Thus, the covalent hypochlorite group was oxidized to the perchlorate anion. An excellent material balance was obtained for this reaction. Again only one oxygen from each ozone was added to the substrate. Furthermore, it was found that with a deficiency of O_3 or with short reaction periods, the only products were nitronium perchlorate and unreacted chlorine nitrate. Other intermediate oxidation products were not observed and, hence, must have been more reactive than $ClONO_2$. The white solid was readily identified as $NO_2^+ClO_4^-$ by its infrared spectrum[30] and comparison to an authentic sample. This reaction represents a new process for preparing nitronium perchlorate. Its main advantage consists of the elimination of ClO_2, one of the two shock-sensitive materials required for the conventional[31] $NO_2^+ClO_4^-$ synthesis.

The $BrONO_2$-O_3 System. The $BrONO_2$-O_3 reaction has previously been reported[6] to yield O_2BrONO_2. We reinvestigated this system since it now appeared to be a promising synthetic route to the novel and interesting compound $NO_2^+BrO_4^-$. All effort to this end, however, failed since at or below −45°, the only product was O_2BrONO_2, while at higher temperatures, degradation of the bromyl intermediate was encountered.

The CF_3OCl-O_3 System. Prolonged contact of trifluoromethyl hypochlorite with neat ozone at −45° did not result in any oxygenation of the chlorine or other reaction. Thus, CF_3OClO_3, a compound recently obtained by another synthetic approach,[32] was not observed.

General Aspects. Comparison of the results of the present study raises an interesting question. Whereas covalent hypochlorite groups are generally oxidized by O_3 to the O_2ClO group, *i.e.*, to chlorine (+V), the chlorine in $ClONO_2$ is oxidized to the +VII state. This is surprising since $ClOClO_3$ and $ClONO_2$ are both covalent hypochlorites of similar structure and reactivity, and the perchlorato and nitrato group are of similar electronegativity. Comparison of the resulting ozonization products, however, reveals a marked difference. The products, in which the original hypochlorite chlorine is oxidized to the +V oxidation state, are mainly covalent and polarized toward the $ClO_2^+X^-$ type structure where X^- can be, for example, ClO_4^- or SO_3F^-. In the case of $ClONO_2$, however, the hypochlorite chlorine ends up in the anion of the product $NO_2^+ClO_4^-$. Since cations are more difficult to oxidize and are stronger oxidizers than anions of the same oxidation state,[16] oxidation of $ClONO_2$ to $NO_2^+ClO_4^-$ is still possible, while formation of a covalent O_3ClO group or of the hypothetical ClO_3^+ cation is not. The ease of NO_2^+ formation is due to the fact that XNO_2 type compounds, such as FNO_2, are strong Lewis bases, whereas $XClO_2$ type compounds are amphoteric.[14,33]

Acknowledgment. We are most grateful to the Office of Naval Research, Power Branch, for support of this work. In addition, we are indebted to Drs. D. Pilipovich and L. R. Grant for helpful discussions.

Registry No. O_3, 10028-15-6; $ClOClO_3$, 27218-16-2; $O_2ClOClO_3$, 52225-66-8; $BrOClO_3$, 32707-10-1; $O_2BrOClO_3$, 52225-67-9; $ClOSO_2F$, 13997-90-5; O_2ClOSO_2F, 24114-30-5; $ClONO_2$, 14545-72-3; $NO_2^+ClO_4^-$, 17495-81-7; ClO_2, 10049-04-4.

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Metal Complexes as Ligands. V.[1] The Crystal and Molecular Structures of Tris(bis(triphenylphosphine)silver(I)) Tris(dithiooxalato)iron(III) and -aluminum(III), $[Ag(P(C_6H_5)_3)_2]_3M(O_2C_2S_2)_3$, M = Fe(III) and Al(III)

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Tris(bis(triphenylphosphine)silver(I)) tris(dithiooxalato)iron(III), A, crystallizes in the trigonal space group $P\bar{3}$ with two molecules per unit cell. The cell dimensions are $a = 19.984$ (6) Å and $c = 15.302$ (11) Å. The cell dimensions of the corresponding, isomorphous, aluminum(III) complex (B) are $a = 19.896$ (5) Å and $c = 15.251$ (6) Å. Intensity data for both A and B were collected with a four-circle computer-controlled diffractometer using the θ-2θ scan technique. In both A and B the carbon atoms in the phenyl rings were constrained to refine as groups of fixed geometry, and all the remaining atoms were refined with anisotropic thermal parameters. Refinement by full matrix least squares of 157 parameters on 2533 data for A and 157 parameters on 1862 data for B gave final R values of 0.051 for A and 0.052 for B. The central metal atom is octahedrally coordinated by the O,O "bites" of three dithiooxalate ligands, and the $Ag(PPh_3)_2^+$ cations interact at the S,S "bite" of each ligand. Average values of selected structural parameters involving the silver and the central metal atom are as follows: For A: Fe–O, 2.003 (6) Å; Ag–S, 2.59 (1) Å; Ag–P, 2.47 (1) Å; ϕ (trigonal twist angle), 36.9°; O–Fe–O (intraligand), 77.8 (2)°; S–Ag–S, 83.3 (1)°; P–Ag–P, 115.2 (1)°. For B: Al–O, 1.889 (8) Å; Ag–S, 2.59 (1) Å; Ag–P, 2.48 (1) Å; ϕ, 47.0°; O–Al–O (intraligand), 82.5 (4)°; S–Ag–S, 83.2 (1)°; P–Ag–P, 113.4 (2)°.

