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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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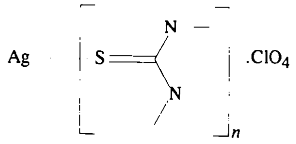
Abstract

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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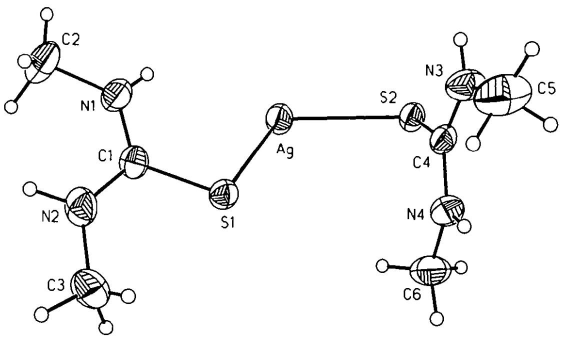

Fig. 1. A 30% displacement ellipsoid plot of the cationic unit in (1) with the atom-numbering scheme.

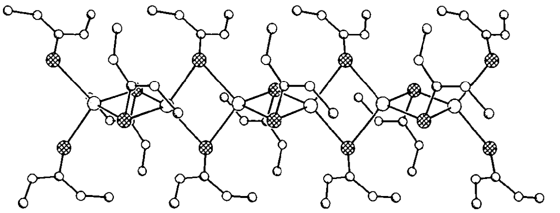

Fig. 2. The polynuclear chain structure of (1).

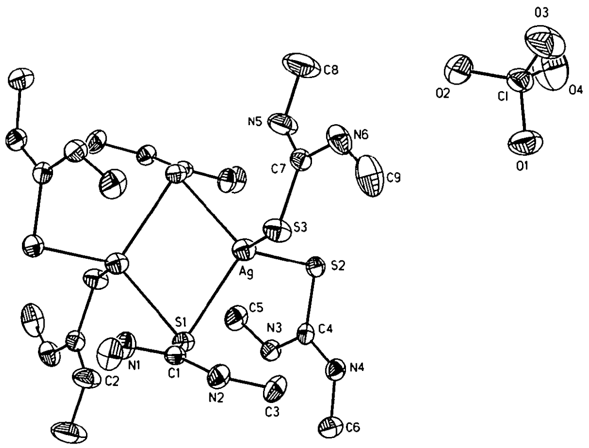

Fig. 3. A 30% displacement ellipsoid plot of (2) with the atomic numbering scheme for the atoms in one asymmetric unit.

and the Ag—S1—Ag′ angle is 76.89 (2)°. The other two non-bridging Ag—S distances, Ag—S2 [2.5663 (8) Å] and Ag—S3 [2.5287 (7) Å], are shorter than the bridging Ag—S bond lengths. As in complex (1), the dmtu ligands are planar in (2); the plane of the bridging dmtu ligand being perpendicular to the Ag_2S_2 lozenge plane. The other two ligands make dihedral angles of 30.52 (5) and 38.19 (6)° with the lozenge plane.

The dmtu ligands in complexes (1) and (2) have the same conformation and bond lengths and angles are normal. Except for C7═S3 in (2) [1.699 (3) Å], all C═S distances in the two structures have nearly the same magnitude and are comparable to the reported mean C═S distance of 1.725 Å for metal–thiourea complexes (Orpen, Brammer, Allen, Kennard, Watson & Taylor, 1989). The perchlorate anion is disordered in (1) but not in (2). A number of hydrogen bonds involving the perchlorate anion and the Ag(dmtu) cations are observed in both structures (Table 5). In complex (2), the $[Ag_2(dmtu)_6]^{2+}$ cations are interconnected by N—H···S hydrogen bonds between the N4 and S2 atoms around the inversion centres.

Experimental

N,*N*′-Dimethylthiourea (2.5 mmol) was dissolved in ethanol and $AgClO_4$ (1.0 mmol) was added with continuous stirring over a period of about 2 h. The solution was filtered and allowed to cool. Slow evaporation of the filtrate at room temperature yielded crystals which under the microscope could be separated into two layers. These were found to correspond to the 1:2 and 1:3 Ag–dmtu complexes.

