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The Crystal and Molecular Structure of Bis[nitratobis(pentamethylenetetrazole)silver(I)]

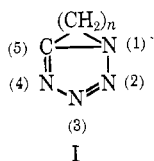
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Received September 13, 1971

The crystal and molecular structure of the dimer of nitratobis(pentamethylenetetrazole)silver(I), $[\text{Ag}(\text{C}_{12}\text{H}_{20}\text{N}_8)\text{NO}_3]_2$, has been determined from three-dimensional single-crystal X-ray diffraction data collected by automated diffractometer methods. The complex crystallizes in the triclinic system $P\bar{1}$ with cell dimensions $a = 9.531$ (5), $b = 9.605$ (5), $c = 11.129$ (5) Å; $\alpha = 107.43$ (4), $\beta = 101.45$ (4), and $\gamma = 108.98$ (4)°. The density calculated for $Z = 2$ is 1.707 g cm $^{-3}$ and the measured density is 1.71 (1) g cm $^{-3}$. The structure was refined by least-squares methods to a conventional R factor of 0.050 based on 1673 "observed" reflections. The coordination polyhedron about the silver atom is a distorted tetrahedron consisting of bonded nitrate and monodentate and bridging tetrazoles. The monodentate tetrazole is coordinated to the silver atom *via* the 4 nitrogen and the bridging tetrazoles are linked to the silver atoms *via* N(3) and N(4). The bond lengths around the silver atom are as follows: 2.238 (10) Å, Ag-N(4) (monodentate tetrazole); 2.216 (10) Å, Ag-N(4); 2.541 (10) Å, Ag-N(3) (bridging tetrazoles); 2.422 (10) Å, Ag-O (nitrate). Infrared and Raman spectral data are consistent with monodentate nitrate.

Introduction

Cyclopolymethylenetetrazoles (I) present an interesting series of compounds from both the pharmacological and the chemical points of view. As drugs, they are



characterized by their strong stimulating action on the central nervous system and, in sufficient dosages, act as convulsants. This activity is ultimately related to the size of the polymethylene ring and it increases monotonically with increasing size of the ring.¹ Chemically, they act as extremely weak Brønsted bases but are capable of forming fairly stable complexes with transition metal ions as well as with molecular Lewis acids. The chemistry of these complexes has been recently reviewed.²

Each of the four nitrogen atoms of the tetrazole ring, in principle, is capable of acting as a coordination site. In general, however, cyclopolymethylenetetrazoles, as well as other 1,5-disubstituted tetrazoles, act as monodentate ligands. Only in the case of transition metal halide complexes do the data seem to indicate that the tetrazole acts as a bridging ligand.³

Only two structures of tetrazole complexes have been determined. The first revealed that the tetrazole in iodopentamethylenetetrazolium monochloride acts as a monodentate ligand and that coordination occurs *via* the 4 nitrogen of the tetrazole ring.⁴ The second and more recent structure determination was that of dichlorobis(1-methyltetrazole)zinc(II). Again, the tetrazoles were monodentate and coordination occurred through the 4 nitrogen. The geometry around the zinc atom is that of a distorted tetrahedron.⁵ There does not seem to be any strong *a priori* reason why the 4

nitrogen should invariably be the coordination site. It seemed likely to us that the coordination site could well depend on the size of the transition metal ion as well as on the coordination number of the metal ion. We, therefore, decided to investigate the structure of $\text{AgNO}_3 \cdot 2\text{PMT}$ where PMT is pentamethylenetetrazole.

Experimental Section

The title compound was prepared as previously described.⁶ Single crystals were grown by slowly evaporating an aqueous solution of the complex. *Anal.* Calcd for $\text{C}_{12}\text{H}_{20}\text{AgN}_8\text{O}_3$: C, 32.29; H, 4.53; N, 28.25. Found: C, 31.95; H, 4.49; N, 28.27.

The infrared spectrum (2000–625 cm $^{-1}$) was obtained with a Perkin-Elmer Model 237B grating infrared spectrophotometer. A Nujol mull of the complex was pressed between NaCl windows and the spectrum was calibrated with polystyrene film. A laser Raman spectrophotometer constructed at this university⁷ was used to obtain the Raman spectrum (1600–600 cm $^{-1}$) of the solid complex contained in a standard nmr tube. The 5145-Å line of an argon laser was employed with the instrument operating at a resolution of 1 cm $^{-1}$.

