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The Crystal and Molecular Structure of Silver Perchlorate–Adiponitrile ($AgClO_4 \cdot 2NC(CH_2)_4CN$)

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The structure of $AgClO_4 \cdot 2NC(CH_2)_4CN$, silver perchlorate–adiponitrile, has been determined by an X-ray diffraction study. The crystals are tetragonal, with $a = 9.07$ Å, $c = 10.27$ Å, and space group $P\bar{4}2_1c$. d(obsd) is 1.65 g cm^{-3} and d(calcd) is 1.66 g cm^{-3} on the basis of two formula units per unit cell. The intensities of 327 independent reflections of which 194 were treated as observed were recorded with a diffractometer. The structure has been refined with a block-diagonal least-squares refinement to a conventional R of 4.6%. The structure is in the form of a two-dimensional polymer with the adiponitrile acting as a bridging ligand between the silver ions. Both Ag(I) and Cl^- are in special positions having $\bar{4}$ symmetry. The silver ion is tetrahedrally coordinated with four nitrile moieties per silver ion. The oxygen atoms of the perchlorate ion are oscillating freely. The chlorine–oxygen distance is 1.45 ± 0.04 Å. The silver–nitrogen distance is 2.28 ± 0.03 Å. The conformation of adiponitrile is GTG.

Introduction

In a previous paper[2] the structure of tin(IV) chloride–glutaronitrile was reported. The nature of the nitrile bonding was shown to be of the acetylene form; that is, tin, the nitrile moiety, and C_1 formed a linear chain: Sn–N–C–C–. This led to bridging between adjacent tins with the formation of a one-dimensional polymer. This result was interesting in that the well-characterized analogous diamines led to chelation rather than bridging.[3] Kubota and Johnston[4a] have studied and characterized complexes of copper(I) perchlorate with various dinitriles, and Kubota, Johnston, and Matsubara[4b] studied several complexes of succinonitrile with silver(I). Their findings indicated that other metal–dinitrile complexes similarly form polymers through possible bridging of the type found for tin(IV) chloride–glutaronitrile. This X-ray crystal structure investigation was undertaken in order to determine with certainty the polymeric nature of silver perchlorate–adiponitrile, the bonding of the nitrile moiety, and the coordination of the silver in the complex.

Experimental Section

$AgClO_4 \cdot 2NC(CH_2)_4CN$ was prepared by the method described in the previous paper for tin chloride–glutaronitrile.[2] This consists of a dropwise addition of a dilute solution of adiponitrile in benzene to a dilute solution of $AgClO_4$ in benzene. In very dilute solution crystallization proceeds slowly enough to yield small single crystals. The crystals decomposed in light after several months but showed no signs of breakdown during collection of the X-ray data. These crystals were stable in air. A single crystal nearly cylindrically shaped, 0.1 mm in diameter and 0.2 mm long, was selected for X-ray study. The lattice parameters of the tetragonal cell were determined with Mo Kα radiation (λ 0.7107 Å); $a = 9.07 \pm 0.03$ Å and $c = 10.27 \pm 0.04$ Å (24°). Each lattice parameter was calculated from 2θ measurements on eight reflections on the GE diffractometer, the uncertainty indicating standard deviations from these measurements. Space group $P\bar{4}2_1c$ was indicated by systematic extinctions shown on Weissenberg photographs: $l \neq 2n$ for hhl zone, and $h \neq 2n$ for $h00$. The density was measured on another crystal by flotation in a solution of carbon tetrachloride and bromoform and was 1.65 g cm^{-3}, compared with 1.66 g cm^{-3} calculated for two formula units per unit cell. The linear absorption coefficient for Mo Kα radiation, which was used in collection of intensity data, is $\mu = 17.6$ cm^{-1}. Absorption corrections were not made inasmuch as the crystal was small and of uniform cross section. The estimated error in intensity due to neglect of absorption effects is <2%. The total number of electrons is $F(000) = 308$. (Ag^+ and Cl^- are in special positions (a) and (b) requiring $\bar{4}$ symmetry.)

