10.3 (0.075 mol) of phosphorous trichloride in 75 ml of ether that had been cooled to $-50°$. The reaction was allowed to warm to room temperature and stirred for 30 min. After centrifugation, the solution was decanted and concentrated. The residue was recrystallized twice from diethyl ether at $-45°$ to give a granular white precipitate which was dried under vacuum for several hours at room temperature. The yield was 10.5 g (50%).

**2,4,6-Triisopropylphenyl(4,4′-dimethyl-2,2′-biphenylylene)phosphine** was prepared in a manner similar to that described for its 2-isopropylphenyl analog. Dichloro-2,4,6-triisopropylphenylphosphine (5.2 g, 16.9 mmol) and 5.64 g (13 mmol) of 2,2′-diiodo-4,4′-dimethylbiphenyl gave 1.62 g (30%) of a white solid having mp 124–126°. This material crystallized only with difficulty: nmr ($CCl_4$, no standard) $\delta$ 2.34 (s, 6, bitolyl methyl), 1.37 (d, 18, isopropyl methyl, $J$ = 7 Hz), 6.65–7.92 (m, 8, aromatic).

*Anal.* Calcd for $C_{29}H_{35}P$: C, 84.02; H, 8.51. Found: C, 84.13; H, 8.23.

**2,4,6-Triisopropylphenyl(4,4′-dimethyl-2,2′-biphenylylene)phosphine tosylimine** was prepared from anhydrous chloroamine T (0.02 g, 3.62 mmol) and 2,4,6-triisopropylphenyl(4,4′-dimethyl-2,2′-biphenylylene)phosphine (1.5 g, 3.62 mmol) in 52% yield, mp 227–228°.

**2,4,6-Triisopropylphenylbis(4,4′-dimethyl-2,2′-biphenylylene)-phosphorane (2)** was prepared from the corresponding tosylimine (1.0 g, 1.72 mmol) and 2,2′-dilithio-4,4′-dimethylbiphenyl (from 1.3 g, 3 mmol, of 2,2′-diiodo-4,4′-dimethylbiphenyl and 6 mmol of 1.5 $N$ $n$-butyllithium solution). After unexceptional work-up, the crude product was purified by dissolving in a minimal amount of boiling tetrahydrofuran and pouring into methanol. The precipitate was collected as a white solid, mp 277.5–278.5°, in 30% yield. Its nmr spectrum was recorded on a Varian HA-60 spectrometer in benzyl ether–1-chloronaphthalene using tetrachloroethane as an internal lock: mass spectrum, $m/e$ (rel intensity) 606 (6), 605 (19, impurity), 595 (3), 594 (12, M), 593 (45), 592 (77), 552 (45), 551 (94, M − $i$-Pr), 536 (47), 535 (100, M − $i$-Pr, $CH_3$, H), 92 (20), 381 (73, M − $C_6H_2(i\text{-}Pr)_3$), 212 (14), 211 (45, M − bitolyl, $C_6H_2(i\text{-}Pr)_3$).

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**Supplementary Material Available.** The derivation of **K** matrix 1 will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only on microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-74-5398.

# Metal Ion–Aromatic Complexes. XX. The Preparation and Molecular Structure of Anthracenetetrakis(silver perchlorate) Monohydrate

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**Abstract:** Anthracenetetrakis(silver perchlorate) monohydrate crystallizes in the monoclinic space group $P2_1/n$ with two molecules per unit cell and with cell constants of $a$ = 24.189 (6) Å, $b$ = 9.325 (2) Å, $c$ = 5.304 (1) Å, and $\beta$ = 90.35 (5)°. The structure was refined by full-matrix least squares including anisotropic temperature factors and anomalous dispersion corrections to a final $R$ of 0.049. The crystal structure is made up of a three-dimensional cross-hatched network of $AgClO_4$ and water with anthracene molecules stacked 5.3 Å apart, one above the other in the channels of the ionic network. The ionic reticulation is composed of pairs of $AgClO_4$ chains bridged by unequal silver–water bonds to yield a two-stranded ribbon which has a ladder-like appearance. The chains are held together by weak Ag–O bonds and van der Waals forces with the ribbons separated by normal van der Waals distances. Each anthracene molecule is unequally bonded *via* its $\pi$-orbitals to silver atoms of four different ribbons, with the short Ag–C interactions at the 1, 4, 5, and 8 positions, rather than the expected 9, 10 positions which have the highest electron density. Each silver is four-coordinate with two interactions to two different perchlorate groups, one to a water of hydration and one to the aromatic. The trend in the Ag–C distances and associated angles indicates that the hydrated silver ion is a weaker Lewis acid than the free silver ion.

The formation of Ag(I)–aromatic complexes has now been well established both in solution studies, as reviewed by Andrews,[2] and by crystallographic determinations of the structures of a number of the complexes in a range of stoichiometries. One to one stoichiometries in single ring aromatics are observed in the structures of benzene (silver perchlorate)[3] and benzene(silver tetrachloroaluminate).[4] Structural studies of complexes of the stoichiometry type $AgAr_2^+$ which have appeared in the literature include bis(cyclohexylbenzene)(silver perchlorate),[5] bis($m$-xylene)(silver perchlorate),[6] and bis($o$-xylene)(silver perchlorate).[7] When the aromatic rings are counted independently, the

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**Table II.** Final Atomic Positional and Thermal Parameters and Estimated Standard Deviations[a]

| Atom | x | y | z | Atom | x | y | z |
|---|---|---|---|---|---|---|---|
| Ag(1) | 0.0910 (1) | 0.8694 (1) | 0.2819 (1) | O(7) | 0.3065 (3) | 0.3623 (9) | 0.8045 (15) |
| Ag(2) | 0.1508 (1) | 0.2767 (1) | 0.2287 (2) | O(8) | 0.2394 (4) | 0.3134 (13) | 0.5116 (13) |
| Cl(1) | 0.0641 (1) | 0.0989 (2) | 0.7987 (4) | O(9) | 0.1761 (3) | 0.0334 (7) | 0.2522 (14) |
| Cl(2) | 0.2522 (1) | 0.3048 (2) | 0.7730 (4) | C(1) | 0.4192 (3) | 0.9503 (8) | 0.1167 (15) |
| O(1) | 0.1135 (3) | 0.1802 (8) | 0.7497 (14) | C(2) | 0.3710 (3) | 0.0276 (9) | 0.1070 (16) |
| O(2) | 0.0558 (3) | 0.0892 (7) | 0.0702 (12) | C(3) | 0.3600 (3) | 0.1322 (9) | 0.3122 (17) |
| O(3) | 0.0172 (3) | 0.1664 (7) | 0.6828 (12) | C(4) | 0.3993 (3) | 0.1584 (8) | 0.4909 (15) |
| O(4) | 0.0708 (3) | 0.9547 (7) | 0.7002 (12) | C(5) | 0.4511 (3) | 0.0805 (8) | 0.4981 (15) |
| O(5) | 0.2521 (4) | 0.1619 (8) | 0.8646 (24) | C(6) | 0.4605 (3) | 0.9722 (8) | 0.3092 (14) |
| O(6) | 0.2129 (3) | 0.3881 (8) | 0.9111 (15) | C(7) | 0.4906 (3) | 0.1069 (8) | 0.6838 (15) |

