The Cr^{2+} and V^{2+} Reduction of μ-Carboxylato-dicobalt(III) Ammine Complexes. Part III.† The Mechanism of Reduction of μ-Benzoato- and μ-*o*-Chlorobenzoato-complexes

By **Karl Wieghardt** and **A. Geoffrey Sykes,*** Department of Inorganic and Structural Chemistry, The University, Leeds LS2 9JT

The μ-benzoato-di-μ-hydroxo- and μ-*o*-chlorobenzoato-di-μ-hydroxo-bis[tri-amminecobalt(III)] complexes are stable to bridge cleavage in aqueous perchlorate solutions $[H^+] = 0{\cdot}01$—$1{\cdot}0$M, $I = 1{\cdot}0$M ($LiClO_4$), during 3 days at 25°. Reduction of the μ-benzoato-complex with Cr^{2+} gives a rate law (i). At 30° $k_{Cr} = (1{\cdot}52 \pm 0{\cdot}06) \times 10^{-3}$

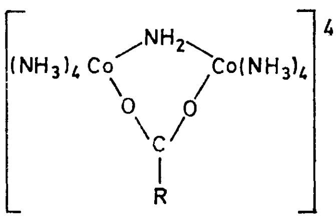
$$\text{Rate} = (k_{Cr}[Cr^{2+}] + k_1[H^+])[(Co^{III})_2] \qquad \text{(i)}$$

l mol^{-1} s^{-1}, $\Delta H^{\ddagger}_{Cr} = 9{\cdot}46 \pm 0{\cdot}28$ kcal mol^{-1} and $\Delta S^{\ddagger}_{Cr} = -40{\cdot}3 \pm 0{\cdot}9$ K^{-1} mol^{-1}, and for the path in which bridge cleavage is rate determining $k_1 = (1{\cdot}8 \pm 0{\cdot}4) \times 10^{-5}$ l mol^{-1} s^{-1}, $\Delta H^{\ddagger}_1 = 18{\cdot}6 \pm 1{\cdot}9$ kcal mol^{-1} and $\Delta S^{\ddagger}_1 = -19{\cdot}2 \pm 6{\cdot}0$ cal K^{-1} mol^{-1}. The rate law for the V^{2+} reduction is (ii) and at 30° $k_V = (6{\cdot}74 \pm 0{\cdot}06) \times$

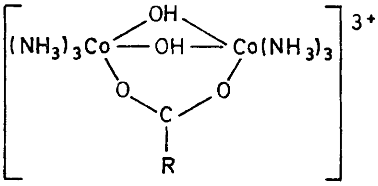
$$\text{Rate} = k_V[V^{2+}][(Co^{III})_2] \qquad \text{(ii)}$$

10^{-2} l mol^{-1} s^{-1}. Rate constants (25°, l mol^{-1} s^{-1}) for the corresponding reductions of the μ-*o*-chlorobenzoato-complex are $k_{Cr} = (1{\cdot}62 \pm 0{\cdot}04) \times 10^{-3}$, $k_1 = (0{\cdot}30 \pm 0{\cdot}10) \times 10^{-5}$ and $k_V = (7{\cdot}9 \pm 0{\cdot}2) \times 10^{-2}$. The ratios k_{Cr}/k_V of 0·023 and 0·021 respectively are consistent with outer sphere Cr^{2+} and V^{2+} reductions. No obvious enhancement in rate results from the presence of the benzene ring or the remote chlorine atom.

NUMEROUS studies of Cr^{2+} reductions of mononuclear penta-amminecarboxylatocobalt(III) complexes have been reported by Taube and colleagues.[1] Inner-sphere pathways have been identified and three categories of reactions involving adjacent attack, adjacent attack with chelation, and remote attack have been defined. As an extension of this work we are carrying out a systematic study of the Cr^{2+} reductions of μ-carboxylato-binuclear cobalt(III) complexes, choosing those organic ligands which have previously provided most significant information. The reduction of the μ-amido-μ-oxalato-complex (I; $R = CO_2H$), has been shown to occur by remote attack.[2] The Cr^{2+} reductions of the μ-amido-μ-formato- and μ-amido-μ-acetato-complexes (I; R = H and Me), are considerably slower and the assignment of outer-sphere mechanisms has been possible.[3] Data for the corresponding V^{2+} reductions have played an important part in these assignments.



