In both cases the decomposition path appears to be successive loss of all ligands to produce an M_3^+ ion. This pattern is like that observed[46] for $Os_3(CO)_{12}$ and $Ru_3(CO)_{12}$ and is quite common for second- and third-row transition metal clusters. A large number of doubly charged ions are observed in the mass spectrum of **4**; this behavior is also seen with $Os_3(CO)_{12}$[46] and reflects the greater stability of third-row transition element clusters toward oxidation.

Both **1** and **4** display strong $M_3(NO)^+$ peaks and in general lose CO in preference to NO. This observation is in accord with experience on mononuclear nitrosyl carbonyls[46,47] and suggests that the nitrosyl ligand is more tightly bound. Indeed, in the case of $Ru_3(CO)_{10}(NO)_2$, Ru_2N^+ (but not Ru_2C^+) is observed after the cluster begins to fragment.

The mechanism of loss of the first nitrosyl ligand appears to vary somewhat between **1** and **4**. In the mass spectrum of $Ru_3(CO)_{10}(NO)_2$, ions below $Ru_3(CO)_6(NO)_2^+$ begin to display NO loss in competition with further CO loss; for $Os_3(CO)_{10}(NO)_2$ the same pattern begins with $Os_3(CO)_8(NO)_2^+$. However, with the osmium cluster a peak ($^{192}Os_3(CO)_8(NO)C^+$ or $^{192}Os_3(CO)_9N^+$) is observed at *m/e* 842—far higher than other deoxygenated fragments, which do not appear until nearly all ligands are gone from the cluster. This observation suggests that some nitrogen is lost as NO_2 from $Os_3(CO)_9(NO)_2^+$.

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Metal Ion–Aromatic Complexes. XII. The Crystal and Molecular Structures of Acenaphthenesilver Perchlorate and Acenaphthylenesilver Perchlorate

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The crystal and molecular structures of acenaphthenesilver perchlorate and acenaphthylenesilver perchlorate have been determined by single-crystal X-ray diffraction from counter-measured intensities at room temperature. Crystals of acenaphthenesilver perchlorate were found to be orthorhombic: a = 18.531 (2) Å, b = 15.586 (5) Å, c = 7.877 (3) Å; space group *Pmnb*, Z = 8. The structure was refined to a conventional R factor of 0.074 by full-matrix least-squares methods based upon 1236 independent reflections. The structure may be described in terms of one-dimensional infinite chains of $AgClO_4$ with the aromatic groups lying on either side of the chain. The Ag–O interactions range from 2.34 to 2.46 Å (±0.02 Å or less). The Ag–C distances are all "short" at 2.44–2.51 Å (±0.01 Å). Crystals of acenaphthylenesilver perchlorate were found to be orthorhombic: a = 6.416 (1) Å, b = 10.286 (2) Å, c = 18.056 (2) Å; space group $P22_12_1$, Z = 4. Disorder and large thermal motions limited the accuracy of this structure determination and full-matrix least-squares refinement converged to a conventional R of 0.20 with 547 independent reflections. The structure consists of one-dimensional chains of alternating aromatic and perchlorate groups and is different from the structure found for acenaphthenesilver perchlorate. The five-membered ring is not involved in bonding to the silver atom.

Introduction

The crystal and molecular structures of a number of complexes between Ag(I) and aromatic moieties have now been determined. These structures cover a wide range of stoichiometries but yet have some common features. $(Aryl)_2Ag^IClO_4$ complexes are formed with cyclohexylbenzene[1] and *o*-,[2] *m*-,[3] and *p*-xylenes.[4] Unfortunately, the last structure is badly disordered and little useful information can be derived from its crystal structure analysis. However, (cyclohexylbenzene)$_2$-$AgClO_4$ and (m-xylene)$_2AgClO_4$ are composed of sheets or chains of $AgClO_4$ in which each Ag(I) is bound to two aromatic entities, one on either side of the chain or sheet such that each silver has two close Ag–C distances at 2.47 ± 0.02 Å. The coordination polyhedron of silver is completed by Ag–O interactions. The next nearest Ag–C distance can vary over wide limits up to the 2.96 Å observed in $C_6H_6 \cdot AgAlCl_4$.[5] On the other hand, a discrete dimer is observed for (o-xylene)$_2AgClO_4$ with Ag–O–Ag bridges and the distorted tetrahedral geometry of Ag(I) is completed by interaction with the aromatic moieties at the usual 2.47 Å distance. One to one stoichiometries are also observed in $C_6H_6 \cdot AgClO_4$,[6] dibenzyl·$AgClO_4$,[7] and indene·$AgClO_4$,[8] but in spite of different coordination numbers and Ag–O distances the common 2.47-Å nearest Ag–C distance persists. Higher ratios of silver to aromatic moieties have been found in naphthalene·$4AgClO_4 \cdot 4H_2O$[9] and anthracene·$4AgClO_4 \cdot H_2O$.[9] Only the naphthalene

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structure does not contain the 2.47-Å Ag–C distance and, in fact, this particular structure could also be described as a clathrate. In contrast to the above aromatics, toluene does not form a stable room-temperature adduct with silver perchlorate.

To further probe the relative importance of steric, anionic, and π-electronic effects in aromatic–silver perchlorate complexes, the study of acenaphthene·$AgClO_4$ and acenaphthylene·$AgClO_4$ was initiated. It is to be noted that acenaphthene and acenaphthylene differ from naphthalene by the replacement of two α hydrogens by a saturated and unsaturated five-membered ring, respectively. The presence of these five-membered rings should make the formation of $4AgClO_4 \cdot 1$(aromatic) more difficult than with naphthalene. In addition, the five-membered unsaturated ring in acenaphthylene presents an alternative binding site for the metal ion as well as affecting the π-electron density in the six-membered rings.

