Synthesis and Crystal Structure of the Silver Perchlorate Adduct of Iron(III) Trisacetylacetonate Monohydrate

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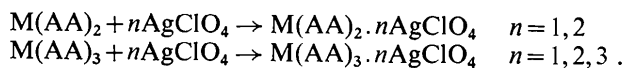
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Crystals of $Fe(acac)_3.AgClO_4.H_2O$ are monoclinic, space group $P2_1/c$, with $a = 12.274$ (5), $b = 11.761$ (5), $c = 17.235$ (5) Å, $\beta = 120.64$ (12)°, $D_m = 1.72$, $D_c = 1.79$ g cm^{-3}, $Z = 4$. The structure was solved from Patterson and electron density maps and refined by full-matrix least-squares methods to $R = 0.066$ for 1672 independent non-zero counter reflexions. The silver ion is located near two chelate rings but is apparently bonded to the 'active methylene' carbon atom of only one ring, Ag–C = 2.29 (2) Å. The silver ion is also bonded to an oxygen atom of the perchlorate group, Ag–O = 2.50 (2) Å and to the hydrate oxygen atom, Ag–O = 2.25 (2) Å. All four atoms lie in approximately the same plane. The perchlorate ion shows enhanced thermal motion but is not greatly distorted from its normal tetrahedral shape. The iron atom is surrounded octahedrally by the oxygens of the three acetylacetonate rings.

Introduction

Ginsberg (1964) and Oestreich (1962) have described the formation of adducts of silver(I) and metal acetylacetonates. Addition of silver perchlorate in benzene or toluene to a solution of the metal acetylacetonate yields adducts which contain up to one silver perchlorate molecule per chelate ring.

$$M(AA)_2 + nAgClO_4 \rightarrow M(AA)_2.nAgClO_4 \quad n = 1,2$$
$$M(AA)_3 + nAgClO_4 \rightarrow M(AA)_3.nAgClO_4 \quad n = 1,2,3 .$$

Structural investigation of these products has been limited to the trisilver dinitrate tris(acetylacetonato)-nickelate(II) monohydrate complex (Watson & Lin, 1966).

Experimental

The compound was prepared by mixing stoichiometric quantities of silver perchlorate and ferric acetylacetonate dissolved in toluene. Dark red crystals of the adduct $Fe(C_5H_7O_2)_3.AgClO_4.H_2O$ were formed on slow evaporation. Unlike most other silver perchlorate complexes, which tend to be deliquescent, the crystals were found to be stable in air for several months and did not decompose on exposure to X-rays.

Weissenberg and precession photographs showed that the crystals were monoclinic with space group $P2_1/c$; systematic absences were $0k0$ for $k \neq 2n$; $h0l$ for $l \neq 2n$.

A crystal with dimensions $0.6 \times 0.4 \times 0.2$ mm was mounted on a standard Philips PW1100 computer controlled X-ray diffractometer. A least-squares fit of the χ, φ and 2θ angles of 25 accurately centred reflexions gave $a = 12.274$ (5), $b = 11.761$ (5), $c = 17.235$ (5) Å,

$\beta = 120.64$ (12)° at 20°C. An approximate value of 1.72 cm^{-3} was obtained for the crystal density by flotation in solutions of thallium malonate. An accurate value was unobtainable as the crystals dissolved slowly in these solutions and halocarbon mixtures. D_c was 1.79 g cm^{-3} for $Z = 4$.

With graphite monochromated Mo radiation ($\lambda = 0.7107$ Å) 1846 independent reflexions were measured by the $\omega-2\theta$ scan technique between $\theta = 3$ and 20°. The scan width was 1° in θ and the scanning speed, 0.02° s^{-1}. The total background scan time and the integration time while scanning over the peak were both 50 s. Detector apertures of 2° in the 2θ plane and 1° at right angles to it were used. Reflexions were rejected if $I < 2\sigma(I)$ where $\sigma(I) = [(0.02N_o)^2 + N_o + K^2N_b]^{1/2}$. N_o is the gross count, N_b the background count, and K the ratio of scan to background time. Of the 1846 measured reflexions 1672 were retained after application of this criterion. Lorentz and polarization corrections were applied to give relative structure factors. No absorption corrections were made, as $\mu = 17.62$ cm^{-1} and A^* varied only from 1.95 to 1.94 over the range $\theta = 3°$ to $\theta = 20°$.

Determination of the structure

A Patterson map gave the positions of the four silver ions in the unit cell. Two consecutive electron density maps located the remaining non-hydrogen atoms except the hydrate oxygen atom. A scaled structure-factor calculation based on the positions of all the known atoms before refinement yielded an R of 0.175, where $R = \sum(|F_o| - |F_c|)/\sum|F_o|$.

Three cycles of full-matrix isotropic least-squares refinement (Busing, Martin & Levy, 1962) reduced R to 0.139. The function minimized was $\sum w(|F_o| - |F_c|)^2$ and unit weights were applied. A difference map was computed and the hydrate oxygen atom located. Apart

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from this peak the map was featureless. Three further cycles of isotropic refinement lowered R to 0·103. Several cycles of anisotropic refinement were executed and R converged to its final value of 0·066. Computations were carried out on a Univac 1106 computer. Scattering factors tabulated by Cromer & Waber (1965) were employed for all atoms.*

Table 1 contains the final atomic coordinates and thermal parameters. Interatomic distances and angles are listed in Tables 2 and 3. Numbers in parentheses are the estimated standard deviations and refer to the least significant digits. Several planes of interest are listed in Table 4. Illustrations of the molecular structure were drawn with the program *ORTEP* (Johnson, 1965).

Discussion

The structure consists of ferric acetylacetonate moieties arranged in a staggered array along z to form a bulky sheet-like structure parallel to the *bc* plane (Fig. 1). Because the three chelate rings of each acetylacetonate molecule are mutually perpendicular, these sheets create 'cylindrical holes' in a direction parallel to y.

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* The table of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30312 (12 pp.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Interatomic distances (Å) with their e.s.d.'s in parentheses*

Interatomic bonded separations

Fe—O(1)	1·98 (1)	C(2)—C(3)	1·38 (2)
Fe—O(2)	2·02 (1)	C(3)—C(4)	1·32 (2)
Fe—O(3)	1·97 (1)	C(7)—C(8)	1·41 (2)
Fe—O(4)	1·99 (1)	C(8)—C(9)	1·38 (2)
Fe—O(5)	2·02 (1)	C(12)–C(13)	1·40 (2)
Fe—O(6)	2·01 (1)	C(13)–C(14)	1·42 (2)
O(1)–C(2)	1·30 (2)	C(1)—C(2)	1·49 (2)
O(2)–C(4)	1·32 (2)	C(4)—C(5)	1·55 (2)
O(3)–C(7)	1·23 (2)	C(6)—C(7)	1·55 (2)
O(4)–C(9)	1·31 (2)	C(9)—C(10)	1·49 (2)
O(5)–C(12)	1·24 (2)	C(11)–C(12)	1·56 (2)
O(6)–C(14)	1·31 (2)	C(14)–C(15)	1·49 (2)
Cl—O(7)	1·27 (3)	Ag—O(8)	2·50 (2)
Cl—O(8)	1·41 (2)	Ag—O(11)	2·25 (1)
Cl—O(9)	1·41 (2)	Ag—C(13)	2·29 (2)
Cl—O(10)	1·39 (2)		

Interatomic non-bonded separations

Ag—O(4)	2·73 (1)	C(2)—C(4)	2·43 (3)
Ag—C(12)	2·87 (2)	C(7)—C(9)	2·45 (2)
Ag—C(14)	2·75 (2)	C(12)–C(14)	2·48 (2)
O(1)–O(2)	2·81 (2)	C(13)–O(8)	3·84 (3)
O(3)–O(4)	2·76 (2)	O(8)—O(11)	4·10 (3)
O(5)–O(6)	2·76 (1)	O(11)–C(13)	4·16 (3)
O(7)–O(8)	2·21 (4)	C(13)–O(4)	3·44 (2)
O(7)–O(9)	2·25 (6)	O(8)—O(4)	3·45 (2)
O(7)–O(10)	2·20 (3)		
O(8)–O(9)	2·12 (3)	O(11)–O(4)	4·10 (3)
O(8)–O(10)	2·33 (3)		
O(9)–O(10)	2·23 (3)		

