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Metal Complexes of Polycyclic Tertiary Amines.
IV. Three Ag(I) Ions with Different Coordination Numbers in the Crystal Structure of Hexamethylenetetramine–Silver(I) Chloride (1/4)

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Crystals of $(CH_2)_6N_4 \cdot 4AgCl$ *are orthorhombic, space group* Pnam, *with* a = *8.594(1),* b = *9.567(1),* c = *16.403(2)* Å, *and* Z = *8. X-ray analysis based on 1824 observed data refined to* R_F = *0.041. All four nitrogen lone pairs of each organic cage molecule serve as ligand sites, giving rise to octahedral* $AgCl_5N$*, tetrahedral* $AgCl_3N$*, and tetragonal pyramidal* $AgCl_4N$ *coordination polyhedra, the first two occupying sites of crystallographic mirror symmetry; these structural units interconnect to form a three-dimensional network. The Ag–N and Ag–Cl bond distances lie in the ranges 2.349(4)–2.411(2) and 2.545(2)–3.191(1)* Å, *respectively.*

Introduction

Silver(I) complexes are predominantly two-coordinate with approximately collinear metal–ligand bonds. Less common, but still frequently found, are Ag(I) ions in trigonal [1–3] and tetrahedral coordination environments. On the other hand, higher coordination numbers such as five [4–6], six [7, 8], and eight [9] are comparatively rare, although it is well known that octahedral coordination occurs in silver(I) halides which adopt the rock-salt structure [10].

We have been exploring Group B metal complexes of hexamethylenetetramine (1,3,5,7-tetraazaadamantane, $(CH_2)_6N_4$) because the multiple donor sites and space-filling properties of the cage-type ligand play a unique role in generating different types of coordination polyhedra in three-dimensional network structures. For example, X-ray analysis of $2(CH_2)_6N_4 \cdot 3CdI_2 \cdot 4H_2O$ showed the presence of tetrahedral CdI_3N and octahedral $CdI_2O_2N_2$ kernels [11], whereas coordination octahedra of the types $CdCl_4N_2$, $CdCl_2O_2N_2$, and $CdCl_3O_2N$ were found in $(CH_2)_6N_4 \cdot 2CdCl_2 \cdot 5H_2O$ [12]. In the present study, the complex $(CH_2)_6N_4 \cdot 4AgCl$, first reported nearly nine decades ago [13], was subjected to crystal structure analysis in a deliberate search for new and unusual coordination geometries around the Ag(I) ions.

Experimental

Crystals of $(CH_2)_6N_4 \cdot 4AgCl$, m.p. 249–251 °C, were obtained from slow evaporation of stoichiometric amounts of the two components in aqueous ammonia. The compound is air-stable for days, but gradually turns yellowish with surface decomposition over a period of several weeks.

A spherically-ground single crystal of radius 0.17 mm was mounted on a goniometer head. Preliminary Weissenberg and precession photographs indicated orthorhombic symmetry and systematic absences consistent with space groups *Pna*2_1 (No. 33) and *Pnma* (No. 62). The crystal was transferred to a Nicolet R3m automated diffractometer, and determination of the orientation matrix and accurate unit-cell parameters were conducted according to established procedures [14].

Intensity data were collected at 22 °C using graphite-monochromatized Mo-Kα radiation ($\bar{\lambda}$ = 0.71069 Å), a scintillation counter, and a pulse-height analyser (details summarized in Table I). The crystal remained stable throughout the diffraction experiment, as three standard reflections monitored every 125 data measurements showed only random deviations (within ±1%) from their mean intensities. Absorption correction was applied using an empirical method based on a pseudo-ellipsoidal analysis of azimuthal (ψ) scans of selected strong reflections [15].

Statistical distributions of normalized structure factors strongly favored the centrosymmetric space group *Pnma*, which was subsequently confirmed in structure analysis. Phase determination by direct

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TABLE I. Data Collection and Processing Parameters.