Compound (1)

Crystal data

$[Ag(C_3H_8N_2S)_2]ClO_4$
$M_r = 415.67$
Triclinic
$P\bar{1}$
$a = 6.397\ (1)$ Å
$b = 10.405\ (1)$ Å
$c = 12.347\ (1)$ Å
$\alpha = 69.78\ (1)°$
$\beta = 85.58\ (1)°$
$\gamma = 78.77\ (1)°$
$V = 756.4\ (2)$ Å^3
$Z = 2$
$D_x = 1.825$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 39 reflections
$\theta = 8–25°$
$\mu = 1.795$ mm^{-1}
$T = 293\ (2)$ K
Thick plate
0.64 × 0.38 × 0.18 mm
Colourless

Data collection

Siemens *P*4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
5227 measured reflections
4205 independent reflections
3459 observed reflections [$I > 2\sigma(I)$]
$R_{int} = 0.0187$

$\theta_{max} = 30.00°$
$h = -1 \rightarrow 8$
$k = -12 \rightarrow 12$
$l = -16 \rightarrow 16$
3 standard reflections monitored every 97 reflections
intensity decay: <3%

Refinement

Refinement on F^2
$R(F) = 0.0384$
$wR(F^2) = 0.1148$
$S = 1.044$
4205 reflections
254 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0769P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.70$ e Å^{-3}
$\Delta\rho_{min} = -0.95$ 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 (Å²) for (1)*

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

	x	*y*	*z*	U_{eq}
Ag	0.24689 (4)	0.50686 (2)	0.50742 (2)	0.05838 (11)
S1	0.43212 (12)	0.70236 (7)	0.50594 (6)	0.0508 (2)
N1	0.3746 (6)	0.6081 (3)	0.7328 (2)	0.0641 (7)
N2	0.6237 (5)	0.7477 (3)	0.6695 (3)	0.0667 (7)
C1	0.4813 (5)	0.6840 (3)	0.6471 (2)	0.0509 (6)
C2	0.4031 (11)	0.5848 (6)	0.8549 (3)	0.0895 (13)
C3	0.7619 (9)	0.8272 (6)	0.5855 (5)	0.0848 (12)
S2	0.02087 (11)	0.56668 (7)	0.32464 (5)	0.0501 (2)
N3	−0.2084 (5)	0.8179 (3)	0.2892 (3)	0.0719 (8)
N4	0.1175 (5)	0.8144 (3)	0.2026 (3)	0.0629 (7)
C4	−0.0261 (5)	0.7471 (3)	0.2673 (2)	0.0493 (5)
C5	−0.2724 (12)	0.9680 (5)	0.2423 (6)	0.113 (2)
C6	0.3169 (7)	0.7504 (6)	0.1656 (5)	0.0934 (14)
Cl	−0.16682 (15)	0.79304 (9)	−0.06276 (7)	0.0681 (2)
O1*A*†	−0.122 (3)	0.9042 (9)	−0.0401 (7)	0.145 (5)
O2*A*†	−0.069 (2)	0.6757 (8)	0.0222 (7)	0.125 (3)
O3*A*†	−0.3667 (15)	0.7786 (19)	−0.0865 (11)	0.145 (4)
O4*A*†	−0.121 (4)	0.834 (3)	−0.1758 (9)	0.228 (11)
O1*B*†	−0.096 (3)	0.715 (3)	−0.1363 (19)	0.229 (12)
O2*B*†	−0.315 (4)	0.887 (2)	−0.063 (4)	0.43 (3)
O3*B*†	0.017 (2)	0.813 (3)	−0.0557 (19)	0.261 (12)
O4*B*†	−0.262 (5)	0.728 (3)	0.028 (2)	0.307 (15)

† Occupancy of 0.5.

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

Ag—S1	2.5401 (8)	N1—C2	1.462 (5)
Ag—S2^{i}	2.5856 (8)	N2—C1	1.321 (4)
Ag—S2	2.5985 (7)	N2—C3	1.446 (6)
Ag—S1^{ii}	2.7272 (9)	S2—C4	1.735 (3)
Ag—Ag^{ii}	3.2073 (7)	N3—C4	1.315 (4)
Ag—Ag^{i}	3.2116 (7)	N3—C5	1.451 (5)
S1—C1	1.734 (3)	N4—C4	1.313 (4)
N1—C1	1.315 (4)	N4—C6	1.438 (5)
S1—Ag—S2^{i}	115.47 (2)	C1—S1—Ag	108.80 (10)
S1—Ag—S2	113.48 (2)	C1—S1—Ag^{ii}	95.65 (10)
S2^{i}—Ag—S2	103.44 (2)	Ag—S1—Ag^{ii}	74.93 (2)
S1—Ag—S1^{ii}	105.07 (2)	C4—S2—Ag^{i}	108.08 (10)
S2^{i}—Ag—S1^{ii}	114.64 (2)	C4—S2—Ag	104.79 (9)
S2—Ag—S1^{ii}	104.43 (2)	Ag^{i}—S2—Ag	76.56 (2)

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

Compound (2)

Crystal data

$[Ag(C_3H_8N_2S)_3]ClO_4$
$M_r = 519.84$
Triclinic
$P\overline{1}$
$a = 9.887$ (1) Å
$b = 10.096$ (1) Å
$c = 10.687$ (1) Å
$\alpha = 90.96$ (1)°
$\beta = 105.68$ (1)°
$\gamma = 95.15$ (1)°
$V = 1022.0$ (2) Å³
$Z = 2$
$D_x = 1.689$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 39 reflections
$\theta = 8$–25°
$\mu = 1.448$ mm^{-1}
$T = 293$ (2) K
Rectangular slab
0.54 × 0.48 × 0.44 mm
Colourless