Table 1. *Positional and thermal parameters*

Positional parameters are given as fractional coordinates ($\times 10^4$) and thermal parameters ($\times 10^{-2}$) are given according to the expression $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Isotropic B (Å)^2
Ag	3410 (1)	983 (1)	3045 (1)	8 (4)	6 (3)	4 (2)	−1 (3)	3 (2)	0 (2)	3·38
Fe	1595 (2)	8911 (2)	3784 (1)	5 (6)	1 (4)	1 (2)	0 (4)	2 (3)	0 (3)	1·31
Cl	3781 (5)	−98 (4)	1399 (3)	12 (15)	6 (11)	6 (7)	0 (11)	6 (9)	0 (7)	3·97
C(1)	8159 (17)	8493 (16)	3835 (14)	8 (52)	8 (46)	8 (33)	−1 (40)	6 (36)	−2 (32)	3·74
C(2)	9548 (17)	8533 (13)	4204 (12)	12 (60)	3 (34)	6 (30)	0 (36)	7 (38)	0 (26)	2·87
C(3)	424 (17)	8488 (16)	5118 (11)	9 (55)	8 (46)	3 (25)	0 (41)	3 (33)	0 (27)	3·70
C(4)	1675 (19)	8499 (14)	5516 (11)	16 (68)	3 (34)	3 (24)	1 (39)	6 (36)	1 (23)	2·88
C(5)	2543 (22)	8367 (18)	6553 (12)	19 (79)	10 (52)	3 (25)	5 (52)	5 (37)	2 (29)	4·55
C(6)	2434 (18)	5448 (13)	3524 (13)	12 (59)	2 (33)	7 (32)	0 (35)	6 (38)	1 (26)	3·07
C(7)	2645 (15)	6751 (13)	3662 (10)	8 (50)	3 (35)	2 (20)	−1 (34)	3 (27)	0 (21)	1·97
C(8)	3831 (16)	7206 (13)	3891 (11)	9 (51)	3 (36)	3 (23)	−1 (35)	3 (28)	0 (23)	2·48
C(9)	4108 (15)	8350 (14)	4007 (9)	7 (47)	5 (40)	1 (19)	1 (35)	2 (24)	0 (21)	2·02
C(10)	5374 (15)	8767 (16)	4220 (12)	5 (46)	8 (45)	5 (26)	−2 (36)	3 (29)	0 (28)	3·54
C(11)	275 (18)	156 (19)	1068 (11)	11 (58)	12 (56)	2 (23)	−2 (46)	2 (31)	1 (28)	4·27
C(12)*	840 (14)	176 (14)	2111 (9)	5 (−)	7 (−)	0 (−)	0 (−)	1 (−)	0 (−)	2·07
C(13)	1304 (15)	1212 (13)	2562 (9)	7 (45)	4 (36)	1 (20)	0 (32)	1 (24)	1 (22)	2·32
C(14)	1550 (15)	1409 (13)	3453 (11)	7 (46)	2 (34)	4 (26)	1 (31)	3 (29)	0 (24)	2·42
C(15)	1677 (20)	2593 (14)	3797 (13)	17 (70)	2 (36)	6 (29)	1 (38)	5 (38)	0 (25)	4·05
O(1)	−117 (10)	8702 (9)	3606 (7)	8 (30)	5 (24)	4 (15)	−1 (21)	4 (18)	0 (15)	2·26
O(2)	2343 (10)	8665 (9)	5123 (7)	10 (33)	5 (24)	2 (14)	1 (22)	2 (18)	1 (14)	2·59
O(3)	1717 (10)	7290 (8)	3555 (7)	8 (31)	2 (21)	4 (15)	0 (21)	4 (19)	−1 (14)	2·30
O(4)	3313 (9)	9127 (8)	3960 (6)	7 (29)	2 (20)	3 (14)	−1 (21)	3 (17)	0 (14)	1·86
O(5)	774 (9)	9274 (8)	2453 (6)	7 (29)	4 (23)	1 (12)	−1 (21)	2 (15)	0 (13)	1·97
O(6)	1570 (10)	593 (8)	3975 (6)	9 (31)	2 (21)	3 (14)	1 (19)	4 (17)	0 (14)	1·98
O(7)	3731 (53)	979 (24)	1358 (50)	127 (16)	12 (3)	114 (14)	6 (6)	116 (14)	4 (5)	21·44
O(8)	3523 (27)	3489 (17)	2054 (16)	55 (6)	14 (2)	15 (2)	5 (3)	25 (3)	3 (2)	10·03
O(9)	2770 (25)	9360 (33)	642 (16)	28 (4)	49 (6)	8 (1)	−8 (2)	2 (2)	−5 (3)	14·20
O(10)	4907 (20)	9490 (15)	1501 (20)	23 (3)	11 (2)	30 (3)	5 (2)	22 (3)	3 (2)	10·34
O(11)	5132 (12)	2036 (11)	3932 (8)	12 (2)	8 (1)	5 (1)	−3 (1)	4 (1)	0 (1)	4·88

