

Crystal Structure of Bis(9-methylhypoxanthine)silver(I) Perchlorate Monohydrate, a Model Complex for the Silver-Poly(I) System

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Abstract: Crystals of the title compound belong to space group $P\bar{1}$ with the following cell parameters: $a = 9.271(3) \text{ \AA}$, $b = 10.187(7) \text{ \AA}$, $c = 19.124(7) \text{ \AA}$, $\alpha = 91.17(4)^\circ$, $\beta = 94.08(3)^\circ$, and $\gamma = 93.78(4)^\circ$. The structure consists of uncoordinated ClO_4^- ions and planar $[(9\text{-methylhypoxanthine})_2\text{Ag}]^+$ cations in which silver is linearly bound to two ligand N(7) atoms. The ligands are syn with respect to N(7)-Ag-N(7). Carbonyl oxygen atoms O(6) are not bound to silver, but they are cross-linked via hydrogen bonding by a water molecule. Such cations associate into dimers by hydrogen-bond formation between the water molecule and a H(1) proton belonging to the other $[(9\text{-methylhypoxanthine})_2\text{Ag}]^+$ cation in the asymmetric unit. The present structure provides a reasonable structural model for the 2:1 poly(I)-Ag complex observed by Shin and Eichhorn at low pH and it suggests assumptions for the structure of the 4:4 complex reported for the same system at higher pH.

Silver reacts with DNA without loss of the helical structure.¹ This behavior is connected with the preference of silver for linear two coordination and its affinity for nitrogen donors on the bases. Propensity to cross-link strands and stabilize multiple helices also extends to synthetic polynucleotides. Interesting results have recently been reported on the polyriboinosinic acid (poly(I)) system by Shin and Eichhorn.² The great affinity of Ag(I) for hypoxanthine residues of poly(I) reported earlier³ was confirmed by this more recent work and two types of complexes were identified. At pH 4, reaction takes place with two residues without exchange of protons, forming a double helix formulated as poly(Ag-I₂). On the other hand, at pH 8, silver reacts according to a 1:1 ratio and displaces one H⁺ ion. On the basis of X-ray fiber diagrams, formation of a four-stranded helix poly(Ag₄-I₄) was proposed.

The 1:2 complex with 9-methylhypoxanthine described in the present paper was prepared under slightly acidic conditions. A crystallographic study was undertaken because the compound was stoichiometrically, and presumably structurally, related to poly(Ag-I₂). This structure also suggests possible arrangements of silver atoms and hypoxanthine moieties in the poly(Ag₄-I₄) complex observed at higher pH.

Experimental Section

Preparation. 9-Methylhypoxanthine (0.10 g) was dissolved in water (25 mL) and 7.0 mL of 0.090 M AgClO_4 in 0.66 M HClO_4 was added. The pH was raised to 4.0 with 1 M NaOH (~1 mL). The cloudy mixture was gently heated and the resulting clear solution was allowed to cool slowly to room temperature. After a few hours, crystals separated from the viscous solution. They were isolated and dried in air. Anal. Calcd: Ag, 20.52; Cl, 6.75; C, 27.42; H, 2.68; N, 21.32. Found: Ag, 20.48; Cl, 6.77; C, 26.85; H, 2.68; N, 20.76.

Crystal Data. $(\text{C}_6\text{H}_6\text{N}_4\text{O})_2\text{AgClO}_4 \cdot \text{H}_2\text{O}$, mol wt 525.61, triclinic, space group $P\bar{1}$, $a = 9.271(3) \text{ \AA}$, $b = 10.187(7) \text{ \AA}$, $c = 19.124(7) \text{ \AA}$, $\alpha = 91.17(4)^\circ$, $\beta = 94.08(3)^\circ$, $\gamma = 93.78(4)^\circ$, $V = 1797.2 \text{ \AA}^3$, $Z = 4$ formula units per cell, $d_c = 1.942 \text{ g cm}^{-3}$, $\mu = 13.0 \text{ cm}^{-1}$, $\lambda = 0.71069 \text{ \AA}$ (graphite monochromator), $t = 22^\circ \text{C}$.

Crystallographic Measurements and Structure Resolution. The crystals were elongated plates of a rather poor quality. Attempts to improve crystal growth by changing concentrations, pH, or cooling rate were unsuccessful. One of the best specimens was selected for space-group determination and used to collect a set of intensity data with which the structure was solved. The final R factor (0.068) was considered to be too high and a second set of data was collected with a new crystal. This set refined slightly better and it is used in this paper. The second crystal had the following dimensions between the indicated pairs of faces: 0.03 (001 and 00 $\bar{1}$), 0.35 (110 and $\bar{1}\bar{1}0$), and 0.20 mm (100 and $\bar{1}00$).

The triclinic Laue symmetry observed on precession photographs was consistent with space groups $P1$ and $P\bar{1}$. Accurate cell parameters

were derived from least-squares refinement of the setting angles for 25 reflections centered in the counter aperture of an Enraf-Nonius CAD-4 diffractometer. Intensity data were collected using the $\omega/2\theta$ scan technique. A fixed slit 4.0 mm wide was used and the scan range (ω) was $(0.75 + 0.35 \tan \theta)^\circ$ extended 25% on either side for background. A scan time of 120 s was imposed, which corresponds to scan speeds of $\sim 0.50^\circ \text{ min}^{-1}$. Prescans at $6.7^\circ \text{ min}^{-1}$, with background counts, were done and all reflections having $I/\sigma(I) < 1$ were labeled "weak" and not remeasured. Three standard reflections were used as a check on instrument and crystal stability. They showed random fluctuations within $\pm 4\%$ about their respective means. Crystal orientation was checked every 100 reflections by recentering three axial reflections. No significant motion of the crystal was detected during data collection.

A total of 4678 independent reflections (hkl , $\bar{h}kl$, $h\bar{k}l$, and $\bar{h}\bar{k}l$, $2\theta \leq 45^\circ$) were measured using Enraf-Nonius option FLAT, a procedure to measure intensity at the ψ position where absorption is minimum. Net intensities, I , and their esd's, $\sigma(I)$, were calculated as described previously.⁴ A set of 2985 reflections with $I \geq 2\sigma(I)$ was retained for the structure determination. An absorption correction was applied (Gaussian integration, grid $10 \times 10 \times 10$); the transmission factors were in the range 0.78–0.96. Finally, the data were corrected for L_p .

The structure was solved by the heavy-atom method and refined by full-matrix least squares initially and by block-diagonal least squares in the latest stages. In group $P\bar{1}$, the asymmetric unit contains two nonequivalent silver atoms, which were located from a Patterson synthesis. The positions of the remaining nonhydrogen atoms were determined from subsequent Fourier maps. Refinement of positional and isotropic thermal parameters of all nonhydrogen atoms using unit weights converged to $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.142$. Hydrogen atoms on N(1), C(2), and C(8) of each ring were then fixed at their calculated positions with isotropic B 's of 6.0 \AA^2 . Those of the methyl groups and water molecules were not located. Anisotropic refinement on all nonhydrogen atoms reduced R to 0.071. At this point, a Fourier map clearly showed that ClO_4^- ion no. 2 is disordered: the abnormally high temperature factor of O(8) suggested partial site occupancy, whereas a spurious peak, O(8'), remained at a suitable distance from Cl(2) to correspond to a bonded oxygen atom. Also, dissymmetric electron density contours suggested the presence of overlapping components for the rest of this ion. Although refinement of a $P1$ structure in group $P\bar{1}$ could lead to apparent disorder, the absence of similar effects elsewhere in the cell ruled out such an explanation. Hence, attempts were made to describe the electron density around Cl(2) in terms of two overlapping ClO_4^- ions in group $P\bar{1}$. Occupancy factors were first refined for O(8) and O(8'), the only resolved components. The refined values normalized to unity (0.60 and 0.40, respectively) were then assumed to hold for their respective ions. Various sets of positions for the tetrahedra were tried, using O(8) and O(8') as pivots, but no real improvement resulted in the R factor. Since a large amount of computer time had already been spent just to improve this structural detail of limited interest, anisotropic refinement was terminated using individual positions for O(8) and O(8') only. In the