Crystal Data and Data Collection.—The crystal system of $[\text{Ag}(\text{PMT})_2\text{NO}_3]_2$ is triclinic and the space group is $P\bar{1}$ with $a = 9.531$ (5), $b = 9.605$ (5), $c = 11.129$ (5) Å; $\alpha = 107.43$ (4), $\beta = 101.45$ (4), $\gamma = 108.98$ (4)°; formula weight 446.28; $V = 868.3$ Å 3 ; $\rho_{\text{obsd}} = 1.71$ (1) g cm $^{-3}$ (floatation in bromoform-benzene), and $\rho_{\text{calcd}} = 1.707$ (1) g cm $^{-3}$ for $Z = 2$. Unit cell parameters were obtained from a least-squares refinement⁸ of the orientational parameters of 10 reflections measured on a Picker four-circle automatic X-ray diffractometer by a Digital Equipment Corp. (DEC) 4K PDP-8 computer (FACS-I system) coupled to a DEC 32K disk file. Reflection intensities were measured with Cu K α (1.5418-Å) radiation under the control of a computer program using a "wandering" ω -step-scan procedure which also utilized balanced Ni-Co filters.⁹ In order to monitor the alignment and decay of the crystal, the intensities of a reflection located at $\chi = 90^\circ$ parallel to the goniometer arcs (for reorientational movement) and one in general space (for rotational movement) were measured every 100 reflections. Automatic realignment of the crystal was performed if the intensity of any one of the monitor intensities decreased by a preset value. Collection of intensity data at 40 kV and 25 mA on an initial crystal over a period of 23 hr showed a decay of 50% on one monitor

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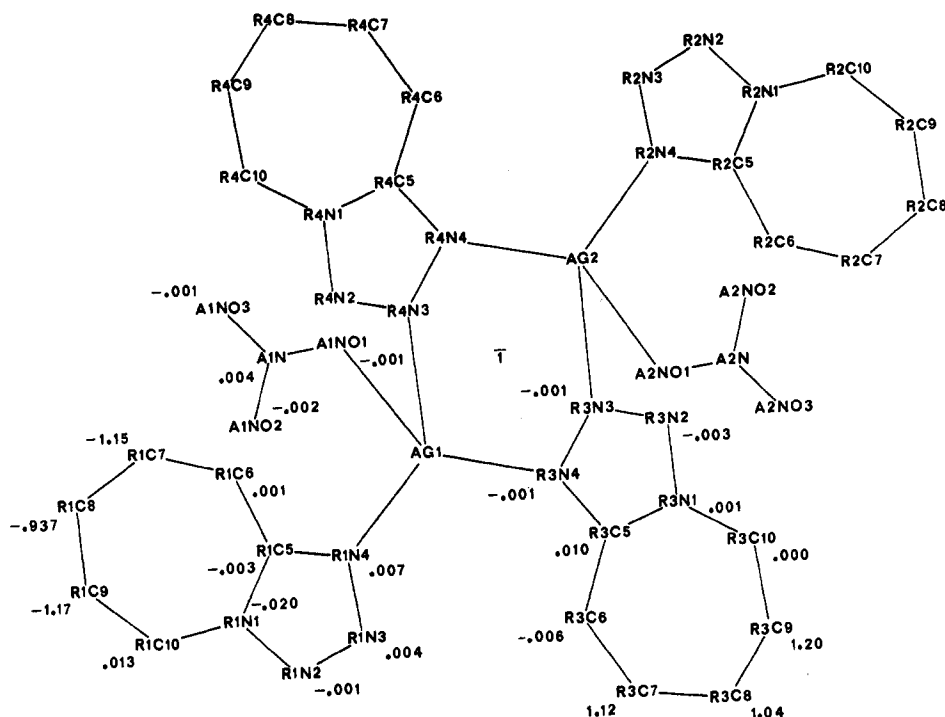


