Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

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

	x	y	z	B_{eq}
Na	0.1407 (2)	0.4212	0.7297 (1)	1.88 (3)
O1	0.5709 (3)	0.3953 (3)	0.8863 (2)	2.15 (6)
O2	0.9773 (3)	0.4782 (3)	0.9961 (2)	2.56 (7)
O3	0.8414 (4)	0.6065 (3)	1.2971 (2)	1.90 (7)
O4	0.8440 (3)	0.2211 (3)	1.2988 (2)	1.87 (7)
O5	0.7160 (3)	0.3503 (3)	1.5988 (2)	2.27 (6)
O6	0.3123 (3)	0.4087 (3)	1.4573 (2)	2.09 (6)
C1	0.7546 (4)	0.4566 (3)	1.0118 (2)	1.51 (7)
C2	0.6628 (4)	0.4976 (4)	1.1857 (3)	1.47 (7)
C3	0.6213 (4)	0.3275 (4)	1.2797 (3)	1.43 (7)
C4	0.5404 (4)	0.3654 (3)	1.4588 (3)	1.43 (7)

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

O1—C1	1.304 (3)	O6—C4	1.242 (3)
O2—C1	1.210 (3)	C1—C2	1.526 (3)
O3—C2	1.414 (3)	C2—C3	1.540 (3)
O4—C3	1.417 (3)	C3—C4	1.532 (3)
O5—C4	1.266 (3)		
O1—C1—O2	124.6 (2)	O4—C3—C2	111.1 (2)
O1—C1—C2	113.2 (2)	O4—C3—C4	113.0 (2)
O2—C1—C2	122.2 (2)	C2—C3—C4	109.6 (2)
O3—C2—C1	110.9 (2)	O5—C4—O6	125.0 (2)
O3—C2—C3	112.1 (2)	O5—C4—C3	116.3 (2)
C1—C2—C3	108.6 (2)	O6—C4—C3	118.7 (2)

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O5^{i}	0.90 (6)	1.59 (6)	2.476 (3)	169 (9)
O5—H6···O1^{ii}	0.71 (8)	1.81 (8)	2.476 (3)	157 (9)
O3—H4···O6^{iii}	0.75 (4)	2.33 (5)	2.961 (3)	142 (4)
O4—H5···O6^{iv}	0.82 (4)	2.11 (4)	2.907 (3)	161 (3)

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

H atoms were located from a difference Fourier map and the coordinates and displacement parameters were refined, except for the disordered H atoms between the O1···O5 hydrogen bond, H1 and H6, whose B_{iso} values were fixed to the average value of B_{eq} of O1 and O5. The occupancy factors of the H atoms converged to 0.58 (2) and 0.42 (2) in the least-squares refinement. The final $\Delta\rho$ map showed no significant peaks around these H atoms, $\Delta\rho$ being at most 0.10 e Å^{-3}. All calculations were performed on a VAX3100 computer at the X-ray Laboratory of Okayama University, Japan.

Data collection: *MSC/AFC Data Collection and Refinement Software* (Rigaku Corporation, 1990). Cell refinement: *MSC/AFC Data Collection and Refinement Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *MITHRIL* (Gilmore, 1984). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, including torsion angles and Na^+ coordination details, have been deposited with the IUCr (Reference: AB1342). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2-Carboxy-9-dihydroxymethyl-1,10-phenanthroline Complexes of Cobalt(II) and Copper(II)

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(*Received 25 July 1995; accepted 1 April 1996*)

Abstract

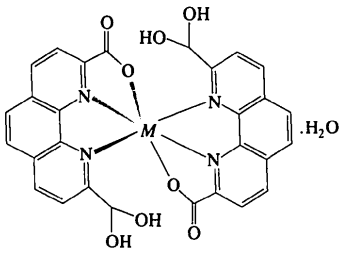
Bis(9-dihydroxymethyl-1,10-phenanthroline-2-carboxylato-*N,N′,O*)cobalt(II) hydrate, $[Co(C_{14}H_9N_2O_4)_2].H_2O$, and bis(9-dihydroxymethyl-1,10-phenanthroline-2-carboxylato-*N,N′,O*)copper(II) hydrate, $[Cu(C_{14}H_9N_2O_4)_2].H_2O$, are isostructural. The stable *gem*-diol ligands are tridentate (two N atoms and one carboxylate O atom) and form a distorted octahedron around the metal center. The total bite angle of the ligand is approximately 150°.