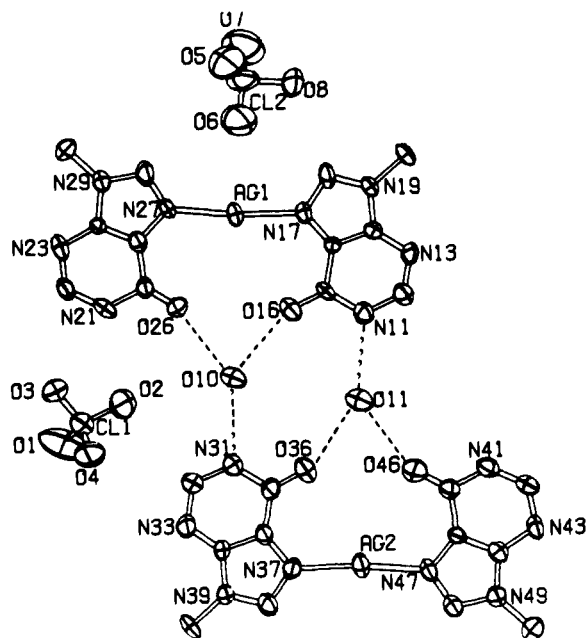


Figure 1. The asymmetric unit of $[(9\text{-methylhypoxanthine})_2\text{Ag}]\text{ClO}_4 \cdot \text{H}_2\text{O}$. The first and second digits in symbols for ring atoms correspond to ring number and atom number in the ring, respectively. O(11) and O(10) are water molecules. Dashed lines represent H bonds. Ellipsoids correspond to 50% probability. Hydrogen atoms at N(1), C(12), and C(18) are not represented.

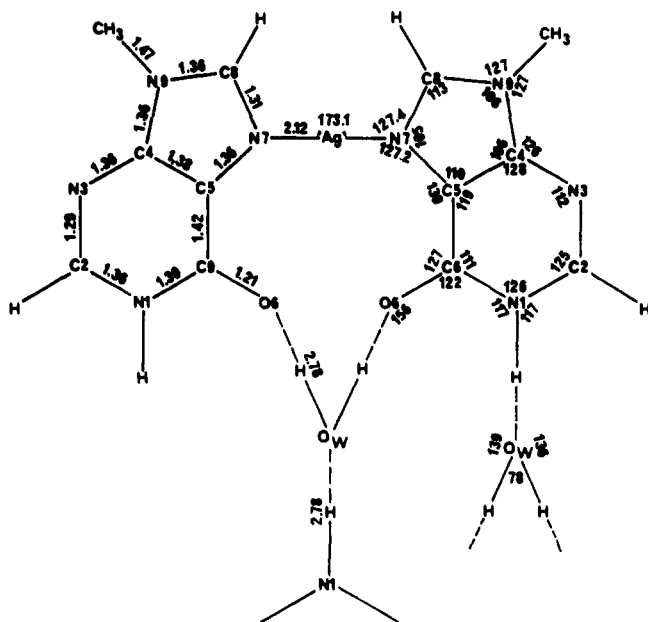


Figure 2. Interatomic distances and bond angles. For ligand molecules, values averaged over the four independent ligands are given. The remaining values have been averaged over the two nearly centrosymmetric halves of the asymmetric unit. Standard deviation on bond lengths are 0.01–0.02 Å except for Ag–N, 0.01 Å, and on bond angles 1° except for the angles at Ag, 0.4°.

final stage of the refinement, individual weights based on counting statistics were used. The final R factor was 0.062, while $R_w = \sum [w(|F_o| - |F_c|)^2] / \sum w|F_o|^2$ was 0.080. The refined coordinates are listed in Table I. Anisotropic temperature factors and hydrogen coordinates are part of the supplementary material.

The form factors used were those of Cromer and Waber,⁵ except for hydrogen.⁶ Anomalous scattering terms f' and f'' were used for Ag and Cl.⁷

Description of the Structure

Besides two ClO_4^- ions, the asymmetric unit includes two

Table I. Refined Coordinates of Bis(9-methylhypoxanthine)-silver(I) Perchlorate Monohydrate ($\times 10^3$, Ag, Cl $\times 10^4$)

