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The Co^{III}—C bond in (1-thia-4,7-diazacyclodecyl-κ^3*N*^{4},*N*^{7},*C*^{10})(1,4,7-triazacyclononane-κ^3*N*^{1},*N*^{4},*N*^{7})-cobalt(III) dithionate hydrate

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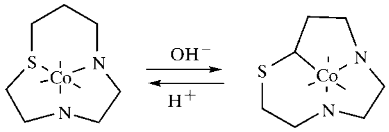
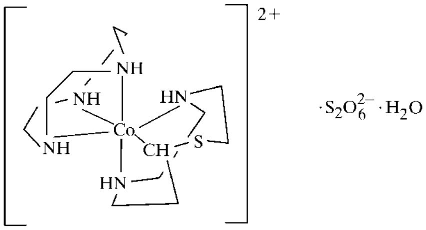
In the title compound, $[Co(C_6H_{15}N_3)(C_7H_{15}N_2S)]S_2O_6{\cdot}H_2O$, the Co—C bond distance is 1.9930 (13) Å, which is shorter than for related compounds with the linear 1,6-diamino-3-thiahexan-4-ide anion in place of the macrocyclic 1-thia-4,7-diazacyclodecan-8-ide anion. The coordinated carbanion produces an elongation of 0.102 (7) Å of the Co—N bond to the 1,4,7-triazacyclononane N atom in the *trans* position. This relatively small *trans* influence is presumably a result of the triamine ligand forming strong bonds to the Co^{III} atom.

Comment

An unusual route for the preparation of alkylcobalt(III) compounds is the coordination of the carbanion formed by the reversible deprotonation of an S-bonded methylene group in thioethercobalt(III) compounds (see *Scheme* below). This method has proved feasible in a number of cases where aminoethyl aminopropyl sulfide (aeaps, 3-thiahexane-1,6-diamine) occupies one face of the octahedron in six-coordinate cobalt(III) compounds (Bjerrum *et al.*, 1988; Kofod, Larsen, Larsen *et al.*, 1992; Kofod, Larsen, Petersen & Springborg, 1992; Kofod *et al.*, 1994). The opposite face of the octahedron was blocked by the neutral amine ligands 1,4,7-triazacyclononane (tacn) or 1,1,1-tris(aminomethyl)ethane (tame), or by a second aeaps ligand. Subsequently, the cyclic thioether 1,4-diaza-7-thiacyclodecane (dathicd) has been shown to react in a similar manner to aeaps (Song *et al.*, 1996). This route for the formation of alkylcobalt(III) compounds is not restricted to coordination compounds with solely saturated amine ligands, but also applies to Schiff base ligands (Chakraborty *et al.*, 1994).



A small number of X-ray crystal structures of cobalt(III) complexes with the C-bonded form of aeaps, *i.e.* the 1,6-diamino-3-thiahexan-4-ide anion, C-aeaps, have been reported. The X-ray crystal structures of $[Co(tame)(C\text{-}aeaps)]S_2O_6$ and $[Co(tacn)(C\text{-}aeaps)](ClO_4)_2$ both suffered from severe disorder of the cation (Kofod, Larsen, Larsen *et al.*, 1992; Kofod *et al.*, 1994). In both cases, the disorder was explained by the two chelate rings of C-aeaps being partly interchanged. The X-ray crystal structure of $[Co(aeaps)(C\text{-}aeaps)]S_2O_6$ was performed on a twin crystal containing both enantiomeric forms of the complex cation (Bjerrum *et al.*, 1988). In this paper, we report the crystal structure of $[Co(tacn)(C\text{-}dathicd)]S_2O_6$, (I) (C-dathicd is the 1,4-diaza-7-thiacyclodecan-8-ide anion).



(I)

The cyclic thioether dathicd is closely related to the linear thioether aeaps, in that dathicd can be seen as aeaps with the two primary amine groups being linked by a two-carbon chain. This linkage introduces a rigidity to the coordinated ligand which is not present in the analogous compounds with aeaps. This rigidity may be the reason for the better quality of the single crystals.

The $[Co(tacn)(C\text{-}dathicd)]^{2+}$ cation of (I) is shown in Fig. 1. The unit cell contains two independent dithionate anions, each lying about an inversion centre. The cation packs with alternating layers of the anions. One layer consists of one dithionate anion and the other layer consists of the other dithionate anion and the water molecule. There are hydrogen bonds (Table 2) from all possible donors. As illustrated in Fig. 2, the atoms of one end of the cation, *viz.* N22, N11 and N13, are hydrogen bonded to one $S_2O_6{}^{2-}$ layer and the atoms of the other end, *viz.* N21 and N12, are hydrogen bonded to the $S_2O_6{}^{2-}$ layer which also contains the water molecules.

