Metal Ion–Aromatic Complexes. XVIII. The Preparation and Molecular Structure of Naphthalene–Tetrakis(silver perchlorate) Tetrahydrate

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Abstract: Naphthalene–tetrakis(silver perchlorate) tetrahydrate, $C_{10}H_8(AgClO_4)_4 \cdot 4H_2O$, has been prepared and its crystal structure determined by three-dimensional X-ray diffraction techniques from 1796 reflections measured with an automatic diffractometer at ambient room temperature. The crystals are triclinic $P\bar{1}$, $Z = 1$, $\rho_{calcd} = 2.81$ g cm^{-3}, $\rho_{obsd} = 2.8$ g cm^{-3}, with reduced cell constants $a = 7.298$ (1) Å, $b = 11.870$ (1) Å, $c = 7.166$ (1) Å, $\alpha = 91.86$ (1)°, $\beta = 100.53$ (1)°, and $\gamma = 102.38$ (1)°. The A-centered cell, $a = 11.870$ (1) Å, $b = 9.247$ (1) Å, $c = 11.123$ (1) Å, $\alpha = 88.93$ (1)°, $\beta = 96.88$ (1)°, and $\gamma = 101.21$ (1)°, was used for the structure solution and refinement by full-matrix least squares including anisotropic temperature factors for all nonhydrogen atoms to a final R of 0.061. The crystal structure is comprised of parallel series of sheets in the order of –aromatic–$AgClO_4$–water–water–$AgClO_4$–aromatic–. The $AgClO_4$ sheets are made up to two $AgClO_4$ chains held together by weak Ag–O interactions and van der Waals forces. Each silver in the chains is strongly bonded to a water of hydration and all of the water molecules are oriented such that a bimolecular layer between $AgClO_4$ sheets is formed. The aromatic sheet consists of a staggered array in which the long symmetry axis of the naphthalene molecule is parallel to b, but the short symmetry axis is tilted 60° relative to the ab plane. Each naphthalene is associated with four different hydrated silver ions with equal Ag–C bonds of 2.61 (1) Å to each of the α,β positions. This Ag–C distance is unusually long compared to the expected value of 2.47 Å and the structure might be best described as a naphthalene clathrate in a hydrated silver perchlorate host lattice.

Single-ring aromatics were known to form 1:1 complexes with silver ions as early as 1920,[2–4] but the first single-crystal studies of benzene·$AgClO_4$[5] and benzene·$AgAlCl_4$[6] were published nearly 40 years later. There was extensive solution evidence for complexes of the type $AgAr_2^+$ with single-ring aromatics during the intervening years, and the single-crystal structural studies of bis(cyclohexylbenzene)silver perchlorate,[7] bis(*m*-xylene)silver perchlorate,[8] and bis(*o*-xylene)silver perchlorate[9] have now appeared in the literature. Another completed structure which formally conforms to the $AgAr_2^+$ type is that of (1,2-diphenylethane)silver perchlorate.[10]

The extensive solubility studies of Andrews and Keefer, as reviewed by Andrews,[11] led to the postulate that water soluble complexes of the types $AgAr^+$ and Ag_2Ar^{2+} were in equilibrium and that the contribution of the disilver complex was sufficiently small in most cases that it could be neglected in the calculation of an overall argenation equilibrium constant. A molecular orbital theoretical treatment[12] of the electronic requirements of silver–aromatic hydrocarbon complexes indicated that coordination with silver cations may take place at more than one position provided that the second silver attacks a hydrocarbon position sufficiently far from the first that there is no substantial electronic perturbation.

As part of a systematic study of the Ag(I)–aromatic interaction, it was deemed necessary to investigate the possibility of isolating polysilver complexes of the type Ag_nAr^{n+}. Polycyclic or fused-ring aromatics might be expected to form such complexes more readily than single-ring systems since they are much larger, and any electron cloud perturbation introduced by the coordination of one silver ion would tend to be "diluted" by the size of the aromatic system. Accordingly, a study of the naphthalene silver perchlorate system was undertaken. Other fused-ring complexes in which structural studies have been completed include anthracene–tetrakis(silver perchlorate) monohydrate,[19] indene-silver perchlorate,[13a] acenaphthene–silver perchlorate,[13b] and acenaphthylene–silver perchlorate.[13b]

Andrews and Keefer[14] gave as the equilibrium constants for the argenation of naphthalene in aqueous solution at 25° the values of $K_1 = 3.08$ and $K_2 = 0.909$. Kofahl and Lucas[15] found values of $K_1 = 2.94$ and $K_2 = 0.91$ in aqueous potassium–silver nitrate solution at unit ionic strength and 25°. Peyronel and coworkers[16] report the isolation of a solid complex having the composition $2AgClO_4 \cdot$naphthalene. Consideration of the

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free-valence concept of electron density[17,18] would place the two silvers in such a complex at the α and α' positions, respectively.

Neither the 1:1 nor the 1:2 complexes have been isolated in the solid state in this laboratory, but rather a totally unexpected hydrated compound was obtained. A preliminary communication[19] has described the gross features of the complex, naphthalene–tetrakis(silver perchlorate) tetrahydrate. We present here the synthetic and structural details of this complex, which is one of a series of $AgClO_4$ complexes with fused-ring systems.

