| | | | | |
|---|---|---|---|---|
| C76 | 0.5768 (6) | 1.0185 (8) | 0.1296 (2) | 0.040 (2) |
| C81 | 0.5580 (5) | 0.7062 (8) | 0.1336 (2) | 0.033 (2) |
| C82 | 0.6216 (6) | 0.6080 (9) | 0.1232 (2) | 0.053 (3) |
| C83 | 0.6839 (6) | 0.5397 (9) | 0.1486 (3) | 0.066 (3) |
| C84 | 0.6843 (7) | 0.5675 (9) | 0.1855 (3) | 0.061 (3) |
| C85 | 0.6213 (6) | 0.6635 (9) | 0.1963 (2) | 0.058 (3) |
| C86 | 0.5573 (5) | 0.7346 (8) | 0.1712 (2) | 0.045 (2) |
| C91 | 0.5280 (5) | 0.7805 (8) | 0.0580 (2) | 0.029 (2) |
| C92 | 0.5692 (6) | 0.8904 (8) | 0.0422 (2) | 0.042 (2) |
| C93 | 0.6133 (6) | 0.8764 (9) | 0.0091 (2) | 0.054 (3) |
| C94 | 0.6208 (6) | 0.7550 (9) | −0.0068 (2) | 0.053 (3) |
| C95 | 0.5793 (6) | 0.6471 (9) | 0.0083 (2) | 0.048 (2) |
| C96 | 0.5303 (5) | 0.6586 (8) | 0.0407 (2) | 0.039 (2) |
| O1† | 0.8524 (14) | 0.1075 (18) | 0.1689 (9) | 0.210 (9) |
| C1 | 0.8524 (14) | 0.1075 (18) | 0.1689 (9) | 0.210 (9) |
| C2 | 0.8448 (15) | 0.076 (4) | 0.2041 (8) | 0.178 (10) |
| C3 | 0.8298 (14) | −0.058 (3) | 0.2056 (7) | 0.168 (8) |
| O4† | 0.8585 (13) | −0.1174 (19) | 0.1742 (10) | 0.182 (9) |
| C4 | 0.8585 (13) | −0.1174 (19) | 0.1742 (10) | 0.182 (9) |
| C5 | 0.8792 (16) | −0.006 (5) | 0.1517 (6) | 0.199 (12) |

† Occupancies: 19.1% O1 and 80.9% O4.

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

| | | | |
|---|---|---|---|
| Cu—Cl | 2.324 (2) | Cu—P1 | 2.346 (2) |
| Cu—P2 | 2.341 (2) | Cu—P3 | 2.352 (2) |
| Cl—Cu—P2 | 104.23 (8) | Cl—Cu—P3 | 101.47 (8) |
| Cl—Cu—P1 | 103.34 (8) | P2—Cu—P3 | 111.93 (8) |
| P2—Cu—P1 | 115.28 (8) | P1—Cu—P3 | 118.03 (8) |

The position of the Cu atom was estimated using Patterson methods and all the remaining non-H-atom positions were estimated using subsequent Fourier syntheses. All non-H atoms were refined anisotropically and H atoms were inserted in calculated positions with common type-specific refined isotropic displacement parameters (phenyl: C—H = 0.93 Å and $U_{\rm iso}$ = 0.055 Å$^2$; tetrahydrofuran: C—H = 0.97 Å and $U_{\rm iso}$ = 0.252 Å$^2$); a riding model was used in the subsequent refinement. The solvent was found to be disordered, the O atom being distributed between the locations of atoms O1 and O4 only, with refined O-atom occupancies of 19.1 and 80.9%, respectively. No attempt was made to model the solvent as two molecules, however, since thermal motion of the solvent was in any case high. Anisotropic displacement parameters were retained for solvent non-H atoms in order to partially accommodate the variation in bond distances resulting from superposition of the two molecules.

Data collection: *P*3 (Siemens, 1982*a*). Data reduction: *XTAPE* (Siemens, 1982*b*). Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1986). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993).