Formula	$(CH_2)_6N_4 \cdot 4AgCl$
Molecular weight	713.48
Cell constants	$a = 8.594(1), b = 9.567(1), c = 16.403(2)$ Å, $V = 1348.6(3)$ Å^3
D_m (displacement of H_2O)	3.40 g cm^{-3}
D_c ($Z = 4$)	3.515 g cm^{-3}
Space group	*Pnma* (No. 62)
Absorption coefficient μ (Mo-Kα)	64.62 cm^{-1}
Estimated mean μr	1.10
Transmission factors	0.053–0.092
Scan type and speed	ω–2θ; 2.02–8.37 deg min^{-1}
Scan range	1° below $K\alpha_1$ to 1° above $K\alpha_2$
Background counting	stationary counts for ½ of scan time at each end of scan
Collection range	h, k, l; $2\theta_{max} = 60°$
Unique data measured	2072
Observed data with $I > 1.5\sigma(I)$	1824

methods yielded the positions of three independent Ag atoms, two of which lie on mirror planes. The ten remaining non-hydrogen atoms in the asymmetric unit were located in a subsequent difference map. After several cycles of anisotropic least-squares refinement, all methylene H atoms were geometrically generated (C–H bond fixed at 0.96 Å) and included in structure-factor calculations with assigned isotropic thermal parameters. The conventional R_F index for 1824 observed reflections $[|F_o| > 3\sigma(|F_o|)]$ converged to 0.041, and the 'goodness of fit' (defined as $[\Sigma w(F_o^2 - F_c^2)^2/(m - n)]^{1/2}$, where m = number of data and n = number of variables) for n = 95 was 2.42. The weighting function used was $w = [\sigma^2(|F_o|) + 0.0002|F_o|^2]^{-1}$, and an isotropic extinction parameter ϵ in the expression $F_{corr} = F_c(1 + \epsilon F_c^2/\sin 2\theta)^{-1/4}$ [16] refined to the value 2.50(18) × 10^{-6}. The final difference map contained residual extrema at 1.66 to 2.28 eÅ^{-3} in the neighborhood of the Ag atoms, presumably caused by series termination effects.

All computations were performed on a Data General Corporation Nova 3/12 minicomputer with the SHELXTL program package [17]. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated [18]. An attempt to refine the structure with scattering factors for Ag^+ and Cl^- ions produced no significant improvement.

The numbering scheme for the non-hydrogen atoms are shown in Fig. 1; their positional and thermal parameters are listed in Table II. Bond distances and angles are displayed in Table III. Table IV contains hydrogen coordinates and fixed isotropic thermal parameters.

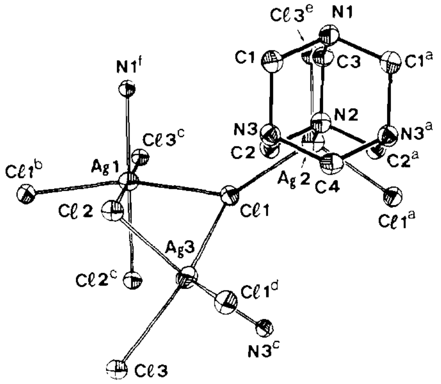

Fig. 1. Coordination geometries around the Ag(I) ions viewed approximately parallel to a and labelling of the atoms. The thermal ellipsoids are drawn at the 40% probability level, and metal-ligand interactions are indicated by open bonds. The symmetry codes are the same as those given in Table II.

Results and Discussion

In the present complex, all four nitrogen lone pairs of each $(CH_2)_6N_4$ cage system serve as donor sites. The three Ag(I) ions in different Wyckoff positions are bridged by chloride ions and organic ligand molecules to yield a three-dimensional polymeric network (Fig. 2). Clearly discernible are octahedral $Ag(1)Cl_5N$, tetrahedral $Ag(2)Cl_3N$, and tetragonal pyramidal $Ag(3)Cl_4N$ coordination polyhedra. The first two polyhedra occupy sites of crystallographic mirror symmetry, $Cl(1)^d$ being the apical ligand in the third (Fig. 1); all three kernels deviate considerably from regular geometry (Table II).

