the molecule has approximately square-pyramidal coordination about each cobalt atom; in II CO_a occupies the unique or axial position of the pyramid. In V the coordination about each cobalt atom is more nearly trigonal bipyramidal with $(CH_3^{(1)})(CH_3^{(3)})Ge–Co^{(1)}–CO_{b'}$, for example, constituting a pseudothreefold axis. A trigonal-bipyramidal configuration is simultaneously assumed at the other cobalt atom, but for clarity this is not explicitly shown in the sketch.

The proposed rearrangement pathway is interesting in that it is the converse of the now widely accepted Berry mechanism[9] for site exchange in trigonal-bipyramidal molecules by way of a square-pyramidal intermediate or transition state. We are not aware that there has been any previous proposal of the converse rearrangement, but, given the premise of a preferred square-pyramidal configuration, it is, *mutatis mutandis*, as natural and appealing as the Berry mechanism.

There are several aspects of the type of phenomenon reported here still to be explored, *e.g.*, the influence of the M–M bond on access to the postulated transition state, whether simultaneous site exchange of CO groups occurs in a manner consistent with the postulated mechanism, etc., and these are under study.[10]

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is believed to occur quite commonly where bridging CO groups are concerned,[6,7] but carbene-like, *i.e.*, terminal CO groups are decidedly stable, whereas stable carbene-like R_2Ge groups have not been observed.[8]

(6) E. A. C. Lucken, K. Noack and D. F. Williams, *J. Chem. Soc. A*, 148 (1967).

(7) J. G. Bullitt, F. A. Cotton, and T. J. Marks, *J. Amer. Chem. Soc.*, **92**, 2155 (1970).

(8) The transient existence of H_2Ge in the gas phase has been postulated by P. Estacio, M. D. Sefcik, E. K. Chan, and M. A. Ring, *Inorg. Chem.*, **9**, 1068 (1970).

(9) (a) R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960); (b) G. M. Whitesides and H. L. Mitchell, *J. Amer. Chem. Soc.*, **91**, 5384 (1969); (c) K. E. DeBruin, K. Naumann, G. Zon, and K. Mislow, *ibid.*, **91**, 7031 (1969).

(10) This work was supported in part by the National Science Foundation under Grant No. GP-7034X. We thank Mr. C. M. Lukehart for generous assistance in recording spectra and Mr. T. J. Marks for useful discussions.

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Chemistry of the Iron–Dithiooxalate Complexes

Sir:

Our studies of the metal–dithiooxalato complexes[1] have revealed two unique characteristics of the coordinated dithiooxalate ligand: (a) the ability of the carbonyl groups to function as donors for Lewis acids,[1] and (b) a conjugated system different from that of the formally analogous 1,2-dithiolate ligands.[2]

The former of these characteristics makes it possible to alter the donor properties of the coordinated sulfur atoms by withdrawing electron density at the oxygen sites, while the latter accounts for the absence of redox properties due to thiol–thione interconversions. A study of the chemistry of the tris(dithiooxalato)iron(III) complex has produced two results which are attributed to the unique properties of the dithiooxalate ligand: (a) isolation of both the high-spin ($^6A_1$ ground state) and low-spin ($^2T_2$ ground state) forms of an iron–sulfur complex by altering the charge distribution within the sulfur ligand, and (b) reversible oxidation which gives rise to a chemically reactive oxidation product. These results, which are summarized in Table I and Figure 1, have not been previously encountered in the thoroughly studied[2,3] iron–sulfur coordination chemistry.

The tetraphenylarsonium, Ph_4As, salt of the tris(dithiooxalato)iron(III) trianion, $Fe(Dto)_3^{3-}$,[4] was prepared by extracting an aqueous solution of $K_3Fe(Dto)_3$ with a dichloromethane solution of Ph_4AsCl. The crude product isolated from the dichloromethane solution was recrystallized from cold nitromethane, whereby crystals of I were obtained. The magnetic moment of I (2.30 BM at 300°K)[6] and the abnormally large Curie–Weiss constant[7] of -42°K are values similar to those obtained for the ferric thioxanthate complexes,[9] in which both the $^6A_1$ and $^2T_2$ states are populated at room temperature.[10] We were unable to observe the existence of a $^2T_2$–$^6A_1$ equilibrium for the $Fe(Dto)_3^{3-}$ complex by epr spectroscopy, since spectra could not be obtained at either 300 or 78°K. At 1°K a strong absorption was observed which is attributed to the $^2T_2$ ground state.