atom	x	y	z
Ag(1)	4323(1)	3256(1)	551(1)
Ag(2)	5454(1)	1881(1)	-5350(1)
N(11)	677(1)	95(1)	-134(1)
N(21)	120(1)	651(1)	-61(1)
N(31)	350(1)	457(1)	-346(1)
N(41)	882(1)	-108(1)	-412(1)
C(12)	765(1)	-1(1)	-114(1)
C(22)	34(1)	720(1)	-20(1)
C(32)	257(1)	552(1)	-366(1)
C(42)	949(1)	-194(1)	-451(1)
N(13)	795(1)	-35(1)	-52(1)
N(23)	27(1)	704(1)	47(1)
N(33)	217(1)	575(1)	-430(1)
N(43)	938(1)	-201(1)	-518(1)
C(14)	719(1)	31(1)	-5(1)
C(24)	115(1)	613(1)	71(1)
C(34)	272(1)	495(1)	-477(1)
C(44)	846(1)	-115(1)	-547(1)
C(15)	628(1)	129(1)	-19(1)
C(25)	208(1)	544(1)	36(1)
C(35)	366(1)	395(1)	-463(1)
C(45)	771(1)	-26(1)	-512(1)
C(16)	598(1)	167(1)	-90(1)
C(26)	215(1)	559(1)	-39(1)
C(36)	412(1)	373(1)	-392(1)
C(46)	789(1)	-18(1)	-438(1)
O(16)	518(1)	250(1)	-111(1)
O(26)	291(1)	507(1)	-77(1)
O(36)	493(1)	292(1)	-371(1)
O(46)	737(1)	62(1)	-401(1)
N(17)	576(1)	174(1)	41(1)
N(27)	280(1)	462(1)	81(1)
N(37)	399(1)	338(1)	-523(1)
N(47)	689(1)	42(1)	-559(1)
C(18)	637(1)	104(1)	92(1)
C(28)	234(1)	486(1)	142(1)
C(38)	325(1)	398(1)	-571(1)
C(48)	716(1)	-3(1)	-620(1)
N(19)	726(1)	18(1)	66(1)
N(29)	132(1)	577(1)	140(1)
N(39)	251(1)	495(1)	-547(1)
N(49)	812(1)	-99(1)	-616(1)
C(19)	808(2)	-78(2)	108(1)
C(29)	50(2)	624(1)	199(1)
C(39)	164(2)	585(1)	-589(1)
C(49)	869(2)	-167(1)	-676(1)
Cl(1)	313(4)	7579(4)	-2404(2)
Cl(2)	4410(5)	2037(5)	2628(2)
O(1)	56(2)	879(2)	-271(1)
O(2)	163(1)	698(2)	-218(1)
O(3)	-39(1)	776(1)	-180(1)
O(4)	-42(2)	675(1)	-290(1)
O(5)	306(1)	138(2)	283(1)
O(6)	431(2)	241(2)	201(1)
O(7)	515(2)	236(2)	322(1)
O(8)	525(2)	80(2)	245(1)
O(8')	404(4)	363(3)	271(1)
O(10)	364(1)	398(1)	-205(1)
O(11)	673(1)	173(1)	-273(1)

nonequivalent AgL_2^+ complex cations (where L = 9-methylhypoxanthine) and a pair of water molecules O(10) and O(11) (Figure 1). Interatomic distances and bond angles are schematically represented in Figure 2.

Both silver atoms are similarly bonded to two imidazolic N(7) atoms, the metal showing the usual linear two coordination. Departure from linearity is significant (N–Ag–N = 173.1 (4)°), but within a range commonly found for silver. The Ag–N bonds (2.13 (1) Å) are somewhat longer than observed in the 1-methylthymine complex (2.081 Å),⁸ but shorter than those of compounds with 1-methylcytosine (2.225 Å),⁹

methyladenine (2.16 Å),¹⁰ and adeninium cation (2.194 and 2.154 Å).¹¹ The shortest distance to a carbonyl oxygen is 3.37 Å, which is well beyond the 3.0-Å limit considered by many authors for bonding interactions.¹¹

Interestingly, the ligands in each AgL_2^+ cation are coplanar and a water molecule forming moderately strong H bonds to carbonyl groups ($\text{O}\cdots\text{O} = 2.78 \text{ \AA}$) helps to keep the six-membered rings syn with respect to N–Ag–N. In turn, that water molecule is tightly attached to the adjacent AgL_2^+ cation via a strong $\text{N}(1)\text{--H}(1)\cdots\text{O}$ hydrogen bond ($\text{N}\cdots\text{O} = 2.78 \text{ \AA}$). Two such water molecules acting as identical three-way links hold two AgL_2^+ ions in a nearly planar centrosymmetric unit. The maximum tilt of any individual ligand with respect to the average plane of the “diaquo dimer” is only 10° .