The authors gratefully acknowledge the support of the Welch Foundation and the US National Science Foundation (grant CHE 8708625). Thanks are due to George Iwaniak for help with data transfer.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CF1023). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Siemens (1982*b*). *XTAPE.* Version 3.0. *Program for Reduction of Data Collected on Siemens R3m/E Diffractometers.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

*Acta Cryst.* (1996). C**52**, 1119–1122

# Diamminebis[dimethylglyoximato(1−)]-cobalt(III) Fluoborate and Perchlorate

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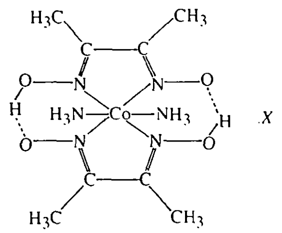
## Abstract

One of the title complexes, *trans*-diamminebis[2,3-butanedione dioximato(1−)]cobalt(III) tetrafluoroborate, $[Co(C_4H_7N_2O_2)_2(NH_3)_2]BF_4$, is isomorphous with the other, *trans*-diamminebis[2,3-butanedione dioximato(1−)]cobalt(III) perchlorate, $[Co(C_4H_7N_2O_2)_2(NH_3)_2]ClO_4$. The octahedral coordination complex has an axial Co—N($NH_3$) bond of 1.953 (2) ($BF_4^-$ salt) or 1.954 (3) Å ($ClO_4^-$ salt).

## Comment

When considering the biochemical reactions of the vitamine $B_{12}$ system, the Co—C bond cleavage step is of great interest (Finke, Schiraldi & Mayer, 1984). It has been revealed that the axial Co—C bond strength in the simple molecular models of vitamine $B_{12}$ is influenced by the ligand located in the opposite position, *i.e.* the 'structural *trans* effect' (Heeg, Elder & Deutsch, 1980). To define a 'zero' for this 'structural *trans* effect' series, the Co—N($NH_3$) bond distance in the structures of *trans*-$[(NH_3)_2Co(Hdmg)_2]X$ (where $X$ = $NO_3^-$, $Br^-$

or $SCN^-$; Hdmg = dimethylglyoxime monoanion) has been determined (Heeg & Elder, 1980; Elder, Nerone & Barrick, 1980). We present here the structures of the title compounds, (1) and (2), to evaluate the reproducibility of the Co—N($NH_3$) bond distance on changing the counterion.



(1) $X = BF_4$
(2) $X = ClO_4$

The crystals of the fluoborate are isomorphous with crystals of the perchlorate. In both, the crystal structure consists of discrete cobaloxime cations located about inversion centres and counteranions located about twofold axes. In the cation, the Co atom displays octahedral coordination, with two Hdmg and two $NH_3$ ligands in *trans* positions. The average Co—N(Hdmg) bond distance of 1.892 Å is identical to those reported previously. The Co—N($NH_3$) bond distance [1.953 (2) Å in the fluoborate and 1.954 (3) Å in the perchlorate] is also in agreement with the average value of 1.956 Å reported previously (Elder, Nerone & Barrick, 1980) and confirms the reproducibility of this bond distance.

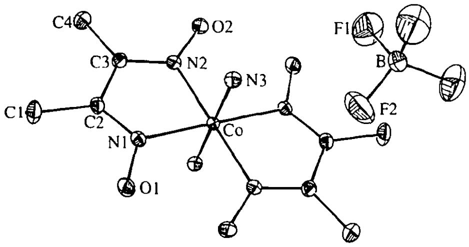


Fig. 1. Molecular structure of the fluoborate showing 30% probability displacement ellipsoids. H atoms are omitted for clarity.

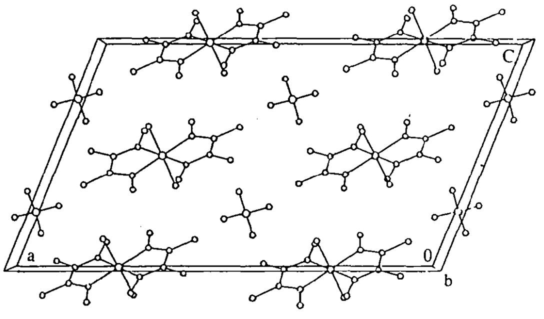


Fig. 2. Packing diagram of the fluoborate.

Besides the hydrogen bonding between O1 and the O2($\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$), the distance of 2.991 Å between O2 and N3($\frac{1}{2} - x, -\frac{1}{2} - y, 1 - z$) might suggest that hydrogen bonding exists between adjacent cations.

## Experimental

The compounds were prepared by the reaction of the chlorite salt of the corresponding complex with fluoboric acid or perchloric acid and purified by recrystallization from water.