Comment

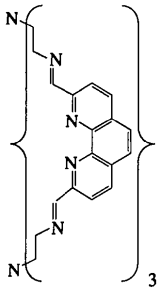
Tridentate phenanthroline ligands are not common. Lee & Trogler (1990) have reported a monosubstituted phenanthroline ligand which coordinates with Cu[1]. The species, however, forms a dimer (M_2L_2) where the phenanthroline N atoms bind one Cu atom and the

substituent N atom binds the second Cu atom. Masood & Hodgson (1994) have reported the synthesis and structure of an unsymmetrical tridentate phenanthroline ligand which binds Ni^{II} in a 1:1 ratio (Cl ions occupy the other coordination sites). To our knowledge, this is the first work involving (ML_2) species, where L is a tridentate phenanthroline moiety.

Recently, structural studies of Schiff base cryptands as free ligands and as transition metal complexes have been reported (Smith *et al.*, 1993; Harding, McKee & Nelson, 1991; Hunter, Nelson, Harding, McCann & McKee, 1990; Jazwinski *et al.*, 1987). In an attempt to synthesize metal complexes of L_1, the cobalt, (I), and copper, (II), complexes were isolated. The ligand 2-carboxy-9-dihydroxymethyl-1,10-phenanthroline is the hydrolysis and oxidation product of L_1. Compounds (I) and (II) are isostructural, with six-coordinate metal centers as shown. Owing to the poor refinement on (II), only bond distances and angles relating to (I) will be discussed.



(I) M = Co
(II) M = Cu



L_1

In (I), the metal center has two short M—N1 (2.04 Å) bonds, two long M—N10 (2.25 Å) bonds and two M—O21 bonds. The Co—N distances observed are either shorter or longer than Co^{II}—N_{phen} distances of 2.11 (1)–2.14 (1) Å (Youinou, Ziessel & Lehn, 1991; Boys, Escobar & Wittke, 1984) observed in high-spin Co^{II} complexes; the Co—N1 distance, however, is not as short as those observed in low-spin Co^{II}–phen complexes (Faus, Julve, Lloret & Muñoz, 1993). The Co—O distances are within expected values (Youinou *et al.*, 1991; Hanton & Raithby, 1980). The variation in the bond lengths is due to the coordination of the carboxyl O21 atom which causes the metal center to shift towards N1, effectively shortening the M—N1 bond while lengthening M—N10. The N1—Co—N10 bond angles of 75° are smaller than those in bidentate phenanthroline species (Boys *et al.*, 1984; Corwin, Fikar & Koch, 1987) but similar to those for phenanthroline-containing macrocycles (Hanton & Raithby, 1980). The total bite angle for the ligand is 150°. Deviation from octahedral metal coordination is thus due to the rigid phenanthroline moiety which cannot span either three ideal equatorial positions or from one ideal axial position to the other.

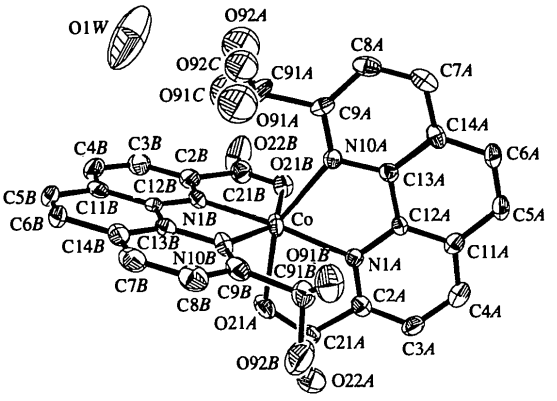


Fig. 1. A perspective view of (I) with displacement ellipsoids shown at 50% probability levels and H atoms omitted for clarity.

