Acta Cryst. (1993). C**49**, 222–224

Structure of Bis[tris(2-aminoethanethiolato)cobalt(III)-μ-S,μ-S',μ-S'']nickel(II) Chloride Trihydrate

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(*Received* 2 *March* 1992; *accepted* 8 *June* 1992)

Abstract. Hexakis(μ-2-aminoethanethiolato)-1κ^3N,-1:3κ^6S;2κ^3N,2:3κ^6S-dicobalt(III)nickel(II) dichloride trihydrate, $[Co_2Ni(C_2H_6NS)_6]Cl_2.3H_2O$, $M_r = 758.4$, triclinic, $P\bar{1}$, $a = 13.624$ (3), $b = 13.943$ (3), $c = 8.205$ (2) Å, $\alpha = 101.29$ (1), $\beta = 90.08$ (1), $\gamma = 69.14$ (2)°, $V = 1424.3$ (6) Å^3, $Z = 2$, $D_x = 1.77$ g cm^{-3}, λ(Mo $K\alpha$) = 0.70930 Å, $\mu = 23.5$ cm^{-1}, $F(000) = 784$, room temperature, $R = 0.035$ for 4379 independent reflections $[F_o > 3\sigma(F_o)]$. The Ni atom is coordinated octahedrally by six thiolato S atoms from two *fac*(S)-$[Co(C_2H_6NS)_3]$ subunits, forming a linear-type S-bridged $Co^{III}Ni^{II}Co^{III}$ trinuclear structure.

Introduction. *fac*(S)-[M(aet)$_3$] (M = Co^{III}, Rh^{III} or Ir^{III}; aet = 2-aminoethanethiolate) and fac(S)-[M(L-cys-N,S)$_3$]$^{3-}$ (L-cys = L-cysteinate) have been recognized as functioning as S-donating terdentate ligands to a variety of metal ions, forming S-bridged polynuclear complexes (Konno, Okamoto & Hidaka, 1991; Konno, Nagashio, Okamoto & Hidaka, 1992, and references therein). For example, the reaction of *fac*(S)-[Co(aet or L-cys-N,S)$_3$]$^{0\ \mathrm{or}\ 3-}$ with octahedral Co^{III} produced a linear-type S-bridged trinuclear complex [Co{Co(aet or L-cys-N,S)$_3$}$_2$]$^{3+\ \mathrm{or}\ 3-}$ (Busch & Jicha, 1962; Konno, Aizawa, Okamoto & Hidaka, 1985), while the reaction of *fac*(S)-[Co(aet)$_3$] with tetrahedral Zn^{II} was found to give a cage-type S-bridged octanuclear complex [{Co(aet)$_3$}$_4$Zn$_4$O]$^{6+}$ (Konno, Nagashio, Okamoto & Hidaka, 1992). It has been proposed that the reaction of *fac*(S)-[Co(aet or L-cys-N,S)$_3$]$^{0\ \mathrm{or}\ 3-}$ with Ni^{II}, which possibly takes a tetrahedral or square-planar geometry besides an octahedral one, gives a linear-type S-bridged trinuclear complex [Ni{Co(aet or L-cys-N,S)$_3$}$_2$]$^{2+\ \mathrm{or}\ 4-}$ (Busch & Jicha, 1962; Aizawa, Okamoto, Einaga & Hidaka, 1988), although no X-ray structural analysis has been presented. Thus, here we report the crystal structure determination of [Ni{Co(aet)$_3$}$_2$]$^{2+}$.

Experimental. The title complex was prepared by modification of a method found in the literature (Busch & Jicha, 1962). To a suspension of *fac*(S)-[Co(aet)$_3$] (0.5 g) in 50 cm^3 of water, $NiCl_2.6H_2O$ (0.7 g) was added and the mixture stirred at 333 K for 30 min. After unreacted starting complex was filtered off, the filtrate was kept in a refrigerator. Crystals of a suitable size for X-ray analysis were grown in 1 d.

