Metal Complexes as Ligands. III.[1] Bonding Interactions of the Anionic Metal Dithiooxalate Complexes with the Coordinately Unsaturated Bis(triphenylphosphine)copper(I) and Bis(triphenylphosphine)silver(I) Complex Cations

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Abstract: Anionic complexes of the multifunctional dithiooxalate ligand, $S_2C_2O_2^{2-}$, are described. The spectroscopic properties of the $M(S_2C_2O_2)_n^{n-}$ complexes indicate that with M = Ni(II), Cu(II), and Zn(II) ($n = 2$) and M = Cr(III), Co(III), Rh(III), and Fe(III) ($n = 3$) these compounds are sulfur bonded chelates. In the aluminum(III) tris complex, the ligand is oxygen chelated. The inert cations accompanying the anionic dithiooxalate complexes are readily replaced by the coordinately unsaturated $M'(P(C_6H_5)_3)_2^+$ (M′ = Ag(I), Cu(I)) complex cations. In the resulting polynuclear complexes, $M(S_2C_2O_2)_n[(P(C_6H_5)_3)_2M']_n$, the following coordination modes have been observed for the bridging ligand: (a) $M\text{-}S_2C_2O_2\text{-}M'$ (M = Ni(II), Cr(III), Co(III), Rh(III); M′ = Cu(I)), (b) $M\text{-}O_2C_2S_2\text{-}M'$ (M = Fe(III), Al(III), Zn(II), Cr(III); M′ = Cu(I), Ag(I)), (c) $M\text{-}OSC_2SO\text{-}M'$ (M = Cr(III), M′ = Ag(I)). The Cr(III)–$(P(C_6H_5)_3)_2M'$ complexes initially isolated in the (a) or (c) mode thermally isomerize to the (b) mode. The linkage isomerism brought about by the $(P(C_6H_5)_3)_2M'$ cations in the Fe(III) complex has been verified by a single-crystal X-ray study. In the $Ni(S_2C_2O_2)_2((P(C_6H_5)_3)_2Ag)_2$ complex the interaction occurs between the Ag(I) and the coordinated sulfurs of the ligand. The synthesis and characterization of the binuclear $[M'(P(C_6H_5)_3)_2]_2S_2C_2O_2$ complexes is described. The ligand in these complexes is bridging in the trans form mode c.

Since the first report[2] on the dithiooxalate ligand and its complexes, a number of studies of the coordination chemistry of these compounds have appeared in the literature;[3] however, it was only recently that certain intriguing characteristics of this system were realized.[4]

In the dithiooxalate dianion ($S_2C_2O_2^{2-}$), the presence of four donor atoms and the possibilities of charge delocalization on any two of these atoms result in a versatile ligand with unique coordination properties. The wide variety of coordination possibilities[5] and the facile delocalization of charge (Figure 1) further indicate that under appropriate conditions the dithiooxalate ligand may coordinate simultaneously to more than one metal ion.

In recent studies we have demonstrated the bifunctional nature of the dithiooxalate ligand. Thus in the planar Ni(II) and Pd(II) bis(dithiooxalate) complexes, the α-diketone moieties of the sulfur coordinated ligands serve effectively as chelates for various stannic halide molecules.[1] In this paper we report further studies on the coordination properties of the dithiooxalate ligand and on the nature of the polynuclear complexes which form when various dithiooxalate complexes are allowed to react with the coordinately unsaturated $M(PPh_3)_2^+$ (M = Ag, Cu) complexes.[6]

Experimental Section

The chemicals in this research were used as purchased. Potassium dithiooxalate was obtained from S. H. Sargent Chemical Co. Tris(triphenylphosphine)copper(I) and -silver(I) chlorides were prepared as described in the literature.[7] Analyses and mass spectra were obtained by the analytical services laboratory of the Chemistry Department of the University of Iowa. Melting points are uncorrected. Metal analyses were performed by atomic absorption spectroscopy.

Physical Measurement. Magnetic susceptibilities were determined at ambient room temperature using a Faraday technique. The calibrant was $Hg(Co(SCN)_4)$.[8] Mass spectra were recorded on a Hitachi RMU6-E spectrometer. Near-infrared spectra were obtained on a Perkin-Elmer 421 recording spectrometer, frequency calibrated with polystyrene. Far-infrared spectra spanning the frequency range 650–100 cm^{-1} were recorded on a Beckman IR 11 spectrometer equipped with a triglycine sulfate crystal detector and frequency calibrated with water vibrations within that wavelength range. Ultraviolet, visible, and near-infrared spectra were obtained on a Cary Model 14 recording spectrophotometer using 1-cm quartz cells. A Debye-Scherrer camera utilizing nickel-filtered copper radiation was used to record the X-ray powder patterns. Nonius Weissenberg and precession cameras were used for the single-crystal preliminary alignments and space group determinations. Intensity data were collected on a Picker FACS-1 automated four-circle diffractometer equipped with a graphite single-crystal monochromator and pulse height analyzer.

Preparation of Complexes. The general synthetic procedure utilized for the synthesis of most of the complexes involved extraction of aqueous solutions of the "parent" $M(S_2C_2O_2)_n^{n-}$ complexes with nonaqueous solutions of the $M'(PPh_3)_3Cl$ complexes (M′ = Cu, Ag) or salts of various large cations. Following separation of the aqueous phase the products were isolated from the nonaqueous solutions by either reducing the volume of the solvent or adding second solvents and cooling to 0°. The crystalline products were washed with ether or pentane and dried under vacuum. Analytical data and physical characteristics are shown in Table I. Specific synthetic information regarding individual complexes is given below.

Tris(tetraphenylarsonium) Tris[(dithioxalato-*S*,*S*′)ferrate(III)]-

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[1] Part II: D. Coucouvanis, N. C. Baenziger, and S. M. Johnson, *J. Amer. Chem. Soc.*, **95**, 3875 (1973).

[2] C. S. Robinson and H. O. Jones, *J. Chem. Soc.*, 62 (1912).

[3] (a) F. A. Dwyer and A. M. Sargeson, *J. Amer. Chem. Soc.*, **81**, 2335 (1959); (b) R. L. Carlin and F. Canziani, *J. Chem. Phys.*, **40**, 371 (1964); (c) W. A. Deskin, *J. Amer. Chem. Soc.*, 80, 5680 (1958).

[4] (a) D. Coucouvanis, *J. Amer. Chem. Soc.*, **92**, 707 (1970); (b) D. Coucouvanis, R. E. Coffman, and D. Piltingsrud, *ibid.*, **92**, 5004 (1970); (c) D. Coucouvanis, *ibid.*, **93**, 1786 (1971).

[5] A number of other structures are possible involving formation of four-membered rings upon chelation. Such structures are not considered as realistic or very probable.

[6] Papers describing this work were presented at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969; and the 162nd National Meeting, Washington, D. C., Sept 1971.

[7] (a) F. Cariati and L. Naldini, *Gazz. Chim. Ital.*, **95**, 3 (1965); (b) S. J. Lippard and J. J. Mayerle, *Inorg. Chem.*, 11, 753 (1972); (c) E. L. Muetterties and C. W. Alegranti, *J. Amer. Chem. Soc.*, **94**, 6386 (1972).

[8] B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958).