In the $Fe(Dto)_3^{3-}$, the proximity of the ligand field to the $^2T_2$–$^6A_1$ cross-over point is suggested by the fact that perturbations reducing the ligand-field strength cause an unpairing of spins and result in a $^6A_1$ ground state.

Specifically, the $Fe(Dto)_3^{3-}$ complex was used as a ligand for the $(Ph_3P)_2Cu^+$ and $(Ph_3P)_2Ag^+$ cations, and by an extraction procedure identical with the one described for I, the crystalline, *high-spin*, X-ray-isomorphous $[(Ph_3P)_2Cu]_3Fe(Dto)_3$ (II) and $[(Ph_3P)_2Ag]_3Fe(Dto)_3$ (III) complexes (Table I) were isolated. The carbonyl stretching frequencies at 1380 cm^{-1} and strong bands at 310 cm^{-1}, which we tentatively assign to the Fe–S stretching vibration, suggest a structure similar to that shown in Figure 1 for these complexes.[11] The epr powder spectrum of III is characteristic of a $S = {}^5/_2$ system with $g = 2.000 \pm 0.002$ and an estimated value for a of 0.5 Gc.[12a]

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(1) D. Coucouvanis, *J. Amer. Chem. Soc.*, **92**, 707 (1970).

(2) J. A. McCleverty, *Progr. Inorg. Chem.*, **10**, 49 (1968).

(3) (a) D. Coucouvanis, *ibid.*, **11**, 233 (1970); (b) D. Coucouvanis, S. J. Lippard, and J. A. Zubieta, *J. Amer. Chem. Soc.*, **90**, 3281 (1968), and references therein; (c) L. H. Pignolet and R. H. Holm, *ibid.*, **92**, 1791 (1970); (d) A. L. Balch, *ibid.*, **91**, 6962 (1969).

(4) The anilinium salt of this anion was first reported in ref 5, but was incorrectly formulated as the ferrous complex $(C_6H_5NH_3)_2Fe(Dto)_2$.

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

(6) The moments of $KBaFe(Dto)_3 \cdot 6H_2O$[7] and $KBaFe(Dto)_3 \cdot 4H_2O$[8] have also been reported as 2.28 and 2.95 BM, respectively.

(7) R. L. Carlin and F. Canziani, *J. Chem. Phys.*, **40**, 371 (1964).

(8) F. A. Dwyer and A. M. Sargeson, *J. Amer. Chem. Soc.*, **81**, 2335 (1959).

(9) The tris(ethyl thioxanthate)iron(III) complex has been reported to have a magnetic moment of 2.57 BM at 300°K and a "pseudo" Curie–Weiss constant of -85°K.[10]

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

(11) Stannic chloride interacts in a similar fashion with the $Fe(Dto)_3^{3-}$ complex anion, and the anion $[Fe(Dto)_3(SnCl_4)_2]^{3-}$ was isolated as the crystalline Ph_4As^+ salt. The C–O absorptions were also observed at 1380 cm^{-1} in this complex.

(12) (a) The spectrum was tentatively analyzed with the spin Hamiltonian[12b]

$$H = g\beta\vec{H}\vec{S} + (a/6)[Sx^4 + Sy^4 + Sz^4 - {}^1/_5S(S + 1)(3S^2 + 3S - 1)]$$

A crystal structure determination of III is currently in progress. (b) B. Bleaney and K. W. H. Stevens, *Rep. Progr. Phys.*, **16**, 108 (1953).

Table I. Analytical Data on the Iron–Dithiooxalate Complexes

	Complex	Mp, °C	% C, calcd (found)	% H, calcd (found)	% N, calcd (found)	% Fe, calcd (found)	$\nu_{C=O}$, cm^{-1}	μ_{eff}^{cor}, BM[c]
I	$(Ph_4As)_3Fe(Dto)_3 \cdot 3CH_3NO_2$	104–107	55.6 (55.51)	3.95 (3.92)	2.40 (2.23)	3.20 (3.23, 3.16)	1622 (sh), 1561 (s)[a,b]	2.30 ± 0.05
II	$[(Ph_3P)_2Cu]_3Fe(Dto)_3$	135–136	62.75 (62.20)	4.14 (4.15)			1382 (s)[a,b]	5.93 ± 0.05
III	$[(Ph_3P)_2Ag]_3Fe(Dto)_3$[e]	145–147	59.10 (58.41)	3.89 (3.98)		2.42 (2.40)	1380 (s)[a,b]	5.81 ± 0.05
IV	$(BzPh_3P)_2Fe(Dto)_2NO$[f]	158–161	62.8 (62.21)	4.27 (4.49)	1.36 (1.31)	5.42 (5.36)	1585 (s, br)[a,b]	2.22 ± 0.05
V	$(Ph_4As)_2Fe(Dto)_2I$[d,g]	230 dec	52.4 (51.22)	3.36 (3.38)		4.72 (4.67)	1615 (s)[a,b]	4.03
VI	$(Ph_4As)_4Fe_2(Dto)_5$	127–130	56.7 (56.37)	3.57 (3.64)		4.99 (4.94)	1615 (s, br)[a,b]	3.5 ± 0.2[h]
VII	$KBaFe(Dto)_3 \cdot 3H_2O$	180 dec	11.13 (10.97)	0.93 (0.89)		8.65 (8.60)	1550 (s), 1516 (s)[a]	2.35 ± 0.05

[a] Nujol null between NaCl plates. [b] KBr disk. [c] Determined by a Faraday technique. [d] Iodine analysis: calcd, 10.67; found, 10.45. [e] Silver analysis: calcd, 14.00; found, 13.91. [f] NO stretch at 1685 cm^{-1}. [g] An infrared absorption found at 190 cm^{-1} is attributed to the Fe–I stretching vibration. [h] Determined by integration of the epr absorption and comparison with III (see above) and the bisacetylacetonatocopper(II) complex.

Upon heating to 70°, violet solutions of the $Fe(Dto)_3^{3-}$ anion in either aqueous $NaNO_2$ or nitroparaffins (CH_3NO_2, $C_2H_5NO_2$) change color owing to the formation of the green $[Fe(Dto)_2NO]^{2-}$ complex. The crys-

