 (4)
C(46)	−0.1105 (10)	0.8557 (9)	0.4215 (10)	4.7 (4)
C(52)	0.3274 (9)	0.9069 (7)	0.3178 (8)	2.4 (3)
C(53)	0.2771 (9)	1.0025 (8)	0.3161 (10)	3.6 (3)
C(54)	0.1829 (10)	1.0125 (8)	0.2067 (10)	4.0 (3)
C(55)	0.1401 (10)	0.9280 (9)	0.1014 (10)	4.5 (4)
C(56)	0.1898 (10)	0.8388 (9)	0.1055 (9)	3.7 (4)
C(62)	0.4234 (10)	0.6129 (8)	0.5580 (10)	4.0 (3)
C(63)	0.4883 (10)	0.5854 (10)	0.6610 (10)	5.8 (4)
C(64)	0.6051 (10)	0.5931 (10)	0.7167 (10)	7.1 (5)
C(65)	0.6620 (10)	0.6378 (10)	0.6790 (10)	6.4 (5)
C(66)	0.5965 (10)	0.6672 (8)	0.5734 (9)	3.7 (3)

Table 2. *Selected geometric parameters* (Å, °) *for* (1)

Co(1)—S(1)	2.200 (4)	Co(2)—S(2)	2.208 (3)
Co(1)—S(5)	2.199 (3)	Co(2)—S(3)	2.201 (4)
Co(1)—S(6)	2.208 (3)	Co(2)—S(4)	2.213 (3)
Co(1)—O(1)	1.943 (8)	Co(2)—O(2)	1.944 (7)
Co(1)—O(5)	1.945 (7)	Co(2)—O(3)	1.932 (7)
Co(1)—O(6)	1.943 (8)	Co(2)—O(4)	1.945 (7)
S(1)—C(16)	1.74 (1)	S(2)—C(22)	1.72 (2)
S(5)—C(52)	1.73 (2)	S(3)—C(32)	1.74 (1)
S(6)—C(66)	1.70 (1)	S(4)—C(42)	1.73 (2)
O(1)—N(11)	1.34 (2)	O(2)—N(21)	1.34 (1)
O(5)—N(51)	1.38 (2)	O(3)—N(31)	1.33 (2)
O(6)—N(61)	1.36 (1)	O(4)—N(41)	1.35 (2)
O(*w*)···O(*ww*)	2.67 (3)	O(*w*)···O(4)	2.88 (1)
O(*w*)···O(6)	2.88 (1)	O(*ww*)···O(5)	2.95 (3)
O(*ww*)···O(1*m*)	2.79 (4)		
S(1)—Co(1)—S(5)	90.5 (1)	S(2)—Co(2)—S(3)	92.0 (1)
S(1)—Co(1)—S(6)	92.2 (1)	S(2)—Co(2)—S(4)	92.3 (1)
S(1)—Co(1)—O(1)	87.8 (2)	S(2)—Co(2)—O(2)	87.0 (2)
S(1)—Co(1)—O(5)	92.6 (2)	S(2)—Co(2)—O(3)	93.9 (2)
S(1)—Co(1)—O(6)	175.5 (3)	S(2)—Co(2)—O(4)	174.9 (3)
S(5)—Co(1)—S(6)	91.1 (1)	S(3)—Co(2)—S(4)	91.1 (1)
S(5)—Co(1)—O(1)	176.0 (2)	S(3)—Co(2)—O(2)	176.8 (2)
S(5)—Co(1)—O(5)	87.2 (2)	S(3)—Co(2)—O(3)	87.4 (3)
S(5)—Co(1)—O(6)	94.0 (2)	S(3)—Co(2)—O(4)	93.1 (2)
S(6)—Co(1)—O(1)	92.6 (2)	S(4)—Co(2)—O(2)	92.1 (2)
S(6)—Co(1)—O(5)	174.9 (3)	S(4)—Co(2)—O(3)	173.7 (2)
S(6)—Co(1)—O(6)	87.7 (2)	S(4)—Co(2)—O(4)	87.6 (2)
O(1)—Co(1)—O(5)	89.2 (4)	O(2)—Co(2)—O(3)	89.6 (3)
O(1)—Co(1)—O(6)	87.8 (3)	O(2)—Co(2)—O(4)	88.0 (3)
O(5)—Co(1)—O(6)	87.7 (4)	O(3)—Co(2)—O(4)	86.3 (3)
Co(1)—S(1)—C(16)	96.7 (4)	Co(2)—S(2)—C(22)	96.6 (4)
Co(1)—S(5)—C(52)	96.2 (4)	Co(2)—S(3)—C(32)	96.2 (4)
Co(1)—S(6)—C(66)	97.1 (4)	Co(2)—S(4)—C(42)	95.7 (4)
Co(1)—O(1)—N(11)	116.5 (6)	Co(2)—O(2)—N(21)	116.0 (6)
Co(1)—O(5)—N(51)	113.5 (6)	Co(2)—O(3)—N(31)	118.1 (6)
Co(1)—O(6)—N(61)	115.7 (6)	Co(2)—O(4)—N(41)	115.2 (6)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (2)