Introduction

In the dithiooxalate dianion ($S_2C_2O_2^{2-}$) (Figure 1), the presence of four donor atoms and the possibilities of charge delocalization on either the O,O or the S,S "bite" results in a versatile ligand with unique coordination properties.[3] The

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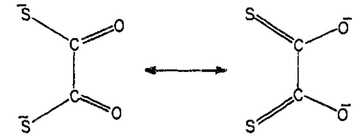

Figure 1. Resonance forms of the $S_2C_2O_2^{2-}$ ligand.

spectroscopic properties of the $M(S_2C_2O_2)_n^{n-}$ complexes indicated that with M = Ni(II), Cu(II), and Zn(II) (n = 2) and M = Cr(III), Co(III), Rh(III), and Fe(III) (n = 3), the ligand coordinates to the metal ions *via* the sulfur atoms. With M = Al(III) n = 3 and M = Zr(IV) n = 4 oxygen chelation was observed.[3b] The inert counterions that accompany the $M(S_2C_2O_2)_n^{n-}$ anions were readily substituted by the $M'(PPh_3)_2^+$ cations[4] (M' = Cu(I) and Ag(I)).

The sulfur-bonded, low-spin, $K_3Fe(S_2C_2O_2)_3$ complex afforded high-spin derivatives of the type $(M'(PPh_3)_2)_3Fe(S_2C_2O_2)_3$. The near ir spectra and X-ray powder patterns of these "adducts" were virtually identical with those of the corresponding Al(III) complexes. Furthermore, the infrared spectra of the Al(III) adducts indicated that the ligands remained O,O chelated to the aluminum atom following the cation exchange.[3b] The available data suggested that the $O_2C_2S_2^{2-}$ ligand in the iron "parent" complex had undergone a major reorientation as a result of the $(PPh_3)_2M'^+$ perturbation. Specifically, it appeared that the ligand had "flipped" from S,S chelation to O,O chelation to the iron atom.

The present X-ray structure determination was undertaken to confirm this change and to compare the structures of the iron and aluminum $(Ag(PPh_3)_2)_3M(O_2C_2S_2)_3$ complexes.

Experimental Section

Crystals of both the iron and the aluminum compound suitable for X-ray diffraction studies were grown from dichloromethane–pentane mixtures. The Fe–Ag_3[5] crystals were well developed hexagonal prisms elongated along c, while the Al–Ag_3 crystals were crescent shaped and showed no well-developed faces.

Preliminary Weissenberg and precession photographs showed that the two compounds were essentially isomorphous, though there were minor differences in the intensity patterns. Upper-layer Weissenberg photographs around c revealed only a threefold axis and there were no systematic extinctions, limiting the space groups to $P3$ and $P\bar{3}$. The latter choice was confirmed by the refinement.

Preliminary cell dimensions were determined from the photographs and by centering of a few reflections on the diffractometer. These were used for the data collection.

Data were collected using a Picker-Nuclear 4 circle diffractometer equipped with a scintillation counter and pulse-height discriminator, automated by a DEC PDP8-I and the FACS-I system. Molybdenum Kα radiation was used for both data sets. A graphite monochromator was used for collection of the Al–Ag_3 data set with a monochromator 2θ angle of 24.53° (graphite 004 reflection). Zirconium filtered radiation (0.0025 in. in diffracted beam) was used for the Fe–Ag_3 data set.[6]

Due to poor crystal quality this first Fe–Ag_3 data set was only collected out to a 2θ angle of 28°. The structure was solved and refined on these data as described below, but esd's for crystal and molecular parameters were high due to low resolution. At the urging of one of the referees we collected a second data set, using graphite monochromatized Mo Kα radiation ($2\theta_m$ = 12.20°, graphite 002 reflection). The details of collection of the second set of data only are set forth below.

The final data for Fe–Ag_3 were collected using a portion of a hexagonal needle which measured approximately 0.020 × 0.020 × 0.034 cm. It was mounted on a glass fiber with the longest dimension (which corresponded to c) approximately parallel to the spindle axis. A θ–2θ scan technique was used with a base width of 1.1° centered on Mo Kα_1 (λ 0.70926 Å) and expanded at high 2θ angles to allow for the α_1–α_2 separation. The range was scanned at 1°/min and background counts were measured for 10 sec at each end of the scan. The $(00\bar{4})$, (400), and $(3\bar{7}0)$ reflections were measured after every 100 data points to check crystal quality and instrumental stability. Data were collected over the hemisphere of reciprocal space $\pm h \pm k$–l out to 2θ of 40° ($\sin\theta/\lambda \leq 0.481$). In all, 9759 data were collected.

Table I. Crystal Data

	Trigonal $P\bar{3}$	
	Al–Ag_3	Fe–Ag_3
a, Å	19.896 (5)	19.984 (6)
c, Å	15.251 (6)	15.302 (11)
V, Å^3	5228	5292
Z	2	2
d_c, g/cm^3	1.45	1.45
d_o, g/cm^3	1.45	1.45
μ, cm^{-1}	8.13	9.30

Data for Al–Ag_3 were collected using a fragment cut from the center of one of the crescent shaped crystals. The fragment was approximately 0.01 × 0.01 × 0.03 cm with the long direction (c) parallel to the fiber and spindle axes. The same data collection technique was used as for Fe–Ag_3, with a base width of 1.0° for the scan. Reflections were collected for the hemisphere of reciprocal space $\pm H \pm K$–L out to a 2θ of 40° ($\sin\theta/\lambda = 0.481$). Three reflections (600, 060, 006) were measured after every 50 data to check crystal quality. In all, 9530 data were collected.

Accurate cell dimensions for the two compounds were determined following data collection by refinement on the 2θ values of 12 reflections between 20 and 30° in 2θ which had been carefully centered on the diffractometer. The FACS-I DOS cell parameter least-squares program was used for Fe–Ag_3, while for Al–Ag_3 a local program was used. The refined cell parameters and other crystal data are given in Table I.