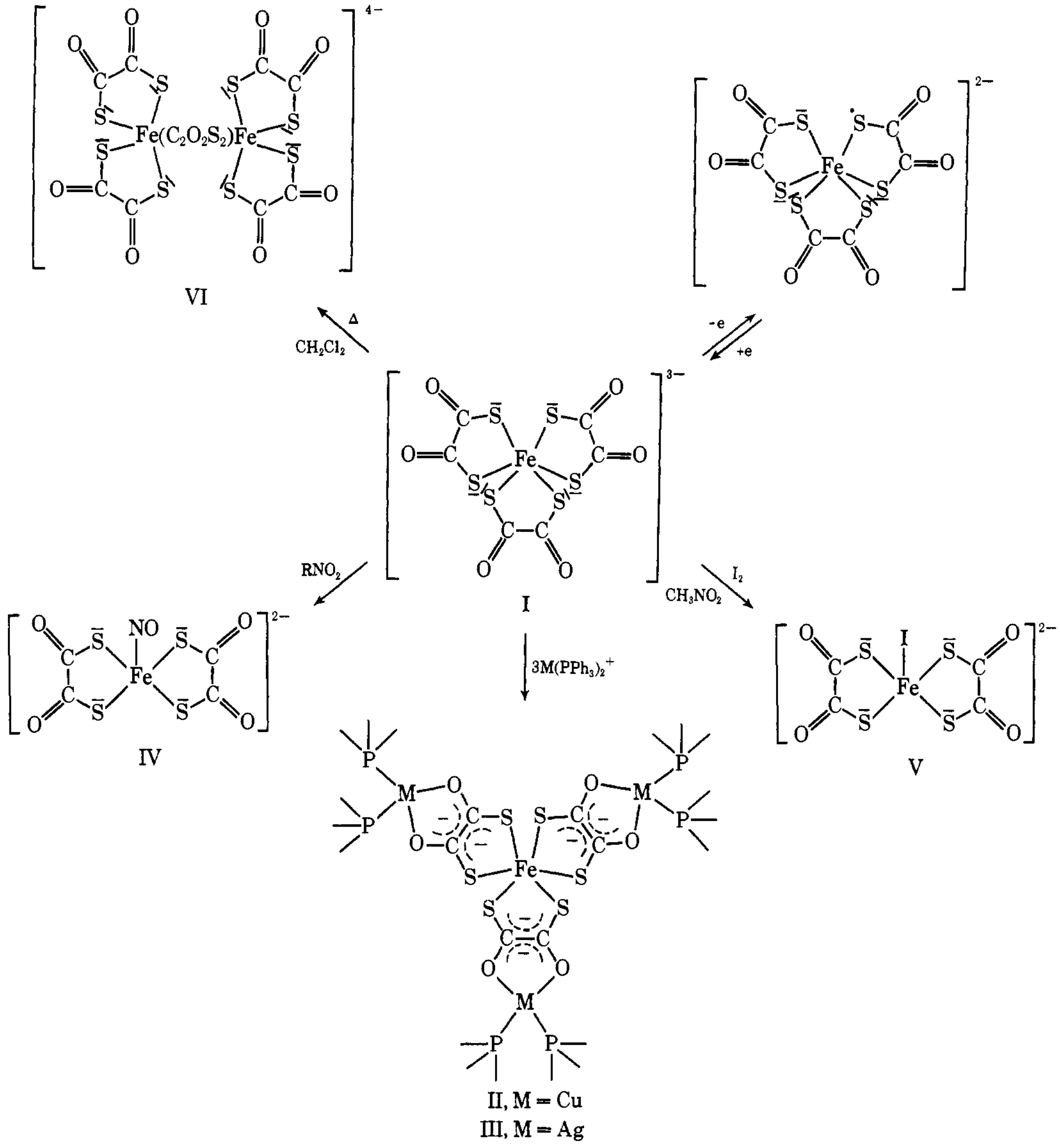

Figure 1.

talline $BzPh_3P^+$ salt of this anion was isolated (IV)[13] and its properties (Table I) suggest a structure similar to that already known for the dithiocarbamate–iron nitrosyl complexes.[8a] The epr spectrum of this complex at $-80°$ consists of a typical triplet with $g = 2.0332 \pm 0.0005$ and $A_{N^{14}} = 14.3 \pm 0.1$ G. These values, as well as the magnetic moment (Table I), compare well with those of other similar nitrosyl complexes in which variations in g and A values seem to reflect the extent of electron delocalization in addition to ring size[14] effects. The magnitude of $A_{N^{14}}$ was used as a probe to investigate the changes brought about by chelation at the oxygen sites of the dithiooxalate ligands. An acetone solution of IV in the presence of excess $SnCl_4$[15] gave a spectrum with $A_{N^{14}} = 12.8 \pm 0.1$ G. This value and the well-resolved tin hyperfine splittings indicate electron delocalization away from the iron atom, and are in agreement with the observed ligand-field characteristics of II and III above.

Unlike other dithiooxalate complexes, I undergoes a reversible one-electron oxidation in dichloromethane at $+0.12 \pm 0.01$ V *vs.* Ag|AgI with Bu_4NClO_4 as the supporting electrolyte.[16] (Figure 1). Chemical oxidation with I_2 in nitromethane occurs readily, and upon dilution with ether, crystals of V (Table I) formed. The magnetic moment of 4.03 BM is very similar to that of the corresponding square-pyramidal[17] dithiocarbamate iron halides,[18] in which the Fe(III) ion is found in the uncommon $^4A_2$ ground state. Refluxing of I in CH_2Cl_2 over a 12-hr period resulted in the formation of VI (Table I), which could be isolated as a brown crystalline material with epr and ir spectra very similar to those of V. The structure of VI, and the nature of the presumed bridging dithiooxalate ligand, are uncertain at present.

Cyclic voltammetry of I in the presence of iodide ion or $(Et)_2NH$, in dichloromethane, has shown that the reversible character of the wave changes as a function of the scanning potential. Thus, when the voltage scan rate is greater than 10 V sec^{-1}, the reduction part of the wave corresponding to the process

$$[Fe(Dto)_3]^{2-} \xrightarrow{+1e} [Fe(Dto)_3]^{3-}$$

is well defined on cycling over a 1-V range. With scan rates less than 10 V sec^{-1}, however, the height of the reduction wave diminishes.[19]

The above observations suggest that the oxidized form of I is depleted from the electrode surface by a reaction following the oxidation. A similar reaction[20] could also be responsible for the formation of V following the chemical oxidation of I. By comparison to the 1,2-dithiolates, the dithiooxalate and thioxanthate complexes are not subject to extensive electron delocalizations. The possibility that the reversible oxidation observed in the iron(III)–thioxanthate and -dithiooxalate complexes results in coordinated, labile, radical anion ligands is at present under study.