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Co(1)	0.78735 (5)	0.0729 (1)	0.63754 (4)	2.46 (2)
Co(2)	1.05291 (5)	−0.1179 (1)	0.88477 (4)	2.98 (2)
Co(3)	0.41979 (5)	0.2285 (1)	0.86907 (4)	2.71 (2)
S(11)	0.8056 (1)	0.2775 (3)	0.67997 (8)	3.24 (5)
S(12)	0.7584 (1)	−0.0458 (3)	0.70088 (8)	3.10 (5)
S(13)	0.6926 (1)	0.1468 (3)	0.61818 (9)	3.34 (5)
S(21)	0.9554 (1)	−0.1681 (3)	0.8836 (1)	4.06 (6)
S(22)	1.0486 (1)	0.0185 (3)	0.95033 (9)	3.61 (5)
S(23)	1.0758 (1)	−0.3205 (3)	0.92733 (9)	4.40 (6)
S(31)	0.4332 (1)	0.1482 (3)	0.94483 (9)	3.80 (5)
S(32)	0.3570 (1)	0.0442 (3)	0.84933 (9)	3.65 (5)
S(33)	0.3430 (1)	0.3726 (3)	0.88365 (8)	3.70 (5)
O(11)	0.8219 (3)	0.1739 (6)	0.5832 (2)	3.1 (1)
O(12)	0.8689 (2)	−0.0098 (6)	0.6537 (2)	3.2 (1)
O(13)	0.7676 (3)	−0.0934 (6)	0.5941 (2)	3.4 (1)
O(21)	1.0303 (3)	0.0432 (7)	0.8406 (2)	3.8 (1)
O(22)	1.1382 (3)	−0.0536 (7)	0.8845 (2)	3.9 (1)
O(23)	1.0640 (3)	−0.2314 (7)	0.8266 (2)	3.7 (1)
O(31)	0.4823 (3)	0.3745 (6)	0.8877 (2)	3.1 (1)
O(32)	0.4850 (3)	0.1078 (6)	0.8495 (2)	3.3 (1)
O(33)	0.4124 (3)	0.3108 (6)	0.8037 (2)	3.0 (1)
N(11)	0.8331 (3)	0.3184 (7)	0.5901 (2)	2.7 (1)
N(12)	0.8752 (3)	−0.1051 (7)	0.6917 (2)	2.6 (1)
N(13)	0.7076 (3)	−0.1204 (8)	0.5846 (2)	3.5 (2)
N(21)	0.9705 (3)	0.0721 (8)	0.8327 (3)	3.5 (2)
N(22)	1.1596 (3)	0.0364 (9)	0.9218 (3)	3.7 (2)
N(23)	1.0807 (3)	−0.3737 (8)	0.8331 (3)	3.3 (2)
N(31)	0.5124 (3)	0.3601 (7)	0.9325 (2)	2.8 (1)
N(32)	0.4716 (3)	−0.0359 (7)	0.8427 (3)	3.0 (2)
N(33)	0.3610 (3)	0.3877 (8)	0.7904 (2)	2.9 (2)
C(111)	0.8235 (4)	0.3851 (9)	0.6326 (3)	2.8 (2)
C(112)	0.8323 (4)	0.5378 (10)	0.6354 (4)	3.9 (2)
C(113)	0.8525 (5)	0.6119 (10)	0.5969 (4)	4.7 (8)
C(114)	0.8643 (5)	0.5375 (10)	0.5550 (4)	4.9 (3)
C(115)	0.8539 (4)	0.3904 (10)	0.5521 (3)	4.2 (2)
C(121)	0.8271 (4)	−0.1356 (9)	0.7170 (3)	2.4 (2)