TABLE II. Fractional Coordinates (×10^5 for Ag and Cl; ×10^4 for N and C) and Anisotropic Temperature Factors (Å^2 × 10^4 for Ag and Cl; ×10^3 for N and C).[a]

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}[b]
Ag(1)	14803(10)	25000	36250(4)	615(5)	384(4)	341(3)		−144(3)		447(2)
Ag(2)	24631(8)	75000	41783(4)	306(3)	446(4)	383(3)		24(3)		378(2)
Ag(3)	33466(8)	42338(6)	20303(3)	810(5)	408(3)	388(3)	48(2)	−47(3)	268(3)	535(2)
Cl(1)	17109(17)	52840(15)	33894(8)	433(8)	317(7)	338(6)	−21(5)	22(5)	−28(6)	363(4)
Cl(2)	49284(15)	25000	29028(11)	388(10)	358(10)	296(8)		−33(8)		347(5)
Cl(3)	33372(26)	25000	6720(8)	435(11)	354(9)	288(8)		−19(8)		359(6)
N(1)	7572(8)	7500	4992(4)	30(3)	24(3)	23(3)		2(2)		26(2)
N(2)	5232(7)	7500	4148(4)	25(3)	29(3)	31(3)		−1(2)		28(2)
N(3)	7541(5)	6220(4)	3698(3)	25(2)	25(2)	27(2)	−2(2)	0(2)	2(2)	25(1)
C(1)	8112(6)	6233(6)	4556(3)	32(3)	26(2)	28(2)	−1(2)	−1(2)	3(2)	29(1)
C(2)	5822(6)	6255(5)	3714(3)	29(2)	25(2)	32(2)	−1(2)	1(2)	−6(2)	29(1)
C(3)	5852(9)	7500	4985(4)	36(4)	31(4)	21(3)		5(3)		29(2)
C(4)	8080(9)	7500	3283(4)	24(3)	31(4)	24(3)		3(3)		27(2)

[a] The exponent takes the form: $-2\pi^2 \Sigma_i \Sigma_j U_{ij} h_i h_j a_i^* \cdot a_j^*$. [b] U_{eq} calculated as one-third or the trace of the orthogonalized U_{ij} matrix.

TABLE III. Bond Distances (Å) and Bond Angles (deg.).