In conclusion we wish to emphasize the similarities of the iron–dithiooxalate complexes to the thioxanthates and dithiocarbamates and, in particular, the interesting cooccurrence of oxidation properties and spin-state equilibria in these complexes.

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[13] The nature of this interesting nitrosyl abstraction reaction is presently under investigation.

[14] C. C. McDonald, W. D. Phillips, and H. F. Mower, *J. Amer. Chem. Soc.*, **87**, 3319 (1965).

[15] In the presence of $SnCl_4$, IV reacts instantly, presumably forming the 2:1 adduct (see ref 1).

[16] (a) F. Rohrscheid, A. L. Balch, and R. H. Holm, *Inorg. Chem.*, **5**, 1542 (1966). (b) The first oxidation wave of $Ni(MNT)_2^{2-}$ was observed at +0.15 V. The voltage scan rate was 0.5 V/sec.

[17] B. F. Hoskins, R. L. Martin, and A. H. White, *Nature (London)*, **211**, 627 (1966).

[18] R. L. Martin and A. H. White, *Inorg. Chem.*, **6**, 712 (1967).

[19] Cyclic voltammetry within the voltage ranges used in this work revealed no redox properties for V.

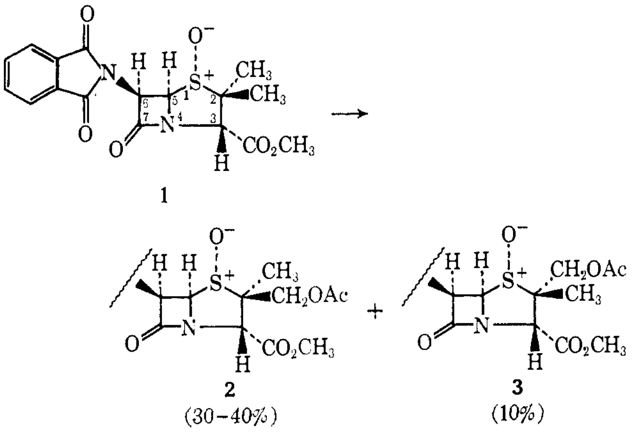
[20] Such a reaction perhaps could be a nucleophilic substitution of Dto^- by I^- or Et_2NH.

Conversion of Penicillin to Cephalosporin *via* a Double Sulfoxide Rearrangement

Sir:

In 1963 Morin and coworkers[1a] reported the chemical conversion of penicillin to deacetoxycephalosporin *via* a cyclic sulfoxide rearrangement. I now wish to report the conversion of penicillin to cephalosporin *via* a *double sulfoxide rearrangement.*

Treatment of methyl phthalimidopenicillinate α-sulfoxide (**1**)[2] with acetic anhydride[3,4] gave a mixture of 2-methylene-substituted penicillins and ring-expansion products. Oxidation of the mixture, followed by chromatography on silica, led to the isolation of the desired sulfoxides **2** and **3**, the stereochemistry being determined from nmr chemical shifts and internal nuclear Overhauser effects (NOE)[5] (see Table I).



1

2
(30–40%)

3
(10%)

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[1] (a) R. B. Morin, B. G. Jackson, R. A. Mueller, E. R. Lavagnino, W. B. Scanlon, and S. L. Andrews, *J. Amer. Chem. Soc.*, **85**, 1896 (1963); (b) see also R. B. Morin, B. G. Jackson, R. A. Mueller, E. R. Lavagnino, W. B. Scanlon, and S. L. Andrews, *ibid.*, **91**, 1401 (1969).

[2] R. D. G. Cooper, P. V. Demarco, and D. O. Spry, *ibid.*, **91**, 1528 (1969).

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[4] R. B. Morin and D. O. Spry, *Chem. Commun.*, 335 (1970).