| Atom | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|
| Ag(1) | 23 (1) | 56 (1) | 336 (3) | 2 (1) | 9 (1) | 1 (1) |
| Ag(2) | 15 (1) | 69 (1) | 390 (3) | 3 (1) | −1 (1) | −5 (1) |
| Cl(1) | 10 (1) | 52 (2) | 227 (7) | 1 (1) | −3 (1) | 23 (3) |
| Cl(2) | 10 (1) | 66 (2) | 275 (8) | 3 (1) | 1 (1) | −12 (4) |
| O(1) | 12 (1) | 128 (10) | 507 (34) | −10 (3) | −9 (5) | 110 (16) |
| O(2) | 24 (2) | 106 (9) | 245 (25) | 9 (3) | 3 (5) | 25 (12) |
| O(3) | 12 (1) | 94 (8) | 375 (28) | 4 (3) | −15 (5) | 63 (12) |
| O(4) | 28 (2) | 77 (8) | 286 (27) | 9 (3) | 9 (5) | −11 (12) |
| O(5) | 34 (3) | 62 (9) | 1284 (77) | 13 (4) | 67 (11) | 108 (22) |
| O(6) | 22 (2) | 99 (10) | 511 (35) | 13 (3) | 51 (6) | 1 (15) |
| O(7) | 15 (1) | 171 (13) | 520 (36) | −13 (4) | −1 (6) | −86 (18) |
| O(8) | 26 (2) | 347 (22) | 242 (29) | 23 (5) | −28 (6) | −61 (21) |
| O(9) | 19 (2) | 75 (8) | 499 (35) | 6 (3) | −5 (6) | −3 (14) |
| C(1) | 11 (1) | 48 (9) | 198 (30) | −5 (3) | −6 (5) | −4 (13) |
| C(2) | 10 (1) | 68 (10) | 236 (32) | −5 (3) | 1 (5) | 22 (15) |
| C(3) | 10 (2) | 58 (9) | 324 (27) | −3 (3) | 6 (6) | 12 (16) |
| C(4) | 11 (1) | 51 (9) | 216 (31) | 1 (3) | 2 (5) | 13 (13) |
| C(5) | 9 (1) | 37 (8) | 208 (30) | −2 (3) | 4 (5) | −9 (12) |
| C(6) | 10 (1) | 46 (8) | 163 (28) | −6 (3) | 1 (5) | −15 (13) |
| C(7) | 10 (1) | 46 (9) | 214 (29) | 1 (3) | −2 (5) | −1 (13) |

[a] Numbers in parentheses here and in succeeding tables are estimated standard deviations in the least significant digits. Anisotropic temperature factors are of the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]10^4$.

structure of 1,2-diphenylethane(silver perchlorate)[8] also conforms to the $AgAr_2^+$ type. Solubility studies[2] suggested that complexes of the type $Ag_2Ar^{2+}$ were in equilibrium with $AgAr^+$, but the only structure of this type reported thus far is that of benzenebis(silver trifluoroacetate).[9] Crystal structures of fused ring aromatics include indene(silver perchlorate),[10] acenaphthene(silver perchlorate),[11] acenaphthylene(silver perchlorate),[11] and naphthalenetetrakis(silver perchlorate) tetrahydrate.[12]

The anthracene–silver(I) system presents a logical extension into more complex aromatic systems which might yield higher silver to aromatic ratios, and the earlier solution work gave few definitive answers concerning the nature of the silver–anthracene interaction. Because of solubility problems with anthracene in purely aqueous solutions, argenation constants are not quoted by Andrews and Keefer[13] although it was presumed that values would approximate those found for phenanthrene: $K_1 = 3.67$ and $K_2 = 1.80$. Kofahl and Lucas[14] also ran into difficulties determining values in an aqueous medium but reported values of $K_1 = 1.35$ and $K_2 = 0.48$ in equimolal water–methanol containing $NaNO_3$ and $AgNO_3$ at ionic strength 0.5. Note that these values are considerably less than those observed for phenanthrene ($K_1 = 2.56$ and $K_2 = 2.22$). Kofahl and Lucas suggest that the anomolously high values for phenanthrene result from appreciable amounts of a trisilver complex but that anthracene is limited to the mono- and disilver complexes. They speculated that the first silver ion in either case coordinates at the meso position. Peyronel and coworkers[15] claim to have isolated both the 1:1 and the 1:2 anthracene–silver perchlorate complexes.

The complex isolated by us proved to be anthracenetetrakis(silver perchlorate) monohydrate, and a preliminary communication[12] has described its gross features. We present here the synthetic and structural details of this complex as part of a continuing study of the Ag(I)–aromatic interaction.

## Experimental Section

Since Hill and Miller[16] had established that toluene(silver perchlorate) can be isolated in the crystalline form only below 22.6°, toluene was selected as the solvent for reactions between $AgClO_4$ and solid aromatics. A saturated solution of silver perchlorate in toluene containing minute traces of water and corresponding to Hill's solution, which was 50.3% $AgClO_4$ by weight, was used in all preparations. One part of a saturated solution of anthracene in toluene was added to two parts of the $AgClO_4$ solution. After standing overnight, pentane was added to the cloud point. Long fibrous crystals, all of which appeared twinned, formed within

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several hours, but approximately 3 days were required for the formation of yellow-green flattened needles suitable for diffraction studies. Large amounts of a brown oily decomposition product, which dissolved any crystals that come in contact with it, accompanied each preparation. Potentiometric titrations for silver were consistently low due to retention of solvent and adsorbed anthracene. *Anal.* Calcd for $C_{14}H_{10}(AgClO_4)_4 \cdot H_2O$: Ag, 42.1. Found: Ag, 39.8.