The intensity data were collected using a General Electric single-crystal orienter and spectrogoniometer equipped with a scintillation counter and pulse height analyzer for detector. The c axis was parallel to the ϕ axis of the single-crystal orienter. Independent reflections were collected by the θ–2θ scan technique (moving crystal–moving counter method), using equal background and scan counting times. Background count was determined by the stationary crystal–stationary counter method. The scan rate in 2θ was 2.0°/min, the takeoff angle was 4°, and counting time was 100 sec/scan and 50 sec for the background count on each side of the peak. Zirconium-filtered molybdenum radiation was used. A total of 327 possible reflections to $2\theta = 45°$ were scanned and 194 were significantly above the statistical fluctuations of the background count. The data were corrected for Lorentz and polarization effects using our SDS Sigma-7 computer.[5] For structure factor calculations, form factors used were from the literature,[6] including the anomalous terms of the form factors for Ag(I) and Cl. Extinction corrections were not made.

Structure Determination and Refinement

From a three-dimensional Patterson map, silver, chlorine, and nitrogen atomic positions were located. Partial structure factors calculated from these atomic positions provided phases for the first electron density map. Three more Fourier maps were calculated to find the rest of the structure.

(1) (a) Eastern Montana College; (b) Montana State University.

(2) D. M. Barnhart, C. N. Caughlan, and M. Ul-Haque, *Inorg. Chem.*, **7**, 1135 (1968).

(3) H. A. Goodwin in "Chelating Agents and Metal Chelates," F. P. Dwyer and D. P. Mellor, Ed., Academic Press, New York, N. Y., 1964.

(4) (a) M. Kubota and D. L. Johnston, *J. Inorg. Nucl. Chem.*, **29**, 769 (1967); (b) M. Kubota, D. L. Johnston, and I. Matsubara, *Inorg. Chem.*, **5**, 386 (1966).

(5) Data reduction NRC-2, three-dimensional Fourier NRC-8, and the block-diagonal least-squares NRC-10 programs were written by F. R. Ahmed and C. P. Saunderson of National Research Council, Ottawa, Ontario, Canada, and adapted for the SDS Sigma-7 computer. The rest of the programs are from the Montana State University Crystallographic Program Library written for the SDS Sigma-7 by C. N. Caughlan, E. L. Enwall, G. D. Smith, and K. D. Watenpaugh.

(6) "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, Table 3.31A.

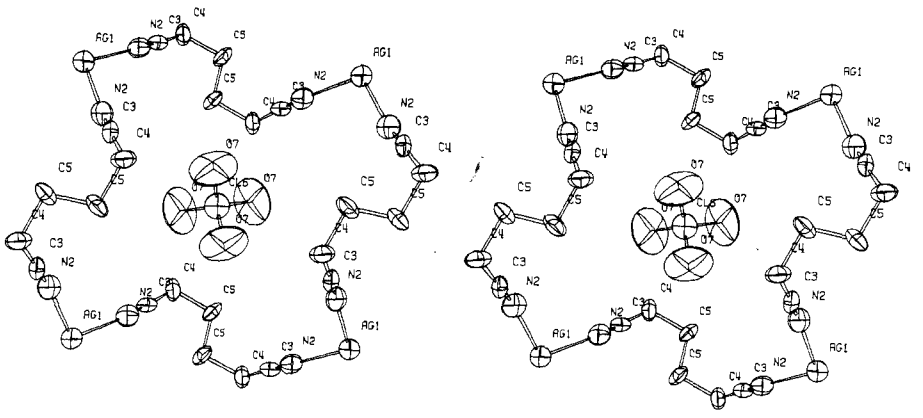


Figure 1.—Stereodiagram down the c axis of the structure of silver perchlorate–adiponitrile. This diagram was drawn using computer program ORTEP, written by Carroll K. Johnson of Oak Ridge National Laboratory and adapted for computation at the University of Washington.

