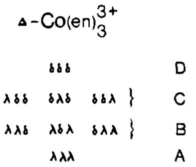
mined from f_λ values range from indeterminate at worst to highly imprecise at best, depending on the individual case.



IV

We showed that D probably amounts to less than a few per cent and could be discarded. If we also discard species C, we can obtain solutions for species A and B, but risk the introduction of systematic errors which could be 20% or larger. Species B is favored over species A by the statistical entropy term $\Delta S_{BA} = R \ln 3$. Neglecting additional entropy contributions, we find that discarding species C leads to an interpolated ΔG_{BA} value of -0.5 ± 0.3 kcal/mol (A = 30%, B = 70%) at 25°. The result that B lies below A in free energy contrasts with nearly all previous studies of Co(en)$_3^{3+}$.[17]

In 0.3 M K_3PO_4, we find that $\Delta G_{BA} = +0.5 \pm 0.3$ kcal/mol, indicating a reversal in the population of species A and B (A = 70%, B = 30%).

These very crude calculations seem to bear out the tendency of phosphate ion to preferentially stabilize species A, which has been attributed to hydrogen bonding.[4-7] A plot of $\Delta\delta_{AB}$ *vs.* f_λ leads to a rather poor linear least-squares fit.

The conformational problem is clearly underdetermined, and we do not presume to have given a full solution from these pmr data. However, the f_λ values obtained from the pmr studies should prove useful in conjunction with strain-energy calculations or additional experimental results.

Acknowledgments. This research was supported by U. S. Public Health Service Grants No. R01-ES00477-04 and R01-GM12769-04. We are grateful to the UCLA Campus Computing Network for their generous support of the computational work. Professor R. M. Wing provided the drawings used in structures I and II.

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[17] A recent reexamination of R-pn and en data for Co(III), however, has resulted in a similar conclusion (B favored over A): C. Hawkins, "Absolute Configuration of Metal Complexes," Wiley-Interscience, New York, N. Y., 1971, pp 102–104.

Metal Ion–Aromatic Complexes. XIII. Trigonal-Planar Silver(I) in the Structure of Indene Silver Perchlorate

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Abstract: The crystal and molecular structure of indene silver perchlorate has been determined by single-crystal X-ray diffraction from 882 counter-measured intensities at room temperature. The structure was refined by full-matrix least-squares methods to a final conventional R of 0.066. Crystals of $C_9H_8 \cdot AgClO_4$ are orthorhombic, *Pbnm*, $Z = 8$, $d_c = 2.15$ g cm^{-3}, $a = 15.390\,(2)$ Å, $b = 8.525\,(1)$ Å, $c = 15.213\,(1)$ Å. The structure consists of isolated dimeric units (indene·AgClO$_4$)$_2$ in a half-open hinge (99°) arrangement where the leaves of the hinge are the organic groups and the pin corresponds to the silver ions with their associated perchlorate groups. The silver, chlorine, and two oxygen atoms of each perchlorate group lie in a crystallographic mirror plane. This same mirror interrelates the rest of the molecule. Such an arrangement leads to one silver atom bound to only olefin parts of the molecule in a distorted linear configuration. The other silver is in a trigonal-planar arrangement with the two aromatic parts [Ag–C = 2.47 (2) Å] and an oxygen of a perchlorate [Ag–O = 2.46 (2) Å]. This is the first reported instance of a trigonal-planar Ag(I) coordination involving aromatic ligands.

In earlier publications[1] we have postulated that a fundamental distinction exists between the nature of the metal–carbon bond in silver–aromatic complexes and silver–olefin complexes.[2] In general, a "short" silver–carbon distance of 2.47 ± 0.02 Å has been found in the silver(I)–aromatic complexes regardless of stoichiometry, anion, and packing considerations.[2-6] The next shortest silver–carbon distance varies over wide limits from 2.56 to 2.94 Å. The silver–carbon distances found for silver–olefin complexes, on the other

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[1] For a general review of the literature and a historical introduction, see ref 3a.

[2] I. F. Taylor, Jr., E. A. Hall, and E. L. Amma, *J. Amer. Chem. Soc.*, 91, 5745 (1969).