(I)



(II)

An extensive range of μ-carboxylato-di-μ-hydroxo-complexes, (II), has recently been prepared from the tri-μ-hydroxo-bis[tri-amminecobalt(III)] complex.[4] The procedure involved would seem to be more flexible

---

† References 2 and 3 respectively constitute Parts I and II of this series.

[1] For recent reviews see for example H. Taube, *Ber. Bunsengesellschaft*, 1972, **76**, 967; *Pure and Appl. Chem.*, 1970, **24**, 289; H. Taube and E. S. Gould, *Accounts Chem. Res.*, 1969, **2**, 321.

[2] K. L. Scott, M. Green, and A. G. Sykes, *J. Chem. Soc.* (*A*), 1971, 3651.

[3] K. L. Scott and A. G. Sykes, *J.C.S. Dalton*, 1972, 1832.

[4] K. Wieghardt, *J.C.S. Dalton*, 1973, 2548.

yielding a much wider range of complexes than it has so far been possible to prepare in the μ-amido-series (I). We report here the Cr^{2+} and V^{2+} reductions of the μ-benzoato-di-μ-hydroxo- and μ-*o*-chlorobenzoato-di-μ-hydroxo complexes. It has been established that both oxygen atoms of the carboxylato-ligand are bonded to cobalt atoms, and by analogy with studies with the μ-amido-μ-formato- and μ-amido-μ-acetato-complexes,[3] adjacent inner-sphere attack seems unlikely. Furthermore Cr^{2+} is unable to utilize electron lone pairs on μ-hydroxo-ligands for inner-sphere electron transfer.[5] The possibility that hydroxo-bridge cleavage provides a pathway for inner-sphere electron transfer is examined in this study.

The Stability of Complexes.—No visible spectrophotometric changes were observed for *ca.* 10^{-3}M-solutions of the μ-benzoato- and μ-*o*-chlorobenzoato-complexes (I; R = C_6H_5 and *o*-C_6H_4Cl) in both 0·01M and 1·0M perchloric acid during 72 h at 25°, I = 1·0M ($LiClO_4$). The tri-μ-hydroxo-bis[triamminecobalt(III)] and di-μ-hydroxo-bis[aquotri-amminecobalt(III)] complexes are known to have significantly different spectra.[6] It is concluded that there is no appreciable build-up of bis-aquo-species resulting from hydroxo-bridge cleavage of the μ-benzoato- and μ-o-chlorobenzoato-complexes. Spectrophotometric changes would also be expected if cleavage of the carboxylato-bridge were occurring. These observations do not of course rule out bridge cleavage as an effective pathway when Cr^{2+} is present to scavenge the aquo-product.

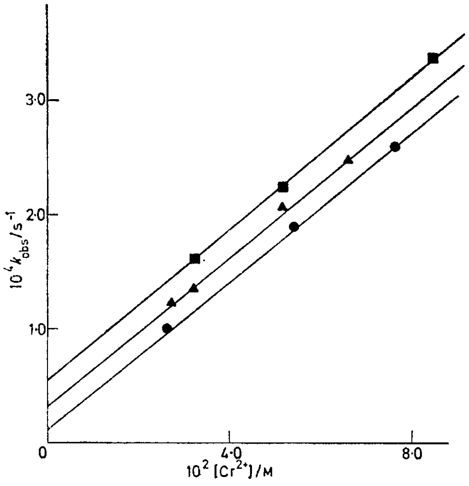


FIGURE 1 The Cr^{2+} reduction of the μ-benzoata-di-μ-hydroxo-complex. The dependence of first-order rate constant k_{obs} at 45° on the concentration of Cr^{2+} at $[H^+]$ = 0·10 (●), 0·40 (▲), and 0·73M (■); I = 1·0M ($LiClO_4$)