Experimental Section

Acenaphthenesilver Perchlorate.—Anhydrous silver perchlorate was dissolved in toluene to form a saturated solution. This was added to a saturated solution of acenaphthene in toluene in an anhydrous environment. As the toluene evaporated clear, colorless, diffraction-quality crystals were obtained. *Anal.* Calcd for acenaphthene·$AgClO_4$: Ag, 29.9. Found: Ag, 29.6. Due to their reactivity toward water vapor, the crystals were mounted in thin-walled glass capillaries with the "c" axis approximately parallel to the capillary axis. Preliminary oscillation and Weissenberg data, $hk0$, $hk1$–$hk7$, showed the crystals to be orthorhombic, with the systematic absences, $h0l$, $h + l = 2n + 1$; $hk0$, $k = 2n + 1$. Thus, the space group is $Pmnb$ (nonstandard setting of space group no. 62, $Pnma$) or the noncentric $P2_1nb$ (nonstandard setting of space group no. 33, $Pna2_1$).[10] The crystal was aligned on a Picker full-circle, four-angle card programmed, automatic diffractometer by variations of well-known techniques.[11] A least-squares fit of the χ, ϕ, and 2θ angles of 32 reflections accurately centered on the diffractometer were used to determine the lattice constants at ambient room temperature (λ 0.71068 Å for Mo Kα): $a = 18.531$ (2) Å, $b = 15.586$ (5) Å, $c = 7.877$ (3) Å. For $Z = 8$, the calculated density is 2.11 g cm^{-3}. The observed density was 2.10 (1) g cm^{-3} found by flotation methods in a halocarbon solution. A crystal $\sim$0.19 × 0.36 × 0.61 mm mounted as described above (0.61 mm = c) was used to collect the intensity data. The linear absorption coefficient (μ) was calculated to be 26.0 cm^{-1} with Mo Kα radiation. With this μ and the above crystal dimensions the maximum variation in transmission coefficient was found to be 0.43–0.62.[12] No absorption corrections were made. A total of 2600 independent hkl reflections were measured by the θ–2θ scan technique to $2\theta = 60°$ with unfiltered Mo Kα[13] radiation at room temperature for 84 sec at 0.0167°/sec and background counts were made for 20 sec (B_1 and B_2) at ±0.70° in 2θ of the peak maxima, $I(\text{net}) = [I(\text{sum}) - 2.102(B_1 + B_2)]$. Reflections were considered absent if the integrated intensity was less than $2.5[2.102 \cdot (B_1 + B_2)^{1/2}]$. By this criterion 1236 reflections were retained. A standard reflection was measured every tenth reflection to ensure stability of operation and to monitor any crystal decomposition. The total variation in the intensity of the standard reflection was less than 3% of the net intensity while the variation from one measurement of the standard reflection to the next was well within the counting statistics, $\sigma[I(\text{net})] = [I(\text{sum}) + (2.102)^2(B_1 + B_2)]^{1/2}$. The intensities of several symmetry-related reflections were recorded and the variation of intensity from one reflection to its symmetry-related one was less than 3% of the total integrated intensity. The half-width at half-peak-height for an average reflection was 0.18° at a takeoff angle of 3.7° indicating a mosaic spread such that all the reflection is counted during the 1.4° scan. The 0.18° is not an absolute value of the mosaic spread but is dependent upon other instrumental factors as well.

Acenaphthylenesilver Perchlorate.—Anhydrous silver perchlorate was added as a saturated solution in toluene to a saturated solution of acenaphthylene in toluene in an anhydrous environment. Clear, colorless, diffraction-quality crystals were formed as the toluene evaporated. The crystals were not obtained in sufficient quantity for chemical analysis. Due to their reactivity toward moisture the crystals were sealed in thin-walled capillaries with the "c" axis approximately parallel to the capillary axis. Preliminary Weissenberg and precession photographic data, $hk0$, $hk1$–$hk9$, $hk10$, $0kl$, showed the crystals to be orthorhombic with the systematic absences $0k0$, $k = 2n + 1$ and $00l$, $l = 2n + 1$, uniqly determining the space group as $P22_12_1$ (the nonstandard setting of space group no. 18, $P2_12_12$).[14] A crystal 0.38 × 0.41 × 0.84 mm (c = 0.84 mm) mounted as described above was used to collect the intensity data. The crystal was aligned as was acenaphthene·$AgClO_4$. A least-squares fit of the χ, ϕ, and 2θ angles of 14 reflections was used to determine the room-temperature lattice constants (λ 0.71068 Å for Mo Kα): $a = 6.416$ (1) Å, $b = 10.286$ (2) Å, $c = 18.056$ (2) Å; with $Z = 4$ the calculated density is 2.00 g cm^{-3} and the measured density is 1.9–2.2 g cm^{-3}. Acenaphthylene·$AgClO_4$ undergoes decomposition in halocarbon solvents—thus, the range in density. A total of 1900 independent hkl reflections were measured by the θ–2θ scan technique to $2\theta = 60°$ with unfiltered Mo Kα radiation[13] at room temperature for 65 sec at 0.0167°/sec and background counts were measured for 20 sec (B_1 and B_2 at ±0.54° in 2θ of the peak maxima, $I(\text{net}) = I(\text{sum}) - 1.65(B_1 + B_2)$. Reflections were considered absent if the integrated intensity was less than $1.5[1.65(B_1 + B_2)^{1/2}]$. A total of 547 intensities were retained by this criterion. A standard reflection was measured every tenth reflection to ensure stability of operation and to monitor any crystal decomposition. The total variation in the standard reflection during data collection was less than 5% of the net intensity while the variation from one measurement of the standard reflection to the next was well within counting statistics: $\sigma[I(\text{net})] = [I(\text{sum}) + (1.65)^2 \cdot (B_1 + B_2)]^{1/2}$. The intensities of several symmetry-related reflections were recorded and the variation of intensity from one to another was less than 5% of the integrated intensity. The half-width at half-peak-height for an average reflection was 0.14° at a 3.7° takeoff angle. The linear absorption coefficient (μ) was calculated to be 18.7 cm^{-1} with Mo Kα radiation. With this μ and the above crystal dimensions the maximum variation in transmission coefficient[12] was found to be 0.48–0.53. No absorption corrections were made.

For both data sets, the takeoff angle, source-to-crystal distance, and crystal-to-counter distance were 3.7°, 18 cm, and 23 cm, respectively. The receiving aperture at the counter was 6 mm wide and 8 mm high. The counting rate never exceeded 5000 counts/sec and, thus, no attenuators were used. Lorentz–polarization corrections were made to reduce the intensities

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(11) (a) W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **22**, 457 (1967); (b) K. Knox in "Master Card Program for Picker Four-Angle Programmer," prepared by F. C. Carter, Picker Instruments, Cleveland, Ohio, 1967, p 11.

(12) Transmission coefficients computed with local variation of GONO-9 originally written by W. C. Hamilton, Brookhaven National Laboratory, Upton, N. Y. This program was not operating to our satisfaction at the time of data collection and structure solution. After solution, in view of the disorder, it was not considered profitable to make the complete absorption correction. Although the variation 0.43–0.62 is large, it must be borne in mind that these are the extremes and frequently those reflections represented by these values suffer from other errors as well. Furthermore, 80–90% of the data usually fall within much narrower limits.

(13) The use of unfiltered radiation is unconventional and upsetting to referees. However, with care and consideration of various factors such as cell dimensions, width of peaks, etc., a gain in intensity of almost a factor of 2 over Zr-filtered radiation can be accomplished. Particular care needs to be exercised for axial and $hk0$, $0kl$, $h0l$ zonal reflections. In addition, Zr-filtered radiation gives an incorrect low-angle background. A Nb filter is better, but in our experience, not good enough. We generally examine preliminary diffraction data for each crystal to decide whether or not the unfiltered technique can be used profitably. In addition, Mo Kβ contributions from very intense Mo Kα reflections to other reflections are computed and subtracted out. This procedure has been shown to work well. For example, four structures of air-stable, well-formed crystals (the only types of crystals to really compare) refined to R factors of 0.035–0.056 with commensurate esd's and have been published. The limited agreement in the present structure is mainly determined by the disorder and the nature of these crystals themselves. There has been little to distinguish six structures of these types of complexes with data taken using Zr filters from six others taken without filters. This concept is not original with us—see R. A. Young, *Trans. Amer. Crystallogr. Ass.*, **1**, 42 (1965).

(14) See ref 10, pp 104, 546.