[3] (a) E. A. Hall Griffith and E. L. Amma, *ibid.*, **93**, 3167 (1971); (b) E. A. Hall and E. L. Amma, *Chem. Commun.*, 622 (1968).

[4] R. W. Turner and E. L. Amma, *J. Amer. Chem. Soc.*, **88**, 3243 (1966).

[5] H. G. Smith and R. E. Rundle, *ibid.*, 80, 5075 (1958).

[6] (a) E. A. Hall and E. L. Amma, *ibid.*, **91**, 6538 (1969); (b) I. F. Taylor, Jr., and E. L. Amma, *Chem. Commun.*, 1442 (1970).

hand, show no such regularity with the shortest distance ranging from 2.31 to 2.45 Å[7–12] and with the two shortest distances in each case being equal. The only exceptions to these general rules for silver(I)–aromatic complexes occur in the structures of tetrakis(silver perchlorate)naphthalene tetrahydrate[6] and acenaphthene silver perchlorate.[13] The former has silver–carbon distances of 2.60 Å or greater and might be best described as a clathrate. The latter structure contains two silver species each of which is bound to two rings on either side of a mirror plane with silver–carbon distances of 2.44 (1), 2.51 (1), 2.48 (1), and 2.51 (1) Å.

The molecule indene (C_9H_8) contains a six-membered aromatic ring and a five-membered ring with a localized carbon–carbon double bond. Thus, this molecule represents an opportunity to observe both a silver–aromatic interaction with the six-membered ring and a silver–olefin interaction with the localized double bond in the five-membered ring simultaneously. The results of an X-ray crystallographic study of indene silver perchlorate are reported here.

Experimental Section

A saturated toluene solution of silver perchlorate was added to a toluene solution of indene in an anhydrous environment. Clear, colorless, diffraction-quality crystals were formed as the toluene evaporated. However, the crystals were not obtained in sufficient quantity for chemical analysis. Because of their reactivity toward moisture, the crystals were mounted in thin-walled glass capillaries with the *c* axis approximately parallel to the capillary axis. Preliminary Weissenberg and precession photographic data *hk*0, *hk*1. . .*hk*8, *h*0*l*, and 0*kl* showed the crystals to be orthorhombic, with the systematic absences, *h*0*l*, $h + l = 2n + 1$, and 0*kl*, $k = 2n + 1$. Thus, the space group is *Pbnm* (nonstandard setting of space group no. 62, *Pmna*) or the noncentric *Pbn*2$_1$ (nonstandard setting of space group no. 33, *Pna*2$_1$).[14] The crystal was aligned on a Picker full-circle diffractometer by variations of well-known techniques.[15] A least-squares fit[15c] of the χ, ϕ, and 2θ angles of 28 reflections accurately centered on the diffractometer were used to determine the lattice constants at 23–25° (λ 0.71068 Å for Mo Kα): $a = 15.390$ (2) Å, $b = 8.525$ (1) Å, $c = 15.213$ (1) A. With $Z = 8$ the calculated density is 2.15 g cm^{-3} and the observed density is between 1.6 and 2.2 g cm^{-3}. A more accurate value was unattainable because the crystals decompose very rapidly in halocarbon solution. A crystal ~0.16 × 0.28 × 0.94 mm (0.94 mm = *c*) mounted as described above was used to collect the intensity data. The linear absorption coefficient μ was calculated to be 27.0 cm^{-1} with Mo Kα radiation. With this μ and the above crystal dimensions the variation in transmission coefficient was found to be 0.51–0.65. No absorption corrections were made, however, since error in intensity measurements due to crystal decomposition probably outweighed simple absorption effects. A total of 2200 independent *hkl* reflections were measured by θ–2θ scan techniques with unfiltered Mo Kα radiation[16,17] at room temperature for 102 sec at 0.017°/sec, and background counts were made for 40 sec (B_1 and B_2). Reflections were considered absent if the integrated intensity was less than $2[2.55(B_1 + B_2)]^{1/2}$. By this criterion 882 reflections were retained as being nonzero. 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 4% of the net intensity while the variation from one measurement of the standard reflection to the next was well within counting statistics, $\sigma I(\text{net}) = [I(\text{scan}) + (2.55)^2(B_1 + B_2)]^{1/2}$. The intensities of several symmetry-related reflections were recorded and the variation of intensity from one reflection to its symmetry-related partner was less than 4% of the total integrated intensity. The take-off 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 × 8 mm high. The half-width at half-peak height for an average reflections was 0.17° at a take-off angle of 3.7° indicating a mosaic spread such that all the reflection is counted during the 1.7° scan. The 0.17° is not an absolute value of the mosaic spread but is dependent upon other instrumental factors as well. The counting rate never exceeded 5000 counts/sec and thus no attenuators were used. The pulse height analyzer was set such that 90% of the scattered radiation was counted. Lorentz-polarization corrections were made to reduce the intensities to relative structure factors.