* During the anisotropic temperature refinement of C(12), the temperature factor coefficients formed a 'non-positive definite' test determinant, and consequently the thermal parameters of this atom could not be refined.

Table 3. *Interatomic bond angles* (°) *with their e.s.d.'s in parentheses*

O(1)—Fe——O(2)	89·3 (5)		C(2)—C(3)—C(4)	127·7 (16)
O(3)—Fe——O(4)	88·4 (4)		C(7)—C(8)—C(9)	123·8 (15)
O(5)—Fe——O(6)	86·4 (4)		C(12)–C(13)–C(14)	122·8 (14)
Fe——O(1)—C(2)	129·3 (11)		O(7)—Cl——O(8)	111·4 (22)
Fe——O(2)—C(4)	124·7 (11)		O(7)—Cl——O(9)	113·8 (37)
Fe——O(3)—C(7)	128·8 (10)		O(7)—Cl——O(10)	111·8 (17)
Fe——O(4)—C(9)	128·3 (9)		O(8)—Cl——O(9)	97·7 (17)
Fe——O(5)—C(12)	127·3 (9)		O(8)—Cl——O(10)	113·3 (15)
Fe——O(6)—C(14)	127·3 (9)		O(9)—Cl——O(10)	108·0 (17)
O(1)—C(2)—C(3)	122·2 (16)		C(13)–Ag——O(8)	106·2 (8)
O(2)—C(4)—C(3)	126·5 (15)		C(13)–Ag——O(11)	132·7 (5)
O(3)—C(7)—C(8)	126·3 (14)		O(8)—Ag——O(11)	119·4 (7)
O(4)—C(9)—C(8)	123·5 (15)			
O(5)—C(12)–C(13)	126·0 (12)		C(13)–Ag——O(4)	86·0 (4)
O(6)—C(14)–C(13)	122·8 (14)		O(8)—Ag——O(4)	82·3 (5)
			O(11)–Ag——O(4)	110·5 (4)
O(1)—C(2)—C(1)	115·1 (16)			
O(2)—C(4)—C(5)	111·3 (16)		O(1)—Fe——O(3)	91·8 (4)
O(3)—C(7)—C(6)	114·6 (14)		O(1)—Fe——O(5)	88·5 (4)
O(4)—C(9)—C(10)	116·0 (14)		O(1)—Fe——O(6)	92·5 (4)
O(5)—C(12)–C(11)	115·9 (15)		O(2)—Fe——O(3)	93·0 (4)
O(6)—C(14)–C(15)	116·7 (14)		O(2)—Fe——O(4)	90·9 (4)
			O(2)—Fe——O(6)	89·4 (4)
C(1)—C(2)—C(3)	122·7 (15)		O(3)—Fe——O(5)	91·3 (4)
C(3)—C(4)—C(5)	122·0 (16)		O(4)—Fe——O(5)	91·3 (4)
C(6)—C(7)—C(8)	119·1 (15)		O(4)—Fe——O(6)	87·3 (4)
C(8)—C(9)—C(10)	120·5 (15)			
C(11)–C(12)–C(13)	117·9 (14)		O(1)—Fe——O(4)	179·8 (4)
C(13)–C(14)–C(15)	120·2 (14)		O(2)—Fe——O(5)	175·2 (4)
			O(3)—Fe——O(6)	175·0 (4)