TABLE I

FINAL ATOMIC POSITIONAL AND THERMAL PARAMETERS FOR ACENAPHTHENESILVER PERCHLORATE[a]

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ag(1)	0.2500 (–)	0.0921 (01)	−0.0196 (02)	C(10)	0.4326 (08)	0.2115 (11)	0.3384 (20)
Ag(2)	0.2500 (–)	−0.2087 (01)	0.1923 (02)	C(11)	0.4121 (07)	0.1809 (09)	0.1782 (17)
Cl(1)	0.2500 (–)	0.0737 (04)	0.4152 (07)	C(12)	0.3735 (07)	0.2282 (09)	0.0639 (20)
Cl(2)	0.7500 (–)	0.1097 (04)	0.1593 (08)	O(2)	0.2500 (–)	0.1364 (09)	0.2800 (17)
C(1)	0.4744 (09)	0.0641 (11)	0.3106 (20)	O(4)	0.7500 (–)	0.1970 (11)	0.1111 (22)
C(2)	0.4730 (09)	0.1412 (11)	0.4376 (20)	O(5)	0.7500 (–)	0.0581 (10)	0.0093 (21)
C(3)	0.4145 (09)	0.2921 (13)	0.3867 (24)	O(1)	0.2500 (–)	0.4952 (48)	0.1560 (83)
C(4)	0.3746 (08)	0.3462 (11)	0.2675 (28)	*O(1)*[b]	0.7500 (–)	0.3787 (31)	0.0745 (59)
C(5)	0.3547 (08)	0.3119 (10)	0.1098 (21)	O(3)	0.3113 (14)	0.0249 (17)	0.4181 (31)
C(6)	0.6454 (07)	0.3122 (10)	0.4097 (21)	*O(3)*	0.3038 (19)	0.0988 (23)	0.5271 (44)
C(7)	0.6252 (07)	0.3967 (11)	0.3859 (17)	O(6)	0.6749 (13)	0.0960 (15)	0.2337 (30)
C(8)	0.5845 (08)	0.4457 (10)	0.5122 (21)	*O(6)*	0.7165 (17)	0.0824 (21)	0.2819 (40)
C(9)	0.4337 (07)	0.0974 (10)	0.1561 (19)				

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ag(1)	21 (01)	40 (01)	183 (04)	00 (–)	00 (–)	16 (02)
Ag(2)	23 (01)	55 (01)	175 (04)	00 (–)	00 (–)	27 (02)
Cl(1)	23 (02)	29 (03)	99 (09)	00 (–)	00 (–)	3 (04)
Cl(2)	63 (03)	32 (03)	117 (12)	00 (–)	00 (–)	−2 (05)
C(1)	27 (06)	53 (10)	150 (32)	9 (06)	−35 (13)	5 (16)
C(2)	31 (06)	45 (09)	194 (37)	4 (06)	−46 (13)	8 (16)
C(3)	24 (06)	55 (11)	230 (43)	−13 (07)	7 (14)	−42 (20)
C(4)	17 (05)	38 (09)	315 (48)	−11 (06)	14 (15)	3 (19)
C(5)	14 (05)	31 (08)	201 (36)	−8 (05)	29 (12)	3 (15)
C(6)	14 (04)	27 (07)	214 (35)	−00 (05)	−19 (11)	−20 (15)
C(7)	14 (04)	47 (09)	89 (26)	−8 (05)	−12 (09)	−3 (14)
C(8)	14 (05)	48 (08)	143 (30)	−1 (05)	−9 (11)	−6 (15)
C(9)	11 (04)	41 (08)	138 (30)	−4 (05)	−1 (10)	17 (15)
C(10)	14 (04)	46 (09)	150 (34)	−6 (05)	−11 (10)	5 (17)
C(11)	15 (04)	28 (07)	87 (25)	−5 (05)	5 (10)	8 (12)
C(12)	16 (05)	25 (07)	136 (31)	−5 (05)	9 (10)	36 (12)
O(2)	37 (06)	33 (08)	99 (28)	00 (–)	00 (–)	16 (12)
O(4)	71 (09)	29 (09)	206 (39)	00 (–)	00 (–)	−38 (16)
O(5)	62 (09)	40 (08)	160 (34)	00 (–)	00 (–)	−18 (16)

Atom	*B*, Å	Atom	*B*, Å	Atom	*B*, Å
O(3)	9 (2)	*O(1)*	6 (3)	*O(6)*	4 (1)
O(1)	13 (5)	O(3)	5 (1)	O(6)	7 (7)

[a] Anisotropic temperature factors of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}kh + 2\beta_{13}hl + 2\beta_{23}kl)] \times 10^4$. [b] Italic atoms are related to those which are not italic but which have the same numbers by disorder.

TABLE II

FINAL ATOMIC POSITIONAL AND THERMAL PARAMETERS FOR ACENAPHTHYLENESILVER PERCHLORATE[a]

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ag(1)	0.0210 (30)	0.5000 (–)	0.0000 (–)	C(3)	−0.028 (15)	0.473 (16)	0.351 (09)
Ag(2)	0.0211 (07)	0.0000 (–)	0.0000 (–)	C(4)	0.125 (10)	0.475 (07)	0.381 (04)
Ag(1)[b]	0.0586 (61)	0.5000 (–)	0.0000 (–)	C(5)	0.269 (08)	0.403 (04)	0.404 (03)
Cl(1)	0.3063 (23)	0.2554 (24)	0.0681 (07)	C(6)	0.264 (08)	0.138 (05)	0.407 (03)
O(2)	0.3451 (80)	0.1104 (55)	0.0580 (24)	C(7)	0.156 (10)	0.031 (07)	0.385 (04)
O(4)	0.3158 (84)	0.3641 (57)	0.0232 (24)	C(8)	0.018 (11)	0.033 (09)	0.355 (05)
O(1)	0.256 (08)	0.249 (08)	0.126 (03)	C(9)	−0.074 (10)	0.108 (06)	0.333 (04)
O(3)	0.432 (40)	0.239 (31)	0.070 (13)	C(10)	−0.068 (09)	0.355 (05)	0.337 (03)
C(1)	−0.299 (39)	0.141 (27)	0.301 (13)	C(11)	0.014 (09)	0.263 (06)	0.356 (02)
C(2)	−0.280 (19)	0.340 (14)	0.292 (06)	C(12)	0.190 (07)	0.259 (06)	0.395 (02)

Atom	β_{11}	β_{22}	β_{33}	β_{13}	β_{13}	β_{22}
Ag(1)	670 (80)	127 (19)	34 (06)	00 (–)	00 (–)	23 (09)
Ag(2)	441 (27)	177 (12)	37 (04)	00 (–)	00 (–)	23 (05)

Atom	*B*, Å^2	Atom	*B*, Å^2	Atom	*B*, Å^2
Ag(1)	14 (16)	Cl(1)	2 (2)	O(2)	1 (7)
O(1)	6 (9)	C(4)	2 (8)	C(9)	1 (3)
O(3)	15 (5)	C(5)	1 (5)	C(10)	1 (3)
C(1)	14 (2)	C(6)	1 (7)	C(11)	1 (5)
C(2)	9 (2)	C(7)	2 (8)	C(12)	1 (5)
O(4)	7 (7)				

[a] Anisotropic temperature factors of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}kh + 2\beta_{13}hl + 2\beta_{23}kl)] \times 10^4$. [b] Related to Ag(1) by disorder.

to relative structure factors. The pulse height analyzer was set such that 90% of the scattered radiation was counted.

Solution of Structures

Acenaphthene·AgClO$_4$.—The centric space group was assumed and the structure was solved and refined on this basis (*vide infra*). A three-dimensional Patterson function[15] was computed which showed the silver and chlorine atoms to be in two sets of the special positions of mirror symmetry. The remainder of the

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[15] Patterson and electron density syntheses were calculated using "ERFR-3, A Three-Dimensional Fourier Summation Program Adapted for the IBM 7040 from ERFR-2 of Sly, Shoemaker, van den Hende," by D. R. Harris.

atoms were located by standard heavy atom methods.[16] In the latter stages of the solution of the structure an electron density map showed possible disorder in three of the six oxygen atoms, a not uncommon problem with structures containing perchlorate ions. A three-dimensional difference Fourier map determined half-atom positions for the disordered oxygen atoms. Five cycles of full-matrix anisotropic least-squares with isotropic temperature factors for the disordered atoms yielded 0.074, 0.068, and 0.322 for R, the weighted R, and the standard error of an observation of unit weight.[17] Further attempts to refine the disordered oxygen atoms in terms of their site occupancy proved to be meaningless and were abandoned. The final parameter shifts were 0.1σ or less.

Acenaphthylene · $AgClO_4$.—Four molecules of acenaphthylene · $AgClO_4$ can be accommodated in the four general positions of $P22_12_1$, or part of the molecule could be placed on the special twofold positions. A three-dimensional Patterson map[15] readily showed that the silver atoms occupied the two special twofold positions $(x, {}^1/_2, 0;\ \bar{x}, 0, {}^1/_2$; and $\bar{x}, 0, 0;\ \bar{x}, {}^1/_2, {}^1/_2)$ with a chlorine atom in general positions. The remaining atoms were found by standard heavy-atom techniques.[16] It was soon apparent that even one of the silver atoms was disordered. At this point in the refinement an attempt was made to define the occupancy of the disordered silver atom by assigning to it the temperature factor of the ordered silver atom. Ag(1) had an occupancy of 0.68 and *Ag(1)* had an occupancy of 0.32 based on the above assumption. A three-dimensional difference Fourier map indicated large thermal parameters for all carbon atoms and the two oxygen atoms not bound to the silver atoms. A final three cycles of full-matrix least-squares refinement with anisotropic temperature factors for two silver atoms and isotropic temperature parameters for the remaining atoms reduced R to a final value of 0.200 with a weighted R of 0.204 and a standard error of 0.57 of an observation at unit weight.[16] Further refinement was not deemed profitable.

For Both Structures.—We minimized the function $\Sigma w(|F_o| - |F_c|)^2$ and the observations were weighted on counting statistics and a 4% intensity factor.[18] The scattering factors for Ag(I), neutral chlorine, oxygen, and carbon were from Cromer and Waber.[19] The effects of anomalous dispersion were included in the structure factor calculations by addition to F_c;[20] the values for $\Delta f'$ and $\Delta f''$ for silver were those given by Cromer.[21]

The final tabulation of observed and calculated structure factors is filed elsewhere.[22] Unobserved data were not used in the refinement, but are listed with the calculated structure factors elsewhere.[22] Final atomic coordinate and temperature parameters are enumerated in Tables I and II. Interatomic distances, angles, and errors[23] are shown in Table III including the least-squares plane of the acenaphthene molecule. Root-mean-square components of thermal displacement where appropriate are listed in Table IV.

TABLE III

INTERATOMIC DISTANCES AND ANGLES FOR ACENAPHTHENE · $AgClO_4$

Bonded Distances, Å

Ag(1)–C(6)	2.51 (1)	Ag(1)–C(7)	2.44 (1)
Ag(2)–C(5)	2.51 (1)	Ag(2)–C(4)	2.48 (1)
Ag(1)–O(2)	2.46 (1)	Ag(1)–O(5)	2.34 (2)
Ag(2)–O(2)	2.42 (1)	Ag(2)–O(4)	2.40 (2)
C(1)–C(2)	1.56 (2)	C(3)–C(4)	1.46 (3)
C(6)–C(12)	1.44 (2)	C(6)–C(7)	1.38 (2)
C(7)–C(8)	1.46 (2)	C(1)–C(9)	1.52 (2)
C(10)–C(2)	1.54 (2)	C(10)–C(3)	1.35 (2)
C(11)–C(9)	1.37 (2)	C(11)–C(10)	1.40 (2)
C(12)–C(5)	1.40 (2)	C(4)–C(5)	1.40 (2)
C(11)–C(12)	1.37 (2)	C(8)–C(9)	1.36 (2)
Cl(1)–O(2)	1.45 (1)	Cl(1)–O(3)	1.37 (3)
Cl(1)–O(1)	1.35 (7)	Cl(1)–O(3′)	1.39 (4)
Cl(1)–O(1′)	1.46 (5)	Cl(2)–O(4)	1.41 (2)
Cl(2)–O(5)	1.43 (2)	Cl(2)–O(6)	1.52 (2)
Cl(2)–O(6′)	1.22 (3)		

Selected Nonbonded Distances Less Than 4 Å

Ag(1)–C(9)	3.68 (1)	Ag(1)–C(11)	3.66 (1)
Ag(1)–C(12)	3.19 (1)	Ag(1)–Cl(1)	3.44 (1)
Ag(1)–C(8)	3.13 (1)	Ag(1)–O(3)	3.78 (2)
Ag(1)–O(1′)	3.23 (5)	Ag(1)–O(1)	3.24 (7)
Ag(1)–O(6)	3.66 (2)	Ag(1)–O(6′)	3.47 (3)
Ag(2)–C(3)	3.11 (2)	Ag(2)–C(10)	3.61 (1)
Ag(2)–C(11)	3.61 (1)	Ag(2)–C(12)	3.14 (1)
Ag(2)–O(1′)	3.38 (5)	Ag(2)–O(1)	3.40 (8)
Ag(2)–O(3′)	3.60 (3)	Ag(2)–O(5)	2.84 (2)

Angles, Deg

C(2)–C(1)–C(9)	103.9 (1.5)	C(1)–C(9)–C(11)	111.5 (1.4)
C(9)–C(11)–C(10)	111.0 (1.4)	C(11)–C(10)–C(2)	110.3 (1.5)
C(10)–C(2)–C(1)	103.9 (1.2)	C(9)–C(8)–C(7)	121.8 (0.8)
C(8)–C(7)–C(6)	123.0 (1.4)	C(7)–C(6)–C(12)	116.3 (1.6)
C(6)–C(12)–C(11)	122.4 (1.5)	C(12)–C(11)–C(9)	111.0 (1.7)
C(11)–C(9)–C(8)	106.3 (1.6)	C(11)–C(12)–C(5)	117.6 (1.5)
C(12)–C(5)–C(4)	121.4 (1.6)	C(5)–C(4)–C(3)	118.6 (1.6)
C(4)–C(3)–C(10)	118.7 (1.7)	C(3)–C(10)–C(11)	120.0 (1.4)
C(10)–C(11)–C(12)	123.4 (1.5)	Ag(1)–C(7)–C(6)	76.7 (0.8)
Ag(1)–C(6)–C(7)	70.7 (0.8)	Ag(2)–C(5)–C(4)	72.6 (0.8)
Ag(2)–C(4)–C(5)	74.8 (0.8)	C(6′)–Ag(1)–C(6)	101.2 (0.7)
C(7′)–Ag(1)–C(7)	143.4 (0.7)	C(4′)–Ag(2)–C(4)	136.8 (0.9)
C(5′)–Ag(2)–C(5)	101.3 (0.8)	C(6)–Ag(1)–C(7)	32.4 (0.5)
C(4)–Ag(2)–C(5)	32.6 (0.5)	Ag(1)–O(5)–Cl(2)	122.0 (0.7)
Ag(1)–O(2)–Cl(1)	121.1 (0.8)	Ag(2)–O(2)–Cl(1)	127.4 (0.8)
Ag(2)–O(4)–Cl(2)	110.7 (0.8)	Ag(1)–O(2)–Ag(2)	111.5 (0.5)
O(2)–Ag(2)–O(4)	99.8 (0.5)	Ag(2)–O(5)–Cl(2)	89.9 (1.1)
O(2)–Cl(1)–O(1)	108.0 (1.1)	O(2)–Cl(1)–O(3)	112.8 (1.1)
O(2)–Cl(1)–O(1′)	106.1 (1.5)	O(2)–Cl(1)–O(3′)	91.3 (2.0)
O(4)–Cl(2)–O(5)	108.6 (1.1)	O(4)–Cl(2)–O(6)	103.7 (1.0)
0(5)–Cl(2)–O(6′)	117.2 (1.7)	O(6′)–Cl(2)–O(6)	96.4 (1.7)