Both sets of data were reduced in the same manner except where noted.[7] Net intensities and their standard deviations were calculated according to the formulas

$$I = C - \frac{t_c}{2t_b}(B_1 + B_2)$$

$$\sigma^2(I) = C + \frac{t_c^{\,2}}{4t_b^{\,2}}(B_1 + B_2)$$

where C is the total count over the peak, taken for scan time t_c, and B_1 and B_2 are background counts, each taken for time t_b. Lorentz and polarization factors were then applied to the data (including the polarization factor for the monochromator). A decay correction amounting to 6% (13%) over the data collection period was applied to the Fe–Ag_3 (Al–Ag_3) data.

Equivalent data were then averaged and assigned standard deviations as the larger of

$$\sigma(I_{av}) = (\Sigma\sigma^2(I))^{1/2}/N$$

or

$$\sigma(I_{av}) = (\Sigma(I - I_{av})^2)^{1/2}/(N - 1)$$

where N is the number of reflections being averaged. For Al–Ag_3 (Fe–Ag_3) the processing finally yielded 3196 (3315) unique reflections of which 1867 (2535) had $I > 3\sigma(I)$. No absorption corrections were performed (μ_{Al-Ag_3} = 8.1 cm^{-1}, μ_{Fe-Ag_3} = 9.3 cm^{-1}).

The least-squares program used minimizes the function $\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^{\,2}$. The weighting scheme used gave $w = 0.0$ to those reflections with $F^2 < 3\sigma'(F^2)$ and $w = 1/\sigma^2(F)$ to all other reflections. Finite differences were used to calculate $\sigma(F)$ from $\sigma(F^2)$ and F^2: $\sigma(F) = F - [F^2 - \sigma'(F^2)]^{1/2}$, $\sigma'^2(F^2) = \sigma^2(F^2) + (pF^2)^2$, where p (0.04 for both crystals) is a factor used to reduce the weight of very intense reflections, which are more subject to systematic errors, and $\sigma(F^2) = (Lp)^{-1}\sigma(I)$.

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(5) Throughout this paper the abbreviations Fe–Ag_3 and Al–Ag_3 will be used for the $(Ag(PPh_3)_2)_3Fe(O_2C_2S_2)_3$ and $(Ag(PPh_3)_2)_3Al(O_2C_2S_2)_3$ complexes.

(6) The Fe–Ag_3 data set was collected before the monochromator was available.

(7) Programs for the 1BM 360/65 used were PTAPE, a local paper to magnetic tape program, MAGPIK, INCOR, and ORDER general data reduction programs.

Table II. Coordinates and Thermal Parameters in $Al(O_2C_2S_2)_3[Ag(PPh_3)_2]_3$[a]

Atom	x	y	z	B_{11}[b]	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Al	$-{}^1/_3$[d]	${}^1/_3$[d]	0.2850 (4)	2.4 (2)	2.4[c]	3.1 (4)	1.2[c]	0.0[d]	0.0[d]
Ag	−0.03722 (6)	0.34278 (6)	0.25617 (7)	3.18 (6)	3.58 (6)	5.04 (7)	1.86 (5)	−0.15 (5)	−0.53 (5)
P(1)	0.0249 (2)	0.2627 (2)	0.2427 (2)	3.5 (2)	3.6 (2)	4.4 (2)	2.1 (2)	0.5 (2)	−0.0 (2)
P(2)	0.0564 (2)	0.4849 (2)	0.2484 (2)	3.2 (2)	3.1 (2)	4.1 (2)	1.4 (2)	−0.2 (2)	−0.2 (2)
S(1)	−0.1644 (2)	0.2851 (2)	0.1689 (2)	3.9 (2)	5.1 (2)	4.0 (2)	2.7 (2)	−0.7 (2)	−1.6 (2)
S(2)	−0.1239 (2)	0.3452 (2)	0.3834 (2)	3.5 (2)	6.5 (2)	3.3 (2)	2.8 (2)	−0.5 (2)	−0.3 (2)
O(1)	−0.2882 (5)	0.2895 (4)	0.2120 (5)	2.7 (4)	2.9 (4)	3.1 (5)	1.5 (4)	0.0 (4)	−0.3 (3)
O(2)	−0.2453 (4)	0.3595 (4)	0.3544 (5)	2.5 (4)	3.8 (4)	2.6 (5)	1.7 (4)	−0.3 (3)	−0.4 (3)
C(1)	−0.2201 (8)	0.3037 (6)	0.2332 (8)	2.6 (7)	2.2 (6)	3.0 (8)	1.6 (6)	0.0 (6)	0.1 (5)
C(2)	−0.1971 (7)	0.3386 (6)	0.3264 (8)	2.6 (7)	2.2 (6)	2.7 (8)	0.8 (6)	0.2 (6)	0.3 (6)

	x_g	y_g	z_g	ϕ[e]	θ	ρ
PHEN(1)	−0.0974 (4)	0.0941 (4)	0.1657 (4)	162.5 (4)	−21.6 (3)	−38.7 (3)
PHEN(2)	0.1053 (3)	0.2403 (4)	0.4135 (4)	−96.0 (6)	52.0 (3)	31.9 (6)
PHEN(3)	0.1703 (4)	0.3332 (3)	0.1097 (4)	−60.3 (4)	−39.5 (3)	−82.0 (4)
PHEN(4)	−0.0205 (4)	0.5873 (3)	0.3056 (4)	58.4 (3)	15.4 (3)	−41.5 (3)
PHEN(5)	0.1462 (4)	0.5551 (4)	0.0661 (5)	−47.4 (7)	−59.4 (4)	49.5 (7)
PHEN(6)	0.1899 (3)	0.5199 (3)	0.3900 (4)	−76.7 (4)	43.0 (3)	−88.9 (4)