(i) Octahedral coordination about Ag(1)			
Ag(1)–Cl(1)	2.699(1)	Ag(1)–Cl(2)	3.191(1)
Ag(1)–Cl(2)^{c}	2.839(1)	Ag(1)–Cl(3)^{c}	2.937(2)
Ag(1)–N(1)^{f}	2.411(2)		
Cl(1)–Ag(1)–Cl(2)	83.0(1)	Cl(1)–Ag(1)–Cl(2)^{c}	84.7(1)
Cl(1)–Ag(1)–Cl(3)^{c}	97.1(1)	Cl(1)–Ag(1)–N(1)^{f}	96.3(2)
Cl(2)–Ag(1)–Cl(2)^{c}	96.2(1)	Cl(2)–Ag(1)–N(1)^{f}	92.0(2)
Cl(3)–Ag(1)–N(1)^{f}	86.6(2)		
(ii) Tetrahedral coordination about Ag(2)			
Ag(2)–Cl(1)	2.567(1)	Ag(2)–Cl(3)^{e}	2.545(2)
Ag(2)–N(1)	2.380(6)		
Cl(1)–Ag(2)–Cl(1)^{a}	111.4(1)	Cl(1)–Ag(2)–Cl(3)^{e}	114.7(1)
Cl(1)–Ag(2)–N(2)	104.0(2)	Cl(3)^{e}–Ag(2)–N(2)	106.9(2)
(III) Tetragonal pyramidal coordination about Ag(3)			
Ag(3)–Cl(1)	2.821(2)	Ag(3)–Cl(1)^{d}	3.137(2)
Ag(3)–Cl(2)	2.578(2)	Ag(3)–Cl(3)	2.778(2)
Ag(3)–N(3)^{c}	2.349(4)		
Cl(2)–Ag(3)–Cl(1)	93.1(1)	N(3)^{c}–Ag(3)–Cl(1)	88.1(2)
Cl(2)–Ag(3)–Cl(1)^{d}	80.9(1)	N(3)^{c}–Ag(3)–Cl(1)^{d}	84.3(2)
Cl(2)–Ag(3)–Cl(3)	93.6(1)	N(3)^{c}–Ag(3)–Cl(3)	94.2(2)
Cl(1)–Ag(3)–Cl(1)^{d}	121.2(1)	Cl(1)–Ag(3)–Cl(3)	147.7(1)
Cl(3)–Ag(3)–Cl(1)^{d}	91.0(1)	N(3)^{c}–Ag(3)–Cl(2)	163.4(2)
(iv) Chlorine bridges between pairs of silver(I) atoms			
Ag(1)–Cl(1)–Ag(2)	139.6(1)	Ag(1)–Cl(1)–Ag(3)	78.4(1)
Ag(1)–Cl(1)–Ag(3)^{c}	69.4(1)	Ag(2)–Cl(1)–Ag(3)	124.6(1)
Ag(2)–Cl(1)–Ag(3)^{c}	127.4(1)	Ag(3)–Cl(1)–Ag(3)^{c}	99.9(1)
Ag(1)–Cl(2)–Ag(3)	73.5(1)	Ag(1)–Cl(2)–Ag(1)^{d}	139.8(1)
Ag(3)–Cl(2)–Ag(1)^{d}	76.0(1)	Ag(3)–Cl(2)–Ag(3)^{b}	80.1(1)
Ag(3)–Cl(3)–Ag(1)^{d}	71.5(1)	Ag(3)–Cl(3)–Ag(2)^{g}	140.6(1)
Ag(3)–Cl(3)–Ag(3)^{b}	73.3(1)	Ag(1)^{d}–Cl(3)–Ag(2)^{g}	128.8(1)

(continued overleaf)

TABLE III. *(continued)*

(v) Hexamethylenetetramine ligand			
N(1)–C(1)	1.482(6)	N(1)–C(3)	1.478(10)
N(2)–C(2)	1.478(6)	N(2)–C(3)	1.473(9)
N(3)–C(1)	1.490(6)	N(3)–C(2)	1.478(7)
N(3)–C(4)	1.476(6)		
C(1)–N(1)–C(1)[a]	109.8(6)	C(1)–N(1)–C(3)	108.0(4)
C(2)–N(2)–C(2)[a]	107.4(6)	C(2)–N(2)–C(3)	109.0(4)
C(1)–N(3)–C(2)	108.2(4)	C(1)–N(3)–C(4)	109.0(4)
C(2)–N(3)–C(4)	107.6(4)		
N(1)–C(1)–N(3)	111.0(4)	N(2)–C(2)–N(3)	111.7(4)
N(1)–C(3)–N(2)	111.6(6)	N(3)–C(4)–N(3)[a]	112.1(6)
C(1)–N(1)–Ag(1)[f]	110.4(4)	C(3)–N(1)–Ag(1)[f]	110.2(5)
C(2)–N(2)–Ag(2)	110.7(3)	C(3)–N(2)–Ag(2)	110.0(5)
C(1)–N(3)–Ag(3)[d]	113.0(3)	C(2)–N(3)–Ag(3)[d]	108.8(3)
C(4)–N(3)–Ag(3)[d]	110.1(3)		

Symmetry code: [a](x, 1½ – y, z); [b](x, ½ – y, z); [c](–½ + x, y, ½ – z); [d](½ + x, y, ½ – z); [e](½ – x, 1 – y, ½ + z); [f](1 – x, 1 – y, 1 – z); [g](½ – x, 1 – y, –½ + z).