Equation of Least-Squares Plane of the Type[a]

$$Ax + By + Cz - D = 0$$

$$A = 0.8573,\ B = 0.3260,\ C = -0.3984,\ D = 6.8800$$

Deviation of Atoms from the Least-Squares Plane, Å

C(1)	0.022 (11)	C(7)	−0.014 (10)
C(2)	−0.018 (12)	C(8)	−0.034 (10)
C(3)	−0.024 (13)	C(9)	0.014 (10)
C(4)	−0.008 (12)	C(10)	0.004 (10)
C(5)	−0.003 (10)	C(11)	0.029 (10)
C(6)	0.021 (10)	C(12)	0.012 (10)

[a] x, y, and z refer to atom positional parameters in ångströms. All atoms were equally weighted in the least-squares plane: J. S. Rollett, "Computing Methods in Crystallography," Pergamon Press, New York, N. Y., 1965, p 22.

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(16) Structure factor calculations and least-squares refinements were performed with a local version of "ORFLS, A Fortran Crystallographic Least-Squares Program," by W. R. Busing, K. O. Martin, and H. A. Levy, Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

(17) $R = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|]$; $R_w = \{\Sigma w[|F_o| - |F_c|]^2/[\Sigma w|F_o|]^2\}^{1/2}$; standard error $= [\Sigma w(F_o - F_c)^2/\text{NO} - \text{NV}]^{1/2}$; NO = 1236, NV = 173.

(18) G. H. Stout and L. H. Jensen, "X-Ray Structure Determination, A Practical Guide," Collier-Macmillan, London, 1968, p 457.

(19) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

(20) J. A. Ibers and W. C. Hamilton, *ibid.*, **17**, 781 (1964).

(21) D. T. Cromer, *ibid.*, **18**, 17 (1965).

(22) A listing of structure factor amplitudes will appear immediately following this article in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

(23) W. R. Busing, K. O. Martin and H. A. Levy, "ORFFE, A Fortran Crystallographic Function and Error Program," Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

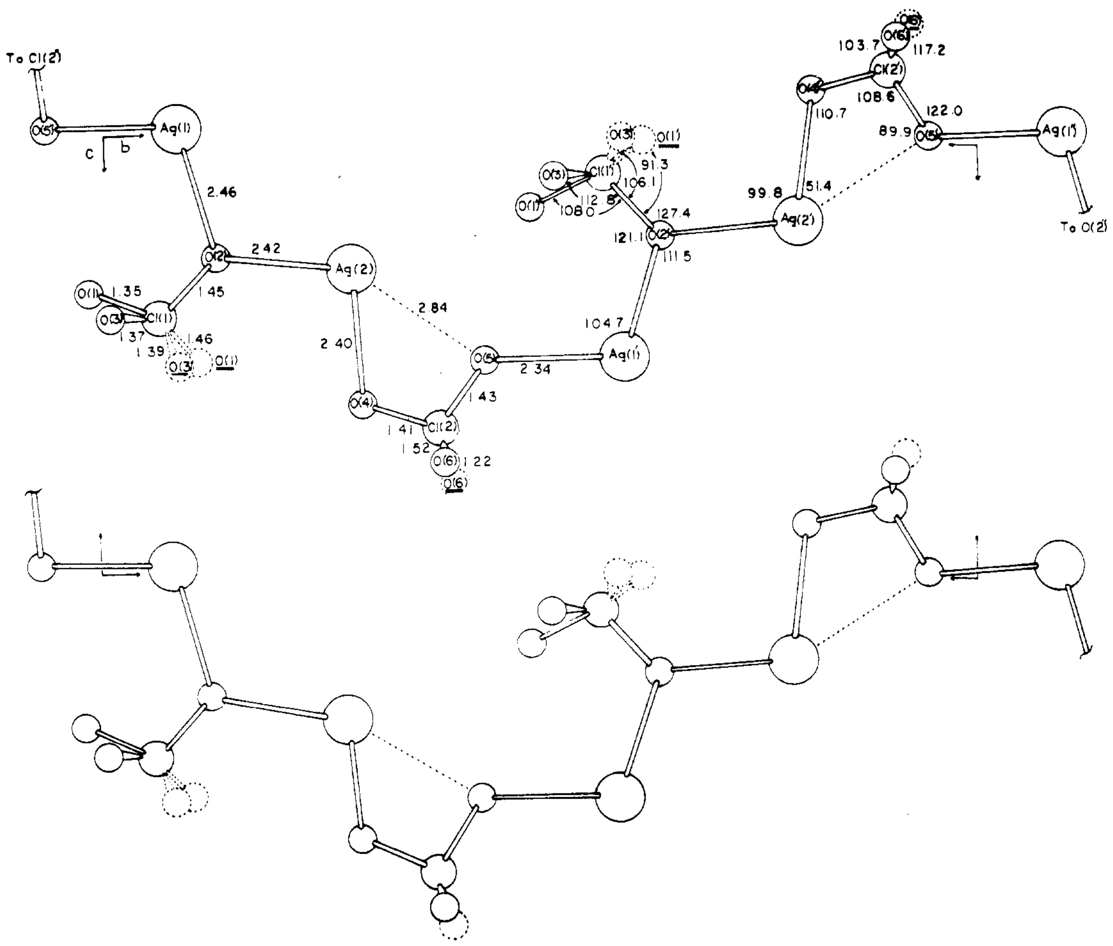

Figure 1.—View of the $AgClO_4$ chain in the acenaphthene·$AgClO_4$ structure as seen down the *a* axis onto the *bc* plane. The acenaphthene molecules are not shown for reasons of clarity. The extremes of the periodically bent chain are Ag(1) and Ag(1′). The prime and doubly primed atoms are related to the unprimed by x, $^1/_2 + y$, $^1/_2 - z$ and x, y, $1 + z$, respectively. The atoms related to O(1), O(3), and O(6) by disorder are underlined and shown dotted. All atoms shown except for O(1), O(3), O(6), and their disordered mates lie in the mirror plane at $x = {}^1/_4$.