The crystals, which were both light sensitive and hygroscopic, were sealed in thin-walled glass capillaries with the "*c*" axis parallel to the capillary axis. Preliminary Weissenberg and precession photographic data (*hk*0, *hk*1 · · · *hk*6, *h*0*l*, 0*kl*) showed that the crystals were monoclinic with the systematic extinctions for *h*0*l*, $h + l = 2n + 1$, and for 0*k*0, $k = 2n + 1$, defining the space group uniquely as $P2_1/n$, a variation of space group $P2_1/c$.[17] A single crystal ~0.20 × 0.25 × 0.50 mm was mounted about the needle axis and aligned on a Picker full-circle, card-controlled diffractometer by variations of well-known techniques.[18] The cell constants for the $P2_1/n$ cell used in the refinement, obtained from a least-squares fit of the $\chi$, $\phi$, and $2\theta$ angles of 15 accurately centered general reflections at a takeoff angle of 2.0° with Mo K$\alpha$ radiation ($\lambda$ 0.71068 Å) at ambient temperature, were found to be $a$ = 24.189 (6) Å, $b$ = 9.325 (2) Å, $c$ = 5.304 (1) Å, and $\beta$ = 90.35 (5)°. Constants for the reduced cell, $P2_1/c$, were $a$ = 5.304 (1) Å, $b$ = 9.325 (2) Å, $c$ = 24.732 (6) Å, and $\beta$ = 102.04 (5)°. The calculated density with two molecules per unit cell is 2.84 g cm$^{-3}$ while the observed density is greater than 2.7 g cm$^{-3}$ measured by flotation in bromoform–carbon tetrachloride solution. A more accurate value of the density was precluded by the fact that decomposition takes place in these solvents.

The intensities of 4035 independent *hkl* reflections in the quadrants *hkl* and $\bar{h}kl$ were measured by the $\theta$–$2\theta$ scan technique to $2\theta$ = 60° using Zr-filtered Mo K$\alpha$ radiation at room temperature. Reflections were scanned for 45 sec and backgrounds were estimated by stationary counting for 10 sec at $2\theta$ ±0.75° from the peak maximum. The takeoff angle, source-to-crystal, and crystal-to-counter values were 3.7°, 18 cm, and 23 cm, respectively, and the receiving aperture at the counter was 6 mm wide × 8 mm high. The half-width at half-peak height for an average reflection was 0.45° in $2\theta$, indicating a satisfactory low mosaic spread. This is not an absolute measure of the mosaic spread since this quantity depends upon instrumental factors as well, but it does indicate that the reflection was completely covered in this angular range. The counting rate never exceeded 5000 counts per second and no attenuators were used.

Integrated intensities were calculated assuming a linear variation background from the function $I_{net} = I_{scan} - 2.25(B_1 + B_2)$ where $I_{scan}$ is the number of counts during the scan, $B_1$ and $B_2$ are background constants, and 2.25 is a constant used to scale the total background time to the total scan time. A standard reflection[19] was measured after every tenth reflection to monitor stability of the electronic operation and any crystal decomposition and to provide a basis for the scaling of the data. An analysis of the standard peak revealed that the crystal underwent a gradual decomposition during the data collection period with a total gross loss of intensity of ~10%. Over short range periods of time the variation from one standard peak to the next was of the order of $\sigma$ or less where $\sigma(I_{net}) = [I_{net} - (2.25)^2(B_1 + B_2)]^{1/2}$. In order to compensate for loss of intensity due to decomposition, $I_{net}$ for each general reflection was scaled by $I_t/I_0$ where $I_0$ is the integrated intensity of the average standard peak and $I_t$ is the integrated intensity of the standard peak taken immediately prior to the general reflection. Reflections were considered to be absent if the integrated net intensity was less than $2[(2.25)^2(B_1 + B_2)]^{1/2}$ ($2\sigma$ of background).

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(19) It may appear that use of only one standard reflection is unusual and misleading. However, considerable care and thought are generally applied to the choice of a standard reflection. A reflection of average intensity in the middle of the $\chi$, $\phi$, and $2\theta$ range and with general *hkl* indices is chosen. We have compared such a procedure with use of three standards for several structures and have found the results quite adequate.