A black crystal, 0.15 × 0.13 × 0.13 mm, was used for data collection on an Enraf–Nonius CAD-4 diffractometer; 50 kV and 26 mA. Unit-cell dimensions were determined by least-squares refinement of 25 reflections with $22 < 2\theta < 26°$. Intensities were measured using ω–2θ scans, with scan rate varied from 1 to 5° min^{-1} (in ω) and scan width $(0.8 + 0.35\tan\theta)°$. The intensities of three standards, monitored every 2 h of X-ray exposure time, remained constant within experimental e.s.d. throughout data collection; orientation (for the same three reflections) was monitored after every 200 scans of 5658 unique reflections measured ($2\theta \leq 56°$; $-10 \leq h \leq 10$, $-18 \leq k \leq 18$, $0 \leq l \leq 10$). 4379 reflections with $F_o > 3\sigma(F_o)$ were used for structure determination. Intensities were corrected for Lorentz and polarization effect, but not for absorption. The structure was solved by standard Patterson methods and successive difference Fourier maps. The ethylene H atoms in the aet ligands were fixed by geometrical constraints (C—H = 0.95 Å) and isotropic thermal parameters ($U = 0.05$ Å^2). The H atoms attached to the amine N and water O atoms were not included in the calculation. One of two independent Cl atoms (Cl2) and one of three water O atoms (O3) exhibited disorder; they appeared to be distributed in two different locations with a site-occupancy factor of 0.5. The structure was refined by full-matrix least squares using anisotropic thermal parameters for non-H atoms; number of refined parameters was 307; $R = 0.035$ and $wR = 0.040$ $\{w = 1.3295/[\sigma^2(F_o) + 0.001120(F_o)^2]\}$, $S = 1.38$; $\Delta_{\max} = 0.01\sigma$; $|\Delta\rho|_{\max}$ in the final difference Fourier map = 0.71 e Å^{-3}. All calculations were performed with *SHELX*76 (Sheldrick, 1976) on a Facom M-780/20 computer. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

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0108-2701/93/020222-03$06.00

Table 1. *Final atomic coordinates and equivalent isotropic thermal parameters* (Å²) *for non*-H *atoms*

$B_{\mathrm{eq}} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	*y*	*z*	B_{eq}
Ni	0.25002 (4)	0.48385 (3)	0.11494 (5)	1.89 (2)
Co*a*	0.26657 (4)	0.26533 (3)	0.07404 (6)	1.73 (2)
S1*a*	0.18888 (9)	0.39663 (7)	0.2970 (1)	2.19 (4)
S2*a*	0.18427 (8)	0.37763 (6)	−0.0895 (1)	2.04 (4)
S3*a*	0.40018 (8)	0.32487 (7)	0.0777 (1)	2.19 (4)
N1*a*	0.3319 (3)	0.1566 (2)	−0.1319 (4)	2.59 (15)
N2*a*	0.3452 (3)	0.1694 (2)	0.2214 (4)	2.70 (16)
N3*a*	0.1419 (3)	0.2218 (2)	0.0844 (4)	2.35 (14)
C1*a*	0.0579 (3)	0.3923 (3)	0.2737 (5)	2.62 (19)
C2*a*	0.0685 (4)	0.2788 (3)	0.2373 (5)	2.80 (19)
C3*a*	0.2695 (4)	0.3034 (3)	−0.2762 (5)	2.89 (19)
C4*a*	0.2865 (4)	0.1887 (3)	−0.2886 (5)	3.04 (20)
C5*a*	0.4516 (4)	0.2822 (4)	0.2679 (6)	3.59 (22)
C6*a*	0.4516 (4)	0.1716 (4)	0.2532 (7)	4.29 (26)
Co*b*	0.23158 (4)	0.70299 (3)	0.14631 (5)	1.74 (2)
S1*b*	0.29255 (9)	0.60184 (7)	0.3339 (1)	2.16 (4)
S2*b*	0.32633 (8)	0.56453 (7)	−0.0521 (1)	2.10 (4)
S3*b*	0.09920 (8)	0.64159 (7)	0.1216 (1)	1.97 (4)
N1*b*	0.1816 (3)	0.7828 (2)	−0.0359 (4)	2.57 (14)
N2*b*	0.1379 (3)	0.8224 (2)	0.3227 (4)	2.51 (15)
N3*b*	0.3545 (3)	0.7498 (3)	0.1810 (4)	2.94 (16)
C1*b*	0.4249 (4)	0.6016 (3)	0.3214 (6)	3.23 (21)
C2*b*	0.4172 (4)	0.7127 (4)	0.3226 (6)	3.77 (23)
C3*b*	0.2449 (4)	0.6068 (3)	−0.2206 (4)	2.74 (18)
C4*b*	0.2260 (4)	0.7217 (3)	−0.2073 (5)	2.96 (19)
C5*b*	0.0393 (4)	0.7042 (3)	0.3318 (5)	2.73 (18)
C6*b*	0.0332 (4)	0.8171 (3)	0.3612 (6)	3.12 (21)
Cl1	0.2891 (1)	0.9607 (1)	−0.0200 (1)	3.61 (5)
Cl2*a*	0.0179 (9)	0.0400 (7)	0.1849 (9)	3.74 (29)
Cl2*b*	0.4399 (8)	09494 (6)	0.3688 (10)	3.17 (19)
O1	0.1794 (3)	0.9462 (3)	0.6466 (4)	5.06 (19)
O2	0.2127 (4)	0.0415 (4)	0.3944 (5)	7.01 (24)
O3*a*	0.0284 (20)	0.0370 (15)	0.1777 (23)	2.86 (67)
O3*b*	0.4603 (19)	0.9305 (16)	0.3448 (26)	3.71 (75)