C(122)	0.8368 (4)	−0.2376 (10)	0.7550 (3)	3.2 (2)
C(123)	0.8928 (4)	−0.3005 (10)	0.7660 (3)	3.9 (2)
C(124)	0.9399 (4)	−0.2624 (10)	0.7402 (3)	4.3 (2)
C(125)	0.9311 (4)	−0.1665 (10)	0.7021 (3)	3.4 (2)
C(131)	0.6648 (4)	−0.0146 (10)	0.5918 (3)	3.3 (2)
C(132)	0.6036 (4)	−0.0502 (10)	0.5797 (4)	4.6 (2)
C(133)	0.5875 (5)	−0.1832 (10)	0.5609 (4)	6.0 (3)
C(134)	0.6325 (5)	−0.2867 (10)	0.5541 (4)	5.4 (3)
C(135)	0.6913 (5)	−0.2563 (10)	0.5660 (4)	4.5 (2)
C(211)	0.9280 (4)	−0.0177 (10)	0.8499 (3)	3.5 (2)
C(212)	0.8672 (5)	0.0176 (10)	0.8398 (4)	4.6 (2)
C(213)	0.8503 (5)	0.1386 (10)	0.8130 (4)	6.3 (3)
C(214)	0.8945 (5)	0.2289 (10)	0.7970 (4)	6.0 (3)
C(215)	0.9535 (5)	0.1951 (10)	0.8066 (4)	5.0 (3)
C(221)	1.1230 (4)	0.0808 (10)	0.9560 (3)	3.3 (2)
C(222)	1.1495 (5)	0.1740 (10)	0.9921 (3)	4.5 (2)
C(223)	1.2076 (6)	0.2171 (10)	0.9935 (4)	6.7 (3)
C(224)	1.2427 (5)	0.1748 (10)	0.9587 (4)	6.5 (3)
C(225)	1.2185 (4)	0.0826 (10)	0.9231 (3)	5.2 (3)
C(231)	1.0859 (4)	−0.4329 (10)	0.8784 (3)	3.7 (2)
C(232)	1.1023 (5)	−0.5819 (10)	0.8823 (4)	5.1 (3)
C(233)	1.1115 (6)	−0.6614 (10)	0.8415 (4)	5.9 (3)
C(234)	1.1072 (5)	−0.5943 (10)	0.7966 (4)	5.2 (3)
C(235)	1.0909 (5)	−0.4509 (10)	0.7926 (4)	4.3 (2)
C(311)	0.4939 (4)	0.2619 (10)	0.9646 (3)	3.2 (2)
C(312)	0.5246 (5)	0.2603 (10)	1.0110 (3)	4.3 (2)
C(313)	0.5734 (5)	0.3490 (10)	1.0241 (3)	4.7 (3)
C(314)	0.5920 (4)	0.4457 (10)	0.9897 (4)	4.3 (2)
C(315)	0.5612 (4)	0.4483 (10)	0.9443 (3)	3.6 (2)
C(321)	0.5194 (4)	−0.1257 (10)	0.8363 (4)	4.0 (2)
C(322)	0.5092 (5)	−0.2724 (10)	0.8299 (4)	5.3 (3)
C(323)	0.4508 (5)	−0.3273 (10)	0.8305 (4)	5.2 (3)
C(324)	0.4037 (5)	−0.2354 (10)	0.8363 (4)	4.5 (2)
C(325)	0.4129 (4)	−0.0852 (10)	0.8421 (3)	3.1 (2)
C(331)	0.3229 (4)	0.4249 (10)	0.8243 (3)	3.1 (2)
C(332)	0.2719 (4)	0.5092 (10)	0.8083 (4)	4.4 (2)