Table I. Analytical Data and Physical Properties of the Complexes

Complex	% C calcd (found)	% H calcd (found)	% metal calcd (found)	Color	Mp, °C	% yield	μ_{eff}^{corr} BM
$Fe(S_2C_2O_2)_3(Ph_4As)_3 \cdot 3CH_3NO_2$	55.61 (55.51)	3.95 (3.92)	Fe 3.20 (3.23, 3.16)	Violet	104–107	43	2.30 ± 0.05
$Rh(S_2C_2O_2)_3(Ph_4As)_3 \cdot 3CH_3NO_2$[a]	54.15 (53.43)	3.87 (3.94)		Brown	104 dec	25	Diamagnetic
$Al(S_2C_2O_2)_3(Ph_4As)_3$	60.94 (61.56)	3.93 (4.15)		Light brown	110 dec	30	Diamagnetic
$Cr(S_2C_2O_2)_3K(Me_3PhN)_2 \cdot H_2O$[b]	38.85 (38.81)	4.08 (3.80)		Dark green	180 dec	80	3.85 ± 0.03
$Cr(S_2C_2O_2)_3((PPh_3)_2Cu)_3$	62.90 (62.31)	4.17 (3.94)	Cu 8.76 (8.69)	Brown	175 dec	50	3.86 ± 0.03
$Cr(S_2C_2O_2)_3((PPh_3)_2Ag)_3$	59.28 (58.67)	3.93 (3.61)		Light brown	131 dec	41	3.86 ± 0.05
$Cr(S_2C_2O_2)_3((PPh_3)_2Cu)_3$[c]	62.90 (62.12)	4.17 (4.06)		Brown	190 dec	80	3.79 ± 0.03
$Cr(S_2C_2O_2)_3((PPh_3)_2Ag)_3$[c]	59.28 (59.99)	3.93 (4.04)		Light brown	174–177 dec	80	3.95 ± 0.05
$Co(S_2C_2O_2)_3((PPh_3)_4Ag)_3$	68.54 (68.56)	4.66 (4.72)	Co 1.51 (1.40)	Dark brown	159 dec	46	Diamagnetic
$Co(S_2C_2O_2)_3((PPh_3)_2Ag)_3$	59.10 (59.35)	3.92 (3.96)	Co 2.54 (2.42)	Light brown	130 dec	47	Diamagnetic
$Co(S_2C_2O_2)_3((PPh_3)_2Cu)_3$	62.70 (62.70)	4.15 (4.19)	Co 2.70 (2.57)	Brown	161–164 dec	41	Diamagnetic
$Ni(S_2C_2O_2)_2((PPh_3)_4Ag)_2$	68.03 (67.49)	4.63 (4.83)	Ni 2.25 (2.24)	Red	170 dec	61	Diamagnetic
$Ni(S_2C_2O_2)_2((PPh_3)_2Ag)_2$[d]	58.37 (58.39)	3.87 (3.61)	Ni 3.75 (3.64)	Red	165 dec	54	Diamagnetic
$Ni(S_2C_2O_2)_2((PPh_3)_2Cu)_2$[e]	61.88 (61.51)	4.10 (4.15)	Ni 3.98 (4.06)	Violet	176 dec	48	Diamagnetic
$Fe(S_2C_2O_2)_3((PPh_3)_2Ag)_3$[f]	59.10 (58.41)	3.89 (3.98)	Fe 2.42 (2.40)	Black	145–147	40	5.81 ± 0.05
$Fe(S_2C_2O_2)_3((PPh_3)_2Cu)_3$	62.75 (62.20)	4.14 (4.15)		Black	135–136	45	5.93 ± 0.05
$Rh(S_2C_2O_2)_3((PPh_3)_2Cu)_3$	61.46 (61.12)	4.07 (4.05)	Cu 8.56 (8.59)	Brown	170 dec	36	Diamagnetic
$Al(S_2C_2O_2)_3((PPh_3)_2Ag)_3 \cdot 2CHCl_3$[g]	55.21 (55.11)	3.67 (3.71)		Light brown	195 dec	42	Diamagnetic
$Co(S_2C_2O_2)_3K(Me_3PhN)_2$[i]	39.44 (39.72)	3.86 (4.05)		Brown	245 dec	41	Diamagnetic
$Al(S_2C_2O_2)_3((PPh_3)_2Cu)_3$	63.63 (63.50)	4.22 (4.40)		Brown	175 dec	59	Diamagnetic
$Zn(S_2C_2O_2)_2(Ph_4As)_2$	58.24 (57.68)	3.76 (3.62)		Light yellow	195–198	30	Diamagnetic
$Zn(S_2C_2O_2)_2((PPh_3)_2Cu)_2$	61.60 (61.07)	4.08 (4.18)	Cu 8.58 (8.41)	Brown	150 dec	84	Diamagnetic
$(Ph_3P)_2Cu(S_2C_2O_2)Cu(PPh_3)_2$	68.67 (68.17)	4.64 (4.58)		Orange	205–207	68	Diamagnetic
$(Ph_3P)_2Ag(S_2C_2O_2)Ag(PPh_3)_2$	64.51 (63.80)	4.34 (4.54)	Ag 15.51 (15.52)	Yellow	168–170	58	Diamagnetic
$(Ph_3P)_2Cu(S_2C_2(NH)_2)Cu(PPh_3)_2$[h]	68.67 (68.22)	4.83 (5.00)		Orange	170 dec	51	Diamagnetic

[a] Nitrogen analysis: calcd, 2.34; found, 2.44. [b] Nitrogen analysis: calcd, 3.78; found, 3.77. [c] Cr–O, M–S (M = Ag, Cu) isomer. [d] Silver analysis: calcd, 13.79; found, 13.73. [e] Copper analysis: calcd, 8.61; found, 8.56. [f] Silver analysis: calcd, 14.00; found, 13.91. [g] Chloroform identified by its mass spectrum. [h] Nitrogen analysis: calcd, 2.16; found, 2.17. [i] Nitrogen analysis: calcd, 3.86; found, 3.97.

Trisnitromethane, ($Fe(S_2C_2O_2)_3(Ph_4As)_3 \cdot 3CH_3NO_2$). A solution of $K_3Fe(S_2C_2O_2)_3$ was prepared by adding a solution of 1.2 g (0.003 mol) of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in 100 ml of water to a solution of 2.0 g (0.01 mol) of dipotassium dithiooxalate, $K_2S_2C_2O_2$, in 50 ml of water. This solution was extracted with a solution of 4.18 g (0.01 mol) of tetraphenylarsonium chloride, Ph_4AsCl, in 270 ml of dichloromethane, CH_2Cl_2.

Addition of 600 ml of anhydrous ether to the organic phase resulted in the formation of an oil which was redissolved in 250 ml of nitromethane. Crystallization was effected by adding 600 ml of anhydrous ether. X-Ray powder data:[9] 7.78 (s), 6.92 (s), 6.07 (m), 5.79 (m), 4.67 (w), 4.39 (s), 4.15 (m), 3.77 (m), 3.45 (w).

Tris(tetraphenylarsonium) Tris[(dithiooxalato-*S*,*S*′)rhodate(III)]-Trisnitromethane, ($Rh(S_2C_2O_2)_3(Ph_4As)_3 \cdot 3CH_3NO_2$). A solution of $K_3Rh(S_2C_2O_2)$ was prepared by heating (80°) under nitrogen an aqueous solution (25 ml) of 1.0 g (0.005 mol) of $K_2S_2C_2O_2$ and 0.44 g (0.0017 mol) of $RhCl_3 \cdot 3H_2O$ for *ca.* 15 min. A procedure identical with that described above for the synthesis of $Fe(S_2C_2O_2)_3(Ph_4As)_3 \cdot 3CH_3NO_2$ was followed for the synthesis of the crystalline Rh(III) complex. Powder data: 7.82 (s), 6.93 (s), 6.05 (m), 5.79 (m), 4.67 (w), 4.39 (s), 4.17 (m), 3.78 (m), 3.44 (w).

Tris(tetraphenylarsonium) Tris[(dithiooxalato-*O*,*O*′)aluminate-(III)], ($Al(S_2C_2O_2)_3(Ph_4As)_3$). A solution of $K_3Al(S_2C_2O_2)_3$ was prepared by adding 0.27 g (0.002 mol) of $AlCl_3$ to 1.0 g (0.005 mol) of $K_2S_2C_2O_2$ in 75 ml of tetrahydrofuran (THF) and then adding water dropwise until a homogeneous orange solution was obtained. This solution was extracted with a solution of 1.4 g (0.003 mol) of Ph_4AsCl in 100 ml of CH_2Cl_2. The crystalline product was obtained following addition of 150 ml of anhydrous ether to the CH_2Cl_2 system.

Potassium Bis(trimethylphenylammonium) Tris[(dithiooxalato-*S*,*S*′)chromate(III)] Hydrate, ($Cr(S_2C_2O_2)_3K(Me_3PhN)_2 \cdot H_2O$). A solution of 2.0 g (0.01 mol) of $K_2S_2C_2O_2$ and 1.65 (0.003 mol) of $KCr(SO_4)_2 \cdot 12H_2O$ in 30 ml of water was heated under nitrogen to 60° for *ca.* 15 min. The warm solution was filtered into a solution of 1.6 g (0.006 mol) of Me_3PhNI in 20 ml of water. Crystallization was effected by the addition of 450 ml of isopropyl alcohol.