Table 4. *Deviations of the silver ion from certain planes*

Atoms defining the plane	Deviation of Ag⁺ from the plane
C(13), O(4), O(8)	1·35 Å
C(13), O(4), O(11)	0·73
O(4), O(8), O(11)	0·97
O(8), O(11), C(13)	0·17

These 'holes' are filled with silver(I) and perchlorate ions (Fig. 2). A projection of the structure is given in Fig. 3.

Mean values of bond distances and angles of the chelate rings are shown in Fig. 4 and are consistent with the values found in the parent compound, $Fe(acac)_3$, (Iball & Morgan, 1967). The regular octa-
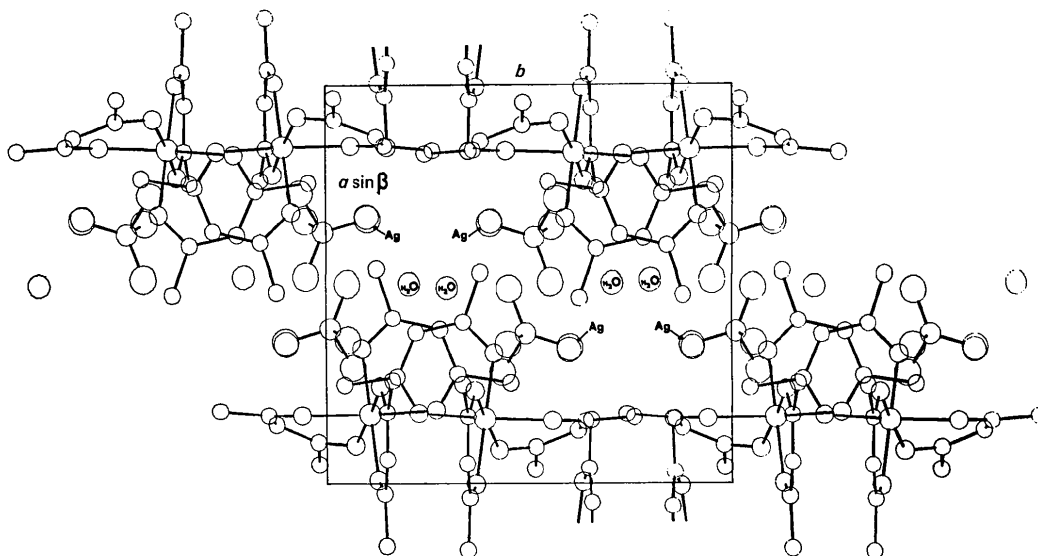

Fig. 1. [001] projection of the structure.

hedral arrangement of the chelate oxygen atoms about the central iron atom is confirmed by the O–Fe–O bond angles which vary from 87·3 to 93·0°.

Each silver ion is surrounded by a perchlorate oxygen O(8), the hydrate oxygen O(11) and the central
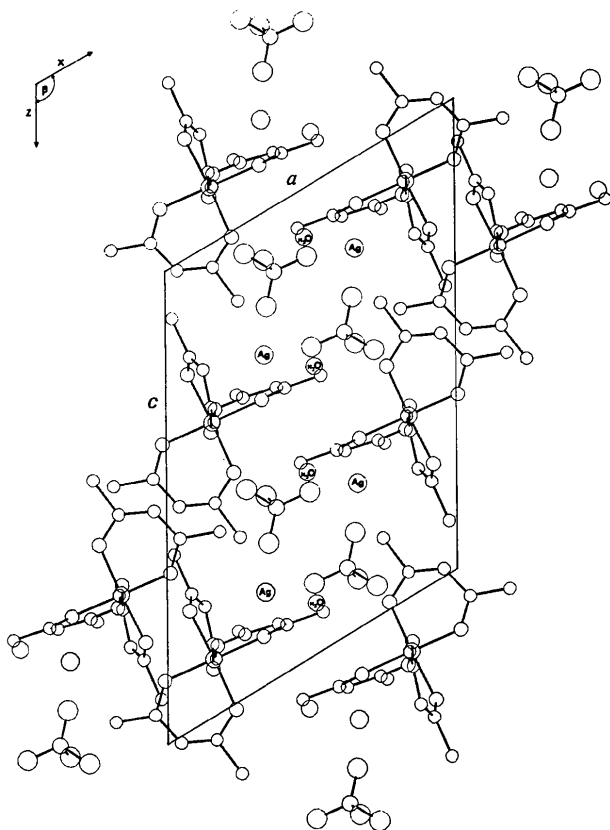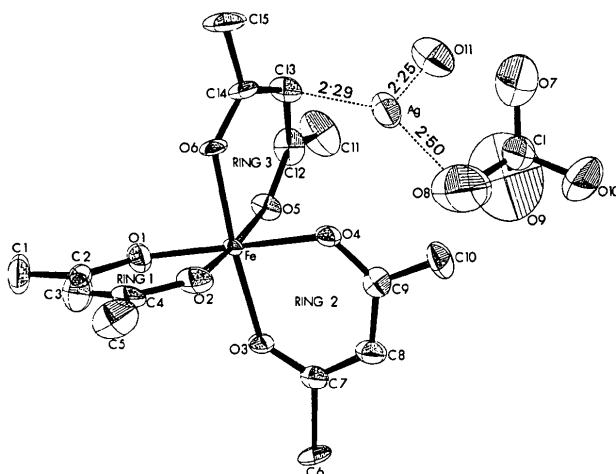

Fig. 2. [010] projection of the structure.

Fig. 3. A view of the structure showing bonding interactions of the silver ion.

carbon atom C(13), of ring 3. All four atoms lie in approximately the same plane.

Considering silver-to-oxygen distances of 2·70 Å or greater to be non-bonding (Rodesiler, Hall Griffith & Amma, 1972), the silver ion is bonded to O(8) (2·50 Å) and to O(11) (2·25 Å). The distance between the silver and the central carbon atom, C(13), of ring 3 is 2·29 Å. This is regarded as an interaction of the silver ion with the electron pair of the methylene carbon similar to that found in the structure of trisilver dinitrate tris(acetylacetonato)nickelate(II) monohydrate (Watson & Lin, 1966), where the Ag–C distance is 2·34 Å. The interatomic distances Ag–C(12) and Ag–C(14) are 2·87 and 2·75 Å respectively and are regarded as too large to represent atomic interactions.

The Ag–O(4) distance is 2·73 Å. There is some doubt as to whether this distance can be considered as a significant bonding interaction owing to the fact that it just exceeds the value of the sum of the silver and oxygen ionic radii, 2·66 Å (Pauling, 1960). In order to establish whether the coordination about the silver ion is three- or fourfold, four planes were calculated each with three of the four atoms O(4), O(8), O(11), C(13). In each case the perpendicular distance of the silver ion to the plane was calculated.

From Table 4 it is seen that the deviation of the silver ion from the first three planes varies markedly from 0·73 to 1·35 Å. All these planes contain the chelate oxygen O(4). The deviation from the fourth plane containing the atoms O(8), O(11) and C(13) is seen to be only 0·17 Å. Thus the silver ion lies almost in the plane of the atoms O(8), O(11) and C(13).

It seems reasonable therefore to consider the coordination about the silver ion in terms of a near planar, distorted trigonal arrangement rather than an irregular fourfold arrangement.