Individual Isotropic Thermal Parameters of Phenyl Carbon Atoms[g]

PHEN(1)		PHEN(3)		PHEN(5)	
C(03)[f]	3.6 (3)	C(15)[f]	3.6 (3)	C(27)[f]	3.9 (3)
C(04)	6.8 (4)	C(16)	5.5 (4)	C(28)	6.2 (4)
C(05)	6.8 (4)	C(17)	6.6 (4)	C(29)	7.0 (4)
C(06)	6.4 (4)	C(18)	5.1 (3)	C(30)	7.7 (4)
C(07)	7.0 (4)	C(19)	5.3 (3)	C(31)	11.1 (6)
C(08)	5.3 (3)	C(20)	3.7 (3)	C(32)	9.2 (5)
PHEN(2)		**PHEN(4)**		**PHEN(6)**	
C(09)[f]	4.1 (3)	C(21)[f]	3.7 (3)	C(33)[f]	3.3 (3)
C(10)	5.9 (4)	C(22)	5.4 (3)	C(34)	4.9 (3)
C(11)	7.0 (4)	C(23)	6.2 (4)	C(35)	6.0 (4)
C(12)	6.6 (4)	C(24)	7.0 (4)	C(36)	6.0 (4)
C(13)	7.3 (4)	C(25)	7.2 (4)	C(37)	5.3 (3)
C(14)	6.4 (4)	C(26)	5.3 (4)	C(38)	4.8 (3)

[a] In this and the following tables the standard deviation of the least significant digit(s) appears in parentheses. [b] In this and Table III the form of the temperature factor (B in units of $Å^2$) is $T = \exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$ for anisotropic and $T = \exp(-B \sin^2 \theta/\lambda^2)$ for isotropic thermal parameters. [c] Derived from B_{11} and symmetry of special position. [d] Fixed by special position symmetry. [e] Group parameters defined in the text. [f] Carbon atom attached to phosphorus. [g] A table of the coordinates of these carbon atoms as derived from the group parameters has been deposited (see paragraph at end of paper).

The scattering factors for the neutral atoms were taken from the tabulation of Doyle and Turner.[8] Real and imaginary dispersion terms[9] for all atoms were included in the calculations.

Structure Determination and Refinement. The three-dimensional Patterson map for Al–Ag_3 was interpreted in the noncentrosymmetric space group to give the position of one silver atom in addition to the assumed Al atom at the origin. Successive cycles of noncentric least squares followed by Fourier maps revealed the location of all the nonhydrogen atoms in the unit cell.

Due to computer limitations the phenyl rings were refined as groups,[10] with the carbon-carbon distance fixed at 1.390 Å and all interior angles at 120°. Noncentric refinement proceeded slowly and the matrix became more and more ill-behaved until a center of symmetry was noted between the two molecules and the shift to the centric space group $P\bar{3}$ was made. The refinement then converged smoothly and rapidly, and several troublesome temperature factors became reasonable. All further refinements were performed in the centric space group.

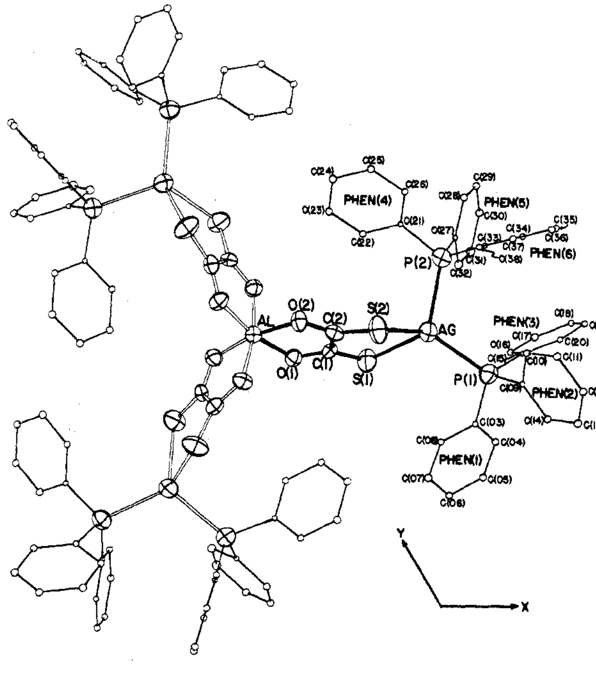

Figure 2. View of the Al–Ag_3 molecule down the c axis. The labeling is shown for the asymmetric unit, and the directions of the a and b axes are indicated. The view and labeling for the Fe–Ag_3 molecule are entirely similar. The thermal ellipsoids of the phenyl carbons are plotted at the 2% probability level for clarity. The other atoms are plotted at the 50% probability level.

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(8) P. A. Doyle and P. S. Turner, *Acta Crystallogr., Sect. A*, **24**, 390 (1968).

(9) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).

(10) The origin of the group coordinate system was taken at the center of the ring, with z normal to the ring, y taken from the center to the para carbon and x to complete a right-handed coordinate system. The program refines x_g, y_g, z_g, the crystal coordinates of the center of the ring, and ϕ, θ, and ρ, the orientation angles of the group as described by Scheringer,[11] and either a single isotropic thermal parameter for all atoms in the group or the individual isotropic thermal parameters of each atom. Scheringer's results were valid only for monoclinic or higher space groups. The procedures in our program have been generalized to any system. Full details will be supplied on request.

(11) C. Scheringer, *Acta Crystallogr.*, **16**, 546 (1963).