Tris[bis(triphenylphosphine)copper(I)] Tris[(dithiooxalato-*S*,*S*′)-chromate(III)], ($Cr(S_2C_2O_2)_3((PPh_3)_2Cu)_3$). A solution of 0.0017 mol of $K_3Cr(S_2C_2O_2)_3$ was prepared as previously described and extracted with a solution of 4.4 g (0.005 mol) of $(Ph_3P)_3CuCl$ in 100 ml of CH_2Cl_2. The crystalline adduct was formed upon the addition of 220 ml of *n*-pentane to the CH_2Cl_2 extract (ν_{C-O} at 1508 cm^{-1}). Powder data: 15.04 (s), 19.68 (s), 8..88 (s), 7.93 (s), 6.60 (m), 6.24 (m), 5.12 (m), 4.57 (m), 4.29 (s), 4.18 (s)

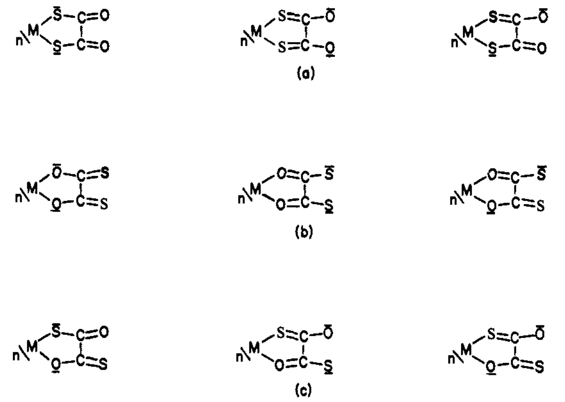

Figure 1. Canonical forms and multifunctional character of the dithiooxalate complexes.

Tris[bis(triphenylphosphine)silver(I)] Tris[(dithiooxalato-*O*,*S*)-chromate(III)], ($Cr(S_2C_2O_2)_3((PPh_3)_2Ag)_3$). This complex was prepared in a similar manner using benzene as a solvent in the extraction procedure (ν_{C-O} at 1622, 1572, and 1440 cm^{-1}).

Tris[bis(triphenylphosphine)metal(I)] Tris[(dithiooxalato-*O*,*O*′)-chromate(III)] (metal = silver, copper) (linkage isomers). Solutions of 2.0 g of either the Cr–Cu or the Cr–Ag adducts in 100 ml of wet CH_2Cl_2 were refluxed for 24 hr. To these solutions 100 ml of *n*-pentane and 250 ml of absolute ethanol were added. Crystals of the isomers formed on standing (ν_{C-O} at 1380 cm^{-1} for both complexes). Powder data for the $Cr(S_2C_2O_2)_3((PPh_3)_2Cu)_3$ linkage isomer: 13.80 (m), 12.77 (m), 11.33 (w), 9.17 (s), 8.25 (s), 9.35 (m), 6.89 (m), 6.29 (m), 4.97 (s), 4.61 (s), 4.40 (s), 4.13 (s).

Potassium Bis(trimethylphenylammonium) Tris[(dithiooxalato-*S*,*S*′)cobaltate(III)], ($Co(S_2C_2O_2)_3K(Me_3PhN)_2$). A solution of $K_3Co(S_2C_2O_2)_3$ was prepared by adding 0.61 g (0.0017 mol) of

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(9) *d* spacing, Å, of some strong lines.

$Na_3Co(CO_3)_3 \cdot 3H_2O$ to a solution of 1.0 g (0.005 mol) of $K_2S_2C_2O_2$ in 50 ml of water, the pH was adjusted to 3 with 2 *N* sulfuric acid, and the solution was heated to 60° for 20 min. After neutralization with $NaHCO_3$, a solution of 1.3 g (0.005 mol) of Me_3PhNI in 20 ml of water was added. Upon addition of 375 ml of isopropyl alcohol crystals of the complex formed.

Tris[tetrakis(triphenylphosphine)silver(I)] Tris[(dithiooxalato-*S*,*S*′)cobaltate(III)], $(Co(S_2C_2O_2)_3((PPh_3P)_4Ag)_3)$. A solution of $K_3Co(S_2C_2O_2)_3$ (0.0017 mol), prepared as previously described, was extracted with a CH_2Cl_2 solution (125 ml) containing 5.2 g (0.02 mol) of Ph_3P and 0.85 g (0.005 mol) of solid $AgNO_3$. Crystallization was effected following concentration of the dried CH_2Cl_2 extract to a volume of 25 ml and cooling to 0°.

Tris[bis(triphenylphosphine)silver(I)] Tris[(dithiooxalato)cobaltate(III)], $(Co(S_2C_2O_2)_3((Ph_3P)_2Ag)_3)$. A solution of $K_3Co(S_2C_2O_2)_3$ (0.0017 mol) was extracted with a solution of 2.7 g (0.01 mol) of Ph_3P in 100 ml of CH_2Cl_2 containing 0.85 g (0.005 mol) of solid $AgNO_3$. The brown crystalline product was obtained after addition of 250 ml of *n*-pentane to the CH_2Cl_2 extract and cooling to 0°.

Tris[bis(triphenylphosphine)copper(I)] Tris[(dithiooxalato-*S*,*S*′)cobaltate(III)], $(Co(S_2C_2O_2)_3((Ph_3P)_2Cu)_3)$. A solution containing 0.0017 mol of $K_3Co(S_2C_2O_2)_3$ (see above) was extracted with a solutionof 4.4 g (0.005 mol) of $(Ph_3P)_3CuCl$ in 100 ml of CH_2Cl_2. Crystals of the product were obtained by adding 250 ml of *n*-pentane to the CH_2Cl_2 extract.

Bis[tetrakis(triphenylphosphine)silver(I)] Bis[(dithiooxalato-*S*,*S*′)nickelate(II)], $(Ni(S_2C_2O_2)_2((Ph_3P)_4Ag)_2)$. An aqueous solution containing 0.0025 mol of $K_2Ni(S_2C_2O_2)_2$ (100 ml) was extracted with a 100 ml CH_2Cl_2 solution containing 5.8 g (0.0022 mol) of Ph_3P and 0.85 g (0.005 mol) of solid $AgNO_3$. Concentrating the CH_2Cl_2 extract to a volume of 25 ml and cooling to 0° caused formation of the red crystalline product. Powder data: 13.55 (w), 11.90 (s), 10.70 (w), 8.42 (s), 5.34 (m), 4.56 (s), 4.37 (s), 3.84 (m), 3.19 (m).

Bis[bis(triphenylphosphine)silver(I)] Bis[(dithiooxalato-*S*,*S*′)nickelate(II)], $(Ni(S_2C_2O_2)_2((Ph_3P)_2Ag)_2)$. A solution of $K_2Ni(S_2C_2O_2)_2$ (100 ml, 0.0025 mol) was extracted with a 100 ml CH_2Cl_2 solution of 2.9 g (0.011 mol) of Ph_3P containing 0.85 g (0.005 mol) of $AgNO_3$. Crystals formed after the addition of 25 ml of acetone and 300 ml of *n*-pentane. Powder data: 11.89 (m), 10.38 (s), 9.09 (s), 6.87 (w), 6.36 (m), 6.00 (w), 5.34 (m), 4.97 (m), 4.38 (m), 3.79 (m).

Bis[bis(triphenylphosphine)copper(I)] Bis[(dithiooxalato-*S*,*S*′)nickelate(II)], $(Ni(S_2C_2O_2)_2((Ph_3P)_2Cu)_2$. A cold solution (5°) of 0.0025 mol of $K_2Ni(S_2C_2O_2)_2$ in 100 ml of water was extracted with a cold solution (5°) of $(Ph_3P)_3CuCl$ (4.0 g, 0.0045 mol) in 200 ml of CH_2Cl_2. Crystals formed upon the addition of 400 ml of chilled *n*-pentane. Powder data: 8.14 (s), 7.51 (m), 6.83 (m), 6.24 (m), 5.70 (m), 5.04 (m), 4.79 (s), 4.42 (s), 3.75 (m), 2.75 (w).

Tris[bis(triphenylphosphine)silver(I)] Tris[(dithiooxalato-*O*,*O*′)ferrate(III)], $(Fe(S_2C_2O_2)_3((Ph_3P)_2Ag)_3)$. A solution of 0.003 mol of $K_3Fe(S_2C_2O_2)_3$ was prepared as described previously. This solution was extracted with a solution of 7.9 g (0.03 mol) of Ph_3P in 300 ml of CH_2Cl_2 containing 1.70 g (0.01 mol) of solid $AgNO_3$. The CH_2Cl_2 extract was diluted with 50 ml of acetone and pentane was added until a permanent cloudiness appeared. Crystals formed on standing at 0°. Powder data: 11.46 (m), 8.36 (s), 7.65 (s), 6.53 (m), 6.06 (w), 5.38 (s), 4.91 (s), 4.58 (s), 3.03 (m).

Tris[bis(triphenylphosphine)copper(I)] Tris[(dithiooxalato-*O*,*O*′)ferrate(III)], $(Fe(S_2C_2O_2)_3((Ph_3P)_2Cu)_3)$. This complex was prepared in a manner exactly analogous to the one described for the silver analog. Anhydrous CuCl was used as a source for copper(I). Powder data: 11.37 (m), 8.25 (s), 7.71 (s), 6.34 (m), 6.05 (m), 5.27 (m), 4.93 (s), 4.54 (s), 3.00 (m).