### Compound (1)

*Crystal data*

$[Co(C_4H_7N_2O_2)_2(NH_3)_2]BF_4$
$M_r = 410.02$
Monoclinic
$C2/c$
$a = 21.526\,(6)$ Å
$b = 6.447\,(1)$ Å
$c = 12.479\,(2)$ Å
$\beta = 112.54\,(2)^\circ$
$V = 1599\,(1)$ Å$^3$
$Z = 4$
$D_x = 1.70$ Mg m$^{-3}$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 13$–$14^\circ$
$\mu = 1.138$ mm$^{-1}$
$T = 296$ K
Prism
0.36 × 0.18 × 0.08 mm
Yellow

*Data collection*

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: $\psi$ scans (Molecular Structure Corporation, 1989)
$T_{min} = 0.718$, $T_{max} = 1.000$
1588 measured reflections
1543 independent reflections

1279 observed reflections $[I > 3\sigma(I)]$
$R_{int} = 0.028$
$\theta_{max} = 25^\circ$
$h = 0 \rightarrow 25$
$k = -7 \rightarrow 0$
$l = -14 \rightarrow 13$
3 standard reflections monitored every 300 reflections
intensity decay: 2.9%

*Refinement*

Refinement on $F$
$R = 0.035$
$wR = 0.049$
$S = 1.48$
1279 reflections
111 parameters
H-atom parameters not refined
Weighting scheme based on measured e.s.d.'s

$(\Delta/\sigma)_{max} = 0.02$
$\Delta\rho_{max} = 0.51$ e Å$^{-3}$
$\Delta\rho_{min} = -0.38$ e Å$^{-3}$
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| Co | 1/4 | 1/4 | 1/2 | 0.0174 (2) |
| O1 | 0.2106 (1) | 0.5068 (3) | 0.6486 (2) | 0.0340 (7) |
| O2 | 0.1922 (1) | −0.1295 (3) | 0.3916 (2) | 0.0323 (7) |

| | | | | |
|---|---|---|---|---|
| N1 | 0.1978 (1) | 0.3301 (3) | 0.5854 (2) | 0.0226 (7) |
| N2 | 0.1887 (1) | 0.0260 (3) | 0.4610 (2) | 0.0223 (7) |
| N3 | 0.3120 (1) | 0.0915 (3) | 0.6306 (2) | 0.0247 (7) |
| C1 | 0.0946 (2) | 0.2673 (5) | 0.6215 (3) | 0.0385 (13) |
| C2 | 0.1462 (1) | 0.2156 (4) | 0.5737 (2) | 0.0253 (7) |
| C3 | 0.1419 (1) | 0.0314 (4) | 0.5017 (2) | 0.0250 (7) |
| C4 | 0.0885 (2) | −0.1293 (5) | 0.4764 (3) | 0.0415 (13) |
| B | 0 | 0.3125 (9) | 1/4 | 0.0359 (16) |
| F1 | 0.0448 (1) | 0.1942 (5) | 0.2235 (3) | 0.0910 (14) |
| F2 | 0.0379 (1) | 0.4270 (5) | 0.3418 (3) | 0.1081 (15) |

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

| | | | |
|---|---|---|---|
| Co—N1 | 1.894 (2) | O1—N1 | 1.352 (3) |
| Co—N2 | 1.890 (2) | O2—N2 | 1.345 (3) |
| Co—N3 | 1.953 (2) | | |
| N1—Co—N2 | 81.18 (9) | N1—Co—N3$^i$ | 87.89 (9) |
| N1—Co—N2$^i$ | 98.82 (9) | N2—Co—N3 | 90.10 (9) |
| N1—Co—N3 | 92.11 (9) | N2—Co—N3$^i$ | 89.90 (9) |

Symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$.

## Compound (2)

*Crystal data*

$[Co(C_4H_7N_2O_2)_2(NH_3)_2]ClO_4$
$M_r = 422.67$
Monoclinic
$C2/c$
$a = 21.560$ (10) Å
$b = 6.438$ (1) Å
$c = 12.510$ (6) Å
$\beta = 111.87$ (4)°
$V = 1612$ (1) Å$^3$
$Z = 4$
$D_x = 1.74$ Mg m$^{-3}$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 13–14°$
$\mu = 1.278$ mm$^{-1}$
$T = 296$ K
Prism
$0.40 \times 0.18 \times 0.09$ mm
Yellow

*Data collection*

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: $\psi$ scans (Molecular Structure Corporation, 1989)
$T_{min} = 0.661$, $T_{max} = 1.000$
1772 measured reflections
1728 independent reflections