**Table III.** Bond Lengths (Å) and Angles (deg)

| | | | |
|---|---|---|---|
| | **Bond Lengths, Å** | | |
| Ag(1)–C(4) | 2.454 (8) | Ag(1)–O(4) | 2.410 (6) |
| Ag(1)–C(3) | 2.560 (8) | Ag(1)–O(6) | 2.485 (7) |
| Ag(2)–C(1) | 2.484 (8) | Ag(1)–O(9) | 2.569 (7) |
| Ag(2)–C(2) | 2.552 (8) | Ag(2)–O(6) | 2.492 (7) |
| | | Ag(2)–O(8) | 2.632 (8) |
| Cl(1)–O(1) | 1.439 (7) | Ag(2)–O(9) | 2.353 (7) |
| Cl(1)–O(2) | 1.459 (7) | | |
| Cl(1)–O(3) | 1.433 (6) | C(1)–C(2) | 1.372 (11) |
| Cl(1)–O(4) | 1.452 (7) | C(1)–C(6) | 1.438 (11) |
| Cl(2)–O(5) | 1.418 (8) | C(2)–C(3) | 1.487 (12) |
| Cl(2)–O(6) | 1.432 (7) | C(3)–C(4) | 1.360 (12) |
| Cl(2)–O(7) | 1.430 (7) | C(4)–C(5) | 1.450 (11) |
| Cl(2)–O(8) | 1.421 (7) | C(5)–C(6) | 1.441 (10) |
| | | C(5)–C(7) | 1.390 (11) |
| | **Nonbonded Distances (Less than 4 Å)** | | |
| Ag(1)–Cl(1) | 3.541 (2) | O(1)–O(5) | 3.408 (13) |
| Ag(2)–Cl(2) | 3.786 (2) | O(1)–O(6) | 3.202 (11) |
| Ag(2)–O(1) | 3.048 (7) | O(1)–O(8) | 3.530 (11) |
| Ag(2)–O(2) | 3.004 (8) | O(1)–O(9) | 3.344 (11) |
| Ag(1)–O(7) | 3.989 (8) | O(2)–O(9) | 3.104 (10) |
| Ag(1)–O(1′) | 3.851 (8) | O(5)–O(9) | 3.911 (15) |
| Ag(1)–O(3′) | 3.928 (7) | O(8)–O(9) | 3.321 (13) |
| Ag(1)–O(4′) | 3.221 (7) | O(4′)–O(9) | 3.570 (10) |
| Ag(2)–Cl(2′) | 3.506 (2) | O(5′)–O(8) | 3.726 (15) |
| Ag(2)–O(1′) | 2.838 (8) | O(6′)–O(8) | 3.319 (11) |
| Ag(2)–O(5′) | 3.308 (10) | O(1′)–O(9) | 3.350 (10) |
| | | O(5′)–O(9) | 3.015 (12) |
| | | O(6′)–O(9) | 3.876 (10) |
| | **Angles, deg.** | | |
| C(2)–C(1)–C(6) | 122.6 (7) | C(3)–Ag(1)–C(4) | 31.4 (3) |
| C(1)–C(2)–C(3) | 118.2 (8) | Ag(1)–C(3)–C(4) | 70.0 (5) |
| C(2)–C(3)–C(4) | 120.1 (8) | Ag(1)–C(4)–C(3) | 78.6 (5) |
| C(3)–C(4)–C(5) | 121.9 (8) | O(2)–Ag(1)–O(4) | 74.0 (2) |
| C(4)–C(5)–C(6) | 118.2 (7) | O(4)–Ag(1)–O(9) | 72.2 (2) |
| C(4)–C(5)–C(7) | 121.4 (7) | O(4)–Ag(1)–C(3) | 124.2 (3) |
| C(6)–C(5)–C(7) | 120.4 (7) | O(4)–Ag(1)–C(4) | 145.9 (2) |
| C(1)–C(6)–C(5) | 118.8 (7) | O(2)–Ag(1)–C(3) | 62.3 (2) |
| C(5)–C(6)–C(7′) | 119.2 (8) | O(2)–Ag(1)–C(4) | 93.4 (2) |
| C(1)–C(6)–C(7′) | 121.9 (8) | O(9)–Ag(1)–C(3) | 58.4 (2) |
| | | O(9)–Ag(1)–C(4) | 89.7 (2) |
| O(1)–Cl(1)–O(2) | 105.1 (3) | C(1)–Ag(2)–C(2) | 31.6 (3) |
| O(1)–Cl(1)–O(3) | 110.3 (4) | Ag(2)–C(1)–C(2) | 76.9 (5) |
| O(1)–Cl(1)–O(4) | 109.2 (5) | Ag(2)–C(2)–C(1) | 71.5 (5) |
| O(2)–Cl(1)–O(3) | 111.1 (6) | O(6)–Ag(2)–O(8) | 45.3 (2) |
| O(2)–Cl(1)–O(4) | 106.4 (7) | O(6)–Ag(2)–O(9) | 91.0 (2) |
| O(3)–Cl(1)–O(4) | 110.0 (4) | O(8)–Ag(2)–O(9) | 83.4 (3) |
| O(5)–Cl(2)–O(6) | 109.4 (5) | O(6)–Ag(2)–C(1) | 73.2 (2) |
| O(5)–Cl(2)–O(7) | 108.4 (6) | O(6)–Ag(2)–C(2) | 66.0 (2) |
| O(5)–Cl(2)–O(8) | 112.7 (7) | O(8)–Ag(2)–C(1) | 106.3 (3) |
| O(6)–Cl(2)–O(7) | 110.5 (5) | O(8)–Ag(2)–C(2) | 81.7 (3) |
| O(6)–Cl(2)–O(8) | 109.1 (5) | O(9)–Ag(2)–C(1) | 142.0 (3) |
| O(7)–Cl(2)–O(8) | 106.7 (5) | O(9)–Ag(2)–C(2) | 156.9 (3) |

Of the 4035 measured reflections, 2151 were considered nonzero by this criteria.

With Mo K$\alpha$ radiation the linear absorption coefficient, $\mu$, was calculated for this compound to be 40.2 cm$^{-1}$. No corrections were made for this absorption since the errors in intensity due to oil of decomposition and to scatter from the capillary probably outweigh simple absorption effects. Corrections for anomalous dispersion effects were included in the refinement. The usual Lorentz–polarization corrections were made and intensities were reduced to structure factors.

**Solution of Structure.** The space group $P2_1/n$ demands, with two molecules per cell of anthracenetetrakis(silver perchlorate), that the eight $Ag^+$ and $ClO_4^-$ ions lie on two sets of general positions and that the center of the anthracene molecules lies upon a crystallographic center of symmetry. Coordinates for the silver and chlorine atoms were readily obtained from examination of an unsharpened three-dimensional Patterson vector map.[20] Using these coordinates for the initial phase determination, all the non-hy-

(20) Patterson and electron density calculations done on IBM 7040 with the ERFR3 program which is a modification of ERFR2 of Sly–Shoemaker–van den Hende by D. R. Harris.

Table IV. Rms Component of Thermal Displacement along Principal Axes (Å) (Esd in Parentheses)

| Atom | 1 | 2 | 3 | Atom | 1 | 2 | 3 |
|---|---|---|---|---|---|---|---|
| Ag(1) | 0.157 (1) | 0.215 (1) | 0.266 (1) | O(7) | 0.187 (11) | 0.244 (10) | 0.313 (11) |
| Ag(2) | 0.171 (1) | 0.211 (1) | 0.236 (1) | O(8) | 0.165 (12) | 0.268 (11) | 0.406 (13) |
| Cl(1) | 0.141 (3) | 0.171 (3) | 0.188 (3) | O(9) | 0.176 (10) | 0.239 (10) | 0.268 (9) |
| Cl(2) | 0.159 (3) | 0.181 (3) | 0.200 (3) | C(1) | 0.135 (14) | 0.165 (13) | 0.189 (12) |
| O(1) | 0.169 (11) | 0.198 (10) | 0.309 (10) | C(2) | 0.150 (14) | 0.177 (13) | 0.198 (13) |
| O(2) | 0.179 (10) | 0.213 (10) | 0.273 (9) | C(3) | 0.152 (14) | 0.178 (14) | 0.217 (13) |
| O(3) | 0.153 (10) | 0.207 (9) | 0.256 (9) | C(4) | 0.146 (14) | 0.174 (12) | 0.182 (13) |
| O(4) | 0.174 (10) | 0.204 (10) | 0.291 (10) | C(5) | 0.124 (14) | 0.160 (12) | 0.179 (12) |
| O(5) | 0.149 (13) | 0.287 (12) | 0.454 (13) | C(6) | 0.125 (15) | 0.157 (13) | 0.183 (12) |
| O(6) | 0.166 (11) | 0.225 (10) | 0.322 (10) | C(7) | 0.142 (13) | 0.166 (12) | 0.177 (12) |

