above 300 mμ superimposed on the n-π* Cotton effect.

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RECEIVED JANUARY 9, 1962

OXIDATION OF CHROMIUM(II) BY IRON(III) IN THE PRESENCE OF CHLORIDE ION

Sir:

The oxidation of Cr^{2+} by Fe^{3+} in aqueous perchloric acid produces Fe^{2+} and $Cr(H_2O)_6{}^{3+}$, but in the presence of chloride ion the complex $Cr(H_2O)_5Cl^{2+}$ is produced along with $Cr(H_2O)_6{}^{3+}$ in proportions depending on the concentrations of Cl^- and H^+.[1] This reaction may proceed *via* the chloro complex of Fe(III) $FeCl^{2+} + Cr^{2+} \rightarrow Fe^{2+} + CrCl^{2+}$ in an inner sphere activated complex mechanism, similar to that observed in the oxidation of Cr^{2+} by $Co^{3+}(NH_3)_5X$.[1,2] Alternatively, Fe^{3+} may enter the activated complex without prior substitution by Cl^-, in a mechanism similar to that taking place in the oxidation of Cr^{2+} by $Co(NH_3)_6{}^{3+}$ in the presence of Cl^-.[3] It is difficult to distinguish between the two mechanisms at room temperature because the equilibrium $Fe^{3+} + Cl^- \rightleftarrows FeCl^{2+}$ is attained too rapidly. At −50° the formation of the $FeCl^{2+}$ complex proceeds quite slowly, therefore this temperature was chosen to distinguish between the two alternative paths.

The solvent used in this investigation was a eutectic aqueous solution of perchloric acid (5.27 *M*) having a melting point of −59.7°.[4] A Pyrex reaction vessel consisting of three compartments was used: two side compartments were connected through a common T-shaped mixing chamber to the main compartment. An inert atmosphere was maintained by a slow stream of CO_2 and the whole vessel was immersed in an ethanol bath, maintained at −50°. A chromous solution was placed in the main compartment, a ferric perchlorate solution in one of the side compartments and a hydrochloric acid solution in the other. By applying a pressure of CO_2 the ferric and the chloride solutions were driven through the common mixing chamber into the chromous solution, which they reached within 0.1 sec. after mixing. The concentrations of the reactants after mixing were: $[Fe^{3+}]$ 0.075 *M*, $[Cl^-]$ 0.075 *M*, $[Cr^{2+}]$ 0.031 *M*.

The oxidation reaction was "instantaneous" and produced a green solution. After warming to room temperature, this solution was separated chromatographically by absorption on a Dowex 50 (8%) cation exchange column and elution with 1 *M* perchloric acid. It consisted mainly of $CrCl^{2+}$ and a smaller amount of $Cr(H_2O)_6{}^{3+}$. The same reaction was carried out in the absence of chloride ion (which was replaced by the pure solvent) and was found to proceed quite slowly at −50°, thus demonstrating the marked catalytic activity of Cl^-. The only chromic species produced in this experiment was the hexaaquochromic ion, as expected.

The assumption that $FeCl^{2+}$ is not formed prior to the oxidation reaction was confirmed by another blank experiment in which Cr^{2+} was replaced by the pure solvent into which the ferric and chloride solutions were injected at −50° as above. After 60 seconds the yellow color of $FeCl^{2+}$ was not yet observed. A very faint color was first noted after three minutes, and even after one hour equilibrium concentration was not attained. These results are in accord with the kinetic data given by Connick and Coppel[5] for this reaction at room temperature. Using their values of the rate constants and activation enthalpies, we found that at the initial ferric and chloride concentrations used by us (0.075 molar) less than 0.4% of the total Fe^{3+} was converted to $FeCl^{2+}$ at −50° after 60 seconds.

The results of these experiments show that the chloride-catalyzed oxidation of Cr^{2+} by Fe^{3+} does not proceed *via* the $FeCl^{2+}$ complex at −50°, but they do not rule out this path at room temperature.

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[1] H. Taube and H. Myers, *J. Am. Chem. Soc.*, **76**, 2103 (1954).

[2] H. Taube, *ibid.*, **77**, 4481 (1955).

[3] H. Taube, *Chem. Soc. Spec. Publ.*, **13**, 57 (1959).

[4] L. H. Brickwedde, *J. Research Natl. Bur. Standards*, **42**, 309 (1949).

[5] R. E. Connick and C. P. Coppel, *J. Am. Chem. Soc.*, **81**, 6389 (1959).

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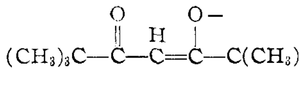
RECEIVED DECEMBER 8, 1961

ABSORPTION INTENSITIES AND ELECTRONIC STRUCTURES OF TETRAHEDRAL COBALT(II) COMPLEXES

Sir:

We wish to report some observations which seem to us to be both novel and important in respect to the problem of the intensities of electronic absorption bands in transition metal complexes.

Using the ligand I, the enolate anion of dipivaloylmethane, hereafter abbreviated DPM, we have prepared the complexes $Co(DPM)_2$



$$(CH_3)_3C-\overset{\overset{O}{\|}}{C}-\overset{H}{C}=\overset{\overset{O-}{|}}{C}-C(CH_3)_3 \quad I$$

and $Zn(DPM)_2$. It has been shown previously that in $Ni(DPM)_2$ the size of the *t*-butyl groups prevents the trimerization which occurs in Ni(II) complexes with less hindered β-diketone enolates so that $Ni(DPM)_2$ is a planar, diamagnetic monomer.[1] $Co(DPM)_2$ has three unpaired electrons

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[1] F. A. Cotton and J. P. Fackler, Jr., *J. Am. Chem. Soc.*, **83**, 2818 (1961); J. P. Fackler, Jr., and F. A. Cotton, *ibid.*, **83**, 3775 (1961).

and, in order to find out whether it also was square planar and hence an example of a high-spin square complex of Co(II)[2], a single crystal X-ray study was undertaken.

It was found that $Co(DPM)_2$ crystallizes in space group $I4_1/a$ with four molecules per unit cell. This requires that the Co atoms lie on $\bar{4}$ axes which in turn requires that the CoO_4 configuration be such that one CoO_2 set lies in a plane perpendicular to that defined by the other CoO_2 set. Although the O-Co-O angles may deviate somewhat from the tetrahedral angle, it can be said that the coördination of Co in this compound is "tetrahedral" in the usual, somewