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Disorder in a Disilver Azacryptate Structure

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In the course of our current program of work on azacryptand chemistry,[1] we have become increasingly alert to the possibility of disorder in cryptate structures arising from alternative positions[2] for the cationic guests. We believe it is worth drawing this facet of azacryptate chemistry to the attention of readers, to avert potential misinterpretation of crystallographic data.

The disilver azacryptate $Ag_2L(ClO_4)_2$ (**1**), obtained[3] by [2 + 3] condensation of tris(aminopropyl)amine with terephthalaldehyde, is an interesting case in point. Because of the "soft" nature of the sp^2 N-donors, ligands of hexaamino type have proved[4] particularly valuable in stabilizing low oxidation states. Higher oxidation states, e.g. Cu(II) or Au(III), are seldom found encapsulated within imino as against amino[5] cryptates. That the product of Ag(I) template condensation of tris(aminopropyl)amine with terephthalaldehyde, as with other dicarbonyls,[2b] is a disilver(I) cryptate comes as no surprise.

The structure of **1** was solved by direct methods,[6-8] which revealed most of the structure shown in Figure 1a. This initial model was refined in several least squares cycles, the resulting difference map revealing a highly significant (ca. 20 e $Å^{-3}$) peak inside the cryptand and only 1.5 Å from Ag1. The short distance from this peak to the silver atom made it unlikely that the peak represents a donor atom and likely that it results from a disorder involving the silver atom. Closer inspection of the difference map revealed an alternative set of atom positions for much of the surrounding section of the cryptand ligand which resulted in coordination geometry for the alternative silver position (Ag1′) which is virtually indistinguishable from that about the (ordered) silver atom Ag2. The refinement was continued as described below using this disorder model; it converged with the major component having approximately 78% occupancy, 22% occupancy for the minor component and conventional $R = 0.048$ (2σ data). The resulting conformations are shown in parts a and b of Figure 1, respectively, and the relationship between the two arrangements is shown in Figure 2.

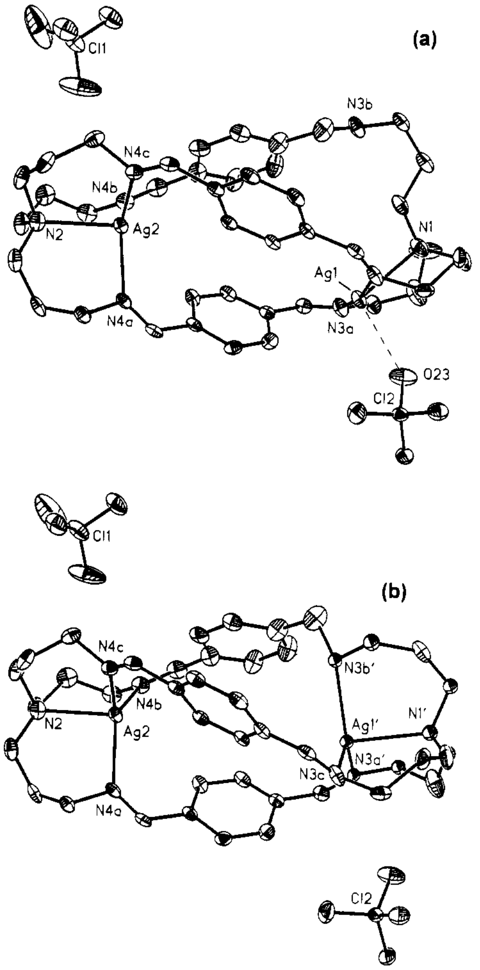

Figure 1. Perspective views (30% probability ellipsoids) of (a) the major and (b) the minor components of the disordered structure. Selected bond lengths (Å): Ag1−N1, 2.500(8); Ag1-N3a, 2.192(6); Ag1-N3c, 2.196(4); Ag1-O23, 2.68(1); Ag2-N2, 2.457(4); Ag2-N4a, 2.293(4); Ag2-N4b, 2.278(4); Ag2-N4c, 2.303(4); Ag1′-N1′, 2.47(3); Ag1′-N3a′, 2.21(2); Ag1′-N3b′, 2.41(2); Ag1′-N3c, 2.43(3) Ag1-Ag, 27.44(1); Ag1′-Ag2, 7.09(2).

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(1) (a) McDowell, D.; Nelson, J. *Tetrahedron Lett.* **1988**, 347. (b) Drew, M. G. B.; McDowell, D.; Nelson, J. *Polyhedron* **1988**, 2229. (c) McKee, V.; McDowell, D.; Nelson, J. *Polyhedron* **1989**, 1143. (d) McKee, V.; Robinson, W.; McDowell, D. *Tetrahedron Lett.* **1989**, 7453. (e) Drew, M. G. B.; Hunter, J.; Harding, C.; McCann, M.; McKee, V. *J. Chem. Soc., Dalton Trans.* **1992**, 11. (f) Dorrity, M.; Malone, J.; Marrs, D.; McKee, V.; Nelson, J. *J. Chem. Soc., Chem. Commun.* **1992**, 383. (g) Drew, M. G. B.; Hunter, J.; Harding, C.; Marrs, D.; Nelson, J. *J. Chem. Soc., Dalton Trans.* **1992**, 3235. (h) Martin, N.; McKee, V.; Nelson, J. *Inorg. Chim. Acta* **1994**, *218*, 5. (i) Harding, C.; Lu, Q.; McKee, V.; Nelson, J. *J. Chem. Soc., Chem. Commun.* **1993**, 1768. (j) Lu, Q.; McKee, V.; Nelson, J. *J. Chem. Soc., Chem. Commun.* **1993**, 1768.

(2) (a) Drew, M. G. B.; Howarth, O. N.; Morgan, G.; Nelson, J. *J. Chem. Soc., Dalton Trans.*, in press. (b) Morgan, G. Ph.D. Thesis, Open University, 1994.

(3) Morgan, G.; McKee, V.; Nelson, J. *Communication to ISMC XIX*; Enschede, The Netherlands, July 1993.

(4) (a) Hunter, J.; Nelson, J.; Harding, C.; McCann, M.; McKee, V. *J. Chem. Soc., Chem. Commun.* **1990**, 1198. (b) McCann, M.; Nelson, J.; Lu, Q. *Inorg. Biochem.* **1993**, *51*, 633. (c) Harding, C.; Nelson, J.; McKee, V. *J. Am. Chem. Soc.* **1991**, *113*, 9684.

(5) (a) Marrs, D.; McKee, V.; Nelson, J.; Harding, C.; Lu, Q. *Inorg. Chim. Acta* **1993**, *211*, 195. Lu, Q.; Latour, J.-M.; Harding, C.; Martin, N.; Marrs, D.; McKee, V.; Nelson, J. *J. Chem. Soc., Dalton Trans.* **1994**, 1471.

(6) Crystal data: $[Ag_2L](ClO_4)_2$, $C_{42}H_{54}Ag_2Cl_2N_8O_8$, yellow block, dimensions 0.62 × 0.60 × 0.36 mm, triclinic, $a = 9.4430(10)$ Å, $b = 15.517(3)$ Å, $c = 16.798(2)$ Å, $\alpha = 106.320(10)°$, $\beta = 101.970(10)°$, $\gamma = 103.640(10)°$, $V = 2194.5(5)$ $Å^3$, $\mu = 1.076$ mm^{-1}, space group $P\bar{1}$, $Z = 2$, $F(000) = 1108$. Data were collected at 123 K on a Siemens P4 four-circle diffractometer using a graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). Using 1.6° ω-scans at 6° min^{-1}, 7985 reflections were collected in the range $4 < 2\theta < 50°$; 7485 unique reflections ($R_{int} = 0.0129$) were used in the refinement. The structure was solved by direct methods.[7] Hydrogen atoms were inserted at calculated positions with a common, fixed isotropic temperature factor except on the minor component of the disorder. All the data were used for refinement of 592 parameters of F^2 which converged with $R_{w2} = 0.1047$, GOOF = 1.091 (and conventional $R_1 = 0.0477$ for $I > 2\sigma I$). All programs used in the structure refinement are contained in the SHELXL-93[8] package.

(7) Sheldrick, G. M.; SHELXS-86. *Acta Crystallogr.* **1990**, *A46*, 467.

(8) Sheldrick, G. M. SHELXL-93, University of Göttingen.

0020-1669/94/1333-4427$04.50/0

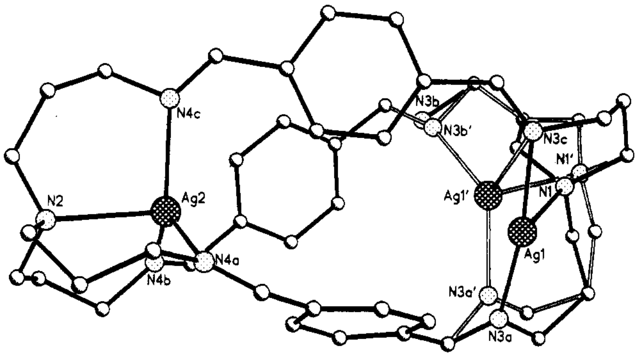

Figure 2. Composite view of the two conformations.

The fully ordered silver atom (Ag2) has approximately trigonal pyramidal coordination geometry. It is bonded to three imine nitrogen atoms in the trigonal plane (out of plane distance 0.20 Å toward the bridgehead amine); the apical bond (Ag2−N2 = 2.457(4) Å) is considerably longer than the other three (mean Ag2−N(imine) = 2.29 Å). The major occupancy site of the second silver atom (Ag1, Figure 1a) lies at the edge of the cryptand cavity and shows rather irregular geometry. Ag1 is coordinated to two imine nitrogen atoms (N3c and N3a), the bridgehead amine (N1), and, *via* a rather long interaction, to one oxygen atom of a perchlorate counterion. As observed for Ag2, the Ag1−N1 distance (2.500(8) Å) is significantly longer than the Ag1−N(imine) bonds (mean 2.194 Å). The difference in mean Ag−N(imine) bond lengths between Ag1 and Ag2 probably reflects ligand constraints about Ag2.

Ag1′ (Figure 1b) is the alternative (22% occupancy) position of the Ag1 atom. As shown in Figure 2, the conformation of the ligand is also disordered in the region around Ag1 and Ag1′. The largest difference is in the conformation about N3b; in the major component this donor is not coordinated and its lone pair is directed out of the cavity. In the minor component the corresponding imine (N3b′) is coordinated to Ag1′ and the lone pair is necessarily directed into the cavity. The positions of the other donor atoms and of some of the methylene carbon atoms (N1, C1a, C1b, C3a, C3b, N3a, and N3b) are also sufficiently different to give rise to separate peaks in the difference Fourier maps. The distances and angles about Ag1′ are less well defined than those at the other metal positions due to the difficulty of locating the minor components of the light atoms from difference maps; however, the strong similarity between the coordination environment at Ag1′ and at Ag2 suggests that the model is essentially correct.

The crystallographic results are supported by magnetic and spectroscopic data. As expected, magnetic susceptibility measurements confirm the diamagnetism of the complex (should confirmation be required), establishing the +1 oxidation state. (In a nonplanar environment, the +III oxidation state is, of course, associated with paramagnetism.) No ESR spectrum is observed, ruling out the +II oxidation state.

Table 1. Comparison of Interatomic Distances (Å) in **1** with Equivalent Distances from ref 12

1 at 123(2) K		ref 12 at 296 K	
Ag2−N2	2.457(4)	Ag1−N1	2.455(5)
Ag2−N4a	2.239(4)	Ag1−N2	2.301(5)
Ag2−N4b	2.278(4)	Ag1−N7	2.286(6)
Ag2−N4c	2.303(4)	Ag1−N6	2.308(5)
Ag1−N1	2.500(8)	Ag2−N4	not listed
Ag1−N3a	2.192(6)	Ag2−N3	2.181(6)
Ag1−N3c	2.196(4)	Ag2−N5	2.198(6)
Ag1−Ag2	7.439(8)	Ag1−Ag2	7.409
Ag1−Ag1′	1.528(4)	Ag2−O	1.586(4)

^{1}H NMR spectra are complex and fluxional in the methylene region at both 298 and 230 K, but the low field (7−9 ppm) part of the spectrum is well resolved. A singlet of relative intensity [4H][9] at 7.1 ppm corresponds to the aromatic CH signal while at 230 K an 8.6 Hz doublet[10] at 8.38 ppm represents the imino CH resonance. Our experience with disilver azacryptates leads us to expect splitting of coordinated imino CH resonances,[1e,5,11] at least at low temperatures, because of coupling to ^{109}Ag [$^{3}J\{^{109}\text{Ag}, {}^{1}\text{H}\} \approx 7-9$ Hz]. The simplicity of the spectrum of **1** suggests that the minor component **1a** of the solid state disorder dominates in solution. However, weak additional features are evident, particularly in the 298 K spectrum, which indicate that additional conformations are increasingly populated as temperature increases.

In summary, **1** exhibits no evidence to support the claim made recently in this journal[12] that the structure is "the first mixed-valence silver(I,III) cryptate" (see Table 1 for a comparison of the two structures). Rather, it seems that failure to interpret disorder in the structure has misled the authors into assigning the electron density corresponding to Ag1′ to a (nonexistent) light atom. The moral is clear: independent corroboration by analytical or spectroscopic techniques is essential before any such claim based on crystallographic data can be accepted.

***Caution*!** Perchlorate salts of silver salts with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with caution. **1** presented no hazard when used in small quantities.

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Supplementary Material Available: A table giving crystal data and details of the structure determination, a drawing depicting the numbering scheme, and tables of atom coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom positions (9 pages). Ordering information is given on any current masthead page.

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(9) Per cryptand strand.

(10) As observed in other disilver cryptates,[1e,9b] this splitting is not resolved in the 298K spectrum.

(11) (a) Marrs, D.; Martin, N.; McKee, V.; Drew, M. G. B.; Nelson, J. Contribution to *Chemistry of Copper and Zinc Triads*; Edinburgh, U.K., July 1992. (b) Marrs, D. Ph.D. Thesis, Open University, 1990.

(12) Shu-Yan, Y.; Qin-Hui, L.; Meng-Chan, S.; Xiao-Yun, H. *Inorg. Chem.* **1994**, *33*, 1251.