Solution of Structure

The centric space group *Pbnm* was assumed to be correct and the structure was solved and refined on this basis (*vide infra*). A three-dimensional Patterson function[18] was computed which showed the silver and chlorine atoms in two sets of the special positions of mirror symmetry $\pm (x, y, {}^1/_4;\ {}^1/_2 + x, {}^1/_2 - y, {}^3/_4)$. The remaining nonhydrogen atoms were located by standard heavy atom techniques.[18,19] In the later stages of the structure solution a three-dimensional map was computed and either large thermal parameters or disorder were noted for the three oxygen atoms bound to Cl(2). Five cycles of full-matrix anisotropic least squares[20a] with isotropic temperature factors for O(4), O(5), and O(6) [bound to Cl(2)] yielded 0.066, 0.066, and 1.103 for *R*, the weighted R_w, and the standard error of an observation of unit weight.[20b] No further attempts were made to refine O(4), O(5), and O(6). The final parameter shifts were 0.1σ or less. We minimized the function $\Sigma w \cdot (|F_o| - |F_c|)^2$ and the observations were weighted on counting statistics and a 4% intensity factor.[21] The scattering factors for

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(7) N. C. Baenziger, H. L. Haight, R. Alexander, and J. R. Doyle, *Inorg. Chem.*, **5**, 1399 (1966).

(8) F. S. Mathews and W. N. Lipscomb, *J. Phys. Chem.*, **63**, 845 (1959).

(9) S. C. Nyburg and J. Hilton, *Acta Crystallogr.*, **12**, 116 (1959).

(10) J. S. McKechnie and I. C. Paul, *J. Chem. Soc. B*, 1445 (1968).

(11) J. S. McKechnie, M. G. Newton, and I. C. Paul, *J. Amer. Chem. Soc.*, **89**, 4819 (1967).

(12) R. B. Jackson and W. E. Streib, *ibid.*, **89**, 2539 (1967).

(13) P. F. Rodesiler and E. L. Amma, submitted for publication in *Inorg. Chem.*

(14) N. F. M. Henry and K. Lonsdale, Ed., "International Tables for X-Ray Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1952, pp 151, 548, 119, 546.

(15) (a) T. C. Furnas, Jr., "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1957. (b) K. Knox, "Master Card Program for Picker Four-Angle Programmer," prepared by F. C. Carter, Picker Instruments, Cleveland, Ohio, 1967, p 11. (c) W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **22**, 457 (1967).

(16) Although the use of unfiltered radiation is somewhat unconventional, we have been able to demonstrate in more than one crystal structure analysis that this is a reliable means of data collection. However, one must use care in this process, especially with axial reflections and *hk*0, 0*kl*, and *h*0*l* data. The utility of this method depends on a number of factors such as cell dimensions, width of peaks, etc. In general, it is no worse than Zr-filtered Mo Kα radiation since this generally gives too low a background estimate at the low angle side of a reflection. We generally examine diffraction peaks from each crystal as to whether or not the unfiltered technique can be used, and if unfiltered radiation is used the background is carefully scrutinized by computer for each reflection. The Mo Kβ contribution from very intense Mo Kα reflections to other reflections is computed and subtracted out when they obviously overlap.

(17) R. A. Young, *Trans. Amer. Crystallogr. Ass.*, **1**, 42 (1965).

(18) 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.

(19) 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, Oak Ridge National Laboratory, Oak Ridge, Tenn., ORNL-TM-305, 1962, on the IBM 7040.