These positions were used for the beginning refinement. Eight cycles of block-diagonal least-square refinement, refining atomic parameters and individual temperature factors, minimizing $\Sigma w(|F_o| - |F_c|)^2$, reduced the R ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$) to 6.8%; weighted $R = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ was 11.3%. Finally six cycles of refinement, refining atomic positions and individual anisotropic temperature factors, reduced the final R to 4.6% (weighted R = 7.2%). Each reflection was weighted using a weighting scheme suggested by Stout and Jensen[7] for the diffractometer data during the refinement. A table of $w(|F_o| - |F_c|)^2$ as a function of F_o and $(\sin\theta)/\lambda$ shows only small variations.

Results and Discussion

Final atomic positions with their standard deviations are listed in Table I, and the anisotropic temperature factors with their standard deviations are given in Table II. The mean-square displacements, calculated from the anisotropic thermal parameters, are given in Table III. Tables IV and V show the interatomic distances and bond angles with their standard deviations. The observed and calculated structure factors are listed in Table VI. Figure 1 is a stereoscopic diagram of the structure viewed along [001], picturing only one asymmetric unit.

The oxygen atoms of the perchlorate ion show considerable oscillation as indicated by the mean-square displacement but are not to be considered disordered. In the structure of *sym*-triphenylcyclopropenium perchlorate, Sundaralingam and Jensen[8] observed a high librational motion for the three oxygens of the perchlorate ion. Although they attempted to treat the oxygen atoms as disordered, finally refinement was based on single atoms with high-temperature factors. The chlorine–oxygen distance in silver perchlorate–adiponitrile of 1.45 ± 0.04 Å is quite normal for a perchlorate ion, although the standard deviation is quite high. The chlorine is tetrahedrally bonded to the oxygens. Out of the six angles of the tetrahedron four are 107 ± 1° and two are 114 ± 1°.

It can be seen from Figure 1 that the adiponitrile molecule acts as a bridging ligand between silver ions, forming a two-dimensional polymer in the (110) plane. The adiponitrile is in the GTG[9] conformation. The Ag^+ ion is tetrahedrally coordinated and there are four nitrile moieties per silver ion. Out of the six angles of a tetrahedron four are 108 ± 1° and two are 112.1 ± 1°. The Ag–N distance of 2.28 ± 0.03 Å can be compared with 2.213 ± 0.014 Å in a silver nitrate–pyrazine

TABLE I

ATOMIC POSITIONS AND THEIR STANDARD DEVIATIONS

	x	y	z
Ag(1)	0.0 (0)[a]	0.0 (0)	0.0 (0)
N(2)	0.1927 (20)	0.0793 (19)	0.1237 (14)
C(3)	0.2613 (21)	0.1140 (19)	0.2073 (15)
C(4)	0.3574 (22)	0.1666 (24)	0.3175 (20)
C(5)	0.5158 (38)	0.0857 (21)	0.3089 (19)
Cl(6)	0.0 (0)	0.0 (0)	0.5 (0)
O(7)	0.1325 (27)	0.0235 (66)	0.5769 (20)

[a] The number in parentheses is the standard deviation and refers to the least significant digits. Estimated standard deviations are calculated in Ahmed's block-diagonal program by $\sigma_i = [(a^{-1})_{ii}(\Sigma w\Delta^2)/(m - n)]^{1/2}$, where $(a^{-1})_{ii}$ is a diagonal element in the matrix inverse to a_{ij}, m is the number of reflections included in the least-squares refinement, n is the number of variable parameters in the structure, and Δ is $|F_o - F_c|$.