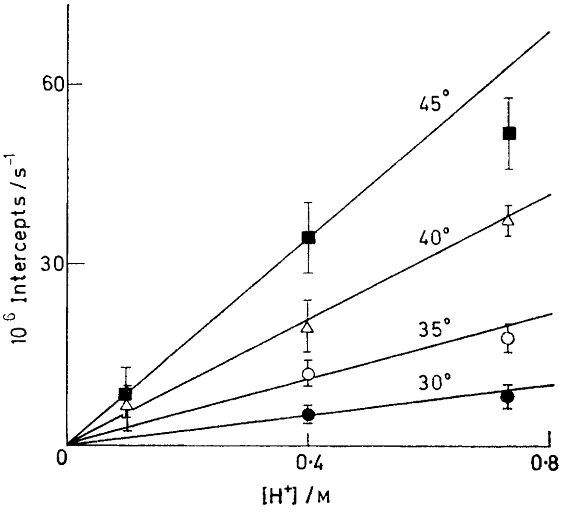


FIGURE 2 The $[H^+]$-dependence of the $[Cr^{2+}]$-independent pathway (intercepts in Figure 1) for the reduction of the μ-benzoato-di-μ-hydroxo-complex, I = 1·0M ($LiCOl_4$)

TABLE 1

First-order rate constants, k_{obs}, for the Cr^{2+} reduction of the μ-benzoato-di-μ-hydroxo-complex, I = 1·0M ($LiClO_4$)

Temp. °C	$[H^+]$ M	$10^2[Cr^{2+}]$ M	$10^3[(Co^{III})_2]$ M	$10^4 k_{obs}$ s^{-1}
30·0	0·05	5·01	1·0	0·74
	0·40	3·25	1·0	0·57
	0·40	5·20	0·9	0·87
	0·40	7·40	0·8	1·22
	0·40	9·12	1·0	1·50
	0·73	5·20	1·0	0·93
	0·73	7·41	1·0	1·29
35·0	0·40	2·70	1·0	0·66
	0·40	5·20	1·0	1·14
	0·40	7·51	1·0	1·63
	0·40	9·12	0·5	1·93
	0·73	2·60	1·0	0·71
	0·73	5·20	1·5	1·21
	0·73	7·50	2·0	1·69
40·0	0·10	2·55	1·0	0·70
	0·10	5·05	1·0	1·27
	0·10	7·70	1·0	1·95
	0·40	2·50	1·0	0·82
	0·40	5·10	1·0	1·48
	0·40	6·61	1·0	1·90
	0·40	8·00	1·0	2·19
	0·73	2·78	1·0	1·07
	0·73	5·11	1·0	1·67
	0·73	7·70	1·0	2·31
45·0	0·07	5·26	1·5	1·85
	0·10	2·65	0·5	1·01
	0·10	5·40	2·0	1·91
	0·10	8·21	1·0	2·92
	0·40	2·70	1·0	1·24
	0·40	3·20	1·0	1·37
	0·40	5·15	1·0	2·08
	0·40	6·60	1·0	2·49
	0·73	3·20	0·8	1·63
	0·73	5·15	1·2	2·24
	0·73	8·40	1·1	3·39

Cr^{2+} *and* V^{2+} *Reductions of the μ-Benzoato-complex.*—Both reactions were monitored at 524 nm (ε = 112 l mol^{-1} s^{-1}) with reductant in large excess, I = 1·0M ($LiClO_4$). Plots of log (OD_t − OD_∞) against time were linear to at least 80%, and sometimes as much as 93% completion with Cr^{2+} as reductant, and to ⩾95% with V^{2+} as reductant. First-order rate constants, k_{obs} were evaluated from gradients (×2·303). Final absorbance OD_∞ values were measured for each run and were consistent (±3%) with equations (1) and (2). No

$$2Cr^{2+} + (Co^{III})_2 \longrightarrow 2Cr^{3+} + 2Co^{2+} \qquad (1)$$

$$2V^{2+} + (Co^{III})_2 \longrightarrow 2V^{3+} + 2Co^{2+} \qquad (2)$$

---

[5] R. S. Taylor and A. G. Sykes, *J. Chem. Soc.* (*A*), 1970, 1991.

[6] M. Linhard and H. Siebert, *Z. anorg. Chem.*, 1964, **364**, 26.

attempt was made to identify the chromium(III) product by ion-exchange separation because of the slowness of the reduction and the possibility of reaction of primary products.[7] It was necessary to wait for at least 24 h to obtain OD_∞ with Cr^{2+} as reductant. The stability of such OD_∞ values was checked in four runs over a period of 3 days and no further absorbance changes were observed.