C(333)	0.2614 (5)	0.5508 (10)	0.7609 (4)	5.8 (3)
C(334)	0.3008 (5)	0.5101 (10)	0.7277 (4)	5.6 (3)
C(335)	0.3514 (4)	0.4297 (10)	0.7434 (3)	4.0 (2)
O(*m*)	1.2312 (5)	−0.2829 (10)	0.8951 (4)	12.4 (3)
C(*m*)	1.2496 (9)	−0.3262 (3)	0.9458 (7)	16.2 (7)

Table 4. *Selected geometric parameters* (Å, °) *for* (2)

Co(1)—S(11)	2.214 (2)	S(21)—C(211)	1.728 (8)
Co(1)—S(12)	2.203 (2)	S(22)—C(221)	1.724 (8)
Co(1)—S(13)	2.202 (2)	S(23)—C(231)	1.731 (9)
Co(1)—O(11)	1.976 (5)	O(21)—N(21)	1.336 (8)
Co(1)—O(12)	1.954 (5)	O(22)—N(22)	1.360 (8)
Co(1)—O(13)	1.951 (6)	O(23)—N(23)	1.352 (8)
S(11)—C(111)	1.710 (8)	Co(3)—S(31)	2.205 (2)
S(12)—C(121)	1.735 (7)	Co(3)—S(32)	2.206 (2)
S(13)—C(131)	1.724 (8)	Co(3)—S(33)	2.207 (2)
O(11)—N(11)	1.348 (8)	Co(3)—O(31)	1.945 (6)
O(12)—N(12)	1.357 (8)	Co(3)—O(32)	1.927 (6)
O(13)—N(13)	1.343 (8)	Co(3)—O(33)	1.943 (5)
O(22)···O(*m*)	2.91 (1)	S(31)—C(311)	1.734 (8)
Co(2)—S(21)	2.190 (2)	S(32)—C(325)	1.728 (9)
Co(2)—S(22)	2.204 (2)	S(33)—C(331)	1.718 (9)
Co(2)—S(23)	2.215 (2)	O(31)—N(31)	1.349 (7)
Co(2)—O(21)	1.938 (5)	O(32)—N(32)	1.348 (7)
Co(2)—O(22)	1.967 (5)	O(33)—N(33)	1.348 (7)
Co(2)—O(23)	1.946 (5)		
S(11)—Co(1)—O(11)	87.0 (2)	Co(2)—S(23)—C(231)	96.9 (3)
S(12)—Co(1)—O(12)	87.9 (2)	Co(2)—O(21)—N(21)	115.8 (5)
S(13)—Co(1)—O(13)	86.6 (2)	Co(2)—O(22)—N(22)	115.7 (4)
Co(1)—S(11)—C(111)	96.9 (3)	Co(2)—O(23)—N(23)	116.9 (4)
Co(1)—S(12)—C(121)	96.9 (2)	S(31)—Co(3)—O(31)	87.3 (2)
Co(1)—S(13)—C(131)	97.5 (3)	S(32)—Co(3)—O(32)	88.0 (2)
Co(1)—O(11)—N(11)	115.1 (5)	S(33)—Co(3)—O(33)	87.1 (2)
Co(1)—O(12)—N(12)	116.1 (4)	Co(3)—S(31)—C(311)	97.1 (3)
Co(1)—O(13)—N(13)	114.7 (4)	Co(3)—S(32)—C(325)	96.3 (2)
S(21)—Co(2)—O(21)	87.8 (2)	Co(3)—S(33)—C(331)	96.8 (3)
S(22)—Co(2)—O(22)	87.5 (2)	Co(3)—O(31)—N(31)	116.4 (5)
S(23)—Co(2)—O(23)	87.5 (2)	Co(3)—O(32)—N(32)	115.6 (4)
Co(2)—S(21)—C(211)	97.4 (3)	Co(3)—O(33)—N(33)	116.1 (4)
Co(2)—S(22)—C(221)	98.1 (2)		

The H atoms, except those of H_2O and MeOH for (1) and MeOH for (2), were placed at calculated positions and given isotropic displacement factors derived from those of the parent atoms. The H atoms were included in the structure-factor calculations but not refined. Both structures were solved by direct methods (Main *et al.*, 1982) and refined by full-matrix least squares (Frenz, 1985).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1088). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Two-Dimensional Open-Frame Host Structure of the Inclusion Compound $[Cd(tenH)_2\{Ni(CN)_4\}_2].4C_6H_5NH_2$ (ten = 1,4-Diazabicyclo[2.2.2]octane)

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Abstract

In the title inclusion compound, bis(1-azonia-4-azabicyclo[2.2.2]octane)cadmium(II) bis[tetracyanonickelate(II)]–aniline (1/4), $[Cd(C_6H_{13}N_2)_2\{Ni(CN)_4\}_2]$.-$4C_6H_7N$, the host contains Cd^{2+} and $[Ni(CN)_4]^{2-}$ in a ratio of 1:2. The two crystallographically independent $[Ni(CN)_4]^{2-}$ anions behave as bidentate bridging ligands, spanning the Cd^{2+} cations with the N atoms of the cyano groups in *trans* positions along both the *a* and *b* axes, building up a two-dimensional network $[Cd(tenH)_2\{NC—Ni(CN)_2—CN—\}_2]_n$ (ten = 1,4-diazabicyclo[2.2.2]octane). Two unidentate tenH ligands coordinate to the Cd in axial positions, the other N-atom end being protonated. The guest aniline molecules accommodated in the interlayer space are hydrogen

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