Table III. Coordinates and Thermal Parameters in $Fe(O_2C_2S_2)_3[Ag(PPh_3)_2]_3$

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe	$-{}^1/_3$[a]	${}^1/_3$[a]	0.2830 (1)	2.77 (6)	2.77[b]	3.26 (11)	1.38[b]	0.0[a]	0.0[a]
Ag	−0.03162 (4)	0.34414 (4)	0.25577 (5)	3.13 (4)	3.49 (4)	4.89 (5)	1.82 (3)	−0.13 (3)	−0.43 (3)
P(1)	0.0296 (1)	0.2643 (1)	0.2430 (2)	3.3 (1)	3.5 (1)	4.2 (1)	1.9 (1)	0.3 (1)	0.1 (1)
P(2)	0.0583 (1)	0.4856 (1)	0.2500 (2)	3.2 (1)	3.3 (1)	4.0 (1)	1.6 (1)	−0.1 (1)	0.0 (1)
S(1)	−0.1561 (1)	0.2896 (2)	0.1652 (2)	4.1 (1)	5.8 (1)	4.2 (1)	3.0 (1)	−0.5 (1)	−1.6 (1)
S(2)	−0.1216 (1)	0.3383 (2)	0.3825 (2)	3.9 (1)	7.0 (2)	3.2 (1)	3.2 (1)	−0.3 (1)	0.1 (1)
O(1)	−0.2794 (3)	0.2937 (3)	0.2058 (4)	3.1 (3)	4.4 (3)	3.3 (3)	2.1 (3)	−0.7 (3)	−0.7 (2)
O(2)	−0.2421 (3)	0.3532 (3)	0.3555 (4)	3.3 (3)	4.2 (3)	3.3 (3)	2.3 (3)	−0.1 (2)	−0.2 (2)
C(1)	−0.2131 (5)	0.3063 (4)	0.2311 (6)	3.5 (5)	2.0 (4)	3.0 (5)	1.2 (3)	0.1 (4)	−0.1 (3)
C(2)	−0.1940 (5)	0.3353 (5)	0.3245 (6)	2.4 (4)	3.2 (4)	3.5 (5)	1.2 (4)	0.3 (4)	0.4 (4)

	x_g	y_g	x_g	ϕ[c]	θ	ρ
PHEN(1)	−0.0941 (3)	0.0965 (3)	0.1663 (3)	161.8 (2)	−21.6 (2)	−39.1 (3)
PHEN(2)	0.1079 (3)	0.2415 (3)	0.4142 (3)	−96.8 (4)	53.1 (3)	32.2 (4)
PHEN(3)	0.1745 (3)	0.3316 (2)	0.1100 (3)	−61.2 (3)	−39.3 (2)	−82.1 (3)
PHEN(4)	−0.0237 (3)	0.5836 (3)	0.3026 (3)	59.8 (2)	13.9 (2)	−42.3 (3)
PHEN(5)	0.1493 (3)	0.5567 (3)	0.0698 (4)	−46.4 (5)	−58.8 (3)	48.7 (6)
PHEN(6)	0.1901 (3)	0.5216 (2)	0.3922 (3)	−77.0 (3)	43.5 (2)	−88.7 (3)

Individual Isotropic Thermal Parameters of Phenyl Carbon Atoms[e]

PHEN(1)		PHEN(3)		PHEN(5)	
C(03)[d]	3.5 (2)	C(15)[d]	3.7 (2)	C(27)[d]	4.2 (2)
C(04)	6.3 (3)	C(16)	5.3 (2)	C(28)	5.7 (2)
C(05)	6.6 (3)	C(17)	6.3 (3)	C(29)	7.2 (3)
C(06)	6.0 (3)	C(18)	5.9 (2)	C(30)	8.1 (3)
C(07)	6.3 (3)	C(19)	5.4 (2)	C(31)	11.0 (4)
C(08)	5.0 (2)	C(20)	4.4 (2)	C(32)	8.2 (3)
PHEN(2)		**PHEN(4)**		**PHEN(6)**	
C(09)[d]	3.8 (2)	C(21)[d]	3.7 (2)	C(33)[d]	3.5 (2)
C(10)	5.6 (2)	C(22)	5.3 (2)	C(34)	4.6 (2)
C(11)	7.8 (3)	C(23)	6.8 (3)	C(35)	6.7 (3)
C(12)	7.5 (3)	C(24)	6.9 (3)	C(36)	6.6 (3)
C(13)	7.8 (3)	C(25)	7.2 (3)	C(37)	6.2 (3)
C(14)	5.9 (3)	C(26)	5.5 (2)	C(38)	5.2 (2)

[a] Fixed by special position symmetry. [b] Derived from B_{11} and symmetry of special position. [c] Group parameters defined in text. [d] Carbon atom attached to phosphorus. [e] A table of the coordinates of these carbon atoms as derived from the group parameters has been deposited (see paragraph at end of paper).

In the last few cycles, the individual thermal parameters of the group atoms were allowed to vary and all nongroup atoms were refined with anisotropic thermal parameters. The final R_1 value was 0.052 with 157 parameters on 1862 data, and the final value of R_2, $(\Sigma w(\Delta F)^2/\Sigma wF_o^2)$ was 0.060. The standard deviation of an observation of unit weight was 1.68. All shifts in the last cycle of least squares were $\leqslant$0.15 of their esd's and most were less than 0.05 esd. There were no peaks with density greater than 0.5 e/Å^3 on the final difference Fourier map.

An attempt was made to fit the hydrogen atoms of the phenyl rings using the group refinement program. The hydrogens were placed 1.0 Å from the attached carbon with 120° C–C–H bond angles. Refinement, however, gave unreasonably large thermal parameters for many hydrogens, so the attempt was abandoned.