Experimental Section

Since the complex between toluene and silver perchlorate is stable only below 22.6° as established by Hill and Miller,[4] toluene was selected as the solvent of choice for reactions between solid aromatics and silver perchlorate. A saturated solution of wet silver perchlorate (a minute trace of water is added if anhydrous silver perchlorate is used) in toluene which corresponded to Hill's solution[2–4] of 50.3% silver perchlorate by weight, was used in each preparation. A saturated solution of naphthalene in toluene was added in equal volumes to the stock silver perchlorate–toluene solution and allowed to reach equilibrium before the addition of pentane to the cloud point. After standing overnight, colorless seed crystals were collected. The volume of the mother liquor was then reduced by one-third in a vacuum desiccator; additional pentane and seed crystals were added. After 2 days a number of colorless, hygroscopic, and light-sensitive rods appeared and were sealed in thin-walled glass capillaries for diffraction studies. The remaining crystalline material was used for chemical analysis. *Anal.* Calcd for $C_{10}H_8(AgClO_4)_4 \cdot 4H_2O$: Ag, 41.9. Found: Ag, 40.7. (Potentiometric titrations of silver–aromatic complexes are consistently low in silver content due to the persistent oil of decomposition and adsorbed aromatic.) A variable amount of oily decomposition product accompanied each preparation.

The crystals were aligned in the capillaries such that the long "c" axis was approximately parallel both to the capillary axis and to the axis of the goniometer head. Preliminary Weissenberg ($hk0$, $hk1 \cdots hk11$) and precession ($h0l$, $0kl$) photographic data showed that the crystals were triclinic[20] and that data would be more conveniently taken using the unconventional A-centered cell which approximates an orthogonal axial system more closely than does the primitive cell. Thus, the systematic absence for all hkl are $k + l = 2n + 1$ absent. A crystal ~0.2 × 0.4 × 0.8 mm was mounted about the needle axis and aligned on a Picker full-circle automatic diffractometer by variations of well-known techniques.[21,22] A least-squares fit to the χ, ϕ, and 2θ angles of 22 accurately centered nonaxial reflections was used in the determination of lattice constants. Using Mo Kα radiation (λ 0.71068 Å) the reduced cell constants for the primitive cell at room temperature were found to be a = 7.298 (1) Å, b = 11.870 (1) Å, c = 7.166 (1) Å, α = 91.86 (1)°, β = 100.53 (1)°, and γ = 102.38 (1)°. The A-centered cell, a = 11.870 (1) Å, b = 9.247 (1) Å, c = 11.123 (1) Å, α = 88.93 (1)°, β = 96.88 (1)°, and γ = 101.21 (1)°, was used for the structure solution and refinement and all subsequent tables and calculations refer to this cell. The calculated density for two molecules of naphthalene$(AgClO_4)_4 \cdot 4H_2O$ per cell is 2.81 g cm^{-3} while the experimental density, measured by flotation in bromoform, is slightly greater than 2.8 g cm^{-3}.

The intensities of 2800 independent hkl reflections were examined by the θ–2θ scan technique using Zr-filtered Mo Kα radiation at room temperature. All reflections in the independent octants, hkl, $\bar{h}kl$, $h\bar{k}l$, and $\bar{h}\bar{k}l$ to $2\theta = 60°$, were measured. Reflections in the layers $hk0 \cdots hk7$ were scanned for 68.7 sec and backgrounds were estimated by stationary counting for 20 sec at $2\theta \pm 1.15°$ from the peak maximum; for layers $hk8 \cdots hk14$ reflections were scanned for 74.8 sec and background taken at $2\theta \pm 1.25°$ from peak maximum. Integrated intensities were calculated assuming a linear variation in background from the function $I_{\text{net}} = I_{\text{scan}} - K(B_1 + B_2)$ where B_1 and B_2 are the background counts and K is 1.72 for $hk0 \cdots hk7$ and 1.87 for $hk8 \cdots hk14$. Reflections were considered to be absent if the integrated net intensity was less than $2[K^2(B_1 + B_2)]^{1/2}$ (2σ of background). Of the 2800 examined reflections 1796 were considered nonzero by this criterion. A standard reflection was measured after every ten reflections to ensure stability of operation, to monitor any crystal decomposition, and to provide a basis for the scaling of the data. Variation in the intensity of the standard reflection was in general within three standard deviations: $\sigma(I_{\text{net}}) = [I_{\text{net}} + K^2(B_1 + B_2)]^{1/2}$. However, at one point late in the data collection (the last 14% in Table I) the laboratory air-conditioning failed in the South Carolina summer and brought about significant crystal decomposition as indicated by a drop of 30% in the intensity of the standard peak. Since it would have been impossible to obtain a crystal with exactly the same size satellite (see below), the data collection was completed with this crystal and this latter section of data was scaled to the earlier data *via* the standard reflection. This procedure was justified by spot checking a number of reflections taken prior to decomposition and found to reproduce the raw intensity within a maximum variation of 8%, but the agreement of most of them was much better.

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 0.7° at the 3.7° takeoff angle, indicating a mosaic spread such that all the reflection (including that of an extremely small satellite) was counted during the scan. The 0.7° should not be interpreted as an absolute value of the mosaic spread since this quantity depends upon instrumental factors as well. The counting rate never exceeded 5000 counts/sec, and no attenuators were used.