The four nonequivalent ligands have the same geometry within experimental errors.¹² Bond lengths and angles agree well with those of similar molecules.^{13,14} The $\text{C}(2)\text{--N}(1)\text{--C}(6)$ angles average 126° , which confirms the presence of a hydrogen atom on N(1), that angle being normally smaller when N(1) is not protonated.¹⁵ The purine rings are planar within 1.5σ (0.015 Å) and the atom-to-plane distances for the exocyclic groups are significant but not unusual: O(46), 0.11 Å; methyl groups, 0.04–0.08 Å; Ag, 0.04–0.12 Å; $\sigma = 0.01 \text{ \AA}$.

Perchlorate ion 1 shows a normal geometry:¹² the Cl–O distances range from 1.37 (2) to 1.44 (2) Å (av 1.39 Å) and the O–Cl–O angles from $105 (1)$ to $115 (1)^\circ$ (av 109°). The spread in bond lengths and angles for ion 2 is due to incomplete resolution of the disordered components (*vide supra*).

The packing pattern (Figure 3) shows the parallel stacking of “diaquo dimers”. Columns of ClO_4^- ions occupy channels parallel to the *a* axis and they interact only moderately with the rest of the structure. Ions 2 act as bridging units between Ag(1) of one dimer and Ag(2) of the next dimer along *c*. One of the contacts ($\text{Ag}(1)\cdots\text{O}(6) = 2.94 (1) \text{ \AA}$) is just within the 3.0-Å limit, while the other ($\text{Ag}(2)\cdots\text{O}(7) = 2.78 (2) \text{ \AA}$) is shorter, but still much longer than found in the adeninium complex (2.64 Å).¹¹ Ion 1 forms weak H bonds with the two N(1)–H(1) groups not already bonded to water: $\text{N}(41)\cdots\text{O}(1) = 3.06 \text{ \AA}$; $\text{N}(21)\cdots\text{O}(2) = 3.10 \text{ \AA}$; $\text{N}(21)\cdots\text{O}(3) = 2.98 \text{ \AA}$; $\sigma = 0.01 \text{ \AA}$.

Discussion

Silver binding to N(7) is not surprising. Metal ions usually bind to that site in N(9)-blocked hypoxanthine or guanine rings.^{14,16} In many of those structures, other ligands in the coordination sphere were found to form intramolecular H bonds to the adjacent carbonyl oxygen O(6). However, no such ligands are available with linearly coordinated silver, with the consequence that the basic character of O(6) must be satisfied differently. This is achieved by water molecules forming H bonds and “cross-linking” the two purine residues of the AgL_2^+ cation.

Shin and Eichhorn² have proposed N(7)–Ag–N(7) bonding for the poly(Ag–I₂) double-helix complex formed at pH 4 and this assumption is fully confirmed by the present crystal structure. Ideally, free hypoxanthine rings could be positioned in syn (Figure 2) or anti configurations with respect to N–

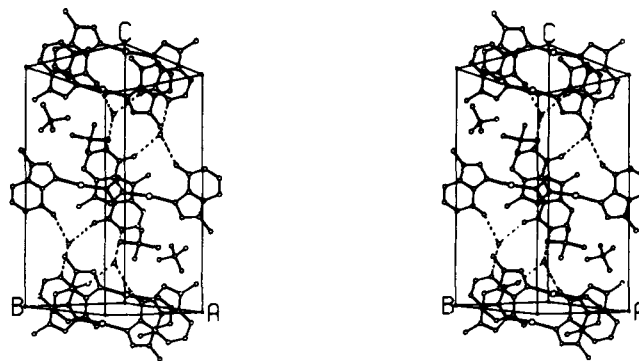


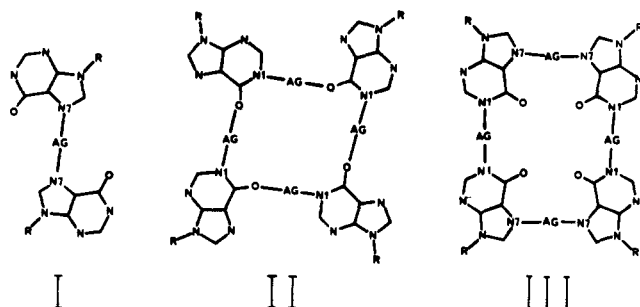
Figure 3. Packing diagram of $[(9\text{-methylhypoxanthine})_2\text{Ag}]\text{ClO}_4\cdot\text{H}_2\text{O}$. Dashed lines correspond to H bonds.