The Fe–Ag$_3$ structure was refined on the first data set from the positions of an intermediate step of the Al–Ag$_3$ refinement, substituting the scattering factor for iron for that of aluminum.

Refinement in the centric space group proceeded smoothly. Attempted anisotropic refinement of the nongroup atoms resulted in a nonpositive definite temperature factor for one of the carbon atoms of the dithiooxalate ligand. As a consequence it was decided to refine both carbons of the ligand isotropically. After the structure had been completely refined on the first data set to an R_1 of 0.052, we collected the second data set as described above. Starting with the final coordinates of the first refinement, convergence with all nongroup atoms refined anisotropically was rapid. No attempt was made to locate or refine the hydrogen atoms. The final R_1 was 0.051 with 157 parameters on 2533 data, and the final R_2 was 0.066. The standard deviation of an observation of unit weight was 2.25. In the last cycle of least squares all shifts were less than 0.1 times their esd's as calculated from the least-squares matrix. The final difference Fourier showed no peaks greater than 0.9 e/Å^3.

The final parameters and their esd's are given in Table II for Al–Ag$_3$ and in Table III for Fe–Ag$_3$. Tables of the observed structure factors and tables of the carbon atom positions generated by the group parameters are available. (See paragraph at end of paper.)

Discussion

The two structures of Al–Ag$_3$ and Fe–Ag$_3$ are isomorphous and consist of two discrete molecules of stoichiometry $M(O_2C_2S_2Ag(PPh_3)_2)_3$ per unit cell. The asymmetric unit consists of one third of the molecule. A view of the molecule[12] showing the labeling used is given in Figure 2.

The structures confirm unequivocally the "flip" of the $O_2C_2S_2^{2-}$ on the iron from S,S bonding to O,O, as both metal ions are bonded to the O,O "bite" of the ligand.

Comparison of the $O_2C_2S_2^{2-}$ ligands in the two structures shows that there is no difference in the bond distances or angles greater than three times their estimated standard deviations (Tables IV and V). The average C–O, C–S, and C–C distances are 1.28, 1.66, and 1.54 Å, respectively, and are consistent with a delocalized structure of the ligand as shown in Figure 3.

The oxygen–oxygen bite distance is very short (average 2.50 Å). The ligand is significantly nonplanar, with deviations of up to 0.24 Å from the best plane through the ligand as a whole. The distortion is best described as a rotation around the carbon–carbon bond by 13.1° for Al–Ag$_3$ and 11.6° for Fe–Ag$_3$, rotating the O(2)C(2)S(2) plane clockwise looking from C(1) to C(2). (This twist is clearly visible in Figure 4.)

The bonding to the ligand is also nonplanar, as the Ag atom lies 0.64 Å (0.68 Å) off the best plane through the ligand for

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(12) Computer drawings were obtained using Johnson's ORTEP thermal ellipsoid plotting program.[13]

(13) C. K. Johnson, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

Table IV. Intramolecular Distances (Å)[a]

	Al-Ag_3	Fe-Ag_3
M-O(1)	1.895 (8)	1.996 (6)
M-O(2)	1.883 (8)	2.010 (6)
Ag-S(1)	2.566 (3)	2.566 (3)
Ag-S(2)	2.612 (2)	2.607 (3)
Ag-P(1)	2.465 (4)	2.455 (2)
Ag-P(2)	2.492 (3)	2.480 (2)
P(1)-C(03)	1.836[b]	1.844[b]
P(1)-C(09)	1.820[b]	1.815[b]
P(1)-C(15)	1.834[b]	1.842[b]
P(2)-C(21)	1.835[b]	1.833[b]
P(2)-C(27)	1.835[b]	1.829[b]
P(2)-C(33)	1.827[b]	1.820[b]
C(01)-S(1)	1.66 (1)	1.68 (1)
C(01)-O(1)	1.28 (1)	1.28 (1)
C(01)-C(02)	1.55 (2)	1.52 (1)
C(02)-S(2)	1.64 (1)	1.67 (1)
C(02)-O(2)	1.29 (1)	1.27 (1)
O(1)-O(2)	2.49 (1)	2.52 (1)
O(1)-O(1)'[c]	2.66 (1)	2.81 (1)
O(1)-O(2)''[c]	2.86 (1)	3.16 (1)
O(1)-S(1)	2.59 (1)	2.58 (1)
O(2)-O(2)'[c]	2.70 (1)	2.88 (1)
O(2)-S(2)	2.61 (1)	2.60 (1)
S(1)-S(2)	3.437 (5)	3.437 (4)

[a] Carbon-carbon distances in the phenyl rings were fixed at 1.390 Å. [b] Due to the group refinement procedure used it was not possible to calculate esd's for these distances. Estimated by comparison to similar distances in the structure, ±0.01 Å for both Al-Ag_3 and Fe-Ag_3. [c] See Figure 5.

Table V. Selected Bond Angles (deg)

