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Bis(tetra-*n*-butylammonium) bis(μ-1,2-dicyanoethene-1,2-dithiolato-$\kappa^3S,S':S'$)bis[(1,2-dicyanoethene-1,2-dithiolato-κ^2S,S')cobalt(III)]

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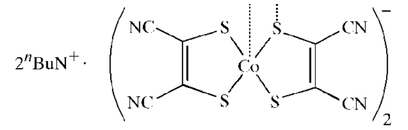
In the title compound, $(C_{16}H_{36}N)_2[Co(C_4N_2S_2)_2]_2$, pairs of $[Co(C_4N_2S_2)_2]^-$ anions combine to form discrete crystallographically centrosymmetric dimers, which stack along the *c* axis, surrounded by the counter-cations. The metal atom in the anion has a five-coordinate distorted square-pyramidal geometry.

Comment

1,3-Dithiolate complexes of transition metals are planar electron acceptors and have received attention in connection with their magnetic and electrical conducting properties. Molecular conductors based on extended 1,3-dithiolate complexes have received special attention recently (Kobayashi *et al.*, 1999, 2001; Moriyama *et al.*, 2001). Furthermore, the discovery of ferromagnetic ordering in $(NH_4)[Ni(mnt)_2]\cdot H_2O$ below 4.5 K (Coomber *et al.*, 1996) has especially stimulated interest in $[M(mnt)_2]$-based compounds (mnt is $S_2C_4N_2^{2-}$, dimercaptomaleodinitrilate). In addition, $[M(mnt)_2]^{n-}$ anions have been used as motifs for supramolecular assembly, taking advantage of their variation in molecular stereochemistry and formal charges (Lewis & Dance, 2000). Among the $[M(mnt)_2]$ salts, however, examples of Co complexes are fewer than those incorporating Ni, Pd or Pt ions. We report here the crystal structure of the title compound, $(^n\mathrm{Bu}_4\mathrm{N})[Co(mnt)_2]$, (I), at 90 K.

Several $[Co(mnt)_2]^{n-}$ salts have been reported, for example, involving the $[Co(mnt)_2]^-$ monoanion (Fettouchi *et al.*, 1995; Rodrigues *et al.*, 1994; Zürcher *et al.*, 1998), the $[Co(mnt)_2]^{2-}$ dianion (Fallon *et al.*, 1997; Fettouchi *et al.*, 1995) and the mixed-valence $[Co(mnt)_2]^{3-}$ anion (Gama *et al.*, 1993; Lam *et al.*, 1995). The monoanion tends to afford an antiferromagnetically interacting dimer, while the dianion often exists in the form of a monomer, showing alternate stacking with counter-cations. The structure of a 1:2 salt, $(^n\mathrm{Bu}_4\mathrm{N})_2[Co(mnt)_2]$, has also been reported (Forrester *et al.*, 1964).

Fig. 1 shows the molecular structure of (I). The $[Co(mnt)_2]$ units form discrete dimers and the components of the dimer are related to each other by a centre of symmetry located between the two metal centres. The metal atom has a distorted square-pyramidal coordination geometry and is displaced by 0.231 (1) Å from the least-squares plane defined by the four S atoms of the basal ligand. The dihedral angle between the Co/S1/S2 and Co/S3/S4 planes is *ca* 19.9°. Factors affecting the displacement of the metal atom from the ligand plane in $[M(mnt)_2]^{n-}$ anions have been discussed by Alvarez *et al.* (1985).



(I)

The important intramolecular and intradimer distances and angles in the anion are listed in Table 1. The coordination distances are virtually identical to those in other $[Co(mnt)_2]^-$ salts (Fettouchi *et al.*, 1995). The long molecular axes of the anions are parallel, being in a slipped configuration, such that the central metal atom is coordinated by the S atom of the adjacent anion, with a Co$\cdots$S distance of 2.3916 (8) Å, which is somewhat longer than the four basal Co—S distances. The intradimer Co$\cdots$Co distance is 3.1150 (8) Å. In contrast with the square-pyramidal $[Co^{III}(mnt)_2]^-$ anion of (I), the dianion of $[Co^{II}(mnt)_2]^{2-}$ is planar, showing D_{2h} geometry (Forrester *et al.*, 1964). The intramolecular distances show significant differences, depending on the formal charges on the anion.