Tris[bis(triphenylphosphine)copper(I)] Tris[(dithiooxalato-*S*,*S*′)rhodate(III)], $(Rh(S_2C_2O_2)_3((Ph_3P)_2Cu)_3)$. A solution containing 0.0017 mol of $K_3Rh(S_2C_2O_2)_3$ (see above) was extracted with a solution of 4.2 g of $(Ph_3P)_3CuCl$ (0.005 mol) in 100 ml of CH_2Cl_2. Crystals of the product formed following addition of 200 ml of *n*-pentane to the CH_2Cl_2 extract.

Tris[bis(triphenylphosphine)silver(I)] Tris[(dithiooxalato-*O*,*O*′)aluminate(III)]–Bischloroform, $(Al(S_2C_2O_2)_3((Ph_3P)_2Ag)_3 \cdot 2CHCl_3)$. A solution containing 0.0017 mol of $K_3Al(S_2C_2O_2)_3$, prepared as previously described, was extracted with a CH_2Cl_2 solution (100 ml) of 4.1 g (0.0045 mol) of $(Ph_3P)_3AgCl$. Crystals formed after addition of 250 ml of pentane. The crude product was recrystallized from a $CHCl_3$–*n*-pentane mixture adding 1 mol of Ph_3P per mol of complex. Powder data of solvent-free complex: 11.44 (m), 8.40 (s), 7.67 (s), 6.51 (m), 6.05 (m), 5.35 (m), 4.90 (s), 4.57 (s), 3.02 (m).

Tris[bis(triphenylphosphine)copper(I)] Tris[(dithiooxalato-*O*,*O*′)aluminate(III)], $(Al(S_2C_2O_2)_3((Ph_3P)_2Cu)_3)$. This compound was prepared in a manner exactly analogous to the one described for the Ag(I) analog.

Bis[bis(triphenylphosphine)copper(I)] Bis[(dithiooxalato)zincate(II)], $(Zn(S_2C_2O_2)_2((Ph_3P)_2Cu)_2)$. A solution of $K_2Zn(S_2C_2O_2)_2$ was prepared by adding 0.72 g (0.0025 mol) of $ZnSO_4 \cdot 7H_2O$ to 1.0 g (0.005 mol) of $K_2S_2C_2O_2$ in 25 ml of water. This solution was extracted with a CH_2Cl_2 solution (100 ml) containing 3.8 g (0.0043 mol) of $(Ph_3P)_3CuCl$. Crystals formed on addition of 200 ml of pentane.

Bis(tetraphenylarsonium) Bis[(dithiooxalato-*S*,*S*′)zincate(II)], $(Zn(S_2C_2O_2)_2(Ph_4As)_2)$. To an aqueous solution of $K_2Zn(S_2C_2O_2)_2$ an aqueous solution of Ph_4AsCl was added. The white precipitate which formed was isolated, dried, and dissolved in dimethylformamide. Addition of ether resulted in the formation of white crystals. Powder data: 10.61 (m), 8.18 (s), 6.99 (s), 6.51 (m), 5.67 (w), 5.37 (m), 4.67 (s), 4.41 (m), 4.28 (s), 4.15 (w).

μ-Dithiooxalato-bis[bis(triphenylphosphine)copper(I)], $((Ph_3P)_2Cu(S_2C_2O_2)Cu(PPh_3P)_2)$. A solution of 0.50 g of $K_2S_2C_2O_2$ (0.0025 mol) in 25 ml of water was extracted with a solution of 4.43 g (0.005 mol) of $(Ph_3P)_3CuCl$ in 150 ml of CH_2Cl_2. Crystals of the product formed after addition of 130 ml of *n*-hexane to the CH_2Cl_2 extract. Powder data: 11.43 (s), 9.93 (m), 8.02 (s), 5.98 (m), 5.53 (m), 4.95 (m), 4.77 (s), 4.43 (s), 4.24 (s).

μ-Dithiooxalato-bis[bis(triphenylphosphine)silver(I)], $((Ph_3P)_2Ag(S_2C_2O_2)Ag(Ph_3P)_2)$. This complex was prepared in a manner similar to the one described for the copper analog using $(Ph_3P)_3AgCl$ as a source for $(Ph_3P)_2Ag^+$. Powder data: 11.59 (s), 9.96 (m), 7.97 (s), 6.06 (m), 5.63 (m), 4.98 (m), 4.68 (s), 4.45 (s), 4.26 (s).

μ-Dithiooxamido-bis[bis(triphenylphosphine)copper(I)], $((Ph_3P)_2Cu(S_2C_2(NH)_2)Cu(Ph_3P)_2)$. Dithiooxamide 0.2 g (0.0017 mol) and KOH (0.3 g, 0.0055 mol) were dissolved in 25 ml of water. This solution was extracted with a 50 ml CH_2Cl_2 solution containing 2.7 g (0.003 mol) of $(Ph_3P)_3CuCl$ and 3.0 g (0.012 mol) of Ph_3P. Addition of 50 ml of *n*-pentane to the CH_2Cl_2 extract caused crystallization of the product. Powder data: 11.40 (s), 9.87 (s), 8.03 (s), 6.03 (w), 5.54 (w), 4.94 (m), 4.75 (s), 4.43 (s), 4.24 (s).

Results and Discussion

Synthesis and Structures. (a) Parent Complexes. The data characterizing the tetraarylphosphonium or -arsonium salts of the anionic dithiooxalate complexes, $M(S_2C_2O_2)_n{}^{n-}$, are summarized in Table I. The use of large cations as counterions allows recrystallization from nonaqueous media and eliminates the difficulties associated with the hydrophilic nature of the alkali or alkaline earth metal salts. The solid-state X-ray structures of the planar[2,10] $Ni(S_2C_2O_2)_2{}^{2-}$ and octahedral[11] $Co(S_2C_2O_2)_3{}^{3-}$ complexes show the ligands coordinated through the sulfurs (Figure 1a). The frequencies of the C–O stretching vibrations occur at 1570 and 1600 cm^{-1}, respectively, for the cobalt(III) and nickel(II) complexes. The presence of C–O absorptions of similar energies in the infrared spectra of the "parent" complexes reported in this study (Table II) is considered as evidence for sulfur (SS) chelated ligands.

The low frequency of the C–O vibrations in the $Al(S_2C_2O_2)_3{}^{3-}$ complex (1360 cm^{-1}) is similar to that found in the corresponding oxalate complex.[12] Such a decrease in the C–O bond order of the coordinated dithiooxalate ligand is expected to occur if the ligand is OO-bonded to the aluminum. Similar evidence for OO-bonded dithiooxalate ligands (Figure 1b) is also found in the infrared spectrum of the zirconium dithiooxalate complex,[13] $Zr(S_2C_2O_2)_4{}^{4-}$. The preference of Al(III) and Zr(IV) for the oxygen atoms of the ligand

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[10] E. G. Cox, W. Wardlaw, and K. C. Webster, *J. Chem. Soc.*, 1745 (1935).

[11] K. R. Butler and M. R. Snow, *Inorg. Nucl. Chem. Lett.*, 8, 541 (1972).

[12] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1970, p 240.

[13] M. Leitheiser and D. Coucouvanis, paper in preparation.

Table II. Vibrational Spectra[a]