Ag–N. The syn structure was observed in the present compound and is proposed as a probable model for poly(Ag–I₂). However, structure I cannot be ruled out even if stabilization by water “cross-linking” would be lost, because that particular orientation of purine rings may have been forced by other factors in the more constrained poly(I)–Ag system.

The ligand hydrogen H(1) is weakly acidic and N(1) becomes available for complexation at higher pH. Structural information on silver compounds with deprotonated hypoxanthine rings is still missing, but one of the reasonable assumptions that can be put forward would be closely related to the “diaquo dimer” structure observed here. Assuming that the two water molecules and four H(1) protons are removed and that the two AgL_2^+ cations are shifted with respect to each other in order to position N(11) and N(21) in front of N(41) and N(31), respectively, reaction of two silver atoms with the four available N(*i*) donors would lead to the planar tetramer III. Such a unit would have a 1:1 stoichiometry with substitution of one H^+ per Ag^+ ion and all the donors bound to silver would be nitrogen atoms, for which silver is known to show a greater affinity than for oxygen.

This model is particularly attractive in connection with the evidence provided by Shin and Eichhorn² for a four-stranded helix in the poly(I)–Ag complex formed at high pH. They have proposed structural unit II in which N(1) and O(6) are coordinated to silver, leaving N(7) free. This model is geometrically reasonable, but it requires coordination with an oxygen donor when a nitrogen donor N(7) is available. Assuming that reaction is forced to take place with O(6) and N(1), the binding curve should not level at a 1:1 Ag:residue ratio, since free N(7) atoms would be expected to accept more silver ions. On the other hand, structure III would make efficient use of both N(1) and N(7) on all four ligands, providing silver with a linear coordination of nitrogen donors only. Extra stabilization could result from water molecules filling the central channel and cross-linking carbonyl groups of adjacent strands. Other arrangements with different relative orientations of the bases are also geometrically and chemically reasonable. For instance, interchanging N(7) and N(1) of two hypoxanthine moieties on opposite corners of the square would lead to a symmetric unit with a fourfold axis, in which all Ag atoms would have the same N(1)–Ag–N(7) coordination. Arrangement III has been preferred because the structure of Figure 2 could be its precursor, thus providing a convenient mechanism for the equilibrium between poly(Ag–I₂) and poly(Ag₄–I₄) noted for intermediate pH values by Shin and Eichhorn.²

Supplementary Material Available: Temperature factors of nonhydrogen atoms, calculated coordinates of hydrogen atoms, individual interatomic distances and bond angles, least-squares planes calculated through purine rings, and table of calculated and observed structure factors with standard deviations ($\times 10$) (24 pages). Ordering information is given on any current masthead page.