Data collection

Siemens *P*4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
5486 measured reflections
4675 independent reflections
4219 observed reflections [$I > 2\sigma(I)$]
$R_{int} = 0.0170$

$\theta_{max} = 27.49°$
$h = -1 \rightarrow 12$
$k = -13 \rightarrow 13$
$l = -13 \rightarrow 13$
3 standard reflections monitored every 97 reflections
intensity decay: <3%

Refinement

Refinement on F^2
$R(F) = 0.0318$
$wR(F^2) = 0.0861$
$S = 1.080$
4675 reflections
314 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0419P)^2 + 0.5561P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.72$ e Å^{-3}
$\Delta\rho_{min} = -0.77$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0479 (17)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (2)*

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

	x	*y*	*z*	U_{eq}
Ag	0.46926 (2)	0.84828 (2)	0.54823 (2)	0.05079 (10)
S1	0.44087 (7)	0.92984 (6)	0.30671 (6)	0.04185 (15)
N1	0.1917 (3)	1.0264 (2)	0.2396 (3)	0.0514 (5)
N2	0.1836 (3)	0.8001 (2)	0.2269 (2)	0.0463 (5)
C1	0.2584 (3)	0.9176 (2)	0.2543 (2)	0.0389 (5)
C2	0.0395 (4)	1.0291 (4)	0.2001 (4)	0.0655 (8)
C3	0.2405 (4)	0.6722 (3)	0.2382 (4)	0.0584 (7)
S2	0.65186 (7)	0.67750 (6)	0.58405 (6)	0.0448 (2)
N3	0.7419 (3)	0.7384 (2)	0.3749 (3)	0.0501 (5)
N4	0.5808 (3)	0.5571 (2)	0.3512 (2)	0.0473 (5)
C4	0.6582 (3)	0.6576 (2)	0.4248 (2)	0.0400 (5)
C5	0.8251 (5)	0.8573 (4)	0.4402 (5)	0.0686 (9)
C6	0.5738 (4)	0.5299 (4)	0.2160 (3)	0.0581 (7)
S3	0.22652 (7)	0.76191 (8)	0.56388 (7)	0.0532 (2)
N5	0.3371 (4)	0.8245 (4)	0.8138 (3)	0.0756 (9)
N6	0.1413 (3)	0.6748 (3)	0.7639 (3)	0.0630 (7)
C7	0.2362 (3)	0.7529 (3)	0.7246 (3)	0.0464 (6)
C8	0.3590 (11)	0.8196 (11)	0.9532 (5)	0.118 (2)
C9	0.0328 (5)	0.5846 (5)	0.6817 (6)	0.0877 (14)
Cl	0.18118 (9)	0.32315 (8)	0.98868 (7)	0.0595 (2)
O1	0.1402 (3)	0.2751 (3)	0.8558 (3)	0.0909 (9)
O2	0.2245 (4)	0.4613 (3)	0.9906 (3)	0.0976 (10)
O3	0.0607 (4)	0.2981 (4)	1.0363 (3)	0.1102 (12)
O4	0.2924 (4)	0.2597 (5)	1.0663 (5)	0.138 (2)

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

Ag—S1	2.6721 (7)	Ag—S3	2.5287 (7)
Ag—S1^{i}	2.6443 (7)	Ag—Ag^{i}	3.3057 (5)
Ag—S2	2.5663 (8)	S1—C1	1.731 (3)
S3—Ag—S2	115.74 (3)	S1^{i}—Ag—S1	103.11 (2)
S3—Ag—S1^{i}	110.05 (3)	C1—S1—Ag^{i}	108.61 (8)
S2—Ag—S1^{i}	113.52 (2)	C1—S1—Ag	98.46 (8)
S3—Ag—S1	107.41 (2)	C4—S2—Ag	98.11 (8)
S2—Ag—S1	105.94 (2)	C7—S3—Ag	107.05 (10)

Symmetry codes: (i) $1-x, 2-y, 1-z$.