A least-squares plane was calculated for the 14 atoms of each phenanthroline ring. The average deviation from the plane of an atom used in the calculation was 0.013 and 0.023 Å for (I) [0.015 and 0.019 Å for (II)] indicating that the phenanthroline rings do not twist significantly. The phenanthroline planes in both complexes are perpendicular to one another [88 and 90° for (I) and (II), respectively].

The ordered diol C—O bond length of 1.39 Å [C91B—O_{av}] observed in (I) agrees well with values of 1.38 (1)–1.42 (1) Å for previously reported diol complexes (Wang, Richardson, Briggs, Jacobson & Jensen, 1986; Mattes & Uckelmann, 1981). The average bond length in the disordered diol [C91A—O_{av} 1.32 Å] varies considerably from the accepted values, but this may be due to the disorder in this portion of the molecule. It is interesting to note that O atoms on C91A are within hydrogen-bonding distance of the water molecule [O92A···O1W 2.61 (2) and O92C···O1W 2.70 (2) Å] and this interaction may be causing the observed disorder. Similar interactions are present in compound (II).

Experimental

Solutions of 1,10-phenanthroline-2,9-dicarboxaldehyde (Chandler, Deady & Reiss, 1981) in DMSO and tris(2-aminoethyl)-amine in CH_3CN were added dropwise to CH_3CN (molar ratio 3:2). After addition was complete, the cream solid was filtered, rinsed with CH_3CN and dried *in vacuo*. The cobalt sample was prepared by combining the above solid with $CoCl_2.6H_2O$ in a 1:1 ratio in water, followed by stirring and filtering. The red–orange filtrate was allowed to evaporate slowly at room temperature to yield (I). The copper sample, (II), was prepared in an analogous manner using $Cu(NO_3)_2.3H_2O$. Neither complex is soluble in common organic solvents but will dissolve (not necessarily intact) in 4 M HNO_3.

Compound (I)

Crystal data

$[Co(C_{14}H_9N_2O_4)_2].H_2O$	Mo $K\alpha$ radiation
M_r = 615.41	λ = 0.71073 Å

Triclinic
$P\bar{1}$
a = 7.778 (2) Å
b = 12.219 (2) Å
c = 12.930 (3) Å
α = 83.24 (3)°
β = 75.71 (3)°
γ = 86.45 (3)°
V = 1182 (1) Å^3
Z = 2
D_x = 1.729 Mg m^{-3}
D_m not measured

Cell parameters from 25 reflections
θ = 5–15°
μ = 0.798 mm^{-1}
T = 203 (2) K
Prismatic
0.18 × 0.12 × 0.12 mm
Orange

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: empirical *via* ψ scan (Sheldrick, 1990)
T_{min} = 0.8583, T_{max} = 0.9007
4478 measured reflections
4145 independent reflections

2368 observed reflections [$F > 4\sigma(F)$]
R_{int} = 0.0218
θ_{max} = 25°
$h = -8 \rightarrow 8$
$k = -14 \rightarrow 14$
$l = 0 \rightarrow 15$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F
R = 0.0644
$wR(F)$ = 0.1056
S = 1.14
2368 reflections
375 parameters
Only coordinates of H atoms refined
Weighting scheme based on measured e.s.d.'s; $w = 1/[\sigma^2(F) + 0.0043(F)^2]$

$(\Delta/\sigma)_{max}$ = 0.016
$\Delta\rho_{max}$ = 1.25 e Å^{-3} (in the area of the diol disorder)
$\Delta\rho_{min}$ = −0.57 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