Of a considerable number of crystals examined from different preparations, all had a propensity toward twinning and likewise all showed at least a small satellite reflection with each diffraction maximum. The stoichiometry indicated a sufficiently interesting structure that we proceeded nontheless. The existence of this satellite, the presence of the glass capillary, and the ever-present small amount of decomposition in these types of crystals as well as the modest linear absorption coefficient of 39.7 cm^{-1} with Mo Kα made us decide that an absorption correction would not be useful. However, 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. With two naphthalene$(AgClO_4)_4 \cdot 4H_2O$ moieties per unit cell the naphthalene molecules must lie on centers of symmetry 0, $^1/_2$, 0 and 0, 0, $^1/_2$ and the Ag and Cl atoms must be in two sets of general positions $\pm(x, y, z;\ x, {}^1/_2 + y, {}^1/_2 + z)$. The Ag and Cl atoms were located from a three-dimensional unsharpened Patterson[23] and with phases based upon these atoms all the other nonhydrogen atoms were located by standard heavy-atom methods. The structure was refined by full-matrix least squares,[24] including anisotropic temperature factors and with weights based on intensity statistics,[25] to yield a final R, weighted R, and standard error of an observation of unit weight of 0.061, 0.070, and 1.08,

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$$\omega = 1/\sigma^2$$

$$\sigma^2(F^2) = S/(\text{Lp})^2[I_{(\text{scan})} + K^2(B_1 + B_2) + (0.44I_{(\text{scan})})^2]$$

$$\sigma^2(F) = S/(\text{Lp})1/F[I_{(\text{scan})} + K^2(B_1 + B_2) + (0.44I_{(\text{scan})})^2]^{1/2}$$

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

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

Atom	x	y	z	Atom	x	y	z
Ag(1)	0.2423 (1)	0.0845 (1)	0.9983 (1)	O(2)	0.2673 (10)	0.5650 (12)	0.1138 (11)
Ag(2)	0.7485 (1)	0.6627 (1)	0.0172 (1)	O(3)	0.3850 (8)	0.5985 (11)	0.2914 (12)
Cl(1)	0.2675 (2)	0.5747 (3)	0.2397 (3)	O(4)	0.2198 (10)	0.7008 (12)	0.2517 (12)
Cl(2)	0.6912 (3)	0.4075 (3)	0.2965 (3)	O(5)	0.6362 (10)	0.2624 (10)	0.3229 (10)
C(1)	0.0472 (9)	0.6548 (13)	0.8931 (12)	O(6)	0.7921 (12)	0.4441 (15)	0.3761 (14)
C(2)	0.0191 (10)	0.7702 (12)	0.9482 (12)	O(7)	0.7165 (8)	0.4111 (10)	0.1782 (10)
C(3)	0.9728 (10)	0.7536 (13)	0.0631 (13)	O(8)	0.6199 (10)	0.5084 (11)	0.3096 (11)
C(4)	0.9505 (9)	0.6128 (12)	0.1143 (12)	O(9)	0.4363 (7)	0.8528 (9)	0.9629 (9)
C(5)	0.9768 (9)	0.4921 (11)	0.0541 (11)	O(10)	0.5539 (8)	0.6289 (9)	0.0610 (9)
O(1)	0.2020 (10)	0.4427 (12)	0.2784 (12)				

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ag(1)	47 (1)	121 (2)	92 (1)	1 (1)	7 (1)	18 (1)
Ag(2)	56 (1)	136 (2)	97 (1)	20 (1)	−3 (1)	−2 (1)
Cl(1)	46 (2)	97 (4)	50 (3)	9 (2)	−2 (2)	2 (3)
Cl(2)	63 (3)	107 (4)	58 (3)	19 (3)	14 (3)	7 (3)
C(1)	35 (9)	103 (16)	69 (14)	13 (9)	6 (9)	23 (12)
C(2)	54 (10)	81 (15)	56 (13)	13 (10)	6 (10)	18 (12)
C(3)	34 (9)	105 (17)	78 (15)	2 (9)	2 (10)	−23 (13)
C(4)	35 (8)	84 (15)	64 (13)	4 (9)	9 (8)	5 (11)
C(5)	28 (8)	69 (13)	49 (12)	14 (8)	3 (7)	7 (10)
O(1)	105 (11)	223 (20)	166 (19)	−60 (11)	−9 (11)	94 (16)
O(2)	121 (12)	207 (18)	96 (14)	28 (11)	43 (11)	3 (13)
O(3)	55 (8)	184 (16)	169 (17)	12 (9)	−32 (4)	−7 (13)
O(4)	104 (11)	196 (18)	150 (17)	62 (11)	5 (11)	−15 (14)
O(5)	140 (12)	131 (14)	118 (14)	20 (10)	60 (11)	40 (11)
O(6)	157 (16)	272 (24)	150 (19)	31 (15)	−90 (14)	−10 (17)
O(7)	85 (9)	146 (14)	100 (13)	16 (9)	49 (9)	8 (11)
O(8)	128 (12)	191 (17)	121 (14)	73 (12)	63 (11)	17 (13)
O(9)	58 (7)	118 (12)	78 (11)	10 (7)	32 (7)	11 (9)
O(10)	78 (8)	120 (12)	75 (11)	16 (8)	10 (8)	−6 (9)

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

respectively.[26] On the last cycle of refinement, the parameter shifts 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.[27a] The effects of anomalous dispersion were included in the structure factor calculations by addition to F_c;[28] the values for $\Delta f'$ and $\Delta f''$ for Ag and Cl were those given by Cromer.[27b] The final tabulation of observed and calculated structure factors is listed in Table Ia.[29] Unobserved data were not used in the structure refinement but are listed with the calculated structure factors in Table Ib.[29] Final atomic positional and thermal parameters are in Table II. Interatomic distances and angles and dihedral angles between normals to planes and their errors[30] were computed using the parameters and variance–covariance matrix from the last cycle of least squares and are listed in Table III. The root-mean-square components of thermal displacement are listed in Table IV. The least-squares plane[31] for the aromatic group is listed in Table V.