Compound	Assignment					
	$A_1, B_2(\lambda_1, \lambda_7)$ C=O stretch[b]	$A_1(\lambda_2)$[b] $\nu_{C-C} + \nu_{C-S}$	$B_2(\lambda_8)$[b]	$A_1(\lambda_3)$[b] C–S stretch?	M–S(O)[h]	Other[c]
$Fe(S_2C_2O_2)_3(Ph_4As)_3 \cdot 3CH_3NO_2$	1561 (s)	1046 (m)			300 (m)	
$Rh(S_2C_2O_2)_3(Ph_4As)_3 \cdot 3CH_3NO_2$	1558 (s)	1043 (m)			307 (m), 290 (m)	
$Al(S_2C_2O_2)_3(Ph_4As)_3$	1360 (s)	1026 (s)		*d*	370 (m)	465 (s),[i] 438 (s, br)
$Cr(S_2C_2O_2)_3K((Me_3Ph)N)_2 \cdot H_2O$	1570 (s)	1050 (s)			325 (s)	
$Cr(S_2C_2O_2)_3((PPh_3)_2Cu)_3$	1508 (s)	1050 (w)	882 (w)	594 (w)	339 (s)	270 (w), 250 (w), 227 (s), 183 (m), 155 (w), 123 (m)
$Cr(S_2C_2O_2)_3((PPh_3)_2Ag)_3$	1622 (m) 1440 (s), 1572 (s)		862 (s, br)		325 (s) 370 (s)	142–260 (m, br)
$Cr(S_2C_2O_2)_3((PPh_3)_2Cu)_3$[e]	1372 (s)	1120 (w)		663 (m)	370 (s)	260 (m), 215 (m), 168 (w)
$Cr(S_2C_2O_2)_3((PPh_3)_2Ag)_3$[e]	1370 (s)	1120 (w)		663 (m)	375 (s, br)	252 (m), 192 (m, br)
$Co(S_2C_2O_2)_3((PPh_3)_4Ag)_3$	1583 (s), 1527 (s)	1045 (w)			329 (m)	
$Co(S_2C_2O_2)_3((PPh_3)_2Ag)_3$	1608 (w), 1530 (s)	1081 (sh)			343 (s, br)	275 (m), 252 (m), 213 (m), 179 (s)
$Co(S_2C_2O_2)_3((PPh_3)_2Cu)_3$	1498 (s)	1100 (s)			344 (m)	293 (w), 247 (s), 191 (s), 122 (s)
$Ni(S_2C_2O_2)_2(Ph_4As)_2$	1605 (s), 1588 (s)	1050 (s)	910 (m)	614 (m)	349 (s)	
$Ni(S_2C_2O_2)_2((Ph_3P)_4Ag)_2$	1603 (s, br)	1051 (s)	909 (m)		348 (s)	
$Ni(S_2C_2O_2)_2((Ph_3P)_2Ag)_2$	1653 (s), 1628 (s)	1034 (s)	884 (m)		345 (s)	274 (m), 251 (m), 220 (m), 209 (m), 199 (m), 173 (m), 162 (m)
$Ni(S_2C_2O_2)_2((Ph_3P)_2Cu)_2$	1528 (s)	1102 (s)	966 (m)		371 (s)	275 (m), 250 (m), 184 (m), 130 (m)
$Fe(S_2C_2O_2)_3((Ph_3P)_2Ag)_3$	1380 (s)			603 (m), 653 (m)	314 (s, br)	275 (s), 208 (m), 167 (m), 138 (m), 110 (w)
$Fe(S_2C_2O_2)_3((PPh_3)_2Cu)_3$	1382 (s)			604 (m) 650 (m)	312 (s)	283 (m), 260 (m), 239 (m), 214 (m), 197 (m), 180 (m), 120 (w)
$Rh(S_2C_2O_2)_3((PPh_3)_2Cu)_3$	1503 (s)	1098 (s)			321 (m)	300 (m), 253 (s), 187 (s), 124 (s)
$Al(S_2C_2O_2)_3((PPh_3)_2Ag)_3$[f]	1395 (s)	1025 (s)		609 (m), 667 (sh)	366 (s)	464 (s), 433 (s), 275 (w), 250 (m), 219 (s), 170 (w), 130 (m), 108 (m)
$Al(S_2C_2O_2)_3((PPh_3)_2Cu)_3$	1402 (s)	1030 (s)		607 (m), 667 (sh)		471 (s), 461 (s), 442 (s) 297 (w), 253 (s), 233 (s) 208 (w), 187 (s), 170 (s), 120 (m)
$Zn(S_2C_2O_2)_2((PPh_3)_2Cu)_2$	1475 (s) 1444 (s)		995 (m)			242 (s, br), 224 (s), 192 (s), 185 (s)
$Zn(S_2C_2O_2)_2(Ph_4As)_2$	1610 (s)	1025 (m)	887 (m)		327 (m)	
$(Ph_3P)_2Cu(S_2C_2O_2)Cu(PPh_3)_2$	1528 (s)		853 (m)			323 (w), 295 (w), 275 (w), 252 (m), 228 (m), 217 (s), 200 (m), 133 (m)
$(Ph_3P)_2Ag(S_2C_2O_2)Ag(PPh_3)_2$	1545 (s)		825 (s)			298 (m), 275 (w), 259 (w), 249 (m), 209 (m), 174 (s), 130 (w), 126 (w)
$(Ph_3P)_2Cu(S_2C_2(NH)_2)Cu(PPh_3)_2$[g]	1465 (s)	1302 (m) 1269 (s)	821 (s) 801 (m)			252 (m), 233 (s), 200 (w), 177 (m), 157 (w)

[a] Frequencies reported in cm^{-1}, s = strong, w = weak, br = broad, m = medium, and sh = shoulder. Near-infrared spectra were taken in Nujol mulls between NaCl plates. Far-infrared, Nujol mulls between high-density polyethylene films. [b] Assignments given in ref 23. [c] Absorptions attributed to noninteracting cations are not included in the table. [d] Region obscured by absorptions due to the cation. [e] Cr–O, M–S coordination isomers (M = Cu, Ag). [f] Compound crystallizes with two $CHCl_3$ molecules of solvation. [g] Assignments made in the table do not apply for this compound. [h] M refers to the central transition metal ion. [i] The spectrum of the complex in this region was obtained from the Me_3PhN^+ "salt."

is in accord with the class A[14] (hard)[15] character of these ions.

In the $Fe(S_2C_2O_2)_3{}^{3-}$ complex the ligands are sulfur bonded. The magnetic moment of this complex is 2.30 BM at 300°K and is appreciably larger than the spin-only value expected for octahedral low-spin Fe(III). Orbital contributions may account for this increase; however, both the magnetic moment and a rather large Curie–Weiss constant of −42°K[3b] are values similar to those obtained for the ferric thioxanthate complexes in which both the $^6A_1$ and $^2T_2$ states are populated at room

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(14) S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev., Chem. Soc.*, **12**, 265 (1958).

(15) R. G. Pearson, *J. Amer. Chem. Soc.*, **85**, 3533 (1963).

temperature.[16] Unlike Co(III), Rh(III), and Cr(III) tris(dithiooxalato) complexes, the $Fe(S_2C_2O_3)_3{}^{3-}$ complex could not be resolved into its optical isomers.[3a] However, the strict isomorphism of the Ph_4As^+ salt of this ion to that of the octahedral $Rh(S_2C_2O_2)_3{}^{3-}$ complex suggests that, at least in the solid state, the $Fe(S_2C_2O_2)_3{}^{3-}$ is an octahedral complex ion.

The $Zn(S_2C_2O_2)_2{}^{2-}$ complex with a given cation is not isomorphous to the planar, X-ray isomorphous, $M(S_2C_2O_2)_2{}^{2-}$ (M = Ni(II), Pd(II), Cu(II)) complexes with the same cation and possibly adopts the tetrahedral or pseudotetrahdral geometry common with other zinc–sulfur complexes.[17]

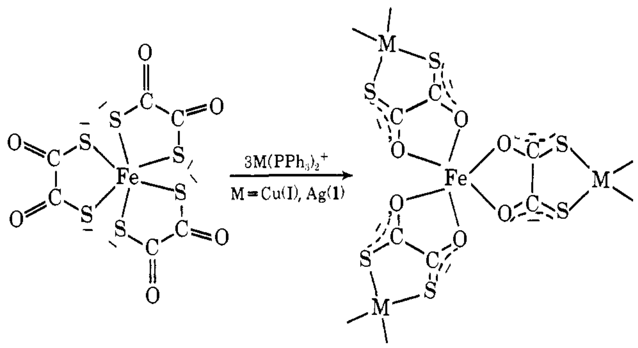
(b) $(PPh_3)_2M^+$ Adducts of the Dithiooxalato Complexes. The inert counterions that accompany the $M(S_2C_2O_2)_n{}^{n-}$ complexes were replaced by the coordinately unsaturated $(PPh_3)_2M^+$ cations (M = Ag, Cu) generated *in situ* from the solid $(PPh_3)_3MCl$ complexes.[7b,c] Table I summarizes the data characterizing the crystalline $M(S_2C_2O_2)_n[(PPh_3)_2M]_n$ adducts. The general extraction procedure (see Experimental Section) used in the synthesis of these compounds (eq 1) allows

$$K_nM(S_2C_2O_2)_n(aq) + n(PPh_3)_3M'Cl \longrightarrow nKCl(aq) + M(S_2C_2O_2)_n[(PPh_3)_2M']_n \quad (1)$$

for an efficient cation exchange and a convenient separation of the dichloromethane soluble adducts from the water soluble alkali metal salt by-products. The adducts are very weakly conducting[18] in CH_2Cl_2 solution and are diamagnetic with the exception of the $Fe(S_2C_2O_2)_3((PPh_3)_2M)_3$ and $Cr(S_2C_2O_2)_3((PPh_3)_2M)_3$ (M = Cu(I), Ag(I)) complexes (Table I).