(20) (a) Application of Hamilton's *R* factor [W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1961)] showed that the anisotropic model was valid at greater than the 99.5% confidence level. All atoms iso $R_w = 0.108$, Ag, Cl anisotropic $R_w = 0.092$, all but those indicated above anisotropic 0.066. (b) $R = \Sigma\{[|F_o| - |F_c|]/\Sigma|F_o|\}$; $R_w = \{\Sigma w[|F_o| - |F_c|]^2/[\Sigma w|F_o|]^2\}^{1/2}$; standard error $= [\Sigma w(F_o - F_o)^2/(\text{NO} - \text{NV})]^{1/2}$, NO = 882, NV = 137.

Table I. Final Atomic Positional and Thermal Parameters for Indene Silver Perchlorate[a]

Atom	x	y	z	Atom	x	y	z
Ag(1)	−0.1167 (01)	0.2769 (02)	0.7500 (—)[b]	C(4)	0.1775 (16)	0.1025 (31)	0.5615 (14)
Ag(2)	0.1643 (02)	0.0956 (03)	0.7500 (—)	C(5)	0.1457 (15)	−0.0267 (26)	0.6043 (15)
Cl(1)	0.1230 (05)	0.4797 (08)	0.7500 (—)	C(6)	0.0537 (15)	−0.0411 (22)	0.6290 (12)
Cl(2)	−0.1544 (05)	0.6580 (09)	0.7500 (—)	C(7)	−0.0968 (13)	0.0932 (24)	0.6268 (12)
O(1)	0.0499 (13)	0.3743 (26)	0.7500 (—)	C(8)	0.1215 (13)	0.2349 (24)	0.5967 (12)
O(2)	0.2009 (11)	0.3759 (23)	0.7500 (—)	C(9)	−0.0451 (13)	0.3297 (21)	0.5487 (13)
O(3)	0.1217 (10)	0.5694 (17)	0.6728 (10)	O(4)	−0.2057 (17)	0.7806 (33)	0.7500 (—)
C(1)	−0.0007 (14)	0.0795 (20)	0.6091 (12)	O(5)	−0.0776 (21)	0.7302 (36)	0.7500 (—)
C(2)	0.0300 (15)	0.2129 (22)	0.5637 (12)	O(6)	−0.1796 (30)	0.5699 (58)	0.6788 (30)
C(3)	0.1194 (17)	0.2316 (28)	0.5387 (12)				

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ag(1)	42 (01)	131 (04)	61 (01)	−1 (02)	00 (—)[b]	00 (—)
Ag(2)	65 (01)	216 (05)	44 (01)	34 (02)	00 (—)	00 (—)
Cl(1)	60 (12)	278 (46)	116 (16)	82 (20)	00 (—)	00 (—)
Cl(2)	38 (04)	137 (13)	180 (10)	2 (10)	00 (—)	00 (—)
O(1)	60 (12)	278 (46)	116 (16)	82 (20)	00 (—)	00 (—)
O(2)	38 (10)	211 (37)	116 (15)	2 (16)	00 (—)	00 (—)
O(3)	102 (10)	301 (31)	91 (10)	−8 (16)	10 (09)	100 (16)
C(1)	72 (13)	93 (32)	50 (11)	2 (20)	−22 (10)	−10 (16)
C(2)	78 (14)	139 (35)	42 (10)	−9 (21)	−9 (11)	9 (17)
C(3)	84 (15)	292 (51)	36 (10)	−63 (27)	2 (11)	−9 (20)
C(4)	105 (17)	190 (41)	60 (13)	30 (25)	−7 (13)	−23 (21)
C(5)	85 (16)	153 (38)	58 (13)	29 (21)	−13 (11)	−19 (20)
C(6)	84 (15)	145 (37)	45 (11)	23 (21)	−14 (11)	−36 (17)
C(7)	65 (14)	201 (40)	47 (11)	22 (20)	−21 (10)	4 (18)
C(8)	69 (12)	195 (39)	47 (10)	−15 (22)	−21 (10)	3 (18)
C(9)	60 (13)	184 (37)	70 (13)	1 (19)	−17 (11)	34 (19)

Atom	B	Atom	B	Atom	B
O(4)	10.8 (1.6)	O(5)	16.3 (1.9)	O(6)	14.8 (3.2)

[a] Anisotropic temperature factors of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)] \times 10^4$. [b] (—) denotes fixed parameter.

silver(I), neutral chlorine, oxygen, and carbon were from Cromer and Waber.[22] The effects of anomalous dispersion were included in the structure factor calculations by addition to F_c;[23] the values for $\Delta f'$ and $\Delta f''$ for silver and chlorine were those given by Cromer.[24]

The final tabulation of observed and calculated structure factors are filed elsewhere.[25] Unobserved data were not used in the refinement but are listed with the calculated structure factors. Final atomic coordinate and temperature parameters are in Table I. Interatomic distances, angles, and errors[26] are shown in Table II. The least-squares plane and root-mean-square components of thermal displacement where appropriate are in Tables IV and III, respectively.