TABLE IV

ROOT-MEAN-SQUARE DISPLACEMENTS FOR ACENAPHTHENE·$AgClO_4$ ALONG THE PRINCIPAL AXES OF THE THERMAL ELLIPSOID, Å

Atom	Axis 1	Axis 2	Axis 3
Ag(1)	0.191 (03)	0.205 (03)	0.253 (03)
Ag(2)	0.199 (03)	0.209 (03)	0.282 (03)
Cl(1)	0.174 (09)	0.191 (10)	0.201 (09)
Cl(2)	0.191 (01)	0.200 (10)	0.331 (09)
C(1)	0.137 (33)	0.251 (24)	0.278 (24)
C(2)	0.147 (32)	0.239 (25)	0.303 (23)
C(3)	0.174 (30)	0.225 (28)	0.318 (27)
C(4)	0.136 (32)	0.235 (26)	0.317 (25)
C(5)	0.097 (39)	0.207 (24)	0.270 (23)
C(6)	0.136 (29)	0.175 (26)	0.273 (23)
C(7)	0.121 (32)	0.184 (25)	0.248 (23)
C(8)	0.150 (27)	0.216 (24)	0.247 (22)
C(9)	0.135 (27)	0.190 (26)	0.242 (25)
C(10)	0.140 (28)	0.217 (28)	0.247 (25)
C(11)	0.137 (28)	0.173 (25)	0.198 (23)
C(12)	0.094 (39)	0.182 (25)	0.245 (23)
O(2)	0.156 (28)	0.216 (24)	0.253 (21)
O(4)	0.151 (32)	0.280 (25)	0.352 (23)
O(5)	0.195 (28)	0.247 (25)	0.329 (23)

Results and Discussion

Acenaphthene·$AgClO_4$.—The structure of acenaphthenesilver perchlorate may be described as a periodically repeating chain of $AgClO_4$ propagating in the *b* direction (Figure 1). The crystallographically independent Ag(1) and Ag(2) atoms lie in a mirror plane

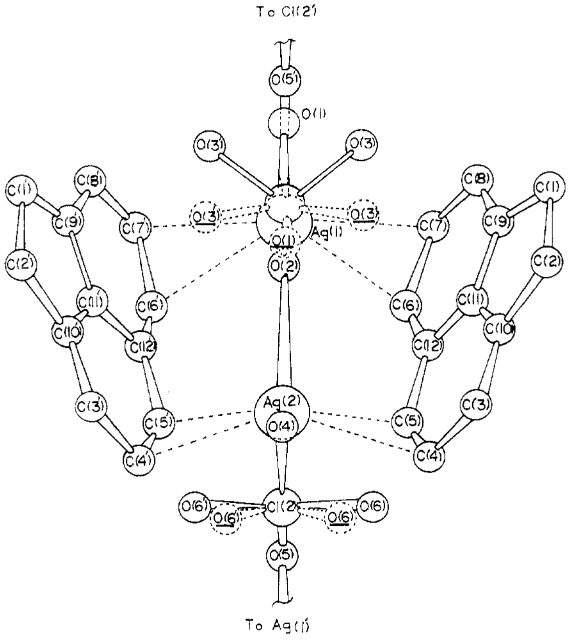

Figure 2.—View of the acenaphthene·$AgClO_4$ dimer. The atoms related to others by disorder are shown dotted and underlined. The primed atoms are related to the unprimed by the mirror plane that vertically bisects this view.

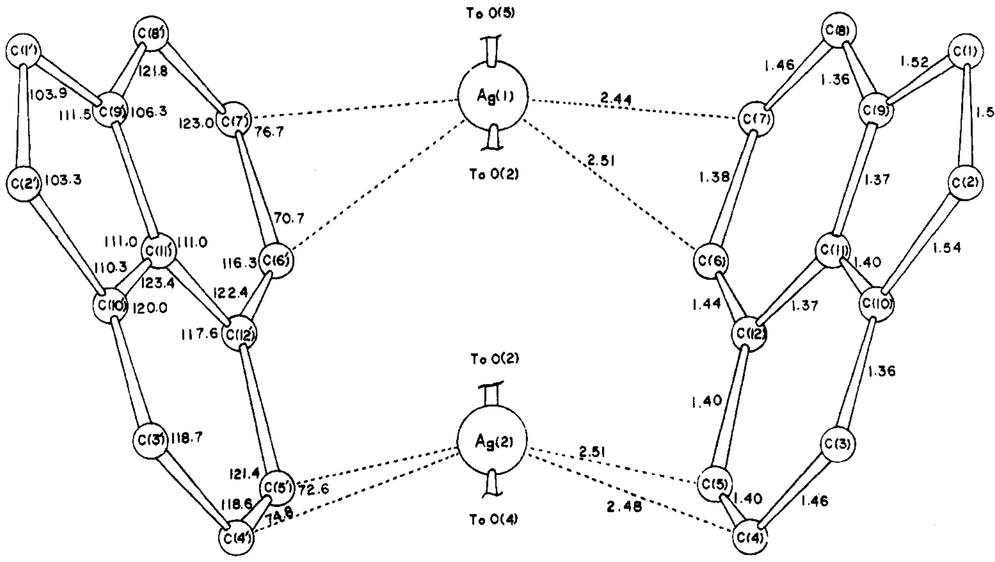

Figure 3.—View of the acenaphthene·$AgClO_4$ structure showning only Ag–C interactions and distances and angles within the acenaphthene molecule. Primed atoms related to the unprimed by the mirror that vertically bisects this view.

along with two oxygens and a chlorine atom of each perchlorate group (Figures 1 and 2). As is seen in Figure 1, each silver is bound to two oxygen atoms of different perchlorate groups and the coordination polyhedron of the metal ion is completed to four by interaction with the π orbitals of the aromatics on either side of the mirror plane (Figure 2). Using the shortest Ag–C distances the silver coordination would be described as distorted tetrahedral (Figures 2 and 3; (Table III). The overall result of this arrangement is that the $AgClO_4$ chains lie in sheets with aromatics on either side such that the packing consists of a sequence of sheets: aromatic···aromatic·ionic·aromatic··· aromatic·ionic·aromatic···. The metal interacts with the same carbon positions as in naphthylene–tetrakis(silver perchlorate) tetrahydrate[9] but with only half the positions; *i.e.*, the effect of the five-membered ring has been to block the C(8)–C(9) and C(3)–C(10) bonds from bonding to silver. Furthermore, in naphthalene·$4AgClO_4·4H_2O$ each naphthalene molecule bonds to four silver ions and consequently, each silver bonds to only one aromatic; however, one silver atom interacts with two aromatics in acenaphthene·$AgClO_4$. The silver–carbon distances in the naphthalene·$4AgClO_4·4H_2O$ structure are 2.60–2.63 Å, in contrast to the present structure where they are much shorter, 2.44–2.51 Å (Table III). The symmetric "long" distances of 2.60 Å led us to suggest a clathrate description of the naphthalene·$4AgClO_4·4H_2O$ structure, not only because of the long Ag–C distances but also because of the fact that it was the first case in which we observed equal Ag–C distances to the nearest bond of the aromatic. In the present structure it is seen that each silver atom is essentially equally bound to four carbon atoms. However, one is somewhat short at 2.44 (1) Å and another is somewhat long at 2.51 (1) Å. It is not clear why Ag(1)–C(7) is shorter than the other three distances, but it may be an apparent result arising from the disorder in the nearby perchlorate group. This is the first reported structure in which the silver–carbon interactions are both symmetric and short.

The naphthalene portion of the molecule has C–C distances that are not significantly different from those found in the naphthalene molecule.[24] The three carbon-carbon single bonds in the five-membered ring show the expected single bond distances[25] and the entire molecule is planar within experimental error (Table III).