Table 2. *Selected bond distances* (Å) *and angles* (°)

Ni—S1*a*	2.417 (1)	Co*a*—N1*a*	1.996 (3)
Ni—S2*a*	2.403 (1)	Co*a*—N2*a*	2.002 (3)
Ni—S3*a*	2.387 (1)	Co*a*—N3*a*	2.004 (3)
Ni—S1*b*	2.406 (1)	Co*b*—S1*b*	2.250 (1)
Ni—S2*b*	2.380 (1)	Co*b*—S2*b*	2.246 (1)
N1—S3*b*	2.408 (1)	Co*b*—S3*b*	2.249 (1)
Co*a*—S1*a*	2.266 (1)	Co*b*—N1*b*	2.012 (3)
Co*a*—S2*a*	2.253 (1)	Co*b*—N2*b*	2.011 (3)
Co*a*—S2*a*	2.252 (1)	Co*b*—N3*b*	2.004 (4)
S1*a*—Ni—S2*a*	81.06 (3)	S2*a*—Co*a*—N3*a*	90.7 (1)
S1*a*—Ni—S3*a*	81.25 (3)	S3*a*—Co*a*—N3*a*	175.7 (1)
S2*a*—Ni—S3*a*	82.20 (3)	N1*a*—Co*a*—N3*a*	92.8 (1)
S1*a*—Ni—S1*b*	95.83 (3)	N2*a*—Co*a*—N3*a*	92.3 (1)
S2*a*—Ni—S1*b*	172.48 (4)	Ni—S1*a*—Co*a*	77.25 (3)
S3*a*—Ni—S1*b*	104.06 (4)	Ni—S2*a*—Co*a*	77.76 (3)
S1*a*—Ni—S2*b*	174.35 (4)	Ni—S3*a*—Co*a*	78.12 (4)
S2*a*—Ni—S2*b*	102.45 (4)	S1*b*—Co*b*—S2*b*	87.72 (3)
S3*a*—Ni—S2*b*	94.76 (3)	S1*b*—Co*b*—S3*b*	87.10 (4)
S1*b*—Ni—S2*b*	81.20 (3)	S2*b*—Co*b*—S3*b*	88.32 (4)
S1*a*—Ni—S3*b*	102.61 (4)	S1*b*—Co*b*—N1*b*	175.4 (1)
S2*a*—Ni—S3*b*	93.89 (4)	S2*b*—Co*b*—N1*b*	87.8 (1)
S3*a*—Ni—S3*b*	174.07 (3)	S3*b*—Co*b*—N1*b*	91.8 (1)
S1*b*—Ni—S3*b*	80.17 (3)	S1*b*—Co*b*—N2*b*	91.9 (1)
S2*b*—Ni—S3*b*	81.69 (3)	S2*b*—Co*b*—N2*b*	175.6 (1)
S1*a*—Co*a*—S2*a*	87.77 (3)	S3*b*—Co*b*—N2*b*	87.3 (1)
S1*a*—Co*a*—S3*a*	87.66 (4)	N1*b*—Co*b*—N2*b*	92.5 (1)
S2*a*—Co*a*—S3*a*	88.71 (4)	S1*b*—Co*b*—N2*b*	88.2 (1)
S1*a*—Co*a*—N1*a*	176.2 (1)	S2*b*—Co*b*—N3*b*	91.2 (1)
S2*a*—Co*a*—N1*a*	88.5 (1)	S3*b*—Co*b*—N3*b*	175.3 (1)
S3*a*—Co*a*—N1*a*	91.5 (1)	N1*b*—Co*b*—N3*b*	92.9 (1)
S1*a*—Co*a*—N2*a*	91.5 (1)	N2*b*—Co*b*—N3*b*	93.1 (1)
S2*a*—Co*a*—N2*a*	176.9 (1)	Ni—Si*b*—Co*b*	78.07 (3)
S3*a*—Co*a*—N2*a*	88.3 (1)	Ni—S2*b*—Co*b*	78.67 (3)
N1*a*—Co*a*—N2*a*	92.1 (1)	Ni—S3*b*—Co*b*	78.04 (4)
S1*a*—Co*a*—N3*a*	88.0 (1)		