Figure 1.—Labeling scheme and deviations from best least-squares planes of the tetrazole rings and nitrate ion. The labeling scheme is as follows: $RXNY$ or $RXCY$ where X is the ring designation ($X = 1, 2$ for centrosymmetrical related monodentate PMT and 3, 4 for centrosymmetrical related bridging PMT) and Y is the number of the carbon on nitrogen in that particular ring; AXN where X is 1 or 2 followed by the atom designation is the nitrate ion.

reflection with extreme darkening of the crystal during which time numerous realignments were required. Thus the data collection was terminated. Another suitable crystal of approximate dimensions $0.37 \times 0.23 \times 0.20$ mm was mounted and exposed to X-rays at 40 kV and 10 mA. During the 29 hr required for data collection, automatic realignment was required three times due to a small rotation of the crystal about the ϕ axis of the diffractometer. The monitor reflections showed a decay in the intensities of approximately 15%. A total of 1782 unique reflections were measured to $(\sin \theta)/\lambda = 0.497$ ($d_{\min} = 1.01 \text{ \AA}$) of which 1673 (94%) were considered observable. Because of the general shape of the crystal and the large linear absorption coefficient of 98.3 cm^{-1} , the transmittance of X-rays was measured as a function of the azimuthal angle, ϕ , for several reflections before and after data collection. The raw intensities were corrected for absorption according to the method of Furnas¹⁰ and for decay as a function of time. These intensities were then converted to relative structure amplitudes with the inclusion of Lorentz and polarization factors.

The scattering factors of Cromer and Waber¹¹ were used for all nonhydrogen atoms. The hydrogen scattering factors were obtained from ref 12.

Structure Analysis

Delaunay reduction¹³ verified that the crystal was triclinic and thus the space group was either $P1$ or $P\bar{1}$. A three-dimensional Patterson map revealed the position of the heavy atom. The statistical distribution of intensities ($N(Z)$ test) indicated that the structure was noncentrosymmetric. However Sim¹⁴ has shown that the presence of a heavy atom in a centrosymmetric molecule can cause the $N(Z)$ test to suggest the wrong symmetry. Assuming a center of symmetry, a structure factor calculation with only an Ag atom and a scale

factor and average temperature factor (5.23 \AA^2) determined from a Wilson plot resulted in an R factor of 0.355, where $R = \Sigma|F_o - F_c|/\Sigma|F_o|$. The contribution of the Ag atom was subtracted from the observed structure factors, and the difference was then used for an $N(Z)$ distribution test. These $N(Z)$ points definitely showed that the lighter atoms were arranged in a centrosymmetrical distribution.

A three-dimensional Fourier map based only on the heavy-atom phases revealed all but five of the light atoms. The other nonhydrogen atoms were found by successive Fourier and structure factor calculations. Full-matrix, unit-weight, least-squares refinement on the structure factors (F 's) using individual isotropic thermal parameters (B 's) was begun at $R = 0.23$. Better atomic positions were obtained by applying the gaussian function to the observed Fourier peaks.¹⁵ Back-shift corrections were made using the gaussian positions from the electron density of the corresponding calculated structure. The new atomic positions were used in a structure factor calculation and after several cycles of refinement on coordinates and isotropic thermal parameters the R factor was reduced to 0.116. Although it was assumed that the tetrazole was coordinated to the Ag atom *via* the 4 nitrogen, it was decided to verify this assumption. The atoms in question were assigned carbon scattering factors and equal isotropic B 's. A least-squares refinement on these B 's resulted in a substantial decrease in the B originally assigned to the nitrogen atom (N(1)) and a slight increase in the B assigned to the carbon atom (C(5)). Thus, the initial assignments of N(1) and C(5) were correct.

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TABLE II
NONHYDROGEN ATOMIC PARAMETERS^a

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Peak Height ($e\text{\AA}^{-3}$)
AG1	-.0877	.0790	.1568	.0180	.0255	.0130	.0126	.0048	.0075	52.6
R1N4	-.3153	.0899	.1685	.0155	.0254	.0111	.0111	.0040	.0071	6.0
R1N3	-.4460	-.0377	.1534	.0174	.0225	.0147	.0073	.0046	.0081	5.7
R1N2	-.5539	.0110	.1732	.0178	.0238	.0133	.0074	.0048	.0076	6.0
R1N1	-.4941	.1686	.1989	.0130	.0230	.0108	.0081	.0041	.0057	7.2
R1C5	-.3479	.2164	.1971	.0140	.0248	.0077	.0101	.0023	.0056	5.2
R1C6	-.2369	.3821	.2223	.0144	.0191	.0150	.0065	.0050	.0069	5.2
R1C7	-.3110	.4572	.1346	.0198	.0249	.0167	.0119	.0076	.0103	4.6
R1C8	-.4406	.5023	.1761	.0204	.0236	.0174	.0113	.0070	.0090	4.5
R1C9	-.5955	.3561	.1377	.0194	.0291	.0163	.0137	.0052	.0105	4.5
R1C10	-.5864	.2646	.2307	.0167	.0268	.0185	.0121	.0088	.0101	5.1
R3N4	.0204	-.0952	.1404	.0168	.0214	.0112	.0101	.0046	.0054	5.8
R3N3	.0402	-.1757	.0265	.0180	.0238	.0116	.0116	.0039	.0062	5.6
R3N2	.0977	-.2764	.0408	.0171	.0237	.0093	.0086	.0035	.0047	5.8
R3N1	.1173	-.2613	.1700	.0140	.0190	.0110	.0070	.0030	.0054	6.4
R3C5	.0708	-.1510	.2280	.0112	.0196	.0136	.0068	.0031	.0063	5.1
R3C6	.0709	-.0999	.3714	.0218	.0314	.0077	.0138	.0066	.0075	3.0
R3C7	.2373	-.0399	.4702	.0234	.0315	.0107	.0140	.0034	.0059	5.0
R3C8	.2896	-.1770	.4700	.0234	.0337	.0112	.0149	.0039	.0096	4.6
R3C9	.3286	-.2545	.3464	.0174	.0271	.0118	.0105	.0031	.0074	5.1
R3C10	.1826	-.3610	.2223	.0198	.0235	.0145	.0121	.0026	.0090	4.7
A1N01	.1274	.3381	.2909	.0238	.0298	.0114	.0105	.0048	.0083	6.8
A1N02	.0816	.2720	.4463	.0484	.0371	.0194	.0040	.0146	.0129	4.6
A1N03	.2905	.4666	.4866	.0306	.0419	.0141	.0056	.0025	.0071	5.1
A1N	.1656	.3586	.4092	.0206	.0226	.0140	.0068	.0055	.0063	5.3
$\sigma \times 10^4$	9-15	10-16	7-12	14-27	16-28	9-17	12-21	10-16	11-17	

^a The anisotropic thermal parameters are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. The limits of the standard deviations are for the light atoms only. The silver atom standard deviation limits are $(7-9) \times 10^{-5}$ and $(10-17) \times 10^{-5}$ for the positional and anisotropic thermal parameters, respectively.

The individual thermal parameters of the previous cycle of refinement were then converted to anisotropic form (β_{ij} 's), and a cycle of refinement on the β_{ij} 's of the Ag atom reduced R to 0.077. Refinement of the remaining light atom anisotropic thermal parameters further decreased R to 0.061. All the hydrogen atom positions (20) were obtained from a difference Fourier map with their electron density ranging from 0.4 to 0.7 (1) $e/\text{\AA}^3$. Thermal parameters (isotropic) for the hydrogen atoms were assigned the same value as those carbon atoms to which they are attached. Inclusion and refinement of the hydrogen atom coordinates alone decreased R to 0.050. The refinement was continued excluding the hydrogen atoms until the parameter shifts were less than half their corresponding standard deviations. The final R factor including refined hydrogen positional parameters is 0.050. A final difference Fourier map was calculated and the largest peak was less than 0.3 $e/\text{\AA}^3$, excluding the region around the Ag atom.

Results

The observed and calculated structure factors are listed in Table I.¹⁶ The structure consists of discrete

(16) Table I, listing structure factor amplitudes, will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number INORG-72-1410. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche.

dimeric units with the two molecules held together by bridging tetrazoles (Figure 1). Two tetrazoles are monodentate and coordinated to the silver atoms through the 4 nitrogen atom while the bridging tetrazoles are bidentate to the silver atoms *via* N(3) and N(4). Table II lists the final atomic coordinates, anisotropic thermal parameters, and peak heights for the nonhydrogen atoms. The hydrogen atom coordinates are given in Table III. The limits of the standard deviations for the light atoms obtained from the least-squares calculations are given in the last row of Tables II and III.

The electron density of C(6) in ring 3 ($3.0 e/\text{\AA}^3$) is lower than those of the other carbon atoms. When this atom was deleted from a structure factor calculation, the difference Fourier map showed the same electron density. Likewise, when this atom was included in a structure factor calculation, the coordinates of the peak in the calculated Fourier map did not change. The limits of the standard deviations from least-squares refinement of its positional and anisotropic thermal parameters are similar to those of the other light nonhydrogen atoms. A final difference Fourier synthesis did not show any excess electron density in the region of R3C6. The electron densities of the hydrogen atoms attached to R3C6 are similar to those of the other hydrogen atoms. It should be noted that the absorption correction applied to the raw intensities is only

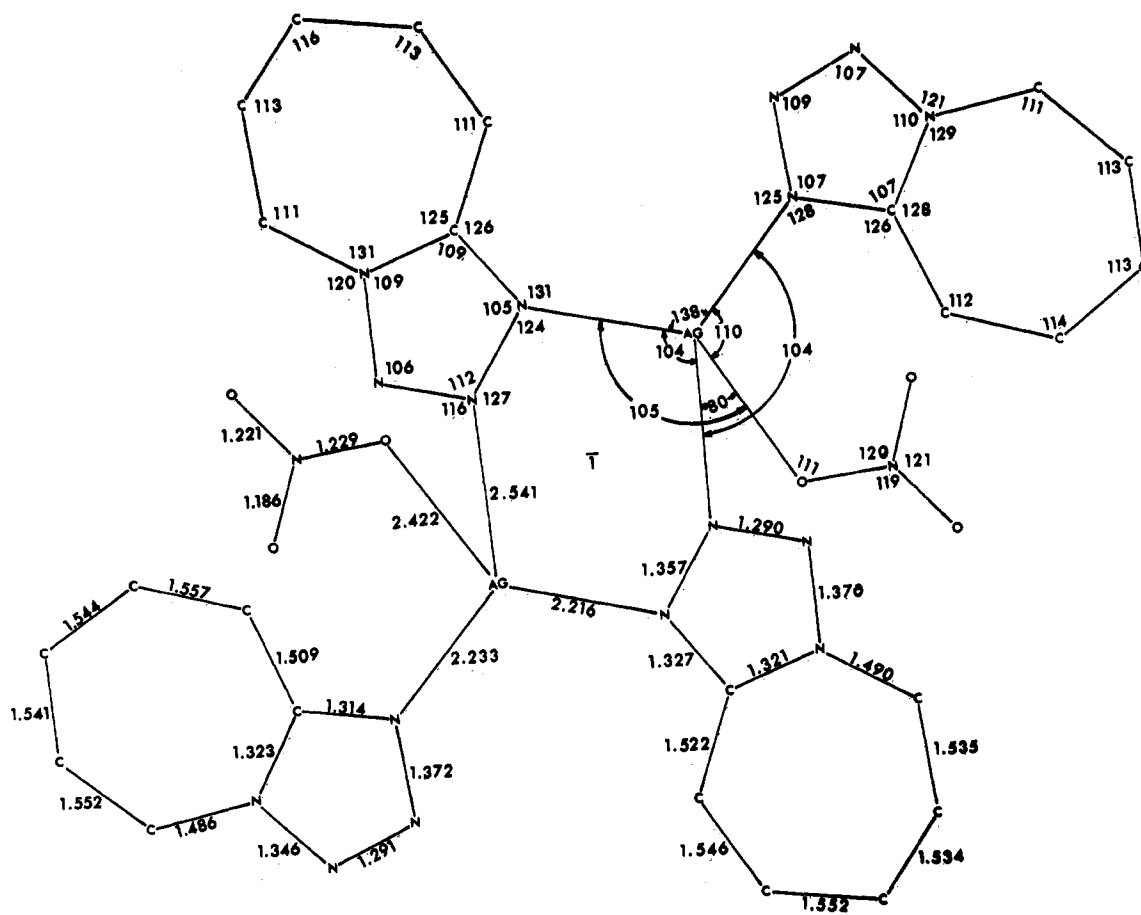


Figure 2.—Bond distances and angles. The limits of the estimated standard deviations for the bond lengths and angles are 0.01–0.02 Å and 0.4–1.0°, respectively.