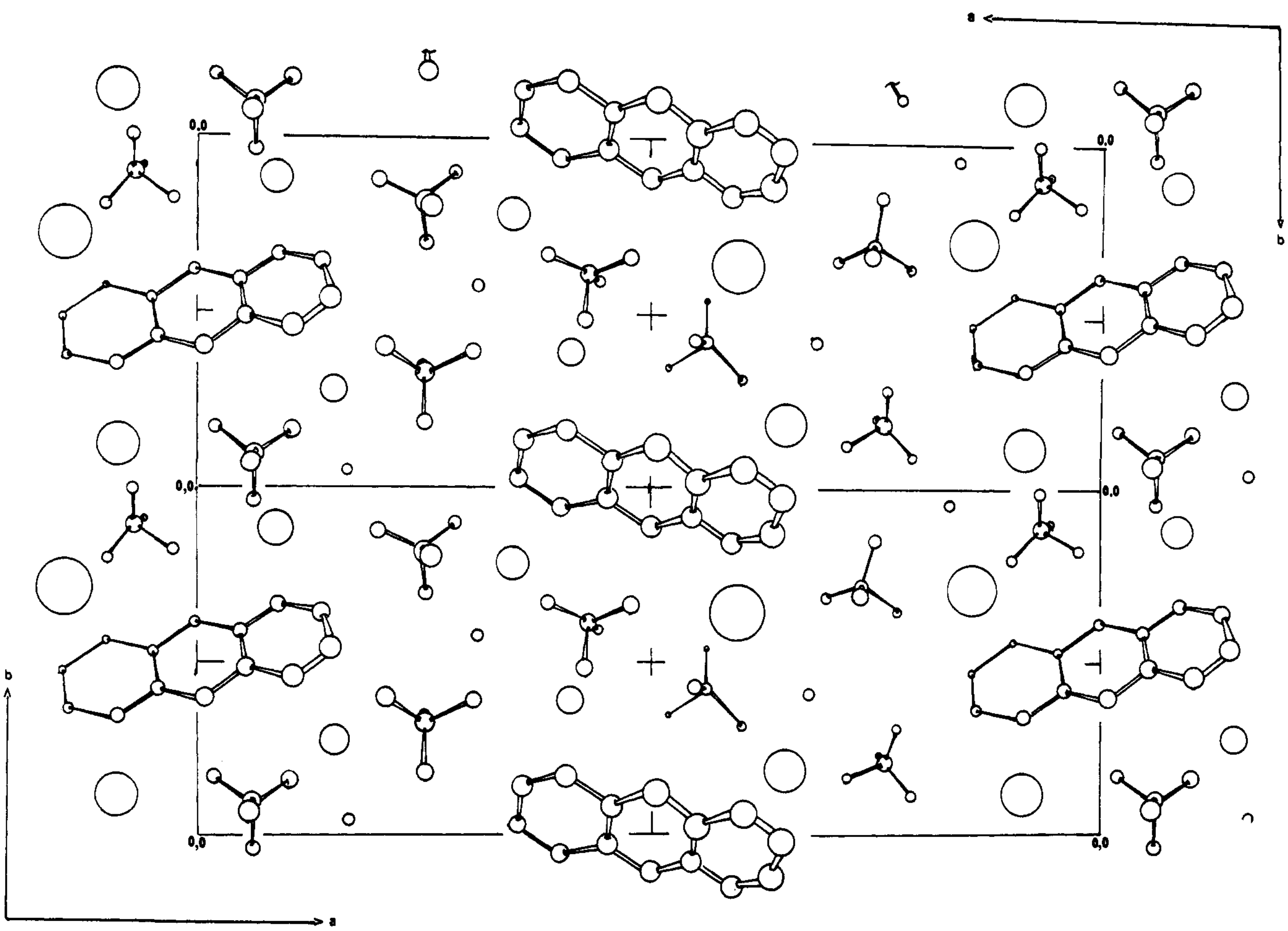


Figure 1. A perspective view down the $c$ axis of the packing diagram of two unit cells of anthracenetetrakis(silver perchlorate) monohydrate, showing the cross-hatched ionic network with the anthracene molecules stacked in the channels of the network. The center of each anthracene molecule lies upon a crystallographic center of symmetry.

drogen atoms were located by standard heavy atom methods. The structure was refined, excluding hydrogens, with a full-matrix least-squares[21] treatment using weights determined by intensity statistics[22] and anisotropic temperature factors. The final conventional $R$, weighted $R$, and standard error of an observation were found to have values of 0.049, 0.057, and 1.78, respectively.[23] The parameter shifts on the final cycle of refinement were all less than 0.1 standard deviation. A final difference electron density map was qualitatively featureless.

The function minimized was $\Sigma w(F_o - F_c)^2$ with weights defined above. Scattering factors for $Ag^+$, $Cl^-$, and neutral O and C were from Cromer and Waber,[24a] and corrections for anomalous dispersion effects were from standard sources.[24,25] Final observed and calculated structure factors are listed in Table IA.[26] Unobserved

(21) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, a Fortran Crystallographic Least-Squares Program," Oak Ridge National Laboratory Report ORNL-TM-305 (1962). The version used incorporates modifications by W. A. Spofford, III.

(22) S. W. Peterson and H. A. Levy, *Acta Crystallogr.*, 10, 70 (1957).

$\omega = 1/\sigma^2$

$\sigma^2(F^2) = S/(\mathrm{Lp})^2[I_{(\mathrm{scan})} + K^2(B_1 + B_2) + (0.04I_{(\mathrm{scan})}{}^2]$

$\sigma^2(F) = S/(\mathrm{Lp}) \cdot 1/F[\mathrm{I}_{(\mathrm{scan})} + K^2(B_1 + B_2) + (0.04I_{(\mathrm{scan})})^2]^{1/2}$

where $S$ = a scale factor, (Lp) is the Lorentz polarization factor, $K$ is the time factor, and the other terms are as defined previously.