References and Notes

- Eichhorn, G. L. "Inorganic Biochemistry"; Elsevier: Amsterdam, 1973; Chapter 34.
- Shin, Y. A.; Eichhorn, G. L. *Biopolymers* **1980**, *19*, 539.
- Eichhorn, G. L.; Butzow, J. J.; Clark, P.; Tarien, E. *Biopolymers* **1967**, *5*, 283.
- Authier-Martin, M.; Hubert, J.; Rivest, R.; Beauchamp, A. L. *Acta Crystallogr., Sect. B* **1978**, *34*, 273.
- Cromer, D. T.; Waber, J. T. *Acta Crystallogr.* **1965**, *18*, 104.
- Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.
- Cromer, D. T. *Acta Crystallogr.* **1965**, *18*, 17.
- Guay, F.; Beauchamp, A. L. *J. Am. Chem. Soc.* **1979**, *101*, 6260.
- Kistenmacher, T. J.; Rossi, M.; Marzilli, L. G. *Inorg. Chem.*, **1979**, *18*, 240.
- Gagnon, C.; Beauchamp, A. L. *Acta Crystallogr., Sect. B* **1977**, *33*, 1448.
- Gagnon, C.; Hubert, J.; Rivest, R.; Beauchamp, A. L. *Inorg. Chem.* **1977**, *16*, 2469.
- Individual bond lengths and angles, best plane equations, and atom-to-plane distances can be found in the supplementary material.
- Thewalt, U.; Bugg, C. E.; Marsh, R. E. *Acta Crystallogr., Sect. B* **1970**, *26*, 1089. Munns, A. R. I.; Tollin, P. *Ibid.* **1970**, *26*, 1101. Rao, S. T.; Sundaralingam, M. *J. Am. Chem. Soc.* **1969**, *91*, 1210.
- Aoki, K. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1260. Sletten, E. *Acta Crystallogr., Sect. B* **1974**, *30*, 1961. Sletten, E.; Kaale, R. *Ibid.* **1977**, *33*, 158.
- Singh, C. *Acta Crystallogr.* **1965**, *19*, 861.
- Hodgson, D. J. *Prog. Inorg. Chem.* **1977**, *23*, 211. Melanson, R.; Rochon, F. D. *Acta Crystallogr., Sect. B* **1978**, *34*, 3594. Kistenmacher, T. J.; Chiang, C. C.; Challopoyl, P.; Marzilli, L. G. *J. Am. Chem. Soc.* **1979**, *101*, 1143. Behrens, N. B.; Cartwright, B. A.; Goodgame, D. M. L.; Skapski, A. C. *Inorg. Chim. Acta* **1978**, *31*, L471. Canty, A. J.; Tobias, R. S.; Chalchit, N.; Gatehouse, B. M., private communication.

Sensitivity of the Cr-Cr Quadruple Bond to Axial Interactions in Dichromium(II) Compounds

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Abstract: X-ray crystallographic studies have been made on five $\text{Cr}_2[\text{RNC}(\text{O})\text{R}']_4\text{L}_2$ -type compounds, $\text{R} = \text{C}_6\text{H}_5$, 2,6- $(\text{CH}_3)_2\text{C}_6\text{H}_3$; 4-(Me_2N) C_6H_4 ; $\text{R}' = \text{CH}_3$, NHPh ; $\text{L} = \text{THF}$, NC_5H_5 , to determine the response of the Cr-Cr bond to the introduction and variation of axial ligands. The structures reported here are for the following compounds, where the numbers in parentheses are the lengths in Å of the Cr-Cr bond: $\text{Cr}_2[(4\text{-Me}_2\text{N-C}_6\text{H}_4)\text{NC}(\text{O})\text{CH}_3]_4\cdot\text{THF}$ (1) (2.006 (2)); $\text{Cr}_2[(2,6\text{-xylyl})\text{NC}(\text{O})\text{CH}_3]_4\cdot 3\text{THF}$ (2) (2.221 (3)); $\text{Cr}_2[(2,6\text{-xylyl})\text{NC}(\text{O})\text{CH}_3]_4\cdot\text{THF}\cdot\text{C}_6\text{H}_5\text{CH}_3$ (3) (2.023 (1)); $\text{Cr}_2[\text{PhNC}(\text{NHPh})\text{O}]_4\cdot 2\text{THF}\cdot\text{C}_6\text{H}_{14}$ (4) (2.246 (2)); $\text{Cr}_2[(2,6\text{-xylyl})\text{NC}(\text{O})\text{CH}_3]_4\cdot 3\text{NC}_5\text{H}_5$ (5) (2.354 (5)). The Cr-Cr bond length is shown to be a sensitive function of both the number of axial ligands present and the donor ability of the axial ligands. Each THF molecule in the axial position is shown to cause an $\sim 0.18\text{-}\text{\AA}$ increase in the length of the Cr-Cr bond. The Cr-Cr bond length is also seen to increase by about $0.12\text{ }\text{\AA}$ upon replacing two axial THF ligands by two pyridine ligands. The basic crystallographic data on the five compounds are as follows. 1: space group, $C2/c$; $a = 21.254$ (4) Å, $b = 10.990$ (2) Å, $c = 20.733$ (4) Å, $\beta = 110.64$ (2)°, $Z = 4$. 2: $Pbcn$; $a = 16.775$ (2) Å, $b = 19.736$ (3) Å, $c = 19.739$ (2) Å, $Z = 4$. 3: $Pbcn$; $a = 16.806$ (2) Å, $b = 19.311$ (3) Å, $c = 14.887$ (3) Å, $Z = 4$. 4: $Pccn$; $a = 24.813$ (5) Å, $b = 13.408$ (3) Å, $c = 18.631$ (3) Å, $Z = 4$. 5: $P2_1/n$; $a = 17.374$ (4) Å, $b = 12.836$ (4) Å, $c = 23.603$ (6) Å, $Z = 4$. These structures are then compared with those of some 30 other quadruply bonded dichromium compounds with bridging ligand chains of the types O-C-O, N-C-O, N-C-N, N-N-N, C-C-O, and C-P-C, and certain trends in the Cr-Cr distance as these ligand types are changed are noted.