Results and Discussion

The structure of indene silver perchlorate may be described as isolated dimeric units, (indene·$AgClO_4$)$_2$, separated by silver–oxygen distances of 2.70 Å (Figure 1) or greater from neighboring dimeric units. This dimer unit is constructed by placing two silver atoms along with the chlorine and two oxygen atoms of each perchlorate group in a mirror plane. The indene molecules are then placed on either side of the mirror plane to form a "V"- or hinge-shaped arrangement with a dihedral angle between the organic groups of 98.7°. Within the dimer unit one of the silver atoms [Ag(1)] is bound only to the π orbitals of the olefin portion of the indene molecule. The other silver atom [Ag(2)] is bound only to the π orbitals of the aromatic ring (Figure 2); *i.e.*, the silver–olefin and the silver–aromatic interactions are mutually exclusive. If the silver–oxygen distances of 2.70 Å (sum of ionic radii = 2.66 Å[27]) or greater are considered to be nonbonding, then Ag(2) would be described as three coordinate, bonded to

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[21] C. H. Stout and L. H. Jensen, "X-Ray Structure Determination, A Practical Guide," Collier-Macmillan, Ltd., London, England, 1968, p 457.

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

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

[24] D. T. Cromer, *ibid.*, **18**, 17 (1965).

[25] These tables will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

[26] W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE, A Fortran Crystallographic Function and Error Program," ORNL-TM-396, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

[27] L. Pauling, "Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 514.

Table II. Interatomic Distances (Å) and Angles (Deg)

	Bonded Distances		
Ag(1)–C(8)	2.36 (2)	Ag(1)–C(7)	2.46 (2)
Ag(2)–C(6)	2.76 (2)	Ag(2)–C(5)	2.47 (2)
Ag(2)–O(2)	2.46 (2)	C(1)–C(2)	1.41 (2)
C(2)–C(3)	1.44 (3)	C(3)–C(4)	1.46 (3)
C(4)–C(5)	1.37 (3)	C(5)–C(6)	1.47 (3)
C(1)–C(6)	1.36 (2)	C(1)–C(7)	1.51 (2)
C(7)–C(8)	1.35 (2)	C(8)–C(9)	1.60 (3)
C(2)–C(9)	1.54 (2)	Cl(1)–O(1)	1.44 (2)
Cl(1)–O(2)	1.49 (2)	Cl(1)–O(3)	1.40 (1)
Cl(2)–O(4)	1.31 (3)	Cl(2)–O(5)	1.33 (3)
Cl(2)–O(6)	1.37 (5)		
	Selected Nonbonded Distances Less Than 4 Å		
Ag(1)–O(1)	2.70 (2)	Ag(1)–O(6′)	2.89 (5)
Ag(1)–O(4′′)	2.73 (3)	Ag(2)–O(1)	2.96 (2)
Ag(2)–O(2′′)	2.79 (2)	Ag(1)–C(1)	3.26 (2)
Ag(1)–C(9)	3.29 (2)	Ag(2)–C(4)	2.88 (2)
Ag(2)–C(1)	3.33 (2)		
	Angles		
C(7′)–Ag(1)–C(7)	99.2 (0.9)	C(8′)–Ag(1)–C(8)	162.2 (1.0)
Ag(1)–C(7)–C(8)	69.8 (1.1)	Ag(1)–C(8)–C(7)	77.9 (1.1)
C(5′)–Ag(2)–C(5)	128.0 (1.2)	C(6′)–Ag(2)–C(6)	83.5 (0.9)
Ag(2)–C(5)–C(6)	85.3 (1.2)	Ag(2)–C(6)–C(5)	62.7 (1.0)
O(4′′)–Ag(1)–O(1)	161.4 (1.0)	O(1)–Ag(1)–O(6′)	92.3 (1.5)
O(6′)–Ag(1)–O(4′′)	93.0 (1.0)	Ag(1)–O(6′)–Cl(2′)	94.8 (2.2)
Ag(1)–O(1)–Cl(1)	159.3 (1.4)	Ag(2)–O(2)–Cl(1)	113.0 (0.9)
Ag(2)–O(2)–Ag(2′)	145.4 (0.8)	O(1)–Ag(2)–O(2)	50.0 (0.8)
O(2)–Ag(2′)–O(2′)	118.8 (0.3)	C(1)–C(2)–C(3)	122.7 (2.0)
C(4)–C(5)–C(6)	122.2 (2.0)	C(5)–C(6)–C(1)	118.3 (1.9)
C(6)–C(1)–C(2)	120.7 (2.0)	C(6)–C(1)–C(7)	128.5 (2.0)
C(1)–C(7)–C(8)	106.6 (1.8)	C(7)–C(8)–C(9)	113.6 (1.7)
C(8)–C(9)–C(2)	99.0 (1.4)	C(9)–C(2)–C(1)	109.9 (1.8)
C(2)–C(1)–C(7)	110.7 (1.7)	C(3)–C(2)–C(9)	127.4 (1.9)
O(2)–Cl(1)–O(1)	104.9 (1.2)	O(1)–Cl(1)–O(3)	109.6 (0.8)
O(2)–Cl(1)–O(3)	109.2 (0.8)	O(4)–Cl(1)–O(4)	99.6 (1.7)
O(5)–Cl(1)–O(6)	120.1 (2.0)	O(4)–Cl(1)–O(6)	105.5 (2.0)
O(2)–Ag(2)–C(5)	116.0 (1.4)	O(2)–Ag(2)–C(6)	109.3 (1.4)
O(3)–Cl(1)–O(3′)	113.8 (1.0)	O(6)–Cl(2)–O(6′)	104.1 (2.5)