Description and Discussion

The crystal structure of naphthalene$(AgClO_4)_4 \cdot 4H_2O$ can be described as comprised of a parallel series of sheets in the order of aromatic–$AgClO_4$–water–water–$AgClO_4$–aromatic–. The naphthalene sheet consists of a staggered array in which the long symmetry axis of the fused rings is parallel to the b axis, but the short symmetry axis is tilted 60° relative to the ab plane to form a layer of aromatic entities parallel to b (Figure 1). Each naphthalene molecule sits upon a crystallographic center of symmetry and is symmetrically bonded to four silver atoms at each of the α,β positions (Figures 1 and 2). The orientation of the silver ions relative to the ring is in agreement with the predictions of Fukui, *et al.*,[12] based upon a molecular orbital charge transfer model. The C–C bond distances are not significantly different from those of the free molecule[32] nor from those observed in the molecular complexes, $(SbCl_3)_2 \cdot$naphthalene[33] and $Cr(CO)_3 \cdot$naphthalene.[34] A comparison of these distances is summarized in Table VI. The naphthalene entity is planar well within experimental error (Table V). The maximum deviation from the least-squares plane is only 0.020 (7) Å.

The $AgClO_4$ sheets, which are parallel to the bc plane, are made up of two $-Ag-OClO_2O-Ag-$ chains held together by weak Ag–O interactions and van der Waals forces. The two chains show only normal van der Waals interactions between them and are alternately shifted relative to one another along the chain direction which makes an angle of 50° with the ab plane of the crystal. Chain 1 has Ag–O distances of 2.59 (1) and 2.77 (1) Å and chain 2 of 2.65 (1) and 2.90 (1) Å.

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(26) $R = \Sigma\ ||F_o - |F_c||/\Sigma\ |F_o|$. Weighted $R = \{[\Sigma w(F_o - F_c)]^2/\Sigma wF_o^2\}^{1/2}$. Standard error $= [\Sigma w(F_o - F_c)^2]^{1/2}/(NO - NV)^{1/2}$. $NO = 1796$; $NV = 172$.

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Table III

Bond Lengths, Å			
Ag(1)–C(1)	2.610 (12)	Ag(1)–O(1)	2.773 (12)
Ag(1)–C(2)	2.599 (12)	Ag(1)–O(2)	2.589 (11)
Ag(2)–C(3)	2.622 (11)	Ag(1)–O(9)	2.338 (8)
Ag(2)–C(4)	2.631 (11)	Ag(2)–O(5)	2.648 (11)
		Ag(2)–O(7)	2.904 (10)
Cl(1)–O(1)	1.404 (10)	Ag(2)–O(10)	2.377 (9)
Cl(1)–O(2)	1.405 (12)		
Cl(1)–O(3)	1.421 (10)	C(1)–C(2)	1.356 (16)
Cl(1)–O(4)	1.407 (10)	C(2)–C(3)	1.444 (20)
Cl(2)–O(5)	1.415 (9)	C(3)–C(4)	1.402 (16)
Cl(2)–O(6)	1.390 (12)	C(4)–C(5)	1.416 (15)
Cl(2)–O(7)	1.383 (10)	C(5)–C(5′)	1.383 (18)
Cl(2)–O(8)	1.396 (10)	C(5′)–C(1)	1.462 (17)
Nonbonded Distances Less Than 4 Å			
Ag(1)–Cl(1)	3.414 (3)	Cl(1)–O(9)	3.822 (9)
Ag(1)–Cl(1′)	3.776 (3)	Cl(1)–C(4)	3.933 (11)
Ag(1)–O(3)	3.804 (12)	Cl(1)–C(5)	3.752 (11)
Ag(1)–O(4)	2.986 (13)	Cl(2)–O(9)	3.681 (9)
Ag(2)–Cl(2)	3.911 (4)	Cl(2)–O(10)	3.713 (10)
Ag(2)–Cl(2′)	3.406 (3)	C(1)–O(1)	3.260 (15)
Ag(2)–O(6)	3.004 (14)	C(1)–O(2)	3.574 (17)
Ag(2)–O(8)	3.888 (11)	C(2)–O(1)	3.217 (16)
Ag(2)–C(5)	3.373 (10)	C(2)–O(6)	3.407 (17)
O(1)–O(9)	3.479 (15)	C(3)–O(4)	3.505 (17)
O(3)–O(9)	3.045 (13)	C(3)–O(6)	3.506 (18)
O(2)–O(9′)	3.534 (13)	C(4)–O(1)	3.890 (17)
O(2)–O(10)	3.458 (14)	C(4)–O(2)	3.871 (15)
O(3)–O(10)	3.413 (16)	C(4)–O(4)	3.329 (16)
O(5)–O(9)	3.235 (13)	C(4)–O(6)	3.800 (20)
O(5)–O(10)	3.086 (14)	C(4)–O(7)	3.180 (14)
O(7)–O(10)	3.208 (13)	C(5)–O(1)	3.523 (16)
O(8)–O(9)	3.051 (13)	C(5)–O(2)	3.369 (16)
O(8)–O(10)	3.035 (15)	C(5)–O(4)	3.653 (17)
O(9)–O(10)	2.847 (12)	C(5)–O(7)	3.479 (14)
Angles (deg)			
C(5)–C(1)–C(2)	120.3 (7)	Ag(1)–C(2)–C(1)	75.4 (7)
C(1)–C(2)–C(3)	121.5 (11)	Ag(1)–C(1)–C(2)	74.5 (7)
C(2)–C(3)–C(4)	118.7 (11)	C(1)–Ag(1)–C(2)	30.2 (4)
C(3)–C(4)–C(5)	119.4 (11)	C(1)–Ag(1)–O(9)	136.9 (4)
C(4)–C(5)–C(5′)	112.1 (7)	C(2)–Ag(1)–O(9)	157.7 (4)
C(4)–C(5)–C(1)	119.4 (11)	C(1)–Ag(1)–O(1)	74.5 (3)
C(1)–C(5)–C(5′)	118.4 (11)	C(2)–Ag(1)–O(1)	73.5 (4)
		O(9)–Ag(1)–O(1)	85.3 (3)
O(1)–Cl(1)–O(2)	107.8 (8)	C(1)–Ag(1)–O(2)	86.9 (4)
O(1)–Cl(1)–O(3)	112.7 (7)	C(2)–Ag(1)–O(2)	102.7 (4)
O(1)–Cl(1)–O(4)	115.1 (8)	O(9)–Ag(1)–O(2)	91.5 (3)
O(2)–Cl(1)–O(3)	106.8 (8)	Ag(2)–C(3)–C(4)	74.9 (6)
O(2)–Cl(1)–O(4)	102.4 (7)	Ag(2)–C(4)–C(3)	74.2 (6)
O(3)–Cl(1)–O(4)	111.1 (7)	C(3)–Ag(2)–C(4)	30.9 (4)
O(5)–Cl(2)–O(6)	108.2 (8)	C(3)–Ag(2)–O(10)	154.6 (4)
O(5)–Cl(2)–O(7)	108.6 (6)	C(3)–Ag(2)–O(5)	119.2 (4)
O(5)–Cl(2)–O(8)	111.3 (7)	C(4)–Ag(2)–O(10)	139.8 (3)
O(6)–Cl(2)–O(7)	110.4 (8)	C(4)–Ag(2)–O(5)	144.6 (4)
O(6)–Cl(2)–O(8)	109.4 (8)	O(5)–Ag(2)–O(10)	75.6 (3)
O(7)–Cl(2)–O(8)	108.9 (7)		