Introduction

The chemistry of compounds containing quadruple metal-metal bonds has developed rapidly since the recognition of the existence of the first such bond.¹ With several of the elements that have shown a consistent tendency to form such bonds, particularly molybdenum and rhenium, the structural patterns are relatively simple. In these cases, the central Mo_2^{4+} and Re_2^{6+} units appear to be structurally rigid and the observed variation in the metal-metal bond distance is relatively small. For example, Mo-Mo quadruple bond lengths range from 2.037 (3) Å in $\text{Mo}_2[(\text{C}_5\text{NH}_4)\text{NC}(\text{O})\text{CH}_3]_4^2$ to 2.183 (2) Å in $\text{Mo}_2(\text{C}_3\text{H}_5)_4^3$ and the known range of Re-Re quadruple bonds is from 2.178 (1) Å in $\text{Re}_2\text{Me}_5^{2-4}$ to about 2.24 Å in several $\text{Re}_2\text{Cl}_8^{2-}$ salts.⁵ With chromium, however, the situation is more complicated.

Quadruply bonded dichromium(II) compounds exhibit a unique variability of the Cr-Cr bond length, covering a range of more than 0.7 Å. The shortest distance, 1.828 (2) Å, is found in $\text{Cr}_2[5\text{-methyl-2-methoxyphenyl}]_4$, and the longest, 2.541 (1) Å, is found in $\text{Cr}_2(\text{O}_2\text{CCF}_3)_4(\text{Et}_2\text{O})_2$.⁷ Apart from the species $[\text{Cr}_2\text{R}_8]^{4-}$ ($\text{R} = \text{CH}_3$ or $1/2\text{C}_4\text{H}_8$)⁸ and $\text{Cr}_2(\text{C}_3\text{H}_5)_4$ ⁹ which contain nonbridging ligands, the numerous examples of $\text{Cr}_2(\text{X}-\text{Y}-\text{Z})_4$ compounds can be divided into two distinctly different groups: (1) First there are the tetracarboxylato compounds which have Cr-Cr distances ranging from 2.283

(2) to 2.541 (1) Å;^{7,10,11} the related $[\text{Cr}_2(\text{CO}_3)_4]^{4-}$ ion has a slightly shorter distance, 2.214 (1) Å.¹¹ All of these molecules have been found to be either disolvated, in which the solvent molecules, L, occupy the axial positions, $\text{Cr}_2(\text{O}_2\text{CR})_4\text{L}_2$, or to have a structure in which the $\text{Cr}_2(\text{O}_2\text{CR})_4$ units are arranged in infinite chains with intermolecular $\text{O}\cdots\text{Cr}$ axial distances of 2.22-2.44 Å.⁷ (2) Then there are the compounds with "supershort" bonds,¹² i.e., $d_{\text{Cr-Cr}} \leq 1.90\text{ }\text{\AA}$. These can generally be characterized as having ligands derived from weak acids and usually have the axial positions blocked as a result of intramolecular steric hindrance.¹³

The rather long metal-metal distances in the carboxylato series have provoked considerable controversy concerning the Cr-Cr bond order.^{14,15} One early report even claimed that in $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2$ and other carboxylato compounds there is no Cr-Cr bond.^{14a} This, however, has been conclusively refuted^{14b,15} by a later ab initio calculation that suggests that the Cr-Cr bond should have its maximum strength at a distance of ca. 2.40 Å.^{14b} Later studies on the carboxylato series $\text{Cr}_2(\text{O}_2\text{CR})_4\text{L}_2$, concerned with examining the factors contributing to the Cr-Cr bond, have shown that the variations of the Cr-Cr bond distance in this series cannot be accounted for solely by postulating linear and independent dependencies on the inductive effect of the R groups and the distance of the axial ligands.¹¹ Recent investigations designed to examine