1309 observed reflections $[I > 3\sigma(I)]$
$R_{int} = 0.007$
$\theta_{max} = 26°$
$h = 0 \rightarrow 26$
$k = 0 \rightarrow 7$
$l = -15 \rightarrow 14$
3 standard reflections monitored every 300 reflections intensity decay: 4.8%

*Refinement*

Refinement on $F$
$R = 0.049$
$wR = 0.055$
$S = 1.81$
1309 reflections
111 parameters
H-atom parameters not refined
Weighting scheme based on measured e.s.d.'s

$(\Delta/\sigma)_{max} = 0.01$
$\Delta\rho_{max} = 1.0$ e Å$^{-3}$
$\Delta\rho_{min} = -1.1$ e Å$^{-3}$
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| Co | 1/4 | 1/4 | 1/2 | 0.0134 (3) |
| O1 | 0.2108 (1) | 0.5068 (5) | 0.6486 (3) | 0.0291 (13) |
| O2 | 0.1922 (1) | −0.1280 (4) | 0.3929 (3) | 0.0264 (12) |
| N1 | 0.1983 (2) | 0.3312 (5) | 0.5861 (3) | 0.0167 (12) |
| N2 | 0.1888 (1) | 0.0258 (4) | 0.4611 (3) | 0.0158 (10) |
| N3 | 0.3109 (2) | 0.0907 (5) | 0.6297 (3) | 0.0204 (13) |
| C1 | 0.0961 (2) | 0.2680 (7) | 0.6253 (4) | 0.0326 (18) |
| C2 | 0.1465 (2) | 0.2171 (6) | 0.5751 (4) | 0.0206 (14) |
| C3 | 0.1425 (2) | 0.0331 (6) | 0.5043 (4) | 0.0206 (14) |
| C4 | 0.0894 (2) | −0.1297 (7) | 0.4796 (5) | 0.0353 (17) |
| Cl | 0 | 0.3123 (2) | 1/4 | 0.0293 (4) |
| O3 | 0.0473 (2) | 0.1911 (9) | 0.2240 (5) | 0.077 (2) |
| O4 | 0.0363 (2) | 0.4350 (10) | 0.3444 (5) | 0.096 (3) |

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

| | | | |
|---|---|---|---|
| Co—N1 | 1.889 (3) | O1—N1 | 1.344 (4) |
| Co—N2 | 1.894 (3) | O2—N2 | 1.327 (4) |
| Co—N3 | 1.954 (3) | | |
| N1—Co—N2 | 81.6 (1) | N1—Co—N3$^i$ | 88.4 (1) |
| N1—Co—N2$^i$ | 98.4 (1) | N2—Co—N3 | 90.1 (1) |
| N1—Co—N3 | 91.6 (1) | N2—Co—N3$^i$ | 89.9 (1) |

Symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$.

For each crystal, data collection was performed with a scan width of $\Delta\omega = (0.65 + 0.35\tan\theta)°$ and a scan rate of $< 5.6°$ min$^{-1}$ in $\omega$. The structures were solved by direct methods and refined anisotropically for all non-H atoms by full-matrix least-squares methods. The H-atom sites were obtained from the individual difference Fourier maps and not refined. All computations were performed on a MicroVAX 3100 computer.

For both compounds, data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1989); program(s) used to solve structures: *TEXSAN*; program(s) used to refine structures: *TEXSAN*; molecular graphics: *ORTEP*II (Johnson, 1976).

This study was supported by the Foundation of the State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Science.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1127). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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# Redetermination of $[Cu_5Cl_{10}(n\text{-}C_3H_7OH)_2]$

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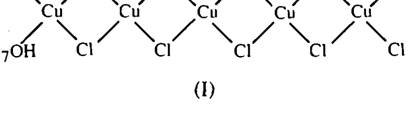
(*Received 21 March 1995; accepted 5 September 1995*)