Representative Dihedral Angles (deg)		
Cl(1)–Ag(1)–C(2)	O(1)–Ag(1)–O(9)	85.4 (7)
C(1)–Ag(1)–C(2)	O(2)–Ag(1)–O(9)	65.1 (7)
C(1)–Ag(1)–O(9)	C(2)–Ag(1)–O(1)	61.0 (5)
C(1)–Ag(1)–O(9)	O(1)–Ag(1)–O(9)	118.7 (5)
C(3)–Ag(2)–C(4)	O(5)–Ag(2)–O(10)	43.2 (8)
C(3)–Ag(2)–O(10)	C(3)–Ag(2)–O(5)	120.9 (8)
C(3)–Ag(2)–C(4)	C(3)–Ag(2)–O(10)	87.2 (10)
C(3)–Ag(2)–O(5)	C(4)–Ag(2)–O(5)	24.7 (6)

Inasmuch as the Ag–O single bond radius sum is 2.18 Å,[35] these Ag–O interactions must be considered to be weak and to have little individual effect on the stabilization of the complex. Their cumulative effect, however, must be to impart considerable stability. Of course, it is still a matter of some debate as to what a "normal" Ag–O distance should be. A number of Ag–O distances have appeared in the literature: 2.34 (5) Å for Ag_3PO_4[36] and Ag_3AsO_4,[37] 2.42 (2) Å for Ag_2MoO_4[38] and $KAgCO_3$,[39] 2.50 Å for Ag_2SO_4,[39] and 2.51 Å for $AgClO_3$.[39] The Ag–O distances of the chains are in contrast to the short Ag–O bond distance of 2.49 (1) Å observed in (*m*-xylene)$_2$·$AgClO_4$[8] and in anthracene $(AgClO_4)_4 \cdot H_2O$,[19] but in agreement with the distances reported for the $AgClO_4$ complexes of benzene,[5] cyclohexylbenzene,[7] and *o*-xylene.[9] The individual perchlorate ions show little evidence of distortion. The Cl–O bond distances range from 1.38 (1) to 1.42 (1) Å while the bond angles (Table III) approach the idealized value of 109° for a tetrahedron.

Conversely, the Ag–O interactions arising from the waters of hydration are of appreciable magnitude. Each silver of chain 1 is associated with the oxygen of a water molecule at 2.34 (1) Å and those of chain 2 at 2.38 (1) Å. All of the water molecules are oriented such that they form a bimolecular layer separating silver perchlorate sheets.

In this case it is extremely difficult to assign a formal coordination number to the silver atoms. Each silver is strongly bound to a molecule of water, less strongly bound (2.65 (1) or 2.59 (1) Å) to the oxygen of a perchlorate group, weakly associated (2.77 (1) or 2.90 (1) Å) with an oxygen of a second perchlorate group, and bonded to the π-electrons of an aromatic ring. If all four interactions are considered, the geometry about each silver atom is best described as a flattened tetrahedron.

It is significant that naphthalene$(AgClO_4)_4 \cdot 4H_2O$ is the first aromatic–Ag(I) complex reported in which the silver is symmetrically bonded to the two nearest carbon atoms. This symmetry is reflected in both the equal Ag–C distances of 2.61 Å average and in the Ag–C–C angles of 75°. Most other known aromatic–Ag(I) complexes[5–9,13,19] demonstrate asymmetry in the two nearest metal–carbon distances with the shorter Ag–C distance of 2.47 (2) Å as a common feature, regardless of stereochemistry, nature of aromatic, stoichiometry, or anion present. A possible exception to this common asymmetry is observed in the structure of acenaphthene·$AgClO_4$,[13b] where each of the two independent silver atoms interacts with two aromatics related by a mirror plane. There the silver–carbon interactions are described by pairs of distances of 2.44 and 2.51 Å and 2.48 and 2.51 Å, respectively, with Ag–C–C angles ranging from 71 to 77°.

It is tempting to consider the structure of naphthalene$(AgClO_4)_4 \cdot 4H_2O$ in terms of a clathrate in which the aromatic is a guest in the water and $AgClO_4$ host lattice. Such a view is lent credence by the unprecedented long Ag–C distance but cannot be verified by comparison with the crystal lattice of hydrated silver perchlorate since this structure is not well known. It would seem more logical to view this molecular complex as an extreme case, but still related to all the other Ag(I)–aromatic complexes known.