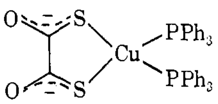
There is evidence to suggest that the alkali metal cations accompanying the $Zn(S_2C_2O_2)_2{}^{2-}$ and $Rh(S_2C_2O_2)_3{}^{3-}$ complexes exchange with $(PPh_3)_2Ag^+$; however, well defined crystalline adducts could not be isolated.

(c) Adducts of the Fe(III), Al(III), and Zn(II) Dithiooxalates. The near-infrared spectra of the $M(S_2C_2O_2)_3((Ph_3P)_2M')_3$ complexes (M = Fe(III) or Al(III) and M′ = Cu(I) or Ag(I)) are virtually identical and are characterized by the low frequency of the C–O vibration which occurs near 1380 cm^{-1}. The far-infrared spectra of the Al(III) and Fe(III), $(PPh_3)_2Cu^+$ adducts differ in the region 550–300 cm^{-1}, normally associated with Al–L and Fe–L vibrations, but show common groups of bands below 300 cm^{-1}. A similar situation occurs with the $(PPh_3)_2Ag^+$ adducts of the iron(III) and aluminum(III) dithiooxalate complexes (Table II). These observations show similar environments for the $(PPh_3)_2M^+$ cations in *both* the Fe(III) and Al(III) complexes, and suggest that *a major reorientation of the ligand has occurred in the initially SS-bonded $Fe(S_2C_2O_2)_3{}^{3-}$ complex as a result of the $(PPh_3)_2M^+$ perturbation.* Specifically, the data indicate that the $(PPh_3)_2M^+$ cations induce a change in the Fe–L coordination from a Fe–SS to a Fe–OO chelation.[19,20]



In order to establish beyond doubt this induced coordination isomerism we have undertaken X-ray crystal structure determinations for the $M(S_2C_2O_2)_3((PPh_3)_2Ag)_3$ complexes (M = Al(III), Fe(III)). The results of these studies[21] verify the conclusions reached previously and unequivocally show M–OO, $(PPh_3)_2Ag$–SS coordination. A *c* axis projection of the structure of the iron complex[22] is shown in Figure 2. Other cases in which addition of $(PPh_3)_2M^+$ to a SS-bonded dithiooxalate complex results in induced linkage isomerization have been observed with the $Sn(S_2C_2O_2)_3{}^{2-}$ and $Zn(S_2C_2O_2)_2{}^{2-}$ complexes.

In $Zn(S_2C_2O_2)_2{}^{2-}$ the lability of the Zn–O bonds makes this compound an excellent source for the



ligand.[13]

(d) Adducts of the Ni(II), Co(III), Cr(III), and Rh(III) Dithiooxalates. The infrared spectra of the $M(S_2C_2O_2)_n((PPh_3)_2Cu)_n$ complexes (M = Cr(III), Co(III), Rh(III) (*n* = 3); M = Ni(II) (*n* = 2)) show the C–O stretching vibrations at frequencies roughly 100 cm^{-1} lower than those of the corresponding "parent" complexes. In the spectra of the $M(S_2C_2O_2)_n{}^{n-}$ "parent" complexes a band near 1050 cm^{-1} has been attributed to a combination of the C–C and C–S vibrations.[23] The same band occurs around 1100 cm^{-1} (Table II) in the spectra of the adducts. Effects of this type, as well as the hypsochromic shifts (Table II) of the M–S stretching vibrations in the $(PPh_3)_2M^+$ adducts, are similar to perturbations observed in the infrared spectra of the $SnCl_4$ adducts of the $Ni(S_2C_2O_2)_2{}^{2-}$ complex. For the latter compounds, X-ray structural determinations have shown that the $SnCl_4$ molecules are chelated by the α-diketone portion of the coordinated ligand.[1] The stoichiometry and magnetic properties of the $(PPh_3)_2Cu^+$ adducts indicate that the coordination about the central metal ion has not changed significantly and probably these molecules adopt structures such as the one shown in Figure 3a. In the $Ni(S_2C_2O_2)_2((PPh_3)_2Ag)_2$ complex, a hypsochromic shift of the C–O stretching frequency and a bathochromic shift of the C–C and C–S combination band are found relative to the corresponding vibra-

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(16) A. H. Ewald and E. Sinn, *Aust. J. Chem.*, **21**, 927 (1968).

(17) D. Coucouvanis, *Progr. Inorg. Chem.*, **11**, 233 (1970).

(18) Limited solubility characteristics did not allow for meaningful molecular weight studies.

(19) The epr spectrum of the polycrystalline $(PPh_3)_2Ag^+$ adduct resembles that of $Fe(Me_2SO)_6(NO_3)_3$: S. A. Cotton and J. F. Gibson, *J. Chem. Soc. A*, 1690 (1971). A different spectrum was obtained for the corresponding $(PPh_3)_2Cu^+$ adduct. A calculation of magnetic resonance line positions and intensities[20] agreed with the experimental spectra. In this calculation the simplified spin Hamiltonian $\mathcal{H} = D(S_z{}^2 - S(S+1)/3) + g_B\mu H \cdot S$ was used with the $S = {}^5/_2$ and $D = 0.26$ and 6.8 GHz for the Fe–Ag and Fe–Cu adducts, respectively.

(20) W. V. Sweeney, D. Coucouvanis, and R. E. Coffman, *J. Chem. Phys.*, in press.

(21) D. Coucouvanis and F. J. Hollander, manuscript in preparation will be submitted to *Inorg. Chem.*

(22) At the present stage of refinement a value of 6.0 has been obtained for R_1.

(23) J. Fujita and K. Nakamoto, *Bull. Chem. Soc. Jap.*, **37**, 528 (1964).

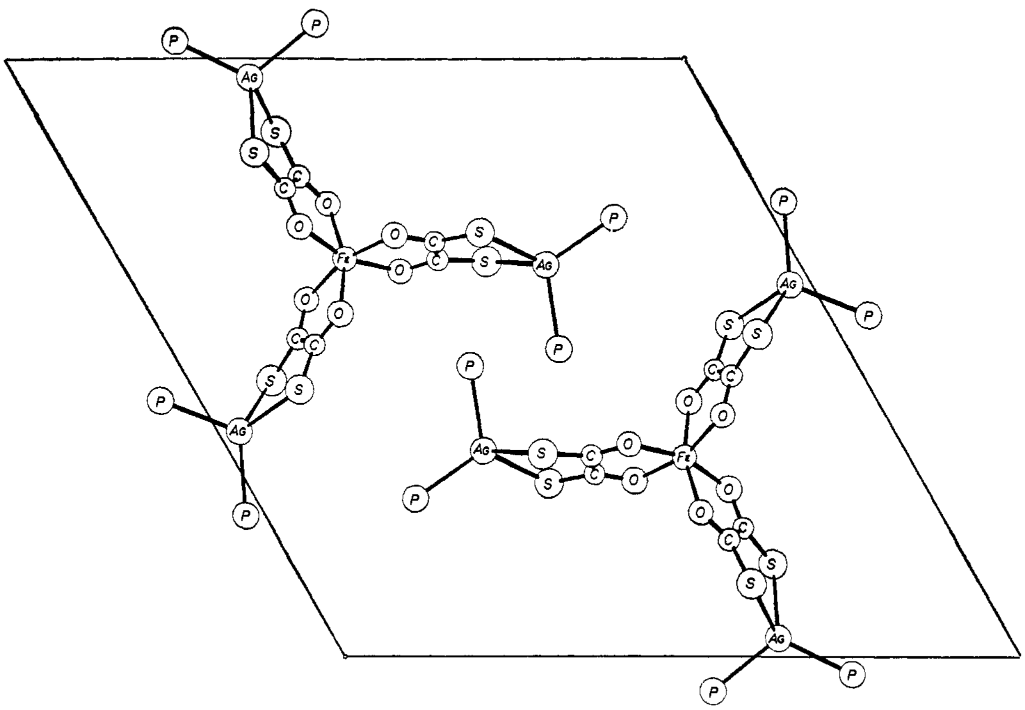

Figure 2. A *c* axis projection of the trigonal ($P\bar{3}$) unit cell contents of the $Fe(S_2C_2O_2)_3((PPh_3)_2Ag)_3$ complex. The PPh_3 phenyl rings have been omitted for clarity. The two iron atoms are located above ($\sim ^1/_4\,c$) and below ($\sim -^1/_4 c$) the *ab* plane.