The average Co—N distance of the tacn amine groups *cis* to the coordinated carbanion (atoms N11 and N12) is 1.977 (7) Å. The Co—N distance for atom N13, which is *trans* to the alkyl group, is 2.0790 (12) Å. Hence, the *trans* influence induced by the alkyl group is 0.102 (7) Å. This is somewhat shorter than but comparable to the *trans* influence we

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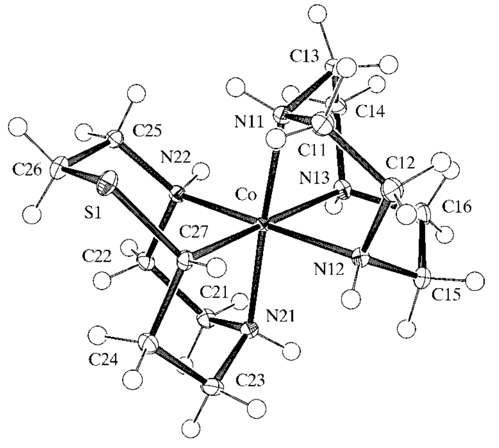

Figure 1
A view of the cation including the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

observed in $[Co(NH_3)_5(CH_3)]^{2+}$ (0.13 Å; Kofod *et al.*, 1997). The smaller *trans* influence in (I) may be a result of the tacn ligand forming strong bonds to the Co^{III} atom, but it could also reflect a difference between a secondary amine and an ammine ligand. The Co—C bond distance in (I) is slightly longer than that in $[Co(NH_3)_5(CH_3)]^{2+}$, by 0.013 (2) Å, and this might also result in a smaller *trans* influence.

Table 3 compares the metal–ligand bond distances in Co^{III} complexes containing C-aeaps or C-dathicd. Although the quality of some of the structures prevents an accurate comparison, it is evident that the Co—C bond distance in (I) is shorter than those in the complexes with C-aeaps. On the other hand, the Co—N distances in the complexes with the C-dathicd ligand are no different from those in the complexes with C-aeaps, which, in turn, display quite some variation. It can also be seen that the *trans* influence tends to become larger on going from a secondary to a primary amine.

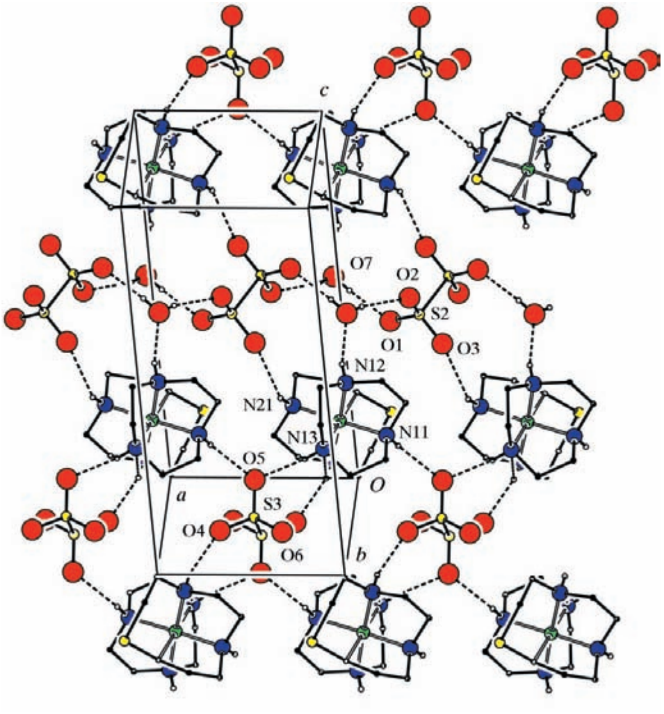

Figure 2
The crystal packing in (I).

Experimental

[Co(tacn)(C-dathicd)]$(ClO_4)_2$ was prepared by dissolving [Co(tacn)-(S-dathicd)]$Cl_3\cdot5H_2O$ (0.65 g) in aqueous NaOH (6 ml, 2 *M*) at 313 K, followed by precipitation with sodium perchlorate (5 g), as described previously by Song *et al.* (1996). The sparingly soluble title dithionate salt, (I), was obtained by precipitation from a solution of the diperchlorate (0.1 g) in water (10 ml) with a saturated aqueous solution of sodium dithionate (2 ml). Single crystals of (I) were grown by slow cooling of a saturated solution in warm water.