(23) $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. Weighted $R = \{[\Sigma w(F_o - F_c)]^2/\Sigma wF_o^2\}^{1/2}$. Standard error $= [\Sigma w(F_o - F_c)^2]^{1/2}/(\mathrm{NO} - \mathrm{NV})]^{1/2}$. NO = 2151; NV = 173.

(24) (a) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, 18, 104 (1965); (b) D. T. Cromer, *ibid.*, 18, 17 (1965).

(25) J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, 17, 781 (1964).

(26) See paragraph at end of paper regarding supplementary material.

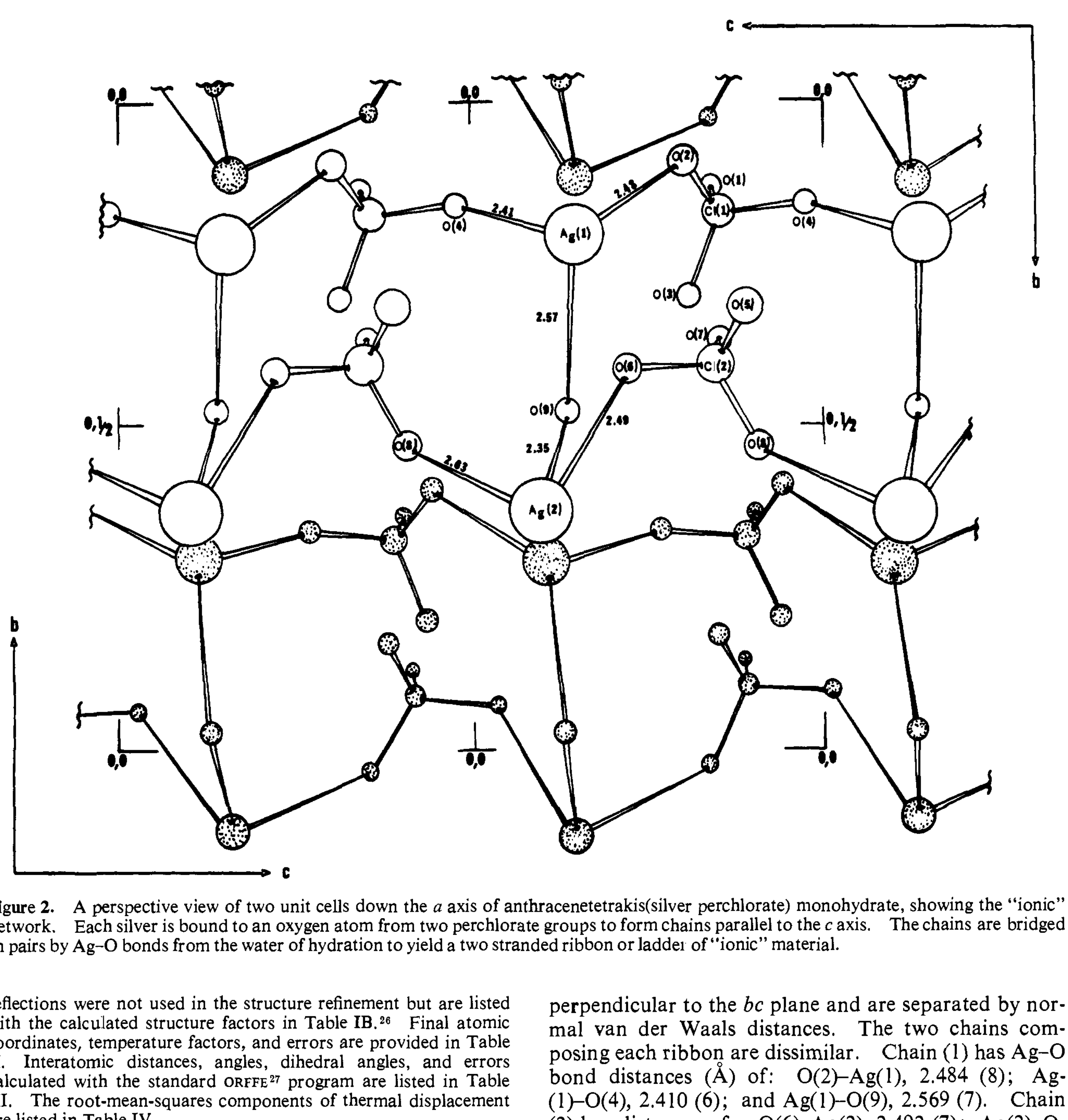


**Figure 2.** A perspective view of two unit cells down the *a* axis of anthracenetetrakis(silver perchlorate) monohydrate, showing the "ionic" network. Each silver is bound to an oxygen atom from two perchlorate groups to form chains parallel to the *c* axis. The chains are bridged in pairs by Ag–O bonds from the water of hydration to yield a two stranded ribbon or laddeı of "ionic" material.

reflections were not used in the structure refinement but are listed with the calculated structure factors in Table IB.[26] Final atomic coordinates, temperature factors, and errors are provided in Table II. Interatomic distances, angles, dihedral angles, and errors calculated with the standard ORFFE[27] program are listed in Table III. The root-mean-squares components of thermal displacement are listed in Table IV.

## Results and Discussion

The molecular structure of anthracenetetrakis(silver perchlorate) monohydrate is composed of a three-dimensional cross-hatched network of ionic material ($Ag^+ClO_4^-$ ions and water molecules) with the anthracene molecules stacked one above the other in the *c* direction in the channels of the ionic network (Figure 1).

The ionic reticulation is composed of chains of $AgClO_4$ propagating in the *c* direction in which each silver is bound to an oxygen of a perchlorate group above and below it. These chains are bridged in pairs by Ag–O–Ag bonds formed by the water oxygens to yield a two-stranded ribbon which has a ladder-like appearance (Figure 2). The ribbons or ladders are stacked perpendicular to the *bc* plane and are separated by normal van der Waals distances. The two chains composing each ribbon are dissimilar. Chain (1) has Ag–O bond distances (Å) of: O(2)–Ag(1), 2.484 (8); Ag(1)–O(4), 2.410 (6); and Ag(1)–O(9), 2.569 (7). Chain (2) has distances of: O(6)–Ag(2), 2.492 (7); Ag(2)–O(8), 2.632 (8); and Ag(2)–O(9), 2.353 (7). Note that chain (1) has two short silver–oxygen interactions with the perchlorate groups and a concomitantly long silver–oxygen interaction with the water molecule. Conversely, chain (2) has one short and one long interaction with the perchlorate groups and a short bond to the water molecule. Since the Ag–O single bond radius sum is 2.18 Å,[28] it is obvious that while these Ag–O interactions, especially those to the perchlorate ions, may be classified as "weak," their cumulative effect is to stabilize the complex. A similar situation is found in bis(*m*-xylene)(silver perchlorate)[6] with a Ag–O distance of 2.49 (1) Å, in indene(silver perchlorate)[10] with one Ag–O distance of 2.46 (2) Å, and in acenaphthene(silver perchlorate)[11] where Ag–O bond lengths range from 2.34 to 2.46 Å (disorder in the perchlorate groups

(27) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE, A Fortran Crystallographic Function and Error Program," Oak Ridge National Laboratory Report ORNL-TM-306 (1964). The version used incorporates modifications by W. A. Spofford, III.

