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Bis(diethylenetriamine)cobalt(II) tetrathiomolybdate(VI) oxotrithiamolybdate(VI)

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Key indicators

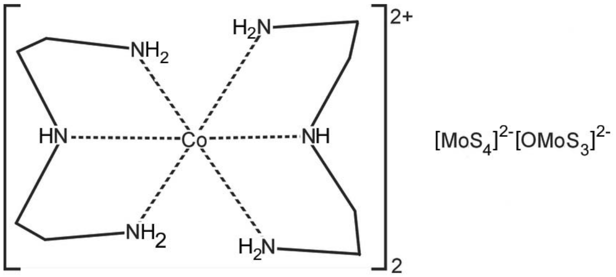
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.009 Å
Disorder in main residue
R factor = 0.041
wR factor = 0.098
Data-to-parameter ratio = 17.1

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

In the crystal structure of the title compound, $[Co(C_4H_{13}N_3)_2]_2[MoS_4][MoS_3O]$, discrete $[MoS_4]^{2-}$ and $[MoS_3O]^{2-}$ anions, as well as $[Co(C_4H_{13}N_3)_2]^{2+}$ cations are found. Both anions occupy the same crystallographic position and are therefore disordered. The Co atom is octahedrally coordinated by six N atoms of the diethylenetriamine ligand whereas the Mo atom shows a distorted tetrahedral geometry.

Comment

During the past few years, a large number of tetrathiomolybdates have been prepared in the presence of an organic cation. Compared to the number of such compounds, those containing a transition metal complex cation are rare and some examples are $[Ni(en)_3]MoS_4$ (en is ethylenediamine; Ellermeier *et al.*, 1999), $[Ni(en)_3]_3(MoS_4)Br_4\cdot 2en$ (Ellermeier, 2002), $[Mn(dien)_2]MoS_4$ (dien is diethylenetriamine; Ellermeier & Bensch, 2002), $[Ni(dien)_2]_2(MoS_4)Br_2$ (Ellermeier, 2002), $[Co_2(tren)_3]$-$(MoS_4)_2$ (tren is triethylenetetramine; Ellermeier & Bensch, 2001), $[(C_6H_5)_4P]_2[M(MoS_4)_2]$ (M = Ni, Fe, Zn) (Müller *et al.*, 1971), and $(Pr_4N)_2[Ni(MoS_4)_2]$ (Callahan & Piliero, 1980).



(I)

The structure of the title compound consists of isolated $[Co(dien)_2]^{2+}$ cations and $[MoS_4]^{2-}$ as well as $[MoS_3O]^{2-}$ anions, which are connected *via* N—H···S hydrogen bonding (Fig. 1 and Table 2). Each Co^{2+} ion is sixfold coordinated by the six N atoms of two tridentate dien ligands within a distorted octahedron. The Co—N distances (Table 1) are between 2.152 (4) and 2.197 (4) Å. The *trans* N—Co—N angles in the title compound are in the range 177.54 (16)–178.61 (17)°. The geometric parameters indicate that the CoN_6 octahedron in the title compound is less distorted than in the analogous en compound. The anion was first refined assuming that only S is bound to Mo. In this case, the Mo—S bonds were between 1.977 (3) and 2.2045 (17) Å with a difference of 0.2275 Å between the longest and the shortest bond. This is a rather large difference; in most tetrathiomolybdates the difference lies between 0.02 and 0.05 Å (Srinivasan *et al.*,

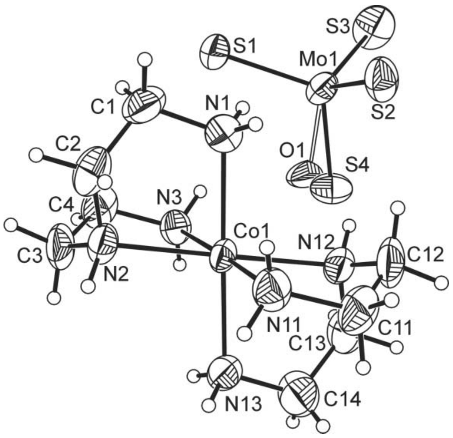


Figure 1
The asymmetric unit of the title compound, with the atom labellling and displacement ellipsoids drawn at the 50% probability level. The Mo—O bond in the disordered anion is shown as an open bond.

2004). Furthermore, the symmetry of the anion would be significantly reduced and the IR spectrum should then show a split Mo—S vibration. The relatively high anisotropic displacement parameters of S4 suggested a slight contamination with oxygen. The refinement of S4 with a split model finally yielded an $[MoS_4]^{2-}$ and an $[MoS_3O]^{2-}$anion which are superimposed in the crystal structure (Table 1). The presence of oxygen was proved with IR spectroscopy. The partial occupancy of the S4 position by oxygen leads to a much more realistic Mo—S bond length and a reasonable Mo—O distance.

Experimental

Cobalt(II) chloride (0.5 mmol) and $(NH_4)_2MoS_4$ (0.5 mmol) were heated for 5 d at 373 K in a mixture of 3 ml diethylenetriamine and 3 ml water in a Teflon-lined steel autoclave. The resulting red–orange crystals (70% yield) were dried under vacuum.