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(36) L. Helmholz, *J. Chem. Phys.*, **4**, 316 (1936).

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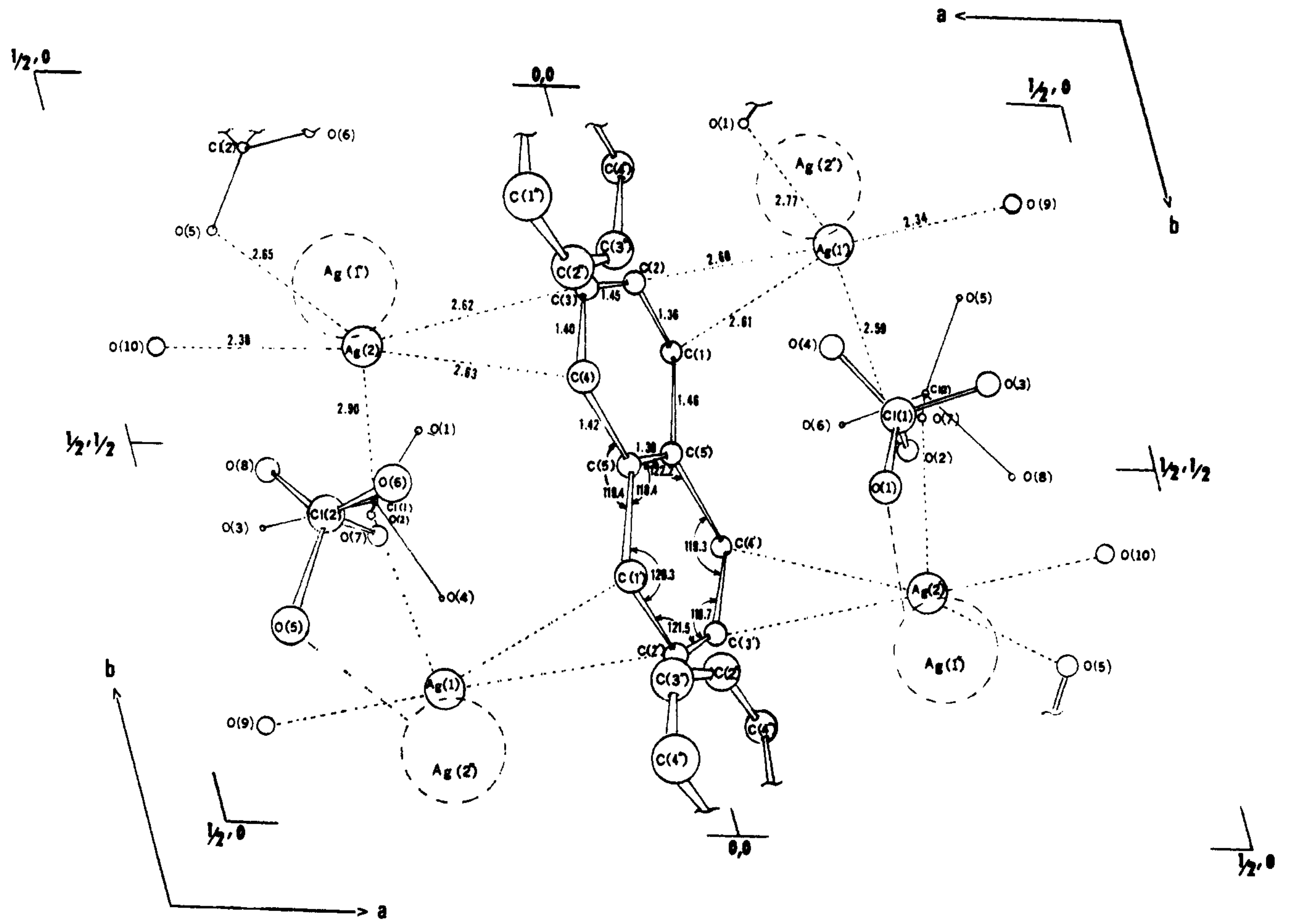

Figure 1. A perspective view of the structure of naphthalene–tetrakis(silver perchlorate) tetrahydrate down the *b* axis showing the sheets and the molecular interactions. The silver atoms represented by large dotted circles are at $z = {}^1/_2$, while the small solid circles represent silver atoms at $z = 0$. A chain of $AgClO_4$ is Cl(2)–O(5)–Ag(2)–O(7)–Cl(2)–O(5)–Ag(2). The hydrate sheets are composed of O(9) and O(10). A crystallographic center of symmetry is midway between C(5) and C(5').

Table IV. Rms Component of Thermal Displacement along Principal Axes (A) (esd in parentheses)

Atom	1	2	3	Atom	1	2	3
Ag(1)	0.174 (2)	0.216 (2)	0.257 (2)	O(2)	0.213 (16)	0.294 (13)	0.303 (15)
Ag(2)	0.190 (2)	0.238 (2)	0.252 (2)	O(3)	0.172 (15)	0.281 (12)	0.344 (16)
Cl(1)	0.163 (6)	0.188 (5)	0.205 (4)	O(4)	0.228 (13)	0.289 (16)	0.321 (15)
Cl(2)	0.181 (5)	0.204 (4)	0.217 (5)	O(5)	0.188 (15)	0.265 (14)	0.335 (15)
C(1)	0.154 (19)	0.177 (19)	0.234 (19)	O(6)	0.192 (20)	0.338 (15)	0.426 (19)
C(2)	0.160 (21)	0.191 (18)	0.209 (20)	O(7)	0.178 (15)	0.249 (12)	0.286 (15)
C(3)	0.148 (20)	0.193 (20)	0.241 (18)	O(8)	0.194 (15)	0.264 (13)	0.342 (15)
C(4)	0.149 (18)	0.189 (17)	0.201 (21)	O(9)	0.159 (14)	0.226 (11)	0.241 (14)
C(5)	0.131 (19)	0.162 (20)	0.182 (20)	O(10)	0.211 (15)	0.226 (12)	0.234 (12)
O(1)	0.182 (15)	0.271 (16)	0.431 (16)				