Table III. Root-Mean-Square Displacements along Principal Axes of the Thermal Ellipsoid, Å

Atom	Axis 1	Axis 2	Axis 3
Ag(1)	0.219 (03)	0.225 (03)	0.269 (03)
Ag(2)	0.228 (03)	0.236 (03)	0.318 (03)
Cl(1)	0.226 (11)	0.237 (11)	0.264 (09)
Cl(2)	0.213 (12)	0.226 (10)	0.460 (13)
O(1)	0.176 (35)	0.368 (25)	0.379 (27)
O(2)	0.212 (28)	0.279 (24)	0.369 (24)
O(3)	0.203 (23)	0.352 (17)	0.419 (19)
C(1)	0.178 (32)	0.212 (31)	0.321 (26)
C(2)	0.208 (31)	0.231 (30)	0.311 (28)
C(3)	0.203 (27)	0.251 (34)	0.383 (33)
C(4)	0.232 (32)	0.278 (31)	0.367 (30)
C(5)	0.216 (31)	0.252 (29)	0.343 (30)
C(6)	0.172 (33)	0.252 (31)	0.338 (28)
C(7)	0.192 (32)	0.269 (27)	0.315 (28)
C(8)	0.202 (29)	0.263 (27)	0.318 (26)
C(9)	0.211 (31)	0.267 (27)	0.326 (26)

Table IV

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

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

$A = -0.9707, B = 0.2400, C = 0.0062, D = -2.1682$

Deviation of Atoms from the Least-Squares Plane, Å[b]

Ag(2)	−0.021 (02)	O(2)	0.006 (02)
C(5)	−0.006 (24)	C(5′)	0.021 (24)

$A = -0.2040, B = -0.4345, C = -0.8772, D = -8.4195$

Deviation of Atoms from the Least-Squares Plane, Å

C(1)	−0.002 (18)	C(4)	−0.011 (26)	C(7)	0.012 (19)
C(2)	0.014 (18)	C(5)	−0.004 (22)	C(8)	−0.032 (19)
C(3)	−0.003 (19)	C(6)	0.009 (19)	C(9)	0.017 (20)

[a] x, y, and z refer to atom positional parameters in ångströms. All atoms were equally weighted in the least-squares plane: ref 14, Vol. II, p 61. [b] It must be borne in mind that Ag(2) and O(2) lie in the crystallographic mirror.