	Al-Ag_3	Fe-Ag_3
O(1)-M-O(2)	82.5 (4)	77.8 (3)
O(1)-M-O(2)''[c]	98.2 (4)	104.2 (3)
O(1)-M-O(2)'[c]	168.7 (5)	161.0 (4)
O(1)-M-O(1)'[c]	88.9 (4)	88.9 (3)
O(2)-M-O(2)'[c]	91.5 (4)	92.2 (3)
S(1)-Ag-S(2)	83.2 (1)	83.3 (1)
P(1)-Ag-P(2)	113.4 (2)	115.2 (1)
S(1)-Ag-P(1)	111.6 (2)	111.9 (1)
S(1)-Ag-P(2)	119.6 (2)	117.4 (1)
S(2)-Ag-P(1)	128.5 (2)	125.9 (1)
S(2)-Ag-P(2)	98.0 (1)	99.6 (1)
Ag-P(1)-C(03)	112.0[a]	111.4[a]
Ag-P(1)-C(09)	117.5[a]	117.6[a]
Ag-P(1)-C(15)	114.2[a]	115.1[a]
Ag-P(2)-C(21)	114.7[a]	114.6[a]
Ag-P(2)-C(27)	119.2[a]	118.4[a]
Ag-P(2)-C(33)	107.3[a]	107.5[a]
Ag-S(1)-C(1)	102.3 (5)	101.6 (3)
Ag-S(2)-C(2)	100.0 (5)	99.9 (3)
M-O(1)-C(1)	116.3 (7)	116.8 (4)
M-O(2)-C(2)	117.5 (7)	118.6 (4)
O(1)-C(1)-S(1)	123.7 (6)	121.2 (4)
O(1)-C(1)-C(2)	112.0 (9)	113.5 (6)
S(1)-C(1)-C(2)	124.4 (7)	125.2 (5)
O(2)-C(2)-S(2)	124.7 (6)	123.6 (4)
O(2)-C(2)-C(1)	110.4 (9)	112.2 (6)
S(2)-C(2)-C(1)	124.9 (7)	124.1 (5)
C(03)-P(1)-C(09)	104.9[b]	105.2[b]
C(03)-P(1)-C(15)	104.6[b]	104.0[b]
C(09)-P(1)-C(15)	102.2[b]	102.0[b]
C(21)-P(2)-C(27)	104.1[b]	104.6[b]
C(21)-P(2)-C(33)	104.8[b]	105.6[b]
C(27)-P(2)-C(33)	105.6[b]	105.0[b]

[a] Due to group refinement procedure, no esd could be calculated. Estimated ±0.5° for Al and ±0.4° for Fe. [b] As for footnote *a* except estimated ±1.0° for Al and ±0.6° for Fe. [c] See Figure 5.

Al-Ag_3 (Fe-Ag_3). The Al(Fe) atom is also displaced from the plane, in the same direction as the Ag but only by 0.05 (0.05) Å.

The bond distances and angles in the triphenylphosphine groups (Tables IV and V) are consistent with those reported for other coordinated triphenylphosphines.[14,15]

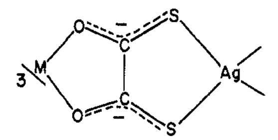

Figure 3. Charge delocalization in the $MO_2C_2S_2Ag$ unit.

The Ag atom is coordinated by two phosphorus atoms and the two sulfurs of an $O_2C_2S_2^{2-}$ ligand. The coordinating atoms lie at the corners of a highly distorted tetrahedron. The Ag-S and Ag-P distances do not change significantly between the two structures (Table IV), but the P-Ag-P angle increases from 113.4° for Al-Ag_3 to 115.2° for Fe-Ag_3 (Table V). Similar changes in the P-CuX-P angle of $(PPh_3)_2$-CuX complexes (where X is a wide variety of ligands) have been explained in terms of steric interactions between the triphenylphosphine and the X ligand.[15,16] In this case, a similar argument can be made, with the important steric interactions between the different "branches" of the complex, specifically between PHEN(4) of one branch and PHEN(1) of the next (Figure 2). This strain is reduced by a general outward movement of the $(O_2C_2S_2Ag(PPh_3)_2)^-$ grouping with the replacement of Al by Fe (see below). Specifically, in Al-Ag_3 there is a nonbonded distance of 3.46 Å between C(24) of one "branch" and C(7) of the next and a distance of 3.47 Å between C(16) and C(32) of the same branch. In Fe-Ag_3 the former has increased to 3.50 Å and the latter has increased to 3.52 Å.

The coordination of the Al and Fe atoms is constrained to have C_3 symmetry by the space group. If the oxygen atoms alone are considered, the symmetry approaches D_3, with the primary distortions being a longer edge for the O(2) triangle than for the O(1) triangle and a displacement of the Al (Fe) atom by 0.03 (0.04) Å toward the O(2) plane (see Figure 5).

The two independent metal-oxygen distances are not significantly different for either Al-Ag_3 or Fe-Ag_3 (Table IV), but there is an increase of 0.10 Å from Al-O to Fe-O, consistent with the increase in ionic radius of Fe(III) with respect to Al(III) ($r_{Al} = 0.50$ Å, $r_{Fe} = 0.64$ Å[17]) and very similar to the increase noted for the iron and aluminum tris(tropolonato) complexes.[18,19]

The change in molecular conformation induced by the increase in metal-oxygen distance can be summarized as a movement of the $O_2C_2S_2Ag$ grouping away from the metal atom by about 0.10 Å combined with a rotation around an axis perpendicular to the crystallographic threefold axis of the molecule. (The angle between the best plane through the ligand and the *xy* plane is 71.1° for Al-Ag_3 and 74.6 for Fe-Ag_3.) The two triphenylphosphine groups do not move outward to the same extent as the rest of the molecule, causing the P-Ag-P angle to open up as noted above.

The changes in the oxygen coordination sphere of the central metal atom are summarized in Figure 5. Comparing the

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(14) M. R. Churchill and T. A. O'Brien, *J. Chem. Soc. A*, 2970 (1968), and references therein.

(15) P. H. Davis, R. L. Belford, and I. C. Paul, *Inorg. Chem.*, 12, 213 (1973), and references therein.

(16) S. J. Lippard and G. J. Palenik, *Inorg. Chem.*, 10, 1322 (1971), and references therein.

(17) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 514-518.

(18) E. L. Muetterties and L. J. Guggenberger, *J. Amer. Chem. Soc.*, 94, 8046 (1972), and references therein.