Table 5. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
Compound (1)				
N3—H3*N*···S1^{i}	0.84 (4)	2.62 (4)	3.43 (1)	162 (3)
N2—H2*N*···O1*B*^{ii}	0.94 (5)	2.17 (6)	2.99 (3)	144 (4)
N2—H2*N*···O3*A*^{iii}	0.94 (5)	2.28 (6)	3.14 (2)	153 (4)
N2—H2*N*···O4*A*^{iii}	0.94 (5)	2.39 (7)	3.06 (3)	128 (4)
N4—H4*N*···O1*A*^{iv}	0.74 (5)	2.22 (5)	2.93 (1)	161 (6)

C2—H2*A*···O3*A*^{iii}	0.92 (7)	2.35 (7)	3.01 (2)	129 (5)
C2—H2*B*···O4*B*^{v}	0.98 (7)	2.52 (8)	3.35 (3)	142 (5)
C3—H3*A*···O4*A*^{iii}	0.94 (9)	2.46 (9)	3.12 (2)	128 (6)
C5—H5*B*···O4*A*^{iv}	1.09 (7)	2.38 (7)	3.43 (3)	162 (4)
C5—H5*B*···O3*B*^{iv}	1.09 (7)	2.52 (6)	3.23 (2)	121 (4)
Compound (2)				
N1—H1*N*···S2^{vi}	0.81 (4)	2.77 (4)	3.505 (2)	152 (3)
N4—H4*N*···S2^{vii}	0.81 (3)	2.60 (3)	3.364 (3)	158 (3)
N1—H1*N*···O4^{viii}	0.81 (4)	2.77 (4)	3.269 (6)	122 (3)
N2—H2*N*···O3^{v}	0.80 (4)	2.69 (4)	3.245 (4)	129 (4)
N2—H2*N*···O1^{v}	0.80 (4)	2.34 (4)	3.101 (4)	159 (4)
N3—H3*N*···O1^{vii}	0.79 (4)	2.33 (4)	3.005 (5)	145 (3)
N6—H6*N*···O2	0.84 (4)	2.70 (4)	3.258 (4)	126 (3)
C2—H2*C*···O3^{viii}	1.00 (6)	2.62 (6)	3.277 (6)	124 (4)
C3—H3*A*···O2^{ix}	0.87 (5)	2.64 (6)	3.330 (5)	137 (4)
C6—H6*C*···O2^{vii}	0.98 (5)	2.57 (5)	3.349 (6)	137 (4)

Symmetry codes: (i) $x-1, y, z$; (ii) $1+x, y, 1+z$; (iii) $1+x, y, z$; (iv) $-x, 2-y, -z$; (v) $-x, 1-y, 1-z$; (vi) $1-x, 2-y, 1-z$; (vii) $1-x, 1-y, 1-z$; (viii) $x, 1+y, z-1$; (ix) $x, y, z-1$.

For both compounds, data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structures: *SHELXTL/PC* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *SHELXTL/PC*; software used to prepare material for publication: *SHELXL93*. Geometrical calculations: *PARST* (Nardelli, 1983).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1251). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(Acetonitrile)[*N,N*-bis(3-aminopropyl)-1,3-propanediamine-*N,N′,N″,N‴*]copper(II) Diperchlorate

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Abstract

The structure of the title compound, $[Cu(C_2H_3N)(C_9H_{24}N_4)](ClO_4)_2$, consists of (acetonitrile)[tris(3-amino-*n*-propyl)amine-*N,N′,N″,N‴*]copper(II) cations and perchlorate anions linked by an extensive network of weak N—H···O and C—H···O hydrogen bonds. The Cu^{II} atom has a coordination geometry intermediate between tetragonal pyramidal (with one of the three primary amine N atoms occupying the apical coordination site) and trigonal bipyramidal (with the tertiary amine and acetonitrile N atoms in the axial positions). Main dimensions include Cu—N(amine) 2.035 (8)–2.121 (8) Å and Cu—N(acetonitrile) 2.099 (7) Å.

Comment

During our investigation of the various factors which affect the coordination geometry of Cu^{2+} ions with tripodal tetraamines (Dittler-Klingemann & Hahn, 1996), we became particularly interested in the importance of protonated complexes. These compounds have recently been shown to be the route between mono- and binuclear complexes (Dittler-Klingemann *et al.*, 1996). The reaction of $Cu(OH)_2$ with tris(3-amino-*n*-propyl)amine (trpn) and NH_4PF_6 under basic conditions yields a trigonal bipyramidal complex, $[Cu(trpn)(NH_3)](PF_6)_2$ (Dittler-Klingemann & Hahn, 1996). However, the reaction of trpn with $Cu(NO_3)_2.3H_2O$ at neutral pH yields the binuclear square-pyramidal complex $[Cu_2(trpn)_2(NO_3)_2](NO_3)_2$ (Dittler-Klingemann *et al.*, 1996). Determination of the complex-formation constants in aqueous solution has shown that the predominant complex in the pH range 6 to 8 is $[Cu(Htrpn)(H_2O)_2]^{3+}$, in which one arm of the amine ligand is protonated and uncoordinated (Dittler-Klingemann *et al.*, 1996). Changing the solvent from protic polar water to aprotic acetonitrile for the crystallization of $[Cu(Htrpn)(H_2O)_2]^{3+}$ induces instead the crystallization of the title com-

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