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

	x	y	z	U_{eq}
Co	0.16446 (13)	0.24186 (9)	0.21122 (7)	0.0258 (3)
N1*A*	0.1906 (7)	0.2409 (5)	0.0507 (4)	0.021 (2)
N10*A*	0.4352 (7)	0.3084 (5)	0.1356 (4)	0.020 (1)
N1*B*	0.0722 (7)	0.2641 (5)	0.3693 (4)	0.024 (2)
N10*B*	0.2596 (7)	0.0892 (5)	0.2979 (4)	0.025 (2)
O21*A*	−0.0741 (6)	0.1645 (5)	0.1978 (4)	0.035 (2)
O22*A*	−0.2109 (8)	0.1168 (5)	0.0769 (5)	0.052 (2)
O21*B*	0.0574 (6)	0.4087 (4)	0.2119 (4)	0.030 (1)
O22*B*	−0.1086 (10)	0.5247 (6)	0.3164 (5)	0.069 (2)
O91*A*†	0.6041 (19)	0.2248 (13)	0.3273 (12)	0.078 (2)
O91*C*‡	0.665 (2)	0.2775 (14)	0.3353 (13)	0.078 (2)
O91*B*	0.5713 (8)	−0.0496 (5)	0.1081 (4)	0.048 (2)
O92*A*†	0.5273 (18)	0.4176 (13)	0.3498 (12)	0.078 (2)
O92*C*‡	0.401 (2)	0.3693 (14)	0.3492 (13)	0.078 (2)
O92*B*	0.2841 (9)	−0.0812 (7)	0.1258 (5)	0.070 (2)
O1*W*	0.3964 (12)	0.3838 (13)	0.5568 (7)	0.160 (2)
C2*A*	0.0616 (9)	0.2055 (6)	0.0147 (5)	0.024 (2)
C21*A*	−0.0864 (9)	0.1556 (6)	0.1027 (6)	0.030 (2)
C3*A*	0.0652 (9)	0.2163 (6)	−0.0937 (6)	0.030 (2)
C4*A*	0.2039 (10)	0.2672 (7)	−0.1658 (6)	0.032 (2)
C5*A*	0.4967 (10)	0.3557 (6)	−0.1977 (5)	0.030 (2)
C6*A*	0.6226 (9)	0.3921 (6)	−0.1551 (5)	0.029 (2)
C7*A*	0.7383 (9)	0.4157 (6)	0.0069 (6)	0.031 (2)
C8*A*	0.7111 (9)	0.3992 (6)	0.1149 (6)	0.031 (2)
C9*A*	0.5590 (9)	0.3453 (6)	0.1766 (6)	0.025 (2)
C91*A*	0.5256 (11)	0.3201 (7)	0.3004 (6)	0.041 (2)
C11*A*	0.3444 (9)	0.3043 (6)	−0.1299 (5)	0.026 (2)
C12*A*	0.3305 (8)	0.2902 (6)	−0.0189 (5)	0.020 (2)
C13*A*	0.4628 (9)	0.3255 (5)	0.0265 (5)	0.022 (2)
C14*A*	0.6102 (8)	0.3775 (6)	−0.0420 (5)	0.024 (2)
C2*B*	−0.0183 (9)	0.3536 (7)	0.3981 (6)	0.029 (2)
C21*B*	−0.0254 (10)	0.4388 (7)	0.3013 (6)	0.032 (2)
C3*B*	−0.0921 (10)	0.3701 (7)	0.5050 (6)	0.037 (2)
C4*B*	−0.0634 (10)	0.2896 (7)	0.5831 (6)	0.034 (2)
C5*B*	0.0804 (10)	0.1050 (7)	0.6288 (6)	0.035 (2)
C6*B*	0.1822 (9)	0.0184 (7)	0.5941 (5)	0.031 (2)
C7*B*	0.3543 (10)	−0.0816 (7)	0.4395 (6)	0.035 (2)
C8*B*	0.4057 (10)	−0.0862 (7)	0.3319 (6)	0.035 (2)
C9*B*	0.3550 (9)	0.0016 (6)	0.2629 (6)	0.029 (2)
C91*B*	0.3981 (10)	−0.0068 (7)	0.1423 (6)	0.035 (2)
C11*B*	0.0364 (9)	0.1940 (7)	0.5552 (6)	0.031 (2)
C12*B*	0.1029 (9)	0.1851 (6)	0.4448 (5)	0.024 (2)
C13*B*	0.2082 (9)	0.0919 (6)	0.4075 (5)	0.025 (2)
C14*B*	0.2502 (9)	0.0071 (7)	0.4803 (6)	0.029 (2)

† Occupancy of 0.52. ‡ Occupancy of 0.48.