(7) G. H. Stout and L. H. Jensen, "X-Ray Structure Determination," The Macmillan Co., New York, N. Y., p 456. A constant of 0.01 was used to allow for instrumental instability; their equation is

$$\sigma_F = \frac{1}{2}\frac{k}{\sqrt{Lp}}\sqrt{\frac{N_T + N_{bg1} + N_{bg2} + (0.01N_{pk})^2}{N_T - N_{bg1} - N_{bg2}}}$$

where σ_F, k, $1/\sqrt{Lp}$, N_T, N_{bg1}, N_{bg2}, and N_{pk} are the standard deviation in F, scale, Lorentz-polarization factor, total counts, background counts on eigher side of the peak, and net peak count, respectively. Weights, w, were $1/\sigma_F^2$.

(8) M. Sundaralingam and L. H. Jensen, *J. Am. Chem. Soc.*, **88**, 198 (1966).

(9) This notation *gauche,trans,gauche* applies to rotational isomers of saturated hydrocarbons. One carbon atom is fixed in space and the directions of the four bonds around it are designated by a, b, c, or d. A unique representation of the carbon skeleton can, therefore, be obtained by denoting the directions of the C–C bonds in order, beginning from one end of the molecule. For a six-carbon-atom chain there are 12 isomers with three *gauche,trans,gauche* isomers designated as GTG′ (abcba), GTG observed here (abcbd), and G′TG′ (abcbc). *TTT* is ababa; GGG is abcda, etc.: S. Mizushima, "Structure of Molecules and Internal Rotation," Academic Press Inc., New York, N. Y., 1954, Part I, Chapter V.

TABLE II

THERMAL PARAMETERS AND THEIR STANDARD DEVIATIONS

Atom	$\beta(1,1)$[a]	$\beta(2,2)$	$\beta(3,3)$	$\beta(2,3)$	$\beta(1,3)$	$\beta(1,2)$
Ag(1)	0.0121 (4)[b]	0.0121 (4)	0.0085 (2)	0.0[c]	0.0[c]	0.0[c]
N(2)	0.0146 (26)	0.0126 (22)	0.0099 (18)	−0.0050 (39)	0.0008 (40)	0.0009 (40)
C(3)	0.0125 (28)	0.0060 (23)	0.0065 (16)	0.0002 (33)	0.0003 (37)	−0.0001 (45)
C(4)	0.0069 (26)	0.0153 (34)	0.0118 (19)	0.0026 (50)	−0.0008 (42)	−0.0019 (43)
C(5)	0.0106 (36)	0.0112 (21)	0.0146 (18)	−0.0041 (41)	0.0007 (71)	0.0108 (86)
Cl(6)	0.0174 (18)	0.0174 (18)	0.0087 (5)	0.0[c]	0.0[c]	0.0[c]
O(7)	0.0343 (43)	0.0616 (85)	0.0281 (26)	−0.0004 (140)	−0.0461 (62)	−0.0173 (158)

[a] The form of anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{23}kl + \beta_{13}hl + \beta_{12}hk)]$. [b] The number in parentheses is the standard deviation and refers to the least significant digits. [c] No standard deviations are given to parameters fixed by symmetry.

TABLE III

MEAN-SQUARE DISPLACEMENT, Å²

	Max	Med	Min
Ag(1)	0.0505	0.0505	0.0450
N(2)	0.0645	0.0612	0.0405
C(3)	0.0521	0.0347	0.0250
C(4)	0.0699	0.0573	0.0283
C(5)	0.0814	0.0658	0.0218
Cl(6)	0.0610	0.0610	0.0480
O(7)	0.2822	0.2333	0.0342

TABLE IV

INTERATOMIC DISTANCES AND THEIR STANDARD DEVIATIONS

Bond	Distance, Å	Bond	Distance, Å
Ag(1)–N(2)	2.28 (3)[a]	C(4)–C(5)	1.62 (5)
N(2)–C(3)	1.11 (4)	C(5)–C(5′)	1.58 (3)
C(3)–C(4)	1.51 (4)	Cl–O	1.45 (4)

[a] The number in parentheses is the standard deviation and refers to the least significant digits.