(19) T. A. Hamor and D. J. Watkin, *Chem. Commun.*, 440 (1969).

Table VI. Comparison of Metal Ion Coordination Geometry in the Aluminum and Iron Tris($O_2C_2S_2Ag(PPh_3)_2$) and Tris(tropolonate) Complexes

Compd	Ligand bite, b, Å	M-O distance, a, Å	b/a	Triangle edge, s, Å	Polyhed height, h, Å	s/h	Twist angle, ϕ, deg
Al-Ag_3	2.49 (1)	1.889 (8)[a]	1.32	2.68 (2)[a]	2.17	1.23	47.0
Fe-Ag_3	2.52 (1)	2.003 (6)[a]	1.26	2.84 (3)[a]	2.29	1.24	36.9
AlT_3[c]	2.490 (6)[a]	1.888 (2)[a]	1.32	2.70 (3)[a]	2.13	1.27	48.1[a]
FeT_3[d]	2.52[b]	2.008 (3)	1.25	2.87[b]	2.27[b]	1.26	38.7[b]

[a] Average of several distances or angles. [b] Derived from quantities reported. [c] E. L. Muetterties and L. J. Guggenberger, *J. Amer. Chem. Soc.*, 94, 8046 (1972). [d] T. A. Hamor and D. J. Watkin, *Chem. Commun.*, 440 (1969).

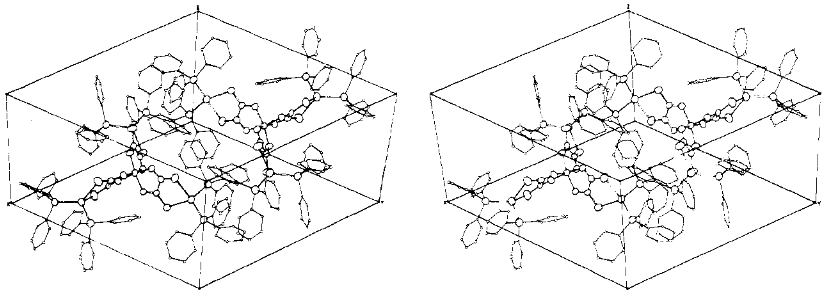

Figure 4. Stereoscopic drawing of the contents of one unit cell of the aluminum compound. Thermal probability ellipsoids as in Figure 1. Again, the view for the iron compound is entirely similar.

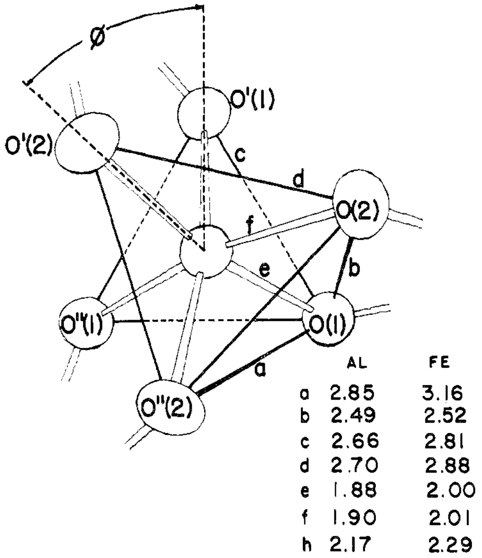

Figure 5. View down c of the coordination sphere of the central metal atom for Al-Ag_3 and Fe-Ag_3. Standard deviations of the distances shown (in Å) are ±0.01 for both structures. The quantity h is the perpendicular distance between the upper and lower triangles of oxygens. The twist angle ϕ is the projected angle between the vectors shown.

iron to the aluminum complex, the twist angle, ϕ, decreases, while the height of the polyhedron and the edges of the triangular faces both increase on changing from aluminum to iron. (In Figure 5, c and d are equivalent to s of Steifel and Brown,[20] and e and f are equivalent to a, the M-O distance.)

This situation compares very closely to that of the tris(tropolonate) complexes AlT_3[18] and FeT_3,[19] where the bite distance is also fixed at ~2.50 Å (Table VI). It is interesting to note that the "compression ratio", s/h, is essentially the same for Al-Ag_3 and Fe-Ag_3 but different than the ratio for AlT_3 and FeT_3. The compression ratio also seems to be independent of the twist angle, ϕ, contrary to the prediction of a relation between the two for ligands of fixed bite.[20]

The ratio b/a of the ligand bite to the metal-oxygen distance is much less than the "ideal" value of 1.41 for a regular octahedron and for the iron complexes is even less than the "ideal" 1.31 for a trigonal prism. However, there does seem to be a strong correlation between the b/a ratio and the angle ϕ, with the smaller ratio corresponding to geometry closer to trigonal prismatic.

Attempts have been made to correlate a value of ϕ intermediate between the trigonal antiprismatic value of 60° and the trigonal prismatic value of 0° with the rapid inversion rates (*via* trigonal twist mechanism) found for such species as the substituted tropolonates.[18,21] While the correlation is not complete, the b/a values and ϕ angles of Al-Ag_3 and Fe-Ag_3 suggest that if a handle were made available for the study of their inversion rates they would probably show the same behavior as the tropolonates.

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Registry No. Al-Ag_3, 42531-96-4; Fe-Ag_3, 42531-93-1.

Supplementary Material Available. A compilation of observed structure factor amplitudes, their estimated standard deviations and the difference $|F_o| - |F_c|$, and tables of the derived carbon atom positions of the phenyl rings will appear immediately 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 \$5.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-2381.

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(20) E. I. Steifel and G. F. Brown, *Inorg. Chem.*, **11**, 434 (1972).

(21) R. H. Holm, *et al.*, *J. Amer. Chem. Soc.*, **94**, 6411 (1972).