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

Co—N1*A*	2.036 (6)	O21*B*—C21*B*	1.261 (9)
Co—N1*B*	2.037 (5)	O22*B*—C21*B*	1.209 (10)
Co—O21*B*	2.154 (5)	O91*A*—C91*A*	1.331 (17)
Co—O21*A*	2.186 (6)	O91*C*—C91*A*	1.329 (19)
Co—N10*B*	2.242 (6)	O91*B*—C91*B*	1.399 (9)
Co—N10*A*	2.250 (5)	O92*A*—C91*A*	1.418 (19)
O21*A*—C21*A*	1.274 (10)	O92*C*—C91*A*	1.187 (16)
O22*A*—C21*A*	1.236 (11)	O92*B*—C91*B*	1.378 (12)
N1*A*—Co—N1*B*	164.0 (2)	O21*B*—Co—N10*B*	150.0 (2)
N1*A*—Co—O21*B*	93.3 (2)	O21*A*—Co—N10*B*	93.1 (2)
N1*B*—Co—O21*B*	75.0 (2)	N1*A*—Co—N10*A*	75.7 (2)
N1*A*—Co—O21*A*	74.9 (2)	N1*B*—Co—N10*A*	114.4 (2)
N1*B*—Co—O21*A*	95.3 (2)	O21*B*—Co—N10*A*	88.9 (2)
O21*B*—Co—O21*A*	97.1 (2)	O21*A*—Co—N10*A*	150.3 (2)
N1*A*—Co—N10*B*	116.6 (2)	N10*B*—Co—N10*A*	96.1 (2)
N1*B*—Co—N10*B*	75.9 (2)		

Compound (II)

Crystal data

$[Cu(C_{14}H_9N_2O_4)_2].H_2O$
M_r = 620.02
Triclinic
$P\bar{1}$
a = 7.793 (2) Å
b = 12.448 (2) Å
c = 13.021 (3) Å
α = 82.10 (3)°
β = 75.06 (3)°
γ = 86.06 (3)°
V = 1208 (1) Å^3
Z = 2
D_x = 1.704 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 32 reflections
θ = 9–11°
μ = 0.974 mm^{-1}
T = 293 (2) K
Parallelepiped
0.09 × 0.06 × 0.05 mm
Red

Data collection

Siemens *R3m/V* diffractometer
ω scans
Absorption correction: none
4508 measured reflections
4169 independent reflections
1517 observed reflections [$F > 3\sigma(F)$]

R_{int} = 0.0157
θ_{max} = 25°
$h = -8 \rightarrow 8$
$k = -14 \rightarrow 14$
$l = 0 \rightarrow 15$
3 standard reflections monitored every 97 reflections
intensity decay: none

Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.004$
$R = 0.1053$	$\Delta\rho_{max} = 0.89$ e Å^{-3}
$wR(F) = 0.2780$	$\Delta\rho_{min} = -0.61$ e Å^{-3}
$S = 3.60$	Extinction correction: none
1517 reflections	Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
200 parameters	
Only coordinates of H atoms refined	
Unit weights applied	