The packing in (I) is illustrated in Fig. 2. The $\{[Co(mnt)_2]_2\}^{2-}$ dimers are stacked in a columnar fashion along the *c* axis. The dimer units are stacked such that the long axes of adjacent dimers make an angle of *ca* 71° with each other. The metal atom of one dimer unit sits 3.923 (1) Å above atom S3^i of the adjacent dimer unit [symmetry code: (i) $-x$, $1-y$, $1-z$]. There is also an S3$\cdots$S3^i contact distance of 3.734 (1) Å between the dimers. The interdimer Co$\cdots$Co distance is 5.063 (1) Å.

The anion columns in (I) are surrounded by the tetrabutylammonium cations. Three of the ^{n}Bu groups in the cation adopt the all-*trans* conformation, but one terminal group, C19—C20, adopts a *gauche* conformation. Presumably, this occurs to reduce steric hindrance between adjacent counter-cations, which have mutual contacts at these ends along the *b* direction.

The corresponding Ni^{III} complex (Mochida *et al.*, 2000) crystallizes in the same space group (*C*2/*c*) and shows similar cell parameters to those of (I). In the Ni^{III} complex, the anions are arranged in the form of a weakly interacting dimer, and the cell volume is larger than that for the Co^{III} complex, by 6.5%.

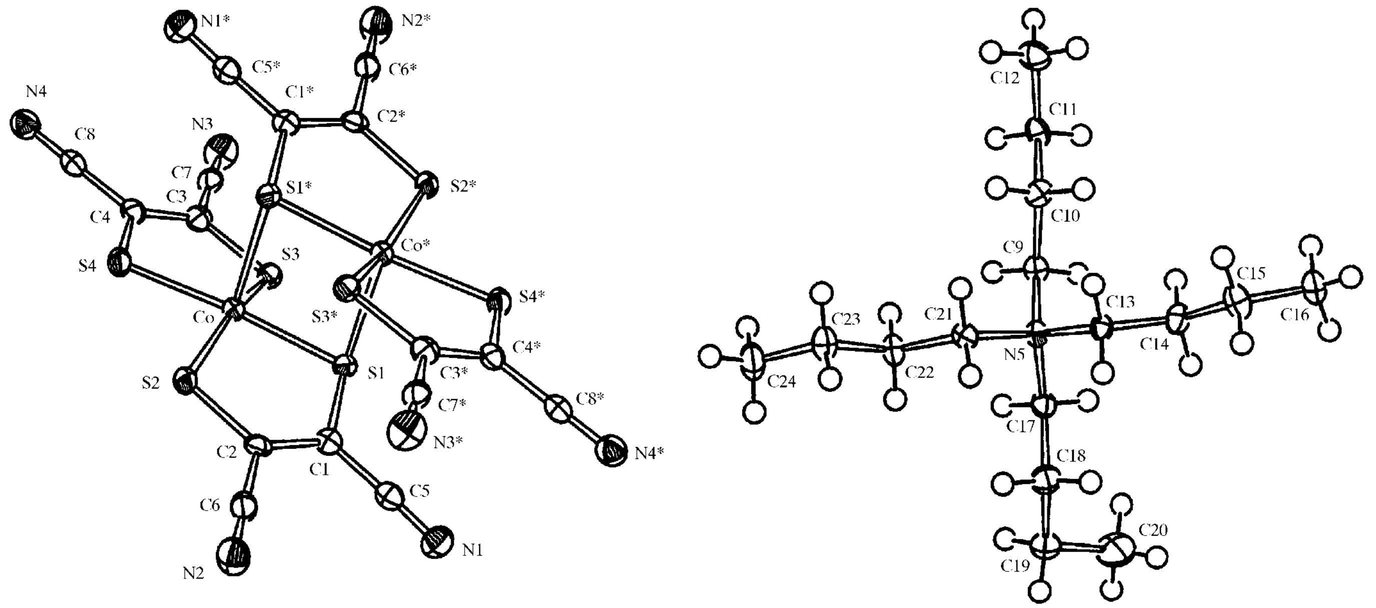


Figure 1

The cation and anion of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 70% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (*) $-x, 1-y, 1-z$.]