(28) L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, p 246.

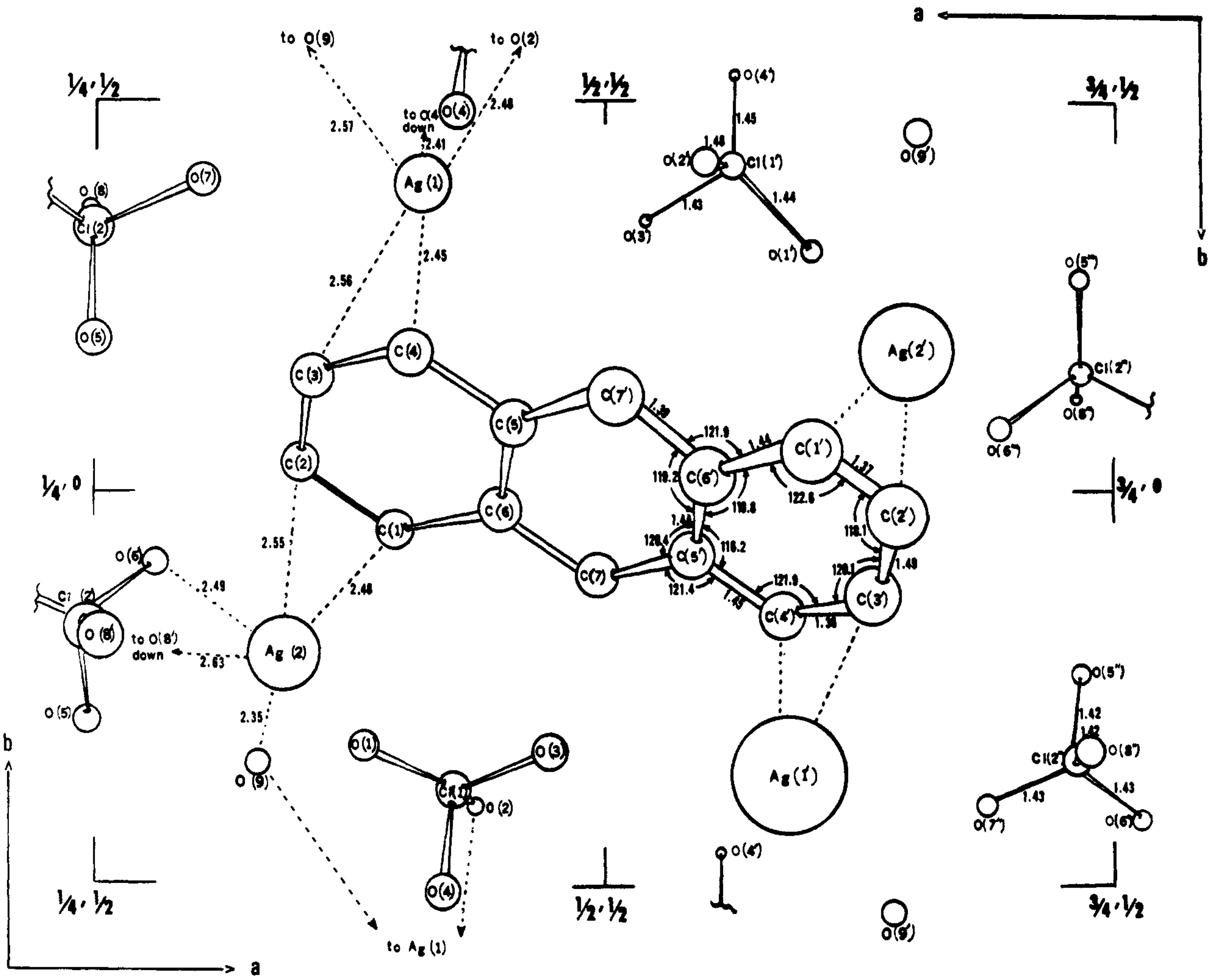

Figure 3. A perspective view of the structure of anthracenetetrakis(silver perchlorate) monohydrate down the $c$ axis showing the ribbons and the Ag–C bonds to the anthracene molecule. A ribbon is Ag(2) bonded to O(8′), O(6′) of a $ClO_4^-$ group, and O(9) of a water group, which is in turn bonded to Ag(1) that is tied to O(4) and O(2). The center of the anthracene molecule is on a crystallographic center of symmetry.

may well modify the Ag–O distances in this last structure). However, much longer distances are reported for the $AgClO_4$ complexes of benzene,[3] cyclohexylbenzene,[5] *o*-xylene,[7] and naphthalene.[12]

The anthracene molecules are stacked one above the other in the channels formed by four ribbons or ladders, such that each molecule has its mid-point on a crystallographic center of symmetry and is separated from neighboring molecules in the $c$ direction by the repeat unit of 5.3 Å. The long molecular symmetry axis makes an angle of 25° with the $ab$ plane of the crystal, while the short axis makes an angle of 44° with this plane (Figure 3). Each anthracene molecule is unequally bonded *via* its $\pi$-orbitals to silver atoms of four different ribbons, with the short Ag–C (~2.47 Å) interactions at the 1, 4, 5, and 8 positions. There are no metal–carbon bonds to the 9,10 positions which would be the expected metal–carbon bond positions based upon free valence or atom polarizability.[29,30] The work of Gold and Tye[31] which dealt with an interpretation of the ultraviolet spectrum of anthracene in sulfuric acid also indicated that protonation always occurred at the 9,10 positions. Fukui[32] and coworkers with a crude theoretical model more correctly predicted the location of the Ag atoms relative to anthracene.