First-order rate constants k_{obs} for the Cr^{2+} studies are listed in Table 1. At constant $[H^+]$ a linear $[Cr^{2+}]$ dependence is obtained, and gradients as observed in Figure 1 are given in Table 2. The $[Cr^{2+}]$-independent intercepts from such plots, Table 2, give an $[H^+]$-dependence, Figure 2. Within the accuracy of our data no $[H^+]$-independent pathway is indicated, and k_{obs} may be expressed as in (3). Values of k_1 and k_{Cr} (with errors)

$$k_{obs} = k_{Cr}[Cr^{2+}] + k_1[H^+] \qquad (3)$$

at each temperature were obtained by a standard least-squares treatment with no weighting factor. Activation parameters, Table 3, were obtained with each k_{obs} value a separate data point, and $[H^+]$, $[Cr^{2+}]$, and temperature as additional variables, using a non-linear least-squares programme[8] with weighting factor $1/k_{obs}^2$.

TABLE 2

The evaluation of rate constants k_{Cr} and k_1, equation (3), for the Cr^{2+} reduction of the μ-benzoato-di-μ-hydroxo complex, $I = 1·0$M ($LiClO_4$), from gradients and intercepts, *e.g.* Figure 1

Temp. / °C	$[H^+]$ / M	10^3 Gradient[a] / l mol⁻¹ s⁻¹	10^6 Intercept[b] / s⁻¹
30·0	0·40	1·58 ± 0·06	5·1 ± 2
	0·73	1·68[c]	8·3[c]
35·0	0·40	2·00 ± 0·06	12·0 ± 2
	0·73	2·00 ± 0·06	18·0 ± 2
40·0	0·10	2·43 ± 0·10	6·8 ± 4
	0·40	2·52 ± 0·10	19·6 ± 4
	0·73	2·52 ± 0·10	37·4 ± 4
45·0	0·10	3·44 ± 0·10	8·4 ± 4
	0·40	3·29 ± 0·10	34·5 ± 6
	0·73	3·40 ± 0·10	52·1 ± 6

[a] From gradients *e.g.* Figure 1. [b] From intercepts *e.g.* Figure 1. [c] Only two data points.

TABLE 3

Summary of kinetic data for the Cr^{2+} reduction of the μ-benzoato-di-μ-hydroxo complex, $I = 1·0$M ($LiClO_4$)

Temp. / °C	10^3k_{Cr} / l mol⁻¹ s⁻¹	10^5k_1 / l mol⁻¹ s⁻¹
30·0	1·52 ± 0·06	1·8 ± 0·4
35·0	1·99 ± 0·06	2·8 ± 0·3
40·0	2·58 ± 0·1	4·7 ± 0·3
45·0	3·34 ± 0·1	7·7 ± 0·6

$\Delta H^\ddagger_{Cr} = 9·46 \pm 0·28$ kcal mol⁻¹; $\Delta H^\ddagger_1 = 18·6 \pm 19·2$ kcal mol⁻¹; $\Delta S^\ddagger_{Cr} = -40·3 \pm 0·9$ cal K⁻¹ mol⁻¹; $\Delta S^\ddagger_1 = -19·2 \pm 6·0$ cal K⁻¹ mol⁻¹.

For the faster V^{2+} reduction, first-order rate constants at 30° conform to the rate law (4), and no $[H^+]$-dependence is observed. Second-order rate constants k_V are

$$-d[(Co^{III})_2]/dt = k_V[V^{2+}][(Co^{III})_2] \qquad (4)$$

listed in Table 4. The temperature dependence was not investigated.

TABLE 4

Rate constants, k_V, for the V^{2+} reduction of the μ-benzoato-di-μ-hydroxo complex at 30°, $I = 1·0$M ($LiClO_4$)

$[H^+]$ / M	$10^2[V^{2+}]$ / M	$10^3[(Co^{III})_2]$ / M	10^2k_V / l mol⁻¹ s⁻¹
0·20	1·10	0·5	6·78
0·20	4·60	2·0	6·83
0·30	1·10	1·0	6·77
0·30	2·30	1·0	6·69
0·70	1·10	0·5	6·74
0·70	4·60	2·0	6·66

Average value $k_V = (6·74 \pm 0·06) \times 10^{-2}$ l mol⁻¹ s⁻¹.