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

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

	x	y	z	U_{eq}
Cu	0.1573 (4)	0.2456 (2)	0.2151 (2)	0.053 (1)
O1*W*	0.398 (3)	0.385 (2)	0.557 (2)	0.178 (7)
O21*A*	−0.090 (2)	0.1687 (13)	0.2049 (13)	0.071 (4)
O22*A*	−0.205 (3)	0.114 (2)	0.080 (2)	0.152 (7)
O22*B*	−0.096 (3)	0.5265 (16)	0.3148 (15)	0.098 (5)
O21*B*	0.0510 (19)	0.4088 (12)	0.2090 (12)	0.063 (4)
O91*A*†	0.609 (5)	0.397 (4)	0.337 (3)	0.110 (6)
O92*A*†	0.564 (6)	0.220 (4)	0.332 (4)	0.110 (6)
O91*C*‡	0.650 (5)	0.273 (3)	0.335 (3)	0.110 (6)
O92*C*‡	0.419 (5)	0.401 (3)	0.353 (3)	0.110 (6)
O91*B*	0.295 (3)	−0.0719 (18)	0.1206 (16)	0.117 (6)
O92*B*	0.567 (3)	−0.0392 (16)	0.1073 (15)	0.105 (5)
N1*A*	0.187 (2)	0.2402 (13)	0.0606 (13)	0.050 (4)
N10*A*	0.435 (2)	0.3142 (13)	0.1372 (10)	0.040 (4)
N1*B*	0.074 (2)	0.2650 (15)	0.3654 (12)	0.051 (4)
N10*B*	0.258 (2)	0.0892 (14)	0.2954 (12)	0.047 (4)
C2*A*	0.058 (3)	0.2039 (15)	0.0210 (14)	0.038 (4)
C21*A*	−0.089 (3)	0.151 (2)	0.118 (2)	0.074 (6)
C3*A*	0.070 (3)	0.2125 (19)	−0.0839 (17)	0.066 (5)
C4*A*	0.204 (3)	0.2640 (17)	−0.1599 (17)	0.056 (5)
C5*A*	0.495 (3)	0.3533 (16)	−0.1942 (16)	0.052 (5)
C6*A*	0.623 (3)	0.3868 (18)	−0.1526 (17)	0.059 (5)
C7*A*	0.735 (3)	0.4148 (16)	0.0071 (16)	0.051 (5)
C8*A*	0.709 (3)	0.4035 (17)	0.1100 (16)	0.055 (5)
C9*A*	0.555 (3)	0.3488 (16)	0.1819 (15)	0.045 (5)
C91*A*	0.522 (3)	0.328 (2)	0.3001 (18)	0.061 (5)
C11*A*	0.338 (3)	0.3001 (17)	−0.1210 (16)	0.049 (5)
C12*A*	0.327 (2)	0.2890 (14)	−0.0150 (13)	0.031 (4)
C13*A*	0.458 (3)	0.3257 (15)	0.0343 (14)	0.041 (4)
C14*A*	0.612 (3)	0.3781 (16)	−0.0442 (15)	0.041 (4)
C2*B*	−0.012 (3)	0.3533 (18)	0.3939 (16)	0.052 (5)
C21*B*	−0.021 (3)	0.436 (2)	0.3015 (18)	0.063 (5)
C3*B*	−0.086 (3)	0.3720 (18)	0.5001 (16)	0.053 (5)
C4*B*	−0.052 (3)	0.2903 (18)	0.5771 (18)	0.062 (5)
C5*B*	0.091 (3)	0.1047 (18)	0.6232 (18)	0.059 (5)
C6*B*	0.185 (3)	0.0221 (19)	0.5918 (17)	0.061 (5)
C7*B*	0.348 (3)	−0.0771 (19)	0.4395 (17)	0.060 (5)
C8*B*	0.399 (3)	−0.083 (2)	0.332 (2)	0.085 (6)
C9*B*	0.352 (3)	0.0035 (18)	0.2624 (16)	0.050 (5)
C91*B*	0.396 (3)	0.000 (2)	0.1406 (18)	0.067 (6)
C11*B*	0.043 (3)	0.1961 (19)	0.5517 (17)	0.059 (5)
C12*B*	0.108 (3)	0.1837 (16)	0.4409 (14)	0.039 (4)
C13*B*	0.206 (2)	0.0935 (15)	0.4048 (13)	0.035 (4)
C14*B*	0.250 (3)	0.0076 (17)	0.4813 (15)	0.049 (5)

† Occupancy of 0.60. ‡ Occupancy of 0.40.