TABLE V

BOND ANGLES AND THEIR STANDARD DEVIATIONS

Atoms	Angles, deg	Atoms	Angles, deg
N(2)–Ag(1)–N(2′)	112.2 (6)[a]	C(3)–C(4)–C(5)	109.3 (15)
N(2)–Ag(1)–N(2″)	108.1 (4)	C(4)–C(5)–C(5′)	106.6 (16)
Ag(1)–N(2)–C(3)	162.7 (17)	O(7)–Cl(6)–O(7′)	114.2 (9)
N(2)–C(3)–C(4)	177.5 (21)	O(7)–Cl(6)–O(7″)	107.2 (7)

[a] The number in parentheses is the standard deviation and refers to the least significant digits.

The perchlorate ions are sandwiched between sheets of polymer, there appearing to be no coordination of oxygen to silver. The closest oxygen–silver distance is 4.5 Å.

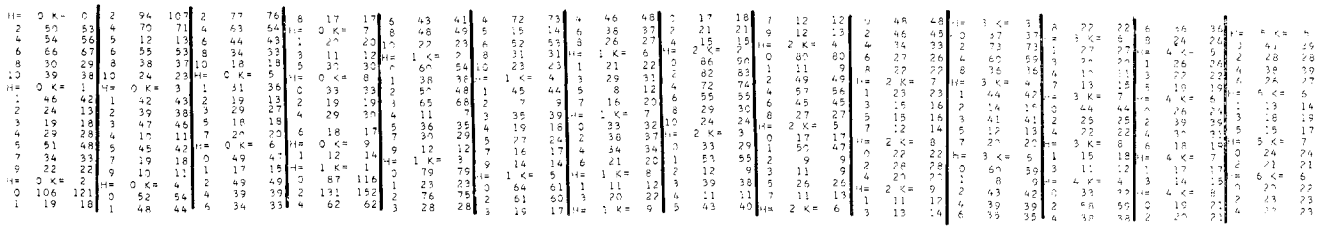
Kubota and Johnston[4a] have shown by ir spectra that complexes of copper(I) perchlorates with various dinitriles show tetrahedral coordination about copper(I), the dinitrile serving as a bridging ligand between two adjacent copper atoms. The bis(dinitrile) complexes are polymeric as suggested by their low solubilities in most organic solvents. The spectra of bis(dinitrile)-copper(I) complexes also indicated that the perchlorate ion is not bonded to copper.

Kubota, *et al.*,[4b] also studied the complexes of succinonitrile with silver(I). From their ir spectra, they demonstrated that both nitrogen atoms of succinonitrile are bound to the metal atoms, and the dinitriles thus serve as bridging ligands between two metal atoms. They also proposed that succinonitrile assumes the *trans* conformation in bis(succinonitrile)silver(I) perchlorate and bis(succinonitrile)silver(I) tetrafluoroborate.

In this work the conformation of the adiponitrile as GTG has been established, and it has been shown that this complex is, in fact, a two-dimensional polymer in the *ab* plane. The silver is tetrahedrally coordinated.

TABLE VI

OBSERVED AND CALCULATED STRUCTURE FACTORS[a]



[a] The columns reading from left to right contain the values of l, F_o, and F_c.

complex,[10] 2.115 ± 0.008 Å in AgNCO,[11] and 2.22 ± 0.05 Å in AgSCN chains.[12] The nitrogen–carbon distance of 1.11 ± 0.04 Å is a little but not significantly shorter than the one observed in the structure of tin(IV) chloride–glutaronitrile (1.16 ± 0.04 Å).

(10) R. G. Vronka and E. L. Amma, *Inorg. Chem.*, **5**, 1020 (1966).
(11) D. Britton and J. D. Dunitz, *Acta Cryst.*, **18**, 424 (1965).
(12) "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 260.

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