Discussion. The final atomic parameters are listed in Table 1.* The molecular structure and numbering scheme are illustrated in the *ORTEP*II (Johnson, 1976) plot given in Fig. 1. Selected bond distances and angles are listed in Table 2.

As shown in Fig. 1, the divalent complex cation consists of two approximately octahedral *fac*(S)-$[\mathrm{Co(aet)_3}]$ subunits and one Ni atom. The Ni atom is situated in a distorted octahedral environment coordinated by six thiolato S atoms from two *fac*(S)-$[\mathrm{Co(aet)_3}]$ subunits, completing the linear-type S-bridged trinuclear structure [Co*A*—Ni—Co*B* = 178.38 (2)°, Ni—Co*A* = 2.925 (1) and Ni—Co*B* = 2.934 (1) Å]. A similar S-bridged trinuclear structure has been observed for $[\mathrm{Co\{Co(aet\ or\ L\text{-}cys\text{-}N,S)_3\}_2}]^{3+\ \mathrm{or}\ 3-}$ (Heeg, Blinn & Deutsch, 1985; Okamoto, Aizawa, Konno, Einaga & Hidaka, 1986).

The average Ni—S distance [2.400 (1) Å] is significantly longer than that found in the related S-bridged trinuclear complex $[\mathrm{Ni\{Co(aet)_2(en)\}_2}]^{4+}$ [average 2.238 (1) Å], in which the Ni atom is coordinated by four thiolato S atoms from two *cis*(S)-$[\mathrm{Co(aet)_2(en)}]^+$ subunits (Konno, Okamoto & Hidaka, 1992). This is in accordance with the fact that the Ni—S distances in six-coordinated $\mathrm{Ni^{II}}$ complexes are usually longer than those in four-coordinated $\mathrm{Ni^{II}}$ complexes (Baidya, Olmstead & Mascharak, 1991, and references therein). The Co—S distances [average 2.253 (1) Å] are within the approximate range of 2.238–2.266 Å observed for $[\mathrm{Ni\{Co(aet)_2(en)\}_2}]^{4+}$ (Konno, Okamoto & Hidaka, 1992), $[\mathrm{Co\{Co(aet)_3\}_2}]^{3+}$ (Heeg, Blinn & Deutsch, 1985) and $[\mathrm{\{Co(aet)_3\}_4Zn_4O}]^{6+}$ (Konno, Nagashio, Okamoto & Hidaka, 1992). The S—Co—S [average 87.88 (4)°] and N—Co—N [average 92.6 (1)°] angles approach the normal values expected for an octahedral geometry, compared with those found in $[\mathrm{Co\{Co(aet)_3\}_2}]^{3+}$ [average S—Co—S = 84.5 (8) and N—Co—N = 94.6 (6)°] (Heeg, Blinn & Deutsch, 1985). The bond distances associated with the aet ligands [average S—C = 1.819 (5), C—C = 1.514 (6)

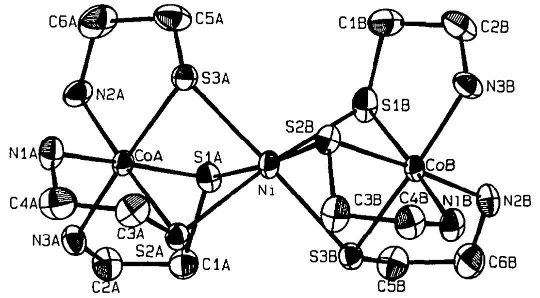

Fig. 1. *ORTEP*II (Johnson 1976) drawing of $[\mathrm{Ni\{Co(aet)_3\}_2}]^{2+}$ (50% probability thermal ellipsoids) with the atom-numbering scheme. H atoms are omitted for clarity.