tions in the parent complex. These changes indicate that the interacting cations induce delocalization of charge toward the sulfur atoms which results in an increase of the C–O bond order. A probable structure for this complex is one in which the $(PPh_3)_2Ag^+$ cation interacts with the complex anion through the already coordinated sulfur atoms[24,25] (Figure 3b). This type of interaction is rather weak and vanishes in the presence of donor molecules that can saturate the coordination sphere of the silver ion. Thus in the presence of an excess of PPh_3 the $Ni(S_2C_2O_2)_2((PPh_3)_2Ag)_2$ adduct is converted to a salt of the nickel dithiooxalate anion with $(PPh_3)_4Ag^+$ [26] as a noninteracting counterion. The $(PPh_3)_2Ag^+$ adduct of the $Co(S_2C_2O_2)_3{}^{3-}$ complex is similar to the $(PPh_3)_2Cu^+$ analog and its infrared spectrum is characterized by strong absorptions at 1533 and 1082 cm^{-1}. The Ag–O interactions, however, are quite weak, and this "adduct" also is converted readily to a $(PPh_3)_4Ag^+$ "salt" in the presence of excess PPh_3. The infrared spectrum of the $Cr(S_2C_2O_2)_3((PPh_3)_2Ag)_3$ complex indicates that in this compound the $S_2C_2O_2{}^{2-}$ ligand is bridging symmetrically in the trans form (Figure 5). This conclusion finds support in (a) the existence of two C–O stretching vibrations, (b) a strong C–S vibration at 862 cm^{-1} "typical" of this type of bonding (*vide infra*), and (c) the existence of two absorptions at 325 and 370 cm^{-1} which can be assigned to the Cr–S and Cr–O stretching vibrations, respectively. This linkage isomerization, which involves rotation about the C–C bond in the ligand, is not surprising in view of the relative affinities of Cr(III) and Ag(I) for sulfur *vs.* oxygen ligands.[27]

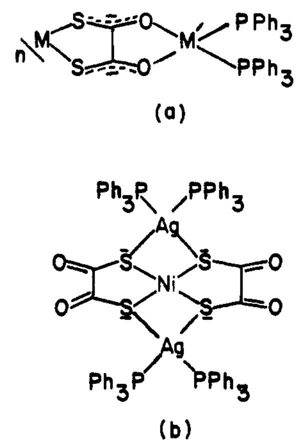

Figure 3. Proposed structures for the $M(S_2C_2O_2)_n((PPh_3)_2M')_n$ complexes: (a) M = Ni(II), Cr(III), Co(III), Rh(III); M′ = Cu(I).

Properties consistent with Cr–SS or Cr–SO coordination were observed for the $Cr(S_2C_2O_2)_3((PPh_3)_2M)_3$ complexes when these compounds were rapidly (within *ca.* 1 hr) crystallized from CH_2Cl_2 or benzene solutions. Prolonged standing of these solutions resulted in products for which the infrared spectra showed the appearance of a new C–O absorption near 1380 cm^{-1}. This band reached maximum intensity after refluxing a CH_2Cl_2 solution of the Cr–SS bonded isomers for *ca.* 8 hr (Figure 4). It appears quite certain that *the observed changes arise from a kinetically controlled linkage isomerization process in which the $Cr–S_2C_2O_2–M$ linkage changes to $Cr–O_2C_2S_2–M$*[28] (Figure 5).

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(24) Bonding of this type has recently been observed[25] in the crystal structures of the $Ni(MNT)_2((PPh_3)_2Ag)_2$ and $Ni(i\text{-}MNT)_2((PPh_3)_2Ag)_2$ complexes: MNT = $SC(CN)C(CN)S^{2-}$, *i*-MNT = $S_2CC(CN)_2{}^{2-}$. An interesting feature of these complexes is the short, 2.90–3.00 Å, Ni–Ag distance.

(25) D. Coucouvanis, N. C. Baenziger, and S. M. Johnson, paper in preparation.

(26) F. A. Cotton and D. M. L. Goodgame, *J. Chem. Soc.*, 5267 (1960).

(27) Consistent with this formulation is the fact that, when treated with an excess of PPh_3, the $Cr(S_2C_2O_2)_3((PPh_3)_2Ag)_3$ complex did not react to give the $(PPh_3)_4Ag^+$ "salt" of the Cr–SS bonded anion.

(28) Attempts were made to effect isomerization of the $Co(S_2C_2O_2)_3((Ph_3)_2M)_3$ complexes but were not successful.

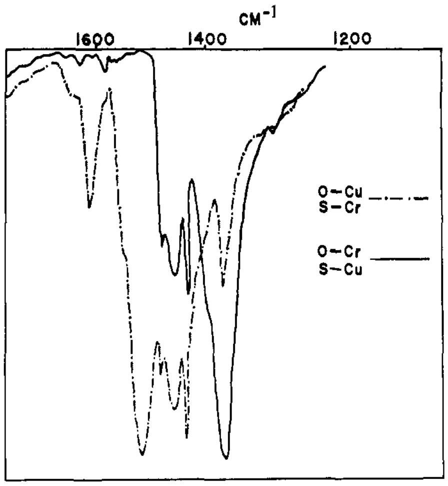

Figure 4. The C–O stretching vibrations in the infrared spectra of the $Cr(S_2C_2O_2)_3((PPh_3)_2M')_3$ linkage isomers (Nujol mulls).

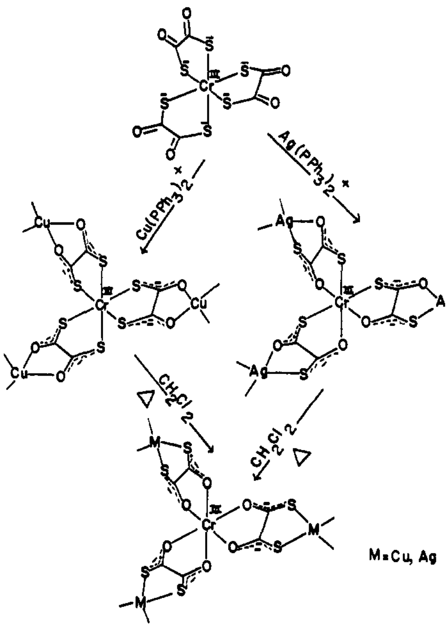

Figure 5. Linkage isomerization in the $Cr(S_2C_2O_2)_3((PPh_3)_2M')_3$ complexes.

Similar cases of coordination isomerism have been reported for other systems. The reaction between $(H_2O)_5CrCN^{2+}$ and Hg^{2+} results in isomerization and formation of the $(H_2O)_5CrNCHg^{4+}$ complex.[29] The same behavior is observed in the $(NH_3)_5CoCN^{2+}$–Hg^{2+} [30] and $(H_2O)_5CrSCN^{2+}$ systems.[31] In the latter the stable $(H_2O)_5CrNCSHg^{4+}$ complex is obtained following aquation and isomerization. In all cases the affinity of Hg^{2+} for the "soft" C and S donor atoms of the ambidentate ligands induces linkage isomerism.

(e) **$(PPh_3)_2M(S_2C_2O_2)M(PPh_3)_2$ Complexes.** Attempts to obtain the $M(PPh_3)_2^+$ adducts of the $Cu(S_2C_2O_2)_2^{2-}$ complex failed and instead products of the composition $(PPh_3)_2Cu^I(S_2C_2O_2)M(PPh_3)_2$ (M = Cu(I), Ag(I)) were isolated. These complexes and the $(Ph_3P)_2Ag(S_2C_2O_2)Ag(PPh_3)_2$ analog are X-ray isomorphous and also could be prepared directly from the appropriate $(PPh_3)_3MCl$ and $K_2S_2C_2O_2$.

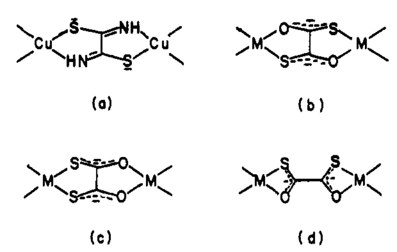

Figure 6. Possible structures for the $((PPh_3)_2M')_2(S_2C_2O_2)$ complexes.