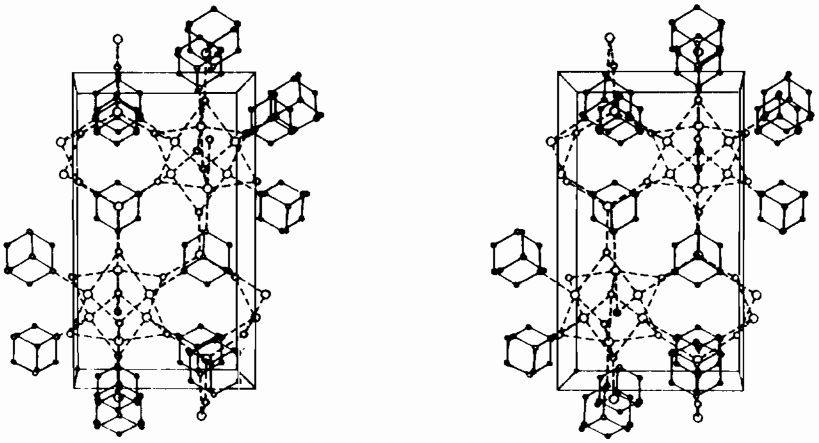

Fig. 2. Stereodrawing of the crystal structure of $(CH_2)_6N_4 \cdot 4AgCl$. The origin of the unit cell lies at the lower left corner, with *a* towards the reader, *b* from left to right, and *c* upwards. Metal–ligand interactions are indicated by dotted lines, and hydrogen atoms have been omitted for clarity.

TABLE IV. Hydrogen Coordinates ($\times 10^4$) and Assigned Isotropic Temperature Factors (Å^2 × 10^3).[a]

	x	*y*	*z*	*U*
H(1a)	7730	5419	4833	36
H(1b)	9229	6220	4553	36
H(2a)	5442	6270	3164	34
H(2b)	5447	5432	3985	34
H(3)	5484	8319	5263	38
H(4a)	7691	7500	2734	29
H(4b)	9197	7500	3274	29

[a] Form of isotropic temperature factor: $\exp(-8\pi^2 U \sin^2\theta/\lambda^2)$.

The observed Ag–Cl bond distances lie in the range 2.545(2)–3.191(1) Å, which brackets the interionic distance of 2.774 Å in crystalline AgCl [19] and the sums, 2.96 and 3.07 Å, of the crystal radii for coordination number six according to Shannon and Prewitt [20, 21] and Pauling [22], respectively. The Ag(3)···Cl(2)[c] separation of 3.375 Å was considered too long and hence excluded from our description of the ligand sites around Ag(3); if it had been included, the coordination about Ag(3) would be distorted octahedral (Fig. 1). There is a good correlation between coordination numbers and weighted mean Ag–Cl bond lengths in the series of Ag(I) coordination polyhedra.

The $(CH_2)_6N_4$ ligand, with a symmetry plane passing through atoms N(1), C(3), and C(4), fully utilizes its four nitrogen lone pairs in metal coordination. The Ag–N bonds [2,349(4)–2.411(2) Å] are in good agreement with those [2.335(6) and 2.406(5) Å] observed in crystalline $(CH_2)_6N_4 \cdot AgNO_3$ [6], in which Ag(I) is five-coordinate and the organic ligand links to only three Ag(I) ions. In the present $(CH_2)_6N_4 \cdot 4AgCl$ complex, the weighted mean dimensions of the $(CH_2)_4N_4$ moiety [C–N = 1.480(3) Å, C–N–C = 108.4(2)°, N–C–N = 111.5(2)°] are comparable to the corresponding values [C–N = 1.476(2), C–N–C = 107.2(1)°, N–C–N = 113.6(2)°] for crystalline hexamethylenetetramine [23]. The small but significant differences in the bond angles in neat and complexed $(CH_2)_6N_4$ are explicable in terms of a reduction in lone pair repulsion of cage bonds through metal coordination.

In conclusion, incorporation of the $(CH_2)_6N_4$ ligand into the simple rock-salt lattice of crystalline AgCl drastically changes the overall crystal structure along with the procreation of new coordination polyhedra. We are continuing our preparative and structural investigation of Group B metal complexes of polycyclic tertiary amines to look for the coexistence of variable coordination geometries involving metal ions of a single type in the same crystal lattice.

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