Crystal data

$[Co(C_6H_{15}N_3)(C_7H_{15}N_2S)]$-$S_2O_6\cdot H_2O$
M_r = 525.54
Triclinic, $P\overline{1}$
a = 7.837 (2) Å
b = 9.135 (2) Å
c = 15.649 (3) Å
α = 89.65 (2)°
β = 76.04 (2)°
γ = 66.99 (2)°
V = 995.8 (4) $Å^3$
Z = 2
D_x = 1.753 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 15.9–21.4°
μ = 1.23 mm^{-1}
T = 122 (2) K
Rod, red
0.22 × 0.12 × 0.08 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: by integration (Coppens, 1970)
T_{min} = 0.816, T_{max} = 0.904
12 912 measured reflections
8747 independent reflections
7372 reflections with $I > 2\sigma(I)$
R_{int} = 0.027
θ_{max} = 35°
$h = -12 \rightarrow 12$
$k = -14 \rightarrow 14$
$l = 0 \rightarrow 25$
5 standard reflections frequency: 166.7 min intensity decay: 3.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.076
S = 1.07
8747 reflections
358 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0286P)^2 + 0.5020P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.66 e $Å^{-3}$
$\Delta\rho_{min}$ = −0.51 e $Å^{-3}$

Table 1
Selected geometric parameters (Å, °).

Co—N12	1.9705 (12)	Co—C27	1.9930 (13)
Co—N21	1.9827 (13)	Co—N22	1.9995 (12)
Co—N11	1.9840 (13)	Co—N13	2.0790 (12)
N12—Co—N21	92.89 (5)	N11—Co—N22	96.91 (5)
N12—Co—N11	84.60 (5)	C27—Co—N22	92.22 (5)
N21—Co—N11	177.43 (5)	N12—Co—N13	84.31 (5)
N12—Co—C27	92.31 (5)	N21—Co—N13	95.26 (5)
N21—Co—C27	86.30 (5)	N11—Co—N13	83.98 (5)
N11—Co—C27	94.32 (5)	C27—Co—N13	176.34 (5)
N12—Co—N22	175.10 (5)	N22—Co—N13	91.20 (5)
N21—Co—N22	85.55 (5)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N11—H11$\cdots$O5$^{\rm iii}$	0.90 (2)	2.30 (2)	3.1052 (17)	150.0 (17)
N12—H12$\cdots$O7$^{\rm i}$	0.83 (2)	2.05 (2)	2.8396 (18)	160 (2)
N13—H13$\cdots$O5	0.83 (2)	2.17 (2)	2.9620 (18)	157.8 (19)
N21—H21$\cdots$O3$^{\rm iv}$	0.85 (2)	2.54 (2)	3.2424 (17)	140.4 (17)
N22—H22$\cdots$O4$^{\rm ii}$	0.87 (2)	2.13 (2)	2.9230 (16)	150.4 (18)
O7—H7$A\cdots$O2$^{\rm i}$	0.75 (3)	2.05 (3)	2.7835 (18)	166 (3)
O7—H7$B\cdots$O1	0.82 (3)	2.01 (3)	2.8059 (18)	163 (2)

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

Table 3
Comparison of metal–ligand bond distances (Å) in complexes containing C-dathicd or C-aeaps.

The numbering of the complexes with C-aeaps corresponds to that of (I).

Bond	(I)†	(II)‡	(III)§	(IV)¶
Co—N11	1.9840 (13)	1.966 (9)	1.992 (12)	1.977 (3)
Co—N12	1.9705 (12)	1.951 (9)	1.954 (12)	
Co—N13	2.0790 (12)	2.047 (10)	2.084 (5)	2.110 (3)
Co—N21	1.9827 (13)	1.992 (11)	2.029 (13)	1.976 (3)
Co—N22	1.9995 (12)	1.992 (11)	1.959 (12)	2.011 (3)
Co—C27	1.9930 (13)	2.05 (2)	2.049 (7)	2.026 (3)

† This work ‡ (II) is [Co(tacn)(C-aeaps)](ClO$_4$)$_2$ (Kofod, Larsen, Larsen *et al.*, 1992) § (III) is [Co(tame)(C-aeaps)]S$_2$O$_6$ (Kofod *et al.*, 1994) ¶ (IV) is [Co(aeaps)-(C-aeaps)]S$_2$O$_6$ (Bjerrum *et al.*, 1988).

The H atoms appeared clearly in the $\Delta\rho$ map calculated after the $U_{\rm eq}$ parameters had been introduced for all non-H atoms. The positions of all H atoms were refined. $U_{\rm iso}$(H) values were constrained to $1.2U_{\rm eq}$(C) for H atoms on C atoms, and to $1.5U_{\rm eq}$(N,O) for H atoms on N or O atoms. The refined C—H distances were in the range 0.93 (2)–1.00 (2) Å, the N—H distances in the range 0.83 (2)–0.90 (2) Å and the O—H distances in the range 0.75 (3)–0.82 (3) Å. The maximum and minimum difference densities were found to be 0.65 and −0.51 e Å^{-3}, respectively, from the Co atom.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *DREADD* (Blessing, 1989); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TR1048). Services for accessing these data are described at the back of the journal.

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