Table III. Electronic Spectra

Compound	10^{-3} ν(max), cm^{-1}	ϵ, l. cm^{-1} M^{-1}
	17.8	2,300
$(Ph_4As)_2Ni(S_2C_2O_2)_2$	19.9	3,500
	32.7	18,500
$[(Ph_3P)_2Ag]_2Ni(S_2C_2O_2)_2$	20.08	3,000
$[(Ph_3P)_2Cu]_2Ni(S_2C_2O_2)_2$	16.53	5,690
	17.70	5,910
	19.08	5,970
$K[(Me_3Ph)N]_2Co(S_2C_2O_2)_3$	17.70	680
	21.98	2,950
$[(PPh_3)_2Cu]_3Co(S_2C_2O_2)_3$	20.41	7,550
	27.03	25,500
$[(PPh_3)_2Ag]_3Co(S_2C_2O_2)_3$	17.24	912
	20.41	2,870
$[(PPh_3)_2Cu]_3Al(S_2C_2O_2)_3$	22.47	11,900
$[(PPh_3)_2Ag]_3Al(S_2C_2O_2)_3$	25.00	3,480
	28.49	10,300
$[(PPh_3)_2Cu]_2Zn(S_2C_2O_2)_2$	23.36	7,500
$[(PPh_3)_2Cu]_3Rh(S_2C_2O_2)_3$	25.19	21,100
$K[(Me_3Ph)N]_2Cr(S_2C_2O_2)_3 \cdot H_2O$	17.00	433
	21.90	1,060
$[(Ph_3P)_2Cu]_3Cr(S_2C_2O_2)_3$	24.39	14,200
$[(Ph_3P)_2Cu]_3Cr(S_2C_2O_2)_3$[a]	21.74	14,700
$[(Ph_3P)_2Ag]_3Cr(S_2C_2O_2)_3$	16.67	456
	20.83	1,910
	31.25	29,900
$[(Ph_3P)_2Ag]_3Cr(S_2C_2O_2)_3$[a]	17.24	365
	22.22	3,500
	32.79	47,800

[a] Cr–O, M–S (M = Ag, Cu) isomer.

The infrared spectra of these complexes are characterized by a sharp C–O absorption and a strong band near 850 cm^{-1} which is probably due to a C–S vibration.

The disodium salt of dithiooxamide, $Na_2S_2C_2(NH)_2$, reacts in a similar manner and the crystalline $(PPh_3)_2Cu(S_2C_2(NH)_2)Cu(PPh_3)_2$ has been isolated. A possible structure for this complex, which is X-ray isomorphous to the dithiooxalate analogs, is shown in Figure 6a.[32] Any of the structures shown in Figure 6 are possible for the dithiooxalate complexes; however, by analogy to the dithiooxamide complex, a structure in which the $S_2C_2O_2^{2-}$ ligand is bridging in the trans form is proposed. In these complexes the strength of the M′–S *vs.* M′–O bonding varies depending on the nature of the coinage metal (M′). The higher C–O and lower C–S stretching frequencies observed when M′ = Ag(I) are in accord with the greater affinity of Ag(I) for sulfur donors. In the $(PPh_3)_2Cu(S_2C_2O_2)Ag(PPh_3)_2$ complex the C–O vibrations are not completely re-

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(29) J. P. Birk and J. H. Espenson, *Inorg. Chem.*, **7**, 991 (1968).

(30) H. Siebert, *Z. Anorg. Allg. Chem.*, **327**, 63 (1964).

(31) J. N. Armor and A. Haim, *J. Amer. Chem. Soc.*, **93**, 867 (1971).

(32) Such a structure has also been postulated for the $(Et)_2Au(S_2C_2(NH)_2)Au(Et)_2$ complex.[33]

(33) R. V. G. Ewens and C. S. Gibson, *J. Chem. Soc.*, 431 (1949).

solved; however, two C–S frequencies are observed at 840 and 827 cm^{-1}.

Electronic Effects. Addition of $Cu(PPh_3)_2^+$ to the oxygen atoms of a SS-coordinated $S_2C_2O_2^{2-}$ ligand leads to a delocalization of charge away from the sulfur atoms. The anticipated decrease in $S \rightarrow M$ σ bonding and possibly a weaker M–S bond are not reflected in the M–S stretching vibrations which occur at *higher* frequencies in the adducts. These effects are very similar to those observed in the spectra of the SnX_4 adducts of the nickel(II) and palladium(II) dithiooxalates and their explanation follows closely the one given previously.[1] Specifically, the expected decrease in $L \rightarrow M$ σ bonding is accompanied by $M \rightarrow S$ backbonding to such an extent that a stronger M–S bond is observed in the adducts. Indirect evidence for the anticipated increase in the ligand field is found in the visible spectra (Table III) of the $M(S_2C_2O_2)_3((PPh_3)_2Cu)_3$ complexes (M = Co(III) and Cr(III)). Thus the $10Dq$ ($^4A_{2g} \rightarrow {}^4T_{2g}$) and ($^1A_{1g} \rightarrow {}^1T_{1g}$) transitions found at 17,000 and 17,700 cm^{-1} in the spectra of the Cr(III) and Co(III) parent complexes are not observed in the spectra of the adducts, presumably due to a hypschromic shift which brings them under the intense charge transfer absorptions (Table III).

Conclusions

The multifunctional nature of the dithiooxalate ligand is demonstrated by the existence of OO-bonded, SS-bonded, and OS-bonded complexes. As expected, the mode of coordination adopted by this ligand depends on the type of the metal ion and its relative affinity for "hard" *vs.* "soft" ligands. Substitution of the inert cations (K) by interacting $M(PPh_3)_2^+$ cations in the $K_nM(S_2C_2O_2)_n$ complexes results in adducts whose structures depend on (a) the kinetic characteristics of the parent complexes and (b) the intrinsic affinity of the metal ions involved for "hard" *vs.* "soft" ligands. It appears that in kinetically inert $M(S_2C_2O_2)_n^{n-}$ complexes the integrity of the $M(S_2C_2O_2)_n^{n-}$ unit is initially maintained and the interaction which takes place depends on the nature of the coinage metal and availability of bonding sites within the $M(S_2C_2O_2)_n^{n-}$ complex. Occasionally the resulting products are not the energetically most stable species. Such is the case with the $Cr(S_2C_2O_2)_3((PPh_3)_2M')_3$ complexes which slowly rearrange to the thermodynamically most stable linkage isomers. With kinetically labile $M(S_2C_2O_2)_n^{n-}$ complexes the relative thermodynamic stabilities of the $M-S_2C_2O_2$ *vs.* $(PPh_3)_2M'-S_2C_2O_2$ interactions determine the bridging mode adopted by the dithiooxalate ligand.

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Bonding, Spectra, and Geometry of the Tetrachlorocuprate Ion $CuCl_4^{2-}$. An *Ab Initio* LCAO–MO–SCF Calculation

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Abstract: The description of the bonding for the ground state of the $CuCl_4^{2-}$ ion in the D_{4h} configuration is compared through the use of three different basis sets of Gaussian functions. It is concluded that a (12,8,5/10,6) set of Gaussian functions contracted to [5,4,2/3,3] gives a description of the ground state which is accurate enough. Doubly occupied MO's which are predominantly metal 3d orbitals are found at lower energy levels than the MO's which are mostly ligand 3p orbitals. Independent SCF calculations for the $CuCl_4^-$ ion (*in vacuo*) allow for electronic relaxation during the ionization process and lead to comparable ionization potentials (IP) for the ligand 3p and metal 3d orbitals. The effect of the crystal environment on the computed ionization potentials is represented by including the electrostatic potential of the crystal in the molecular SCF calculation. This results in a rather uniform increase of the computed IP's. The dependence of the results of a population analysis on the basis set used is exemplified by considering the three different basis sets and the effect of diffuse functions. Independent SCF calculations have been carried out for several excited states of the $CuCl_4^{2-}$ ion in the D_{4h} configuration. The lowest excitations correspond to d–d excitations in the order $^2B_{2g}(d_{xy} \rightarrow d_{x^2-y^2}) < {}^2E_g(d_{xz,yz} \rightarrow d_{x^2-y^2}) < {}^2A_{1g}(d_{z^2} \rightarrow d_{x^2-y^2})$ in agreement with experimental evidence from polarized spectra and magnetic circular dichroism for $PdCl_4^{2-}$ and $PtCl_4^{2-}$. The next excitations correspond to ligand to metal charge transfer. It is found by energy minimization that the most stable configuration of the $CuCl_4^{2-}$ ion corresponds to a flattened D_{2d} structure, with a predicted value of 120° for the Cl–Cu–Cl angle in good agreement with the experimental value of 124° in Cs_2CuCl_3. It is concluded that the distortion with respect to an ideal T_d geometry is an intrinsic property of the $CuCl_4^{2-}$ ion.

The *ab initio* LCAO–MO–SCF calculations of transition metal complexes and organometallics have become feasible in the last few years.[1-15] So far,

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(1) A. J. H. Wachters and W. C. Nieuwpoort, *Int. J. Quantum Chem.*, **5**, 391 (1971), and references therein for NiF_6^{4-}.

(2) J. Demuynck, A. Veillard, and G. Vinot, *Chem. Phys. Lett.*, **10**, 522 (1971) ($Ni(CN)_4^{2-}$).