The dihedral angles formed by Ag(1)–C(7)–C(6) and C(6)–C(7)–C(8) and by Ag(2)–C(5)–C(4) and C(3)–C(4)–C(5) are 98.5 and 94.2°, respectively, indicating that the silver atoms interact with the π electrons of the aromatic rings.

The details of the silver perchlorate interactions are interesting in that Ag(1) is bound to Ag(2) by a bridging oxygen [O(2)] but Ag(2) is bound to Ag(1') *via* a perchlorate group [O(4), Cl(2), O(5)] (Figure 1). The silver–oxygen bond lengths range from 2.34 to 2.46 Å and are considered to be rather short when compared to other aromatic silver perchlorate complexes which show values of 2.49–2.66 Å.[1–3,5,6]

Short silver–oxygen distances have only been observed in silver–aromatic structures which contain water molecules of hydration (naphthalene·$4AgClO_4·4H_2O$ and anthracene·$4AgClO_4·H_2O$) with the short silver–oxygen distances found for the silver atoms bound to the water molecules.[9] Silver–oxygen distances of 2.34 Å have been observed in Ag_3PO_4[26] and 2.42 Å in Ag_3AsO_4[27] and Ag_2MoO_4.[28] For comparative purposes the silver–oxygen distance from the sum of the covalent radii is 2.18 Å.[29] The general conclusion that may be drawn from these silver–oxygen distances is that the metal–anion interaction is important to the stabilization of the structure.

Cl(1), Cl(2), O(2), O(4), O(5), O(1), and its disordered partner *O(1)* all lie in the mirror plane along with

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[27] L. Helmholz and R. Levine, *J. Amer. Chem. Soc.*, **64**, 354 (1942).

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[29] L. Pauling, "The Nature of the Chemical bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 246.

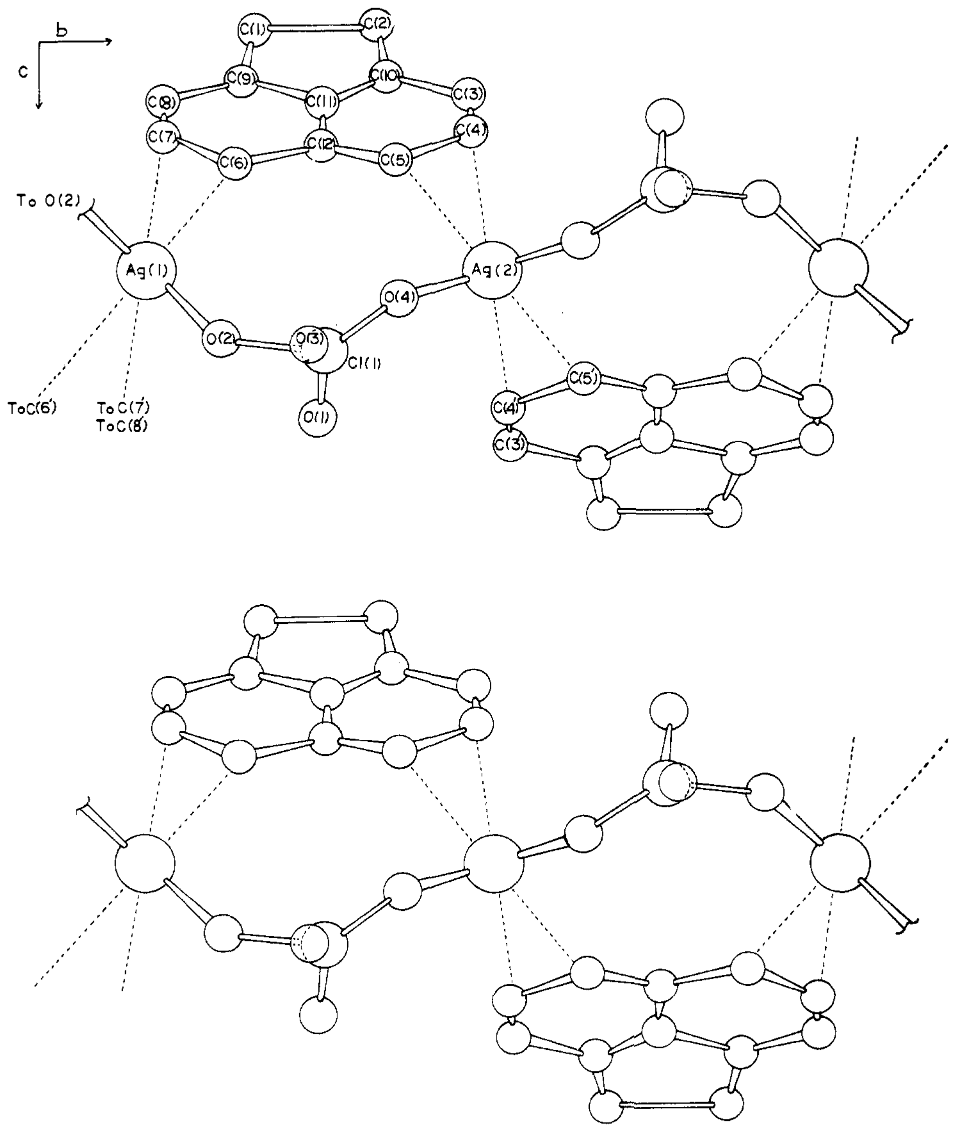


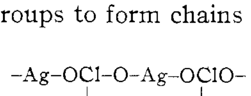
Figure 4.—The structure of acenaphthylene·$AgClO_4$ as viewed down *a* onto the *bc* plane. *Ag(1)* is not shown, but is directly above Ag(1). Primed atoms are related to the unprimed by twofold rotation axes that pass through the Ag atoms perpendicular to the plane of projection.

Ag(1) and Ag(2). O(6) and O(3) are related to O(6') and O(3') by this same mirror. *O(6)* and *O(6')* are the disordered positions of O(6) and O(6'). This disorder in O(6) corresponds to tipping the ClO_4^- tetrahedron with O(4) and O(5) as fixed points (Figure 2, Table III). This should lead to disorder of Cl(2) as well, but only an abnormally large thermal motion for Cl(2) perpendicular to the mirror is observed. This is reasonable since the displacement of the Cl(2) should be much less than that of O(6) for such a disordered arrangement.

This disorder involving O(1) and O(3) corresponds to two possible orientations of the Cl(1) ClO_4^- tetrahedron generated by a 120° rotation about the Cl(1)–O(2) bond.

Acenaphthylene·$AgClO_4$.—The most significant feature of the acenaphthylene·$AgClO_4$ structure is that the Ag^+ is not involved in binding to the five-membered unsaturated ring but rather is bound to the same positions of the fused six-membered rings as in acenaphthene·$AgClO_4$.

The structure may be described as Ag atoms bridged by perchlorate groups to form chains of the type (Figure 4)



$$-Ag-O\underset{\substack{|\\O_2}}{Cl}-O-Ag-O\underset{\substack{|\\O_2}}{Cl}O-$$

Each silver atom then completes its distorted tetrahedral coordination polyhedron by interaction with the π electrons of two different acenaphthylene molecules. The acenaphthylene molecules may also be considered as bridging units along with the perchlorate groups (Figure 4).

This geometrical arrangement between the aromatics and the silver atoms is in contrast to that found above for acenaphthene·$AgClO_4$. In acenaphthene·$AgClO_4$ two silver atoms are bound to the same two aromatic moieties whereas in acenaphthylene·$AgClO_4$ each Ag atom is bound to two aromatics that are bound to two other silver atoms.