Crystal data

$[Co(C_4H_{13}N_3)_2]_2[MoS_4][MoOS_3]$
$M_r = 962.86$
Monoclinic, $P2_1/n$
$a = 7.4164$ (5) Å
$b = 15.9171$ (11) Å
$c = 15.4070$ (12) Å
$\beta = 93.063$ (9)°
$V = 1816.2$ (2) Å^3
$Z = 2$
$D_x = 1.761$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 2.01$ mm^{-1}
$T = 293$ (2) K
Block, red–orange
0.09 × 0.09 × 0.08 mm

Data collection

Stoe IPDS-1 diffractometer
φ scans
Absorption correction: none
11766 measured reflections
3269 independent reflections
2455 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.048$
$\theta_{\rm max} = 25.7°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.099$
$S = 1.02$
3269 reflections
191 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0458P)^2 + 2.2351P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.55$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.60$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0022 (6)

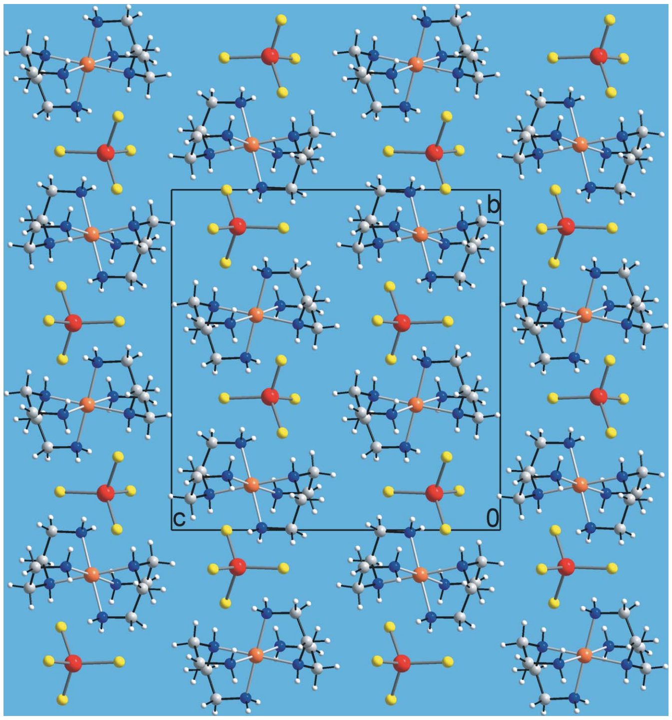


Figure 2
The crystal structure of the title compound, viewed along the *a* axis. The O atoms have been omitted for clarity.

Table 1
Selected geometric parameters (Å, °).

Mo1—O1	1.796 (17)	Co1—N2	2.164 (4)
Mo1—S4	2.050 (6)	Co1—N11	2.182 (4)
Mo1—S2	2.1826 (16)	Co1—N1	2.191 (4)
Mo1—S3	2.1908 (16)	Co1—N13	2.196 (4)
Mo1—S1	2.2041 (14)	Co1—N3	2.197 (4)
Co1—N12	2.152 (4)		
O1—Mo1—S4	14.0 (5)	N12—Co1—N1	98.35 (16)
O1—Mo1—S2	114.5 (5)	N2—Co1—N1	80.64 (16)
S4—Mo1—S2	103.84 (19)	N11—Co1—N1	89.79 (18)
O1—Mo1—S3	112.0 (7)	N12—Co1—N13	80.48 (16)
S4—Mo1—S3	109.2 (2)	N2—Co1—N13	100.55 (16)
S2—Mo1—S3	108.11 (7)	N11—Co1—N13	90.77 (18)
O1—Mo1—S1	102.3 (5)	N1—Co1—N13	178.61 (17)
S4—Mo1—S1	115.37 (18)	N12—Co1—N3	100.80 (17)
S2—Mo1—S1	108.71 (6)	N2—Co1—N3	80.43 (16)
S3—Mo1—S1	111.11 (6)	N11—Co1—N3	177.54 (16)
N12—Co1—N2	178.43 (18)	N1—Co1—N3	90.75 (16)
N12—Co1—N11	81.49 (17)	N13—Co1—N3	88.74 (16)
N2—Co1—N11	97.29 (17)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*···S4$^{\rm i}$	0.90	2.53	3.396 (8)	161
N1—H2*N*···S2	0.90	2.79	3.497 (5)	136
N2—H3*N*···S3$^{\rm ii}$	0.91	2.82	3.613 (5)	147
N3—H4*N*···S1	0.90	2.76	3.567 (4)	150
N3—H5*N*···S3$^{\rm iii}$	0.90	2.58	3.409 (4)	154
N11—H6*N*···S4$^{\rm i}$	0.90	2.30	3.133 (8)	153
N11—H7*N*···S1$^{\rm ii}$	0.90	2.84	3.635 (5)	149
N12—H8*N*···S2	0.91	2.73	3.525 (4)	146
N12—H8*N*···S4	0.91	2.76	3.491 (8)	138
N13—H9*N*···S1$^{\rm ii}$	0.90	2.73	3.574 (5)	157

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D—H···A	D—H	H···A	D···A	D—H···A
N13—H10N···S3^{iii}	0.90	2.61	3.493 (5)	166
N1—H1N···O1^{i}	0.90	2.34	3.18 (2)	155
N11—H6N···O1^{i}	0.90	2.43	3.290 (18)	161

Symmetry codes: (i) $x - 1, y, z$; (ii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (iii) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$.

All H atoms were positioned with idealized geometry and were refined with fixed isotropic displacement parameters [$U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C,N)] using a riding model, with C—H = 0.97 Å, C—H = 0.90 Å or N—H = 0.91 Å. The disordered S and O atoms were refined using a split model and anisotropic displacement parameters. Refinement of their site occupation factors proves that they are occupied 50:50, and this was assumed in the final refinement.

Data collection: *IPDS Software* (Stoe & Cie, 1998); cell refinement: *IPDS Software*; data reduction: *IPDS Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997; program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Bruker, 1998) and *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *CIFTAB* in *SHELXTL*.

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