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*Lists of structure factors, complete bond distances and angles, anisotropic thermal parameters, and H-atom coordinates (calculated) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55500 (24 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1008] and C—N = 1.496 (6) Å] are within the range normally observed for the aet metal complexes (Konno, Nagashio, Okamoto & Hidaka, 1992, and references therein).

The single crystal used in this work consists of the $\Delta\Delta$ and $\Lambda\Lambda$ isomers, which combine to form the racemic compound. All the aet chelate rings possess a distinct *gauche* form with the λ conformation for the $\Delta\Delta$ isomer and the δ conformation for the $\Lambda\Lambda$ isomer, and, furthermore, all the bridging S atoms are fixed to the *S* configuration for the $\Delta\Delta$ isomer and the *R* configuration for the $\Lambda\Lambda$ isomer.

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Acta Cryst. (1993). C**49**, 224–226

Structure of *trans*-Bis[1,2-bis(dimethylphosphino)ethane]dibromoiron(II)

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(*Received* 3 *February* 1992; *accepted* 5 *May* 1992)

Abstract. $[FeBr_2(C_6H_{16}P_2)_2]$, $M_r = 515.94$, monoclinic, $P2_1/n$, $a = 8.739$ (2), $b = 12.743$ (2), $c = 9.533$ (1) Å, $\beta = 91.32$ (1)°, $V = 1061.2$ Å^3, $Z = 2$, $D_x = 1.615$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 45.56$ cm^{-1}, $F(000) = 520$, $T = 293$ K, final $R = 0.043$ for 1178 observed reflections. The structure consists of a neutral *trans*-$[FeBr_2\{1,2\text{-bis(dimethylphosphino)ethane}\}_2]$ molecule with the Fe atom located at a centre of symmetry. The Fe—P bond lengths [2.230 (2) and 2.236 (1) Å] are the same as those in the analogous chloro complex and are indicative of low-spin Fe^{II}. The Fe—Br distance is 2.492 (1) Å.

Introduction. As part of a project involving a mechanistic study of C—H bond activation by iron bis(diphosphine) dihydride complexes, a series of dihalide complexes $[FeX_2(pp)_2]$ [pp = 1,2-bis(dimethylphosphino)ethane (dmpe), 1,2-bis(dipropylphosphino)ethane (dprpe) or 1,2-bis(diphenylphosphino)ethane (dppe); X = Cl, Br] were synthesized and their properties examined (Baker, Field & Hambley, 1988). These dihalide complexes can easily be converted to the corresponding dihydrides by reduction with lithium aluminium hydride in THF (Baker, Field & Young, 1990). In this paper, the structure of $[FeBr_2(dmpe)_2]$ (1) is reported.

Experimental. $[FeBr_2(dmpe)_2]$ was synthesized by stirring a THF solution of anhydrous iron(II) bromide in the presence of dmpe at room temperature for 6 h. The reaction was accompanied by a colour change from yellow–brown to pale green. Removal of the solvent produced a green solid which was characterized as a symmetrical *trans* complex by ^{31}P and ^{1}H NMR spectroscopy. ^{31}P NMR (C_6D_6): δ 58.10 (*s*, 4P). ^{1}H{^{31}P} NMR (C_6D_6): δ 1.482 (*s*, 8 × CH_3); 2.204 (*s*, 2 × PCH_2CH_2P). Details of the synthesis have been published elsewhere (Baker, Field & Hambley, 1988). Pale green crystals of *trans*-$[FeBr_2(dmpe)_2]$ were obtained by slow crystallization from benzene/light petroleum.

Cell constants were determined by a least-squares fit to 25 independent reflections, measured and refined on an Enraf–Nonius CAD-4F diffractometer with a graphite monochromator. The crystallographic data are summarized in Table 1. Data were reduced and Lorentz, polarization and absorption corrections were applied using the Enraf–Nonius *SDP* system (Frenz, 1985). The structure was solved by heavy-atom methods and refined by full-matrix

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0108-2701/93/020224-03$06.00