TABLE III
HYDROGEN ATOM POSITIONAL PARAMETERS

	x	y	z
R1C6H1	-0.18	0.46	0.32
R1C6H2	-0.26	0.42	0.19
R1C7H1	-0.21	0.57	0.15
R1C7H2	-0.36	0.38	0.04
R1C8H1	-0.40	0.58	0.29
R1C8H2	-0.47	0.56	0.13
R1C9H1	-0.69	0.39	0.14
R1C9H2	-0.65	0.27	0.04
R1C10H1	-0.52	0.22	0.22
R1C10H2	-0.69	0.19	0.23
R3C6H1	-0.03	-0.22	0.37
R3C6H2	0.06	-0.10	0.32
R3C7H1	0.25	0.03	0.57
R3C7H2	0.32	0.05	0.47
R3C8H1	0.21	-0.27	0.46
R3C8H2	0.32	-0.22	0.38
R3C9H1	0.39	-0.34	0.36
R3C9H2	0.42	-0.16	0.33
R3C10H1	0.07	-0.46	0.24
R3C10H2	0.22	-0.42	0.15
σ	0.01	0.01	0.01

approximate and no anomalous dispersion correction to the silver atom was applied during refinement. In view of the above considerations, it is puzzling why only the electron density of R3C6 is low.

Interatomic distances and bond angles are shown in Figure 2. The two silver atoms are separated by a distance of 4.251 (2) Å. The estimated standard deviations of the bond lengths are 0.01 Å for the N– and O–Ag distances, 0.015 Å for the tetrazole and nitrate dis-

tances, and 0.02 Å for the C–C distances in the pentamethylene chain. The estimated standard deviations of the bond angles are 0.4° for angles involving the silver atom and 1° for all other angles. Closest intermolecular contacts (3.15–3.50 Å) generally involve the nitrate ions. A stereo ORTEP¹⁷ view of the dimeric unit is shown in Figure 3. The tetrazole rings and nitrate ion are planar with the seven-membered ring of PMT in a chair conformation. Deviations from the best least-squares planes (Table IV) for rings 1 and 3

TABLE IV
EQUATIONS OF BEST LEAST-SQUARES PLANES⁸ FOR TETRAZOLE RINGS AND THE NITRATE ION

Ring 1	$1.250 = 0.960X - 2.192Y + 10.425Z$
Ring 3	$-0.410 = 6.727X + 3.665Y - 1.419Z$
Nitrate	$2.012 = -7.483X + 7.806Y + 1.115Z$

and the nitrate ion are depicted in Figure 1. The silver atom is nonplanar with respect to the tetrazole and nitrate planes with deviations from rings 1 and 3 and nitrate ion being 0.128, -0.112, and -0.565 Å, respectively. The dihedral angles involving the planes of two tetrazole rings and the nitrate ion are 77° (ring 1–ring 3), 91° (ring 1–nitrate ion), and 97° (ring 3–nitrate ion), respectively.

Discussion

Perhaps the most striking feature about the structure

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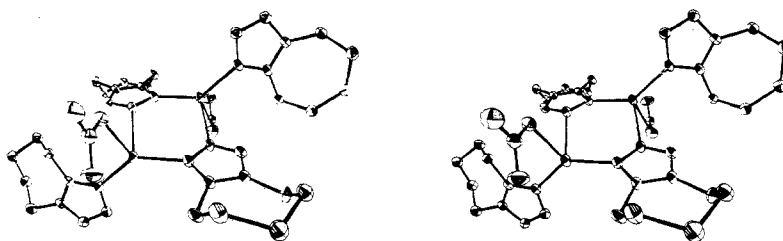


Figure 3.—ORTEP drawing of $[\text{Ag}(\text{PMT})_2\text{ONO}_2]_2$ where PMT is pentamethylenetetrazole. Hydrogen atoms are not shown.