The Cr^{2+} *and* V^{2+} *Reduction of the* μ-o-*Chlorobenzoato-complex.*—The reactions were monitored at 524 nm (ε = 113 l mol⁻¹ cm⁻¹), procedure as before. First-order rate constants k_{obs} obtained with Cr^{2+} as reductant (Table 5) fit the dependence (3). With V^{2+} as reductant the rate law (4) again gives a good fit to experimental data; values of k_V are listed in Table 6. Errors for k_{Cr} and k_V were determined by an unweighted least-squares treatment.

TABLE 5

Experimental first-order rate constants k_{obs} (25°) for the Cr^{2+} reduction of the μ-*o*-chlorobenzoato-di-μ-hydroxo complex, $I = 1·0$M ($LiClO_4$). Rate constants k_1 and k_{Cr} as defined in equation (3) are also given

$[H^+]$ / M	$10^2[Cr^{2+}]$ / M	$10^3[(Co^{III})_2]$ / M	10^4k_{obs} / s⁻¹
0·156	3·02	1·1	0·52
0·156	5·95	1·3	1·02
0·156	12·0	0·7	1·99
0·656	3·02	1·1	0·64
0·656	5·95	0·8	1·16
0·656	12·0	2·0	2·12

$k_{Cr} = (1·62 \pm 0·04) \times 10^{-3}$ l mol⁻¹ s⁻¹. $k_1 = (0·30 \pm 0·10) \times 10^{-5}$ l mol⁻¹ s⁻¹

TABLE 6

Rate constants, k_V, for the V^{2+} reduction of the μ-*o*-chlorobenzoato-di-μ-hydroxo complex at 25°, $I = 1·0$M ($LiClO_4$)

$[H^+]$ / M	$10^2[V^{2+}]$ / M	$10^3[(Co^{III})_2]$ / M	10^2k_V / l mol⁻¹ s⁻¹
0·20	1·40	0·5	7·94
0·20	2·30	1·0	7·74
0·20	4·22	2·0	7·92
0·70	1·10	0·5	8·08
0·70	2·30	1·0	7·84

Average value $k_V = (7·90 \pm 0·2) \times 10^{-2}$ l mol⁻¹ s⁻¹.

DISCUSSION

Both complexes are stable in the absence of reductant, and no spectrophotometric changes consistent with build-up of hydroxo- or carboxylato-bridge-cleaved species were observed. Equilibrium amounts of species resulting from any such bridge cleavage processes are small therefore. With Cr^{2+} (but not V^{2+}) as reductant

---

[7] See comments in ref. 3.

[8] Los Alamos Report LA 2367 (1959) and Addenda by R. H. Moore and R. K. Zeigler.

the direct reduction of the triply-bridged complex is slow and bridge-cleavage processes make a contribution. The data give a good fit to (3), with electron-transfer rate determining for k_{Cr} and bridge cleavage for k_1. The Cr^{2+} scavenges the product of the bridge cleavage which is therefore independent of $[Cr^{2+}]$. We note that k_1 makes only a relatively small contribution and that it is not possible to say with certainty whether or not a term independent of $[H^+]$ and $[Cr^{2+}]$ is making some small contribution. Such a pathway has been detected previously in hydroxo-bridge cleavage processes [9] but, with one exception,[10] generally makes only a small contribution. While hydroxo-bridge cleavage is expected to be effective, earlier studies have indicated that with the μ-amido-μ-acetato- and μ-amido-μ-formato-complexes slow cleavage of the organic bridging ligands can also occur.[3,11] It has not been possible for us to distinguish between these two processes and both may contribute.

For slow Cr^{2+} reduction it is uncertain whether ion-exchange separation techniques will give primary chromium(III) product(s). Thus if an inner-sphere reaction results in the formation of species CrX^{2+} it is possible for them to undergo Cr^{2+}-catalysed or uncatalysed aquation. We have therefore resorted as in previous work [3,12] to determine the k_{Cr}/k_V ratio which is known to be *ca.* 0·020 when both reactions are of the outer-sphere type. The ratio is 0·023 for the μ-benzoato-complex and 0·021 for the μ-*o*-chlorobenzoato-complex. On this basis an outer-sphere mechanism can be assigned to both the Cr^{2+} and V^{2+} reductions. Rate constants *ca.* 10^{-3} l mol^{-1} s^{-1} (25°) are also consistent with outer-sphere electron transfer.