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

Cu—N1*B*	1.94 (2)	O22*B*—C21*B*	1.24 (3)
Cu—N1*A*	1.98 (2)	O21*B*—C21*B*	1.27 (3)
Cu—O21*B*	2.14 (2)	O91*A*—C91*A*	1.34 (6)
Cu—O21*A*	2.25 (2)	O92*A*—C91*A*	1.39 (5)
Cu—N10*B*	2.27 (2)	O91*C*—C91*A*	1.31 (5)
Cu—N10*A*	2.31 (2)	O92*C*—C91*A*	1.31 (4)
O21*A*—C21*A*	1.19 (3)	O91*B*—C91*B*	1.33 (4)
O22*A*—C21*A*	1.27 (4)	O92*B*—C91*B*	1.37 (3)
N1*B*—Cu—N1*A*	166.7 (7)	O21*B*—Cu—N10*B*	154.8 (6)
N1*B*—Cu—O21*B*	77.4 (7)	O21*A*—Cu—N10*B*	92.6 (6)
N1*A*—Cu—O21*B*	93.6 (6)	N1*B*—Cu—N10*A*	112.7 (7)
N1*B*—Cu—O21*A*	95.8 (7)	N1*A*—Cu—N10*A*	76.4 (6)
N1*A*—Cu—O21*A*	75.2 (6)	O21*B*—Cu—N10*A*	88.2 (5)
O21*B*—Cu—O21*A*	96.1 (6)	O21*A*—Cu—N10*A*	151.4 (6)
N1*B*—Cu—N10*B*	78.2 (7)	N10*B*—Cu—N10*A*	95.4 (6)
N1*A*—Cu—N10*B*	111.5 (6)	C21*A*—O21*A*—Cu	114.2 (15)

The structures were solved by direct methods and refined using the full-matrix least-squares method with *SHELXTL-Plus* software (Sheldrick, 1990). The disordered diols in (I) and (II) were modeled by allowing two sets of O atoms to refine with linked occupancy and isotropic displacement parameters. No H atoms were located on the hydroxyl O atoms, the water molecule or the C atom carrying the disordered hydroxyl groups (C91*A*). All other H atoms were located on the difference map and fixed at ideal positions with common isotropic displacement parameters ($U_{iso} = 0.08$ Å^2). The small observed data set for (II) ($F > 3\sigma F$) precluded full anisotropic refinement. Attempts to cool (II) to improve peak intensities were not successful.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989) for (I); *XSCANS* (Siemens, 1994) for (II). Cell refinement: *CAD-4 Software* for (I); *XSCANS* for (II). Data reduction: *CAD-4 Software* for (I); *XSCANS* for (II). For both compounds, program(s) used to solve structures: *SHELXTL-Plus*; program(s) used to refine structures: *SHELXTL-Plus*; molecular graphics: *SHELXTL-Plus*; software used to prepare material for publication: *SHELXTL-Plus*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, together with a displacement ellipsoid plot of (II), have been deposited with the IUCr (Reference: KH1071). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis(*N,N'*-dimethylthiourea-*S*)silver(I) Perchlorate and Tris(*N,N'*-dimethylthiourea-*S*)silver(I) Perchlorate

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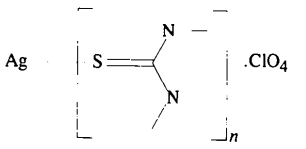
(*Received 29 January 1996; accepted 29 February 1996*)

Abstract

The structures of two different complexes of silver(I) and dimethylthiourea (dmtu) in the stoichiometric ratios 1:2, $[Ag(C_3H_8N_2S)_2]ClO_4$, and 1:3, $[Ag(C_3H_8N_2S)_3]ClO_4$, are described. The 1:2 complex consists of polynuclear cationic chains, whereas the 1:3 complex contains discrete $[Ag_2(dmtu)_6]^{2+}$ cations. In both structures, Ag_2S_2 lozenges with different Ag—S bond lengths are observed and the perchlorate anions are connected to the cations by hydrogen bonds.