is that in addition to having monodentate tetrazoles, bridging tetrazoles are also present. Including the bonded nitrate, the resulting geometry about the silver atom is a distorted tetrahedron. Although most Ag(I) complexes are linear, ligands which act in a bidentate fashion cannot form such structures and thus tend to yield polynuclear species.¹⁸ The two previous structure determinations of tetrazole complexes indicate that the tetrazole ring is monodentate and that the site of coordination is the 4 nitrogen.^{4,5} As mentioned previously, only in the case of transition metal halide complexes of PMT do the data indicate that the tetrazole acts as a bridging ligand.³ The present structure indicates that the preferred site of coordination in the tetrazole ring is at the 4 nitrogen since the Ag–N(4) distances are 0.3 Å shorter than the Ag–N(3) distance. It also indicates however that the 3 nitrogen of the tetrazole ring can be utilized in bond formation.

The Ag–N(4) distances of approximately 2.22 Å may be compared with the silver–nitrogen distance of 2.21 Å in the silver nitrate–pyrazine complex.¹⁹ The Ag–N(3) distance of 2.54 Å is somewhat longer. It should be noted that the silver atom has a large deviation (0.933 Å) from the best least-squares plane of the tetrazole ring containing coordinated N(3) and thus reduces substantially the overlap of the bonding orbitals leading to a weaker covalent bond. The Ag–O(1) distance of 2.42 Å compares well with other silver-bonded nitrate distances (2.3–2.9 Å).^{20,21} Additional evidence for coordinated nitrate in the present complex is found in the infrared and Raman spectra of the solid. Monodentate nitrate is of C_{2v} symmetry and exhibits six bands in the infrared and Raman spectra.²² The ir spectrum²³ shows bands at approximately 665 (m, sh), 830 (w), 1048 (m), 1303 (vs), and 1438 (s) cm^{-1} which do not appear in the spectrum of uncomplexed PMT. These bands can be assigned the NO_2 asymmetric bend, out-of-plane rock, N–O stretch, NO_2 symmetric stretch, and NO_2 asymmetric stretch, respectively, of monodentate nitrate. The Raman spectrum shows three of these bands at 669 (m), 1038 (s), and approximately

1430 (m) cm^{-1} . The PMT vibrations mask the remaining nitrate vibrations in both types of spectra.

The tetrazole ring distances and angles are in good agreement with those of other tetrazole structure determinations.²⁴ The C–C distances in the pentamethylene chain are close to the expected distance of 1.54 Å and the remaining C–C (C(6)–C(5)) and C–N (C(10)–N(1)) distances are in agreement with those previously found.⁴ The major differences between the monodentate and bidentate tetrazoles are in the angles of the tetrazole ring. Within the estimated standard deviation (1°) the N(2)–N(3)–N(4) angle in the bridging tetrazole is at least 3° larger than the corresponding angle in the monodentate tetrazole. This increase and other angle differences in the tetrazole rings may be ascribed to the difference in their coordination behavior.

Two of N–O distances in the nitrate ion (N–O(1) and N–O(3)) are very close to the accepted value of 1.22 Å.²⁵ Within the estimated standard error, there is no increase in the N–O(1) distance as a result of the bonded nitrate. Comparison of the O(2) thermal parameters suggests that the oxygen atom may be moving thus leading to a shorter N–O(2) distance. The O–N–O angles are very close to those expected for the trigonal-planar nitrate ion (120°).

The distorted tetrahedral geometry about the silver atom may be seen by observing the appropriate angles. Four of the six angles required to describe a tetrahedron are much closer to the accepted angle (109.5°) than are the remaining two angles (138 and 80°).

Conclusion

As in previous studies, the present structure indicates that the preferential site of coordination in the tetrazole ring seems to be the 4 nitrogen. However, as suggested previously, the tetrazole can function as a bridging ligand by using additional sites for coordination. There is no evidence to date which suggests any other type of bonding than a σ donation from the nitrogen atom(s) in the tetrazole ring to the acceptor moiety.

Acknowledgments.—Support of this work by Research Grant NS 69061 from the National Institutes of Health is gratefully acknowledged. In addition, we wish to thank Mr. R. L. Vandlen for his advice and help throughout the course of most of this work. Helpful discussions with Dr. A. Tulinsky are also appreciated.

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(23) Abbreviations: v, very; s, strong; m, medium; w, weak; sh, shoulder.