Table V. Least-Squares Plane[a]

Atom	Deviation from plane (Å)
C(1)	0.014 (7)
C(2)	−0.020 (7)
C(3)	0.013 (7)
C(4)	0.001 (6)
C(5)	−0.006 (6)

[a] $Ax + By + Cz - D = 0$ where *x*, *y*, and *z* refer to an internal coordinate system. See J. S. Rollett, "Computing Methods in Crystallography," Pergamon Press, New York, N. Y., 1965, p 22. The esd's for the positional parameters of individual atoms were used as weights.

In the general case, if the silver behaves as an electron acceptor from the aromatic, utilizing a 5s, 5p, or some hybrid orbital thereof, the best position for the metal ion is in the π-cloud above one of the carbon atoms of the ring.[40] If metal → aromatic back-donation is more important,[41] then the best overlap between filled metal "d" orbitals and the antibonding π* molecular orbital of the aromatic is achieved with the metal located in the π-cloud equidistant between two carbon atoms of the

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(41) M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, **18**, C.71 (1951).

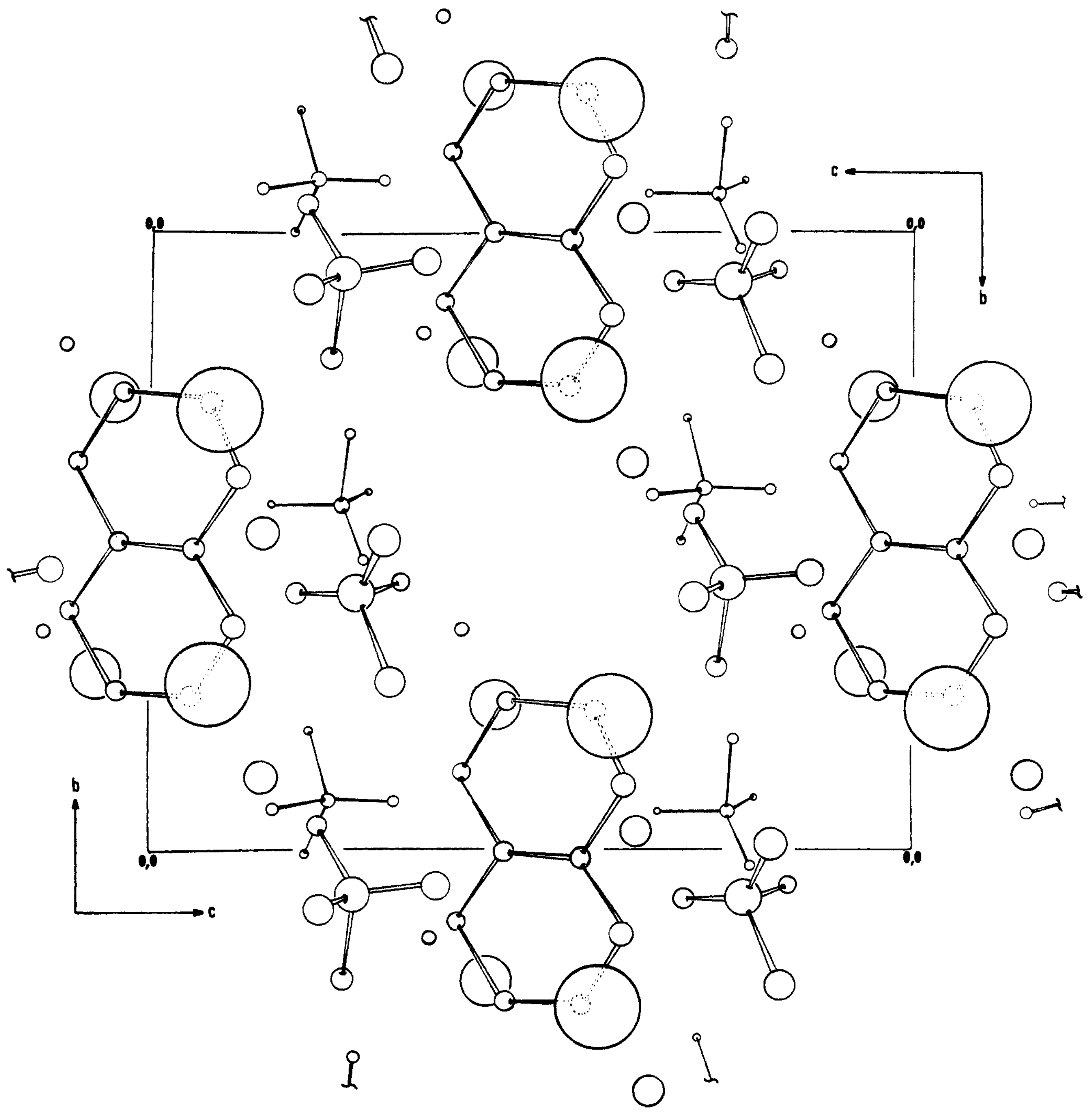
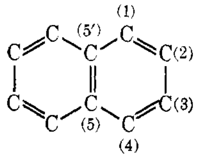


Figure 2. A perspective view of the packing diagram of naphthalene–tetrakis(silver perchlorate) tetrahydrate down the *a* axis of the crystal. The centers of the naphthalene molecules lie upon crystallographic centers of symmetry.