## Abstract

The structure of the title compound, octa-$\mu$-chloro-1:2$\kappa^4$*Cl*,2:3$\kappa^4$*Cl*,3:4$\kappa^4$*Cl*,4:5$\kappa^4$*Cl*-dichloro-1$\kappa$*Cl*,5$\kappa$*Cl*-bis(propanol)-1$\kappa$*O*,5$\kappa$*O*-pentacopper(II), consists of planar bibridged pentameric $Cu_5Cl_{10}L_2$ ($L$ = $n$-propanol) units. Each $Cu^{2+}$ ion assumes approximate square-planar coordination geometry, with Cu—Cl distances ranging between 2.258 (2) and 2.297 (3) Å. The oligomers form stacks parallel to $b$ through the formation of longer semicoordinate bonds which range in length from 2.687 (2) to 3.158 (3) Å. The stacking pattern leaves one semicoordinate site vacant on the Cu(3) atom. The stacks then aggregate into sheets lying parallel to the ($\bar{1}$01) planes through the formation of semicoordinate Cu(3)—Cl(5) bonds of 2.681 (2) Å. The $n$-propyl groups separate these sheets. Large atomic displacements of the C atoms [particularly for atoms C(2) and C(3)] indicate substantial disorder of the propyl groups.

## Comment

The title pentamer, (I), is one of a series of planar bibridged $Cu_nX_{2n}L_2$ oligomers, with $n$ = 2, 3, 4, 5, 6 or 7, $X$ = $Cl^-$ or $Br^-$, and $L$ = $Cl^-$, $Br^-$ or other coordinating ligands (Bond & Willett, 1989; Willett, Bond & Pon, 1990; Bond, Place, Wang, Willett, Liu, Grigereit & Drumheller, 1995). The stacking pattern is denoted as $5(\frac{3}{2},\frac{1}{2})$ in the notation of Geiser, Willett, Lindbeck & Emerson (1986). A phenomenological theory has been developed to describe the stacking pattern (Willett, 1993).



(I)

The structure of the Cu/Cl framework (Fig. 1) and the stacking of the oligomers (Fig. 2) is closely related to that of the parent $CuCl_2$ structure (Wells, 1947). The latter is built up of infinite planar bibridged $(CuCl_2)_n$ chains linked together into layers through semicoordinate bonds. The stacks of pentamers in $Cu_5Cl_{10}L_2$ can be viewed as slabs cut from the $CuCl_2$ layer structure when the $n$-propanol groups are inserted into the chains. This chain termination effect is a common modification of the parent $CuCl_2$ structure (Weiss & Willett, 1993). In the title compound, however, semicoordinate bonds between the stacks link adjacent stacks to form a herringbone pattern (Fig. 3).

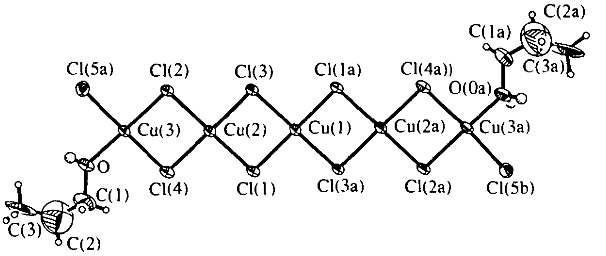


Fig. 1. Displacement ellipsoid illustration of the $[Cu_5Cl_{10}(n\text{-}C_3H_7OH)_2]$ oligomer, with ellipsoids shown at the 50% probability level.

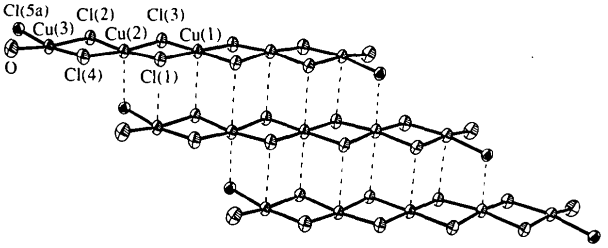


Fig. 2. Displacement ellipsoid illustration of the stacking of the pentamers, with ellipsoids shown at the 50% probability level.

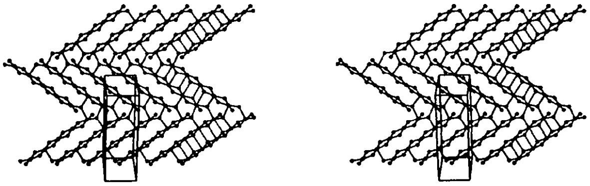


Fig. 3. Stereoview of the sheet structure.

In the present compound, there is less variation in the length of the coordinate Cu—Cl bonds than in other $Cu_nCl_{2n}L_2$ oligomer systems (Willett, 1988). The normal trend of short, long, short, *etc.*, bond-length alternation is found as one proceeds from the end of the oligomer towards the center; however, it is not as pronounced as in other oligomers. In the