C(5), C(5′), and O(2), whereas, Ag(1) would be considered two coordinate bonded to C(8) and C(8′).

A distorted trigonal plane best describes the coordination polyhedra of Ag(2) with the angles about Ag(2) being 116.0 (1.4)° and 128.0 (1.2)° for O(2)–Ag(2)–C(5) and C(5)–Ag(2)–C(5′), respectively. Table IV shows that the maximum deviation from the least-squares plane containing Ag(2), O(2), C(5), and C(5′) is 0.02

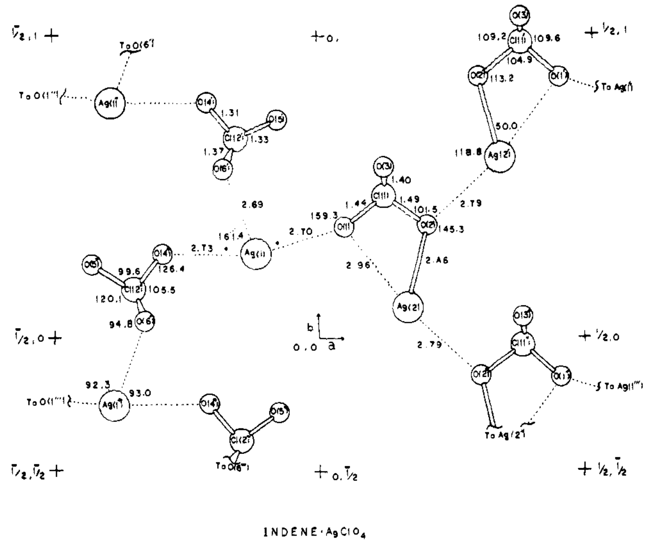

Figure 1. Perspective view of the indene·AgClO$_4$ structure down the *c* axis. Ag(1), Ag(2), Cl(1), Cl(2), O(1), O(2), O(4), and O(5) lie in the mirror plane at $Z = {}^3/_4$ (plane of paper). O(3) and O(6) are above this plane and the symmetry-related O(3') and O(6') are below. The carbon atoms are omitted for clarity. Bonds are indicated by solid lines and dotted lines represent weak or van der Waals interactions.

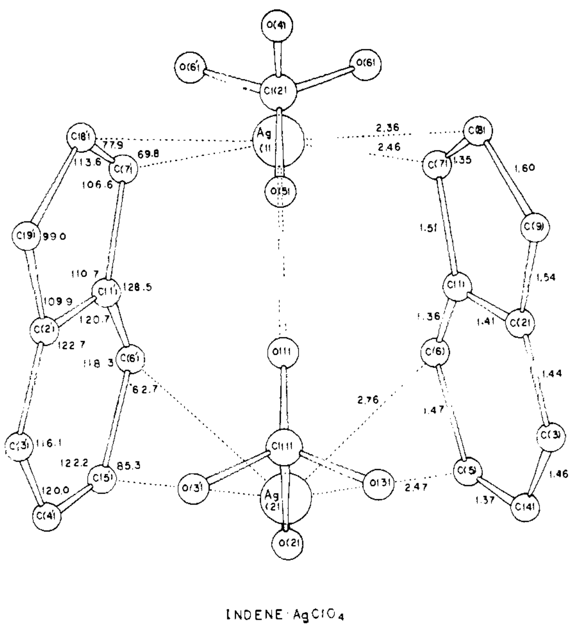

Figure 2. Perspective view of the indene·AgClO$_4$ dimer down the *b* axis with *a* vertical and pointing down the page, showing the relationship between the AgClO$_4$ and aromatic portions of the dimer. The crystallographic mirror is vertical and contains Ag(1), Ag(2), Cl(1), O(1), O(2), Cl(2), O(4), and O(5). The remaining atoms are related to one another by this mirror.