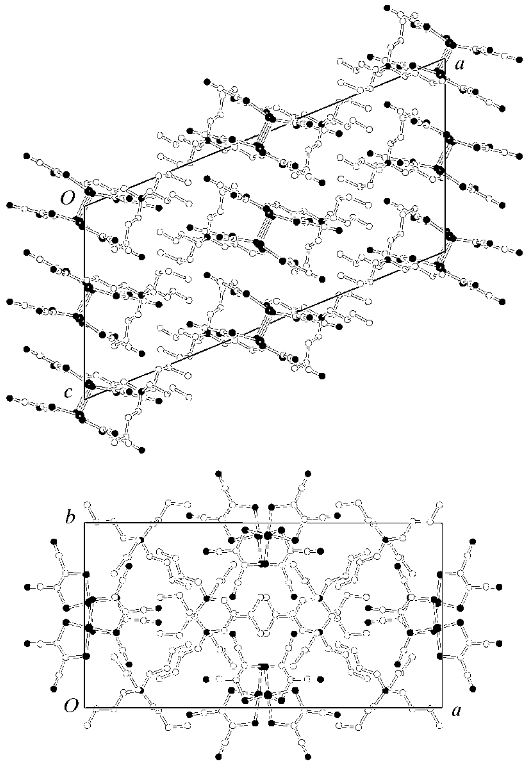


Figure 2

Packing diagrams for (I). Atoms other than C atoms are represented by shaded circles and H atoms have been omitted for clarity.

Experimental

Compound (I) was synthesized according to the literature method of Davison & Holm (1967). Single crystals of (I) suitable for X-ray analysis were grown by vapour diffusion of pentane into a dichloromethane solution of the compound.

Crystal data

$(C_{16}H_{36}N)_2[Co(C_4N_2S_2)_2]_2$
$M_r = 1163.52$
Monoclinic, $C2/c$
$a = 29.457$ (4) Å
$b = 14.060$ (2) Å
$c = 14.703$ (2) Å
$\beta = 112.518$ (5)°
$V = 5625.2$ (14) Å^3
$Z = 4$

$D_x = 1.374$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7543 reflections
$\theta = 1.6$–13.7°
$\mu = 0.93$ mm^{-1}
$T = 90$ K
Prism, black
0.3 × 0.3 × 0.2 mm

Data collection

Rigaku Mercury CCD area-detector diffractometer
ω scans
Absorption correction: analytical (de Meulenaer & Tompa, 1965)
$T_{\min} = 0.827$, $T_{\max} = 0.830$
21 339 measured reflections

6176 independent reflections
4718 reflections with $F^2 > 2\sigma(F^2)$
$R_{\rm int} = 0.050$
$\theta_{\max} = 27.5°$
$h = -37 \rightarrow 38$
$k = -18 \rightarrow 13$
$l = -19 \rightarrow 19$

Table 1

Selected geometric parameters (Å, °).

Co—S1	2.1886 (8)	N1—C5	1.151 (3)
Co—S2	2.1969 (8)	N2—C6	1.147 (3)
Co—S3	2.1812 (8)	C1—C2	1.363 (4)
Co—S4	2.1839 (8)	C1—C5	1.427 (4)
S1—C1	1.744 (3)	C2—C6	1.453 (4)
S2—C2	1.705 (3)	C3—C7	1.440 (4)
S3—C3	1.718 (3)	C3—C4	1.367 (4)
S4—C4	1.727 (3)	C4—C8	1.434 (4)
N3—C7	1.148 (3)	Co—Co$^{\rm i}$	3.1150 (8)
N4—C8	1.147 (3)	Co—S1$^{\rm i}$	2.3916 (8)
S1—Co—S2	90.87 (3)	S3—Co—S4	91.35 (3)
S1—Co—S3	87.28 (3)	Co—S1—C1	103.79 (9)
S2—Co—S3	160.94 (3)	Co—S2—C2	103.14 (9)
S1—Co—S4	174.69 (3)	Co—S3—C3	102.74 (9)
S2—Co—S4	88.76 (3)	Co—S4—C4	102.84 (9)

Symmetry code: (i) $-x, 1-y, 1-z$.

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Refinement

Refinement on F^2
$R(F) = 0.045$
$wR(F^2) = 0.067$
$S = 1.44$
4749 reflections
343 parameters
H-atom parameters constrained

Weighting scheme based on measured s.u.s
$w = 1/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.48$ e Å^{-3}
$\Delta\rho_{\min} = -0.52$ e Å^{-3}

H atoms were treated as riding, with C—H = 0.95 Å.

Data collection: *CrystalClear* (Molecular Structure Corporation & Rigaku, 2001); cell refinement: *CrystalClear*; data reduction: *Crystal Structure* (Molecular Structure Corporation & Rigaku, 2001; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *CRYSTALS* (Watkin *et al.*, 1996); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *CrystalStructure*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1380). Services for accessing these data are described at the back of the journal.

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