Unfortunately, the combination of limited data and disorder in the silver atoms makes the estimated errors sufficiently large that no detailed discussion of interatomic distances is meaningful. In the same sense speculations concerning the reasons for the disordering of the Ag atoms based upon silver–aromatic interactions are meaningless.

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The Crystal Structure of Ethylidyneheptacarbonyl-μ-[1,2-bis(dimethylarsino)tetrafluorocyclobutene]-*triangulo*-tricobalt

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The crystal structure of ethylidyneheptacarbonyl-μ-[1,2-bis(dimethylarsino)tetrafluorocyclobutene]-*trianguló*-tricobalt, $Co_3As_2F_4O_7C_{17}H_{15}$, has been determined from three-dimensional X-ray data collected by counter methods. The compound crystallizes in the monoclinic space group $P2_1/n$; the unit cell contains four molecules and has dimensions $a = 10.568$ (3) Å, $b = 13.462$ (5) Å, $c = 16.394$ (4) Å, $\beta = 90.80$ (2)°. The measured density, 2.0 g/cm³, agrees well with the calculated value, 2.09 g/cm³. The structure was determined by direct phasing methods and refined by full-matrix least-squares technique to a conventional R index of 0.026 and weighted R of 0.032 for 1673 observed reflections. The cobalt atoms have a triangular arrangement with Co(3)–Co(4), Co(3)–Co(5), and Co(4)–Co(5) being 2.440 (1), 2.479 (2), and 2.470 (2) Å, respectively. A carbon atom in the ethylidyne group is symmetrically placed with respect to this triangle with an average C(18)–Co bond length of 1.903 Å (individual esd 0.007 Å). The ffars ligand bridges Co(3)–Co(4) with As(1)–Co(3) = 2.337 (1) Å and As(2)–Co(4) = 2.358 (1) Å; the cyclobutene ring, As(1), and As(2) are coplanar. Seven carbonyl groups are arranged so that Co(3) and Co(4) have one terminal group while Co(5) has two; three carbonyl groups bridge adjacent cobalt atoms, those bridging Co(3)–Co(5) and Co(4)–Co(5) being asymmetrical.

Introduction

Recently, it has been shown that some of the carbonyl groups in $YCCo_3(CO)_9$ ($Y = CF_3, CH_3, Cl$) can be replaced by groups containing phosphorus and arsenic, a reaction which had generally been expected to cleave one or more of the metal–metal bonds. Robinson and Tham[1] have synthesized $CH_3CCo_3(CO)_8L$ [$L = (C_6H_5)_3P, (C_6H_5)_3As, (C_4H_9)_3P, (C_4H_9)_3As$], $CH_3CCo_3(CO)_7L_2$ [$L = (C_6H_5)_3P, (C_4H_9)_3As$], and $ClCCo_3(CO)_8(C_6H_5)_3P$. It has been shown by Cullen[2] that 1,2-bis(dimethylarsino)tetrafluorocyclobutene, ffars, will react with $CH_3CCo_3(CO)_9$ (I) and $CF_3CCo_3(CO)_9$ (II), the ffars displacing two carbonyl groups and forming a bridge between adjacent cobalt atoms. The crystal structure[3] of the product with II has indicated that the molecule contains a tetrahedron of cobalt atoms and two ffars ligands. Physical methods indicate that the product with I, $CH_3CCo_3(CO)_7$ffars, has the same three-point linkage of the aliphatic carbon atom to the cobalt atoms as in the parent compound.[4,5] However, the ffars derivative has bridging carbonyl groups in addition to terminal ones.

Experimental Section

Crystals of the compound were red and multifaceted. Weissenberg photographs of the zones $h0l$–$h3l$ and precession photographs of zones $hk0$–$hk2$ and $0kl$–$1kl$, taken with Cu K radiation, established the crystal system as monoclinic and showed the following absences: $h0l$ for $h + l$ odd; $0k0$ for k odd. The space group is therefore $P2_1/n$ [$\pm(x, y, z)$; $\pm(\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$] (a nonstandard orientation of $P2_1/c$).

Crystal Data.—$Co_3As_2F_4O_7C_{17}H_{15}$, mol wt 733.9, crystallizes in the monoclinic space group $P2_1/n$, with $a = 10.568$ (3) Å, $b = 13.462$ (5) Å, $c = 16.394$ (4) Å, $\beta = 90.80$ (2)°, and $V = 2332$ Å³; $d_{obsd} = 2.0$ g cm^{-3} (Bermann density balance), $d_{calcd} = 2.09$ g cm^{-3}, $Z = 4$, $F(000) = 1424$, λ(Cu Kα) 1.5418 Å, λ(Mo Kα) 0.7107 Å, λ(Mo Kα_1) 0.70926 Å, and μ(Mo Kα) 52.2 cm^{-1}.

A large crystal was cleaved to an approximate cube and ground to a sphere of diameter 0.3 mm. This sphere was mounted with a general orientation to minimize multiple reflections and was used to measure the cell dimensions and collect the intensity data. Cell dimensions were obtained from the least-squares analysis of 2θ values for 19 high-angle reflections, automatically centered and measured on a Picker four-circle diffractometer using Mo Kα_1 radiation. The errors in the cell dimensions are those determined from the least-squares process. The takeoff angle was 0.8° and the ambient temperature was 23°.

Intensities from one quadrant were collected by the θ–2θ scan technique using Mo Kα radiation (niobium filter) and a scintillation counter equipped with pulse height discrimination. The takeoff angle was 4.3°, the detector was positioned 28 cm from the crystal, and the detector aperture was 5.00 mm high and 4.00 mm wide. Each reflection was scanned for 1.8° (extended for the splitting of α_1 and α_2) at a scan rate of 2°/min. For reflections with $2\theta \leq 35°$, the background was counted for 10 sec at each end of the scan range while for reflections with $35° < 2\theta \leq 40°$, the background counts were for 20 sec. Every 50 reflections, two standard reflections were measured. The maximum deviation of any individual standard from the mean was 1.5%. Several reflections which had a high count rate were remeasured at lower beam intensity and provided no evidence for coincidence losses. In this manner, intensities for 2188 reflections, with $2\theta \leq 40°$, were measured.

Intensities were corrected for background, Lorentz–polarization factors, and the absorption for a spherical crystal, μr being 0.78. If the net count for a reflection was less than 2σ, σ = (total count + background)$^{1/2}$, the reflection was considered unobserved. The number of observed reflections was 1673.

Structure Determination.—The phase problem was solved by direct phasing methods.[6,7] E values were determined[8] and the

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[8] All calculations were performed on an IBM 360/50 computer. Programs used were FORDAP, crystallographic Fourier summation and peak searching (A. Zalkin), BUCILS, crystallographic structure factors and full-matrix least squares (University of Canterbury), ORFFE, Fortran crystallographic function and error program (W. R. Busing, K. O. Martin, and H. A. Levy), ORTEP, Fortran thermal-ellipsoid plot program for crystal structure illustrations (C. K. Johnson), MEANPLANE, calculation of weighted mean planes through atom groups with esd's (M. E. Pippy and F. R. Ahmed), and SAP I–IV and DP I–IV, a set of direct phasing programs (S. Hall, F. R. Ahmed, and C. Huber).