(2) Å. To our knowledge this is the first structure reported in which the silver atom involving aromatic donors has trigonal-planar geometry. Related trigonal-planar coordination for Ag(I) in olefin complexes has been observed.[7,8] However, the silver atom including a 2.66-Å Ag–O distance was found to be three-coordinate, but pyramidal in bis(cyclohexylbenzene)silver perchlorate.[3b]

The usual silver–carbon (aromatic) distance of 2.47 Å[3] is seen for Ag(2)–C(5) interaction with the next shortest silver-carbon distance, Ag(2)–C(6), of 2.76 Å. The latter value of 2.76 Å is intermediate in the range of previously observed values.[2,3,5] Furthermore, this same silver [Ag(2)] is also bound to O(2) with a silver-oxygen distance of 2.46 (2) Å which is one of the shortest values found when compared to those found for silver perchlorate–aromatic complexes that range from 2.49 to 2.66 Å.[2–5] This silver–oxygen distance of 2.46 Å is in agreement with our earlier proposal that the role of anions in metal ion–aromatic complexes is important in the stabilization of these structures.[3,13] Shorter silver–oxygen distances (2.34–2.46 Å) have been observed in naphthalene·4AgClO$_4$·4H$_2$O,[6] anthracene·4AgClO$_4$·H$_2$O,[6] and acenaphthene·AgClO$_4$.[13] In the former two cases the short silver–oxygen distances are associated with the oxygen atoms of the water molecules and in the latter case silver–oxygen distances range from 2.34 to 2.46 Å. Silver–oxygen distances of 2.34 Å were observed in Ag$_3$PO$_4$[28] and 2.42 Å in Ag$_3$AsO$_4$[29] and Ag$_2$MoO$_4$.[30] For comparative purposes the silver–oxygen distance obtained from the sum of the respective covalent radii is 2.18 Å.[27] The next shortest Ag(2)–O distance is 2.79 Å, Ag(2)–O(2').

In contrast Ag(1) is bound to the olefin part of the indene molecule with a short distance of 2.36 (2) Å to C(8) and the next shortest distance at 2.46 (2) Å to C(7). This result is in agreement with the general concept that olefins are stronger π bases than are aromatics. These shorter silver–carbon distances are indicative of silver(I)-olefin complexes[7–12] and not silver(I)-aromatic complexes. The coordination polyhedron about Ag(1) may be described as a very distorted linear arrangement. The exact angle is not completely defined since C(7')–Ag(1)–C(7) is 99.2 (9)° and C(8')–Ag(1)–C(8) is 162°, but an average angle would be ∼130°. This assumes Ag(1) is bound only to the olefins and the silver–oxygen distances are considered nonbonding. The shortest Ag(1)–O distance is 2.70 Å, and, consequently, the silver–oxygen interactions are less important in the olefin part of the indene molecule. It is interesting to note that the perchlorate group associated with the silver atom [Ag(1)] bound to the olefin shows considerable thermal motion or disorder, which is compatible with the concept of very weak silver–oxygen interactions.

The remaining silver–oxygen distances range from 2.70 to 2.89 Å and are somewhat longer than the average longest value of 2.66 Å[2–6] observed in other silver perchlorate–aromatic complexes. For this reason these long silver–oxygen distances are considered to be essentially nonbonded.

The chlorine–oxygen distances and angles associated Cl(1) are close to the expected values.[31] The oxygen atoms bound to Cl(2) show considerable thermal motion or possible disorder. Thus, the distortions in chlorine–oxygen bond distances and angles probably are not significant.

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

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

(30) J. Donohue and W. Shand, Jr., *ibid.*, **69**, 222 (1947).

(31) L. E. Sutton, Ed., "Tables of Interatomic Distances and Configurations in Molecules and Ions," Supplement 1956–1959, The Chemical Society, London, 1965, p 585.

The carbon–carbon bond distances and angles in the indene molecule show the expected values.

Consideration of the so-called "super-delocalizability" index described by Fukui and coworkers[32] shows that the index which is related to the π-electron density is highest for carbon positions 7 and 8. This is the position of the carbon–carbon double bond in the five-membered ring and the short silver–carbon distances. The next highest value of the index is found for positions 5 and 6 in the indene molecule. Again this is where Ag(2) binds to the six-membered aromatic ring. Although these calculations are based upon a rather simplified model, they are quite successful in predicting where the silver will interact with the aromatic ring.

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(32) K. Fukui, *et al.*, *Bull. Chem. Soc. Jap.*, **34**, 1076 (1961).