However, in spite of the fact that the relative locations of the silver to the aromatic moiety are similar in the present case and the analogous naphthalene[12b] structure, they should not be considered as similar types of bonding. In the naphthalene case the two short Ag–C distances are equal and long at ~2.6 Å.

Each silver has a formal coordination number of four, two interactions to two different perchlorate groups, one to a water of hydration, and one to the aromatic. Ag(1), which has the weaker interaction with the water of hydration, has Ag–C distances of 2.454 (8) and 2.560 (8) Å with C(4) and C(3), respectively, while Ag(2), which has a much stronger interaction, has slightly elongated Ag–C distances of 2.484 (8) and 2.552 (8) Å with C(1) and C(2), respectively. The asymmetry (difference in the two shortest Ag–C distances) of the silver–aromatic interactions is also reflected by the unequal Ag–C–C angles of 70.0 (5) and 78.6 (5)° for Ag(1) and the Ag–C–C angles of 71.5 (5) and 76.9 (5)° for

(29) R. Daudel, R. Lefebvre, and C. Moser, "Quantum Chemistry," Interscience, New York, N. Y., 1959, p 242.

(30) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961, p 330.

(31) V. Gold and F. L. Tye, *J. Chem. Soc.*, 2172, 2184 (1952).

(32) K. Fukui, A. Imamura, T. Yonezawa, and C. Nagata, *Bull. Chem. Soc. Jap.*, 34, 1076 (1961).

Ag(2). This type of asymmetry in which the shortest Ag–C distance is 2.47 ± 0.02 Å is usually observed in Ag(I)–aromatic complexes while the longer Ag–C distance may be as much as 2.7 Å regardless of stoichiometry, anion, or packing considerations.

The anthracene molecule is planar well within experimental error, and the bond distances and angles are not too dissimilar from that of the free molecule.[33,34] The largest distortion from that of the free molecule is the elongation of the C(2)–C(3) distance from 1.418 Å in free anthracene (measured at 290°K)[34] to 1.487 (12) Å in this complex. Since this is of the order of seven–eight standard deviations, it appears that the distortion is real. While the explanation for this ring distortion is not readily apparent, it should be noted that the distortion is of the same type and in the same direction as the distortion in bis(cyclohexylbenzene)(silver perchlorate).[5] In both cases the C–C bonds adjacent to the carbon of the "longer" Ag–C interaction have been elongated. In the anthracene case, both C(2) and C(3) are the carbons associated with a "long" Ag–C interaction, and the C(2)–C(3) bond shows a much greater distortion. It is unfortunate that comparison with benzene-(silver perchlorate)[3] is impractical because of the disorder in the silver positions and the magnitude of the errors in the C–C bonds in both the *m*-xylene[6] and the *o*-xylene[7] structures preclude an analysis of ring distortion. Similar difficulties exist in most of the other known structures. It is obvious that an adequate explanation of the reason for ring distortion in Ag–aromatic complexes will have to wait until more evidence is available in terms of structures of silver complexes with polysubstituted aromatics.

(33) D. W. J. Cruickshank and R. Sparks, *Proc. Roy. Soc., Ser. A*, **258**, 270 (1960).
(34) R. Mason, *Acta Crystallogr.*, **17**, 547 (1964)

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**Supplementary Material Available.** A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-74-5407.

# Pentaammineruthenium–Guanine Complexes

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**Abstract:** The synthesis of several pentaammineruthenium(II and III)–guanine complexes is reported, in which the metal is believed to be bound to $N_7$. The Ru(III) compounds exhibit a broad low energy guanine-to-metal charge-transfer absorption, while the Ru(II) complexes show a metal-to-ligand charge transfer in the ultraviolet. The effect of Ru(II and III) on the acidity of the protons at $N_1$ and $N_9$ is investigated. Electrochemical potentials are reported for the complexes over a broad pH range. At low pH the Ru(III) nucleoside complexes undergo acid-catalyzed hydrolysis of the sugar–purine bond at a much slower rate than do the corresponding free nucleosides.

The interaction of metal ions with nucleotides has been the subject of considerable investigation for the past several years.[1] Areas of interest include: the effect of metal ions on the stability of nucleic acids,[2,3] synthesis of heavy-atom derivatives as aids in determining the structure of RNA by X-ray crystallography,[4] the participation of metal ions in the biological function of nucleic acids,[5] the use of heavy metal derivatives of nucleosides as cytological stains,[6] and the sequencing of nucleic acids by electron microscopy with the aid of a metal ion complex binding selectively to sites along the polynucleotide chain.[7,8]

Ruthenium is a sufficiently heavy atom to be of use in studies of structure by X-ray and electron microscopy. The aquopentaammineruthenium(II) ion shows a unique selectivity for heterocyclic nitrogen bases. This property has made it possible for us to synthesize a number of purine complexes with a ruthenium ammine species bound to the N-7 site (Figure 1). These complexes are substitution inert for ruthenium in both the 2+ and 3+ oxidation states. This feature simplifies the results and prepares the way for a systematic study of the effect of both a di- and tripositive metal ion on the purine moiety.

## Experimental Section

**Chemicals and Reagents.** Chloropentaammineruthenium(III) chloride was prepared by refluxing hexaammineruthenium(III) chloride, obtained from Matthey Bishop, Inc., in 6 *M* HCl for 4 hr followed by crystallization from 0.1 *M* HCl.[9] The compounds 1-methylguanosine and 2′-deoxy-1-methylguanosine were prepared by methylating the corresponding ribosides (Aldrich Chemical Co.)

(1) R. M. Izatt, J. J. Christensen, and J. H. Rytting, *Chem. Rev.*, **71**, 439 (1971).
(2) G. L. Eichhorn, *et al.*, *Advan. Chem. Ser.*, **No. 100**, 135 (1971).
(3) G. L. Eichhorn, E. Tarien, and J. Butzow, *Biochemistry*, **10**, 2014 (1971).
(4) S. H. Kim, G. J. Quigley, F. L. Suddath, A. McPherson, D. Sneden, J. J. Kim, J. Weinzierl, and A. Rich, *Science*, **179**, 285 (1973).
(5) W. Szer and S. Ochoa, *J. Mol. Biol.*, **8**, 823 (1964).
(6) R. J. Barrnett, *J. Roy. Microsc. Soc.*, **83**, 143 (1964).
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(9) L. H. Vogt, J. L. Katz, and S. E. Wiberly, *Inorg. Chem.*, **4**, 1158 (1965).