Table VI. Bond Distances for Naphthalene and Its Molecular Complexes



Bond	A[a]	B[b]	C[c]	D[d]	D′[e]
C(5′)–C(1)	1.462 (17)	1.421 (8)	1.420 (12)	1.438 (30)	1.404 (30)
C(1)–C(2)	1.356 (16)	1.364 (5)	1.313 (16)	1.375 (30)	1.389 (30)
C(2)–C(3)	1.444 (20)	1.415 (5)	1.343 (18)	1.392 (30)	1.375 (30)
C(3)–C(4)	1.402 (16)	1.364 (5)[f]	1.421 (17)	1.415 (30)	1.383 (30)
C(4)–C(5)	1.416 (15)	1.421 (8)[f]	1.440 (12)	1.406 (30)	1.447 (30)
C(5)–C(5′)	1.383 (18)	1.418 (5)	1.425 (14)	1.439 (30)	1.439 (30)

[a] A, these results. [b] B, free naphthalene.[32] [c] C, $(SbCl_3)_2$·naphthalene.[33] [d] D, $Cr(CO)_3$·naphthalene,[34] Cr–C bonded ring. [e] D′, $Cr(CO)_3$·naphthalene, Cr nonbonded ring. [f] Refers to crystallographically related position.

ring. Since most of the known silver–aromatic interactions are asymmetric with the shorter Ag–C distance invariant at 2.47 Å, it appears that a back-donation interaction is generally of lesser importance.

In the case of naphthalene$(AgClO_4)_4 \cdot 4H_2O$ there is one large and new perturbing effect which has been added to the electronic environment of the system. It may be that the water of hydration has altered the electronic requirements of the silver ion such that the hydrated silver ion is no longer as good an electron acceptor and may be considered to be a weaker Lewis acid than the free silver ion. Hence, back-donation in this case becomes more important relative to the overall Ag–π interaction. It might be more logical to consider the 2.52 (1) Å distance from the silver to the midpoint of the nearest C–C bond as a more accurate measure of the Ag–π interaction rather than the Ag–C distance of 2.61 (1) Å.

It is interesting to note that for anthracene$(AgClO_4)_4 \cdot H_2O$[13] each water of hydration is associated with two silver ions and relatively little perturbing effect upon the "normal" asymmetric Ag–C interaction is observed.

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Supplementary Material Available. Table I, 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-74-743.

Unusual Structural and Magnetic Resonance Properties of Dicyclopentadienylhexacarbonyldichromium

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Abstract: The proton nmr spectra at various temperatures and in solvents of varying polarity have shown that the title compound, **1**, exists as a solvent- and temperature-dependent mixture of anti and gauche rotamers. The barrier to internal rotation ($\Delta G_{298}^{\ddagger}$) is 12.1 ± 0.7 kcal mol^{-1}, which is substantially lower than that in the molybdenum analog, **2**. Marked line broadening, which is reversible, in **1** occurs at temperatures above about $-10°$; presumably some paramagnetic state or species become populated. In order to obtain structural data bearing on these anomalies in the solution properties of **1**, its structure was determined X-ray crystallographically. It is essentially isomorphous with **2**, as expected, belonging to space group $P2_1/c$, with $Z = 2$ and $a = 10.468$ (1) Å, $b = 7.625$ (1) Å, $c = 12.227$ (2) Å, and $\beta = 127.22$ (1)°. The molecule has a crystallographic center of symmetry and has virtual symmetry of C_{2h}. Using 1269 reflections with intensities exceeding three times their estimated standard deviations the structure was refined to discrepancy indices (defined in the usual way) of $R_1 = 0.027$ and $R_2 = 0.033$. Hydrogen atoms were refined isotropically and all other atoms anisotropically. The Cr–Cr distance, 3.281 (1) Å, is far longer than would be expected for an unstrained single bond; it is actually about 0.06 Å longer than the Mo–Mo bond in **2**. There is other evidence of internal steric strain. Reasons for the long Cr–Cr bond and its bearing on other molecular properties are discussed.

Among the great variety of intramolecular rearrangements which have been shown to be the basis for stereochemical nonrigidity in organometallic[1] and metal carbonyl[2] type molecules, one that is of general importance is hindered rotation about metal–metal bonds. This process plays a key role in the rearrangements of certain binuclear metal carbonyl species.[2]

We recently reported a quantitative study of the equilibrium and kinetic aspects of internal rotation in $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6$,[3] in which it was shown that the molecule exists as a mixture of *anti* and *gauche* rotamers, with the equilibrium ratio strongly dependent on solvent polarity. The barrier to internal rotation (~15 kcal/mol) was evaluated from nmr line shape variation over a temperature range.

The results of that investigation raised certain questions pertaining to the nature of the forces causing the barrier and to how the magnitude of the barrier would vary on changing the metal atoms from Mo to Cr. An nmr study of $(\eta^5\text{-}C_5H_5)_2Cr_2(CO)_6$ was therefore undertaken. When the nmr results were found to be different from what might naively have been expected, it was considered worthwhile to conduct an X-ray crystallographic investigation of the structure as well. The results of both phases of the study are reported and discussed here.

Experimental Section

The compound was prepared according to the procedure of King and Stone,[4] and recrystallized from toluene at $-20°$.

Nmr Spectra. Samples were prepared by placing the solid compound, under nitrogen, in nmr tubes closed with serum stoppers. Vacuum degassed solvents were then introduced with a syringe.

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(2) R. D. Adams and F. A. Cotton, *J. Amer. Chem. Soc.*, **95**, 6589 (1973), and references cited therein.

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