Comment

Complexes of copper(I) or silver(I) halides [*M*(I)*X*; *X* = Cl, Br, I] or oxyanions (*X* = NO_3, SO_4, ClO_4) with thiourea (tu) or substituted thioureas (*L*) show stoichiometries of the type $(MX)L_n$ (n = 1–4). Furthermore, complexes with the same stoichiometry may have different structures. Characterized complexes of silver(I) with substituted thioureas are much rarer than their copper(I) counterparts. $[Cu(tu)_2Cl]$ and $[Ag(tu)_2Cl]$ form chain structures, the metal being trigonal planar and coordinated to S atoms from three different thiourea ligands; the *M*—Cl distances are very long (Spofford & Amma, 1968, 1970; Vizzini & Amma, 1966). $[Cu(tu)_3Cl]$ also has a chain structure but the Cu^I atom is tetrahedral, being coordinated to three S atoms (one bridging and two terminal) and to one Cl atom (Okaya & Knobler, 1964). Dimeric ionic complexes of stoichiometry $[ML_3]^+X^-$ have been reported only for copper(I) with thiourea or substituted thioureas and include $[Cu(tu)_3]BF_4$, $[Cu(dmtu)_3]BF_4$ and $[Cu(tu)_3]ClO_4$ (Taylor, Weininger & Amma, 1974; Hanic & Durcanska, 1969). They contain discrete sulfur-bridged dimeric $Cu_2L_6^{2+}$ cations, in which the metal coordination is approximately tetrahedral, and X^- anions. Mononuclear complexes of stoichiometry 1:3 are commonly either monomeric or ionic. The monomeric form, XML_3, has been reported for a complex of copper(I) chloride with *N,N'*-dimethylthiourea, while the ionic form, $[ML_3]^+X^-$, has been reported for complexes of tris(ethylenethiourea)copper(I) sulfate, $[Cu(etu)_3]SO_4$, and tris(tetramethylthiourea)copper(I) tetrafluoroborate, $[Cu(tmtu)_3]BF_4$, all of which contain trigonal copper(I) (Girling & Amma, 1971; Weininger, Hunt & Amma, 1972; Bowmaker, Pakawatchai, Skelton, Thavornyutikarn, Wattanakanjana & White, 1994). For stoichiometry 1:4, the mononuclear ionic structural type has been characterized for tetrakis(ethylenethiourea)copper(I) nitrate, $[Cu(etu)_4]NO_3$, where the copper(I) coordination is tetrahedral and involves S atoms of four independent etu molecules (Bowmaker *et al.*, 1994).



(1) $n = 2$
(2) $n = 3$

We have prepared new 1:2, (1), and 1:3, (2), complexes of silver(I) perchlorate *N,N'*-dimethylthiourea and have determined their crystal structures. Complex (1) consists of polynuclear and (2) of dinuclear cationic units. In both structures, the Ag atoms are tetrahedrally coordinated and form planar Ag_2S_2 lozenges with bridging dmtu ligands.

The asymmetric unit of (1) is shown in Fig. 1 and the polynuclear chain of continuous Ag_2S_2 lozenges which run along the *a* axis is shown in Fig. 2. There are two different lozenges, each exactly centrosymmetric, formed by Ag—S1—Ag'—S1' and Ag—S2—Ag'—S2', with differing Ag—S distances [Ag—S1 2.5401 (8) and Ag—S1' 2.7272 (9); Ag—S2 2.5985 (7) and Ag—S2' 2.5856 (8) Å]. The Ag—S—Ag bond angles are 74.93 (2) and 76.56 (2)° at atoms S1 and S2, respectively. The two lozenges are nearly perpendicular to one another, the dihedral angle between their planes being 86.40 (2)°. The atoms in each dmtu ligand lie in a plane perpendicular to that of the lozenge to which it is attached. The Ag—S—C angles are greater than 95°.

The $[Ag_2(dmtu)_6]^{2+}$ cation of complex (2) is shown in Fig. 3. The lozenge in (2) also has unequal Ag—S bond lengths [Ag—S1 2.6721 (7) and Ag—S1' 2.6443 (7) Å]

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