If the first stage of reduction is outer-sphere then formation of tri-ammine-di-aquo-benzoatocobalt(III) will result. The second stage of the Cr^{2+} (and V^{2+}) reductions is observed to be rapid, and can occur by inner-sphere reduction at the benzoato-ligand,[13] or, since the cobalt(III) has two water ligands, by Cr^{2+} reduction of the conjugate-base hydroxo complex.* The first of these would give a CrX^{2+} complex, in this case benzoatochromium(III), as product, and the second hexa-aquochromium(III). Careful monitoring of absorbance changes did not give any evidence for a secondary reaction involving dissociation of CrX^{2+}. It is also noted that $\log(OD_t - OD_\infty)$ against time plots give good linearity at all hydrogen-ion concentrations. Absorbance changes for the dissociation of CrX^{2+} may be small however, and its formation cannot be categorically ruled out.

At 25° the rate constant for the Cr^{2+} reduction of the μ-*o*-chlorobenzoato-complex ($1{\cdot}62 \times 10^{-3}$ l mol^{-1} s^{-1}) is very similar to that for the μ-benzoato-complex (extrapolated value $1{\cdot}15 \times 10^{-3}$ l mol^{-1} s^{-1}) and the presence of the chlorine atom does not give any appreciable enhancement in rate. We note the rate constant previously reported for the Cr^{2+} reduction of *o*-chlorobenzoatopenta-amminecobalt(III) ($k = 0{\cdot}11$ l mol^{-1} s^{-1} at 25°) [15] is very similar to that for benzoatopenta-amminecobalt(III) ($k = 0{\cdot}153$ l mol^{-1} s^{-1} at 25°).[13] The chlorine atom does not provide a favourable site for inner-sphere Cr^{2+} attack in the mononuclear complex, or in the much slower reaction of the binuclear complex when the carbonyl function has been removed. Indeed in the case of the binuclear complex the chlorine has every opportunity to exercise an influence on the reaction by serving as a site for remote attack, but does not do so.

There is also no evidence for the π-orbital of the benzene ring assisting in any way in the redox process. Electrons transferred from the Cr^{2+} and V^{2+} occupy σ- and π-orbitals respectively. If therefore the overlap of orbitals on the metal with orbitals on the benzene ring had been relevant we would have expected different contributions to result with the two reductants. The k_{Cr}/k_V ratios are as expected for solely outer-sphere attack and no enhancement in one or other of the rate constants is indicated.

EXPERIMENTAL

The preparation and characterization of μ-benzoato $[(NH_3)_3Co{\cdot}\mu(OH,OH,C_6H_5CO_2){\cdot}Co(NH_3)_3](ClO_4)_3,H_2O$ and μ-*o*-chlorobenzoato $[(NH_3)_3Co{\cdot}\mu(OH,OH,C_6H_4ClCO_2){\cdot}Co(NH_3)_3](ClO_4)_3,H_2O$ complexes have been described.[4] Solutions of Cr^{2+} and V^{2+} were prepared as described previously in work from these laboratories; details of the preparation of lithium perchlorate have also been given.[2,3] Rigorous air-free techniques were required in all experiments with Cr^{2+} and V^{2+} as reductant. Absorbance readings were recorded using a Unicam SP 500 spectrophotometer.

K. W. is grateful to the Deutsche Forschungsgemeinschaft for a European Exchange Fellowship and the University of Heidelberg for leave of absence.

[3/2068 *Received*, 9*th October*, 1973]

---

* See for example rate constants for Cr^{2+} reduction of $Co(NH_3)_5H_2O^{3+}$ in ref. 14.

[9] S. W. Foong, R. D. Mast, M. B. Stevenson, and A. G. Sykes, *J. Chem. Soc.* (*A*), 1971, 1266.

[10] R. K. Wharton and A. G. Sykes, *J.C.S. Dalton*, 1973, 440.

[11] K. L. Scott and A. G. Sykes, *J.C.S. Dalton*, 1972, 2364.

[12] K. L. Scott and A. G. Sykes, *J.C.S. Dalton*, 1973, 736.

[13] M. Barrett, J. H. Swinehart, and H. Taube, *Inorg. Chem.*, 1971, **10**, 1983.

[14] D. L. Toppen and R. G. Linck, *Inorg. Chem.*, 1971, **10**, 2635.

[15] E. S. Gould and H. Taube, *J. Amer. Chem. Soc.*, 1964, **86**, 1322.