It is possible that for each of the chelate rings a certain degree of bending can occur about an axis drawn through the dionato oxygens of each ring (Fig. 5).

The bonding of the silver ion to C(13) results in the ring being bent by 15°47' in the direction of the silver ion. This clearly illustrates the significance of the Ag–C(13) interaction. Ring 1 is planar within experimental error. Although the Ag–O(4) interaction is considered to be non-bonding, ring 2 is found to be bent 7°9' about the O(3)–O(4) axis. Although this angle is much smaller than that found for ring 3, it must be considered real and for this reason the Ag–O(4) interaction cannot be entirely discounted. It is concluded that although the Ag–O(4) distance of 2·73 Å reflects a weak interaction, the dionato oxygen O(4) contributes to the stabilization of the structure.

The nature of bonding of the silver ion described above contrasts with the interpretation that was given in an earlier note (Nassimbeni & Thackeray, 1973) reporting the structure obtained from visual intensities. No hydrate oxygen atom was located and consequently the coordination of the silver ion was described in terms of a trigonal pyramidal arrangement with the

silver ion bonded to O(4) (2·66 Å), O(8) (2·51 Å) and C(13) (2·32 Å). The presence of the hydrate oxygen clearly invalidates this earlier description.

Large thermal parameters were found for all the perchlorate oxygens (Fig. 1). Disorder and high thermal motion are not uncommon in perchlorate structures and in the silver perchlorate–dioxane complex the perchlorate oxygen atoms were found to be rotating at room temperature (Prosen & Trueblood, 1956).

Despite the large thermal motion of the perchlorate ion, three Cl–O bond distances (1·39–1·41 Å) and all the tetrahedral angles are close to their expected values. The Cl–O(7) bond distance is contracted to 1·27 Å. No reason is apparent for this shortening.

Although no hydrogen atoms were located in the structure, the water molecule is probably hydrogen bonded to O(2') of an adjacent iron acetylacetonate molecule and O(10') of a neighbouring ClO_4^- ion. The O(11)–O(2') and O(11)–O(10') separations are 2·79 and 2·98 Å which compare favourably with the O–O hydrogen-bonded separations found in ice (Pauling, 1960). The angle O(2')–O(11)–O(10') is 107·7° which is in close agreement with the theoretical tetrahedral angle of 109°28' found in ice.

Of the four perchlorate oxygens only O(8) is seen to be bonded to the silver ion. O(10) is probably stabilized by hydrogen bonding. O(7) and O(9) are not stabilized by any interaction with other atoms. This fact probably accounts for the high B values of O(7) and O(9) in contrast to the smaller values of O(8) and O(10).

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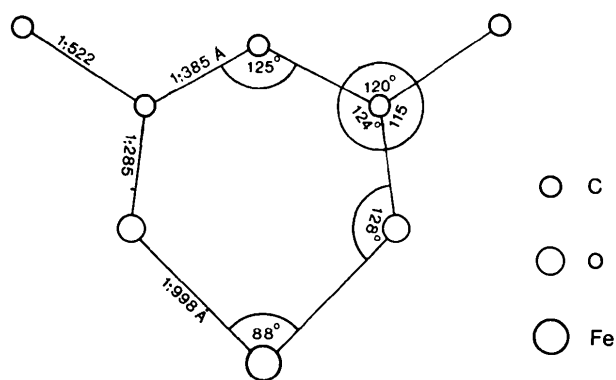CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* 18, 104–109.

Fig. 4. Mean values of bond distances and angles in the acetylacetonate rings.
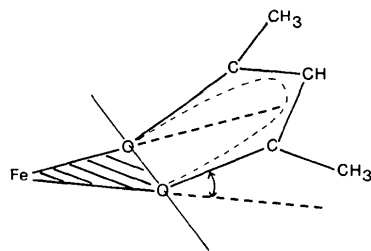

Fig. 5. Bending of the acetylacetonate ring about the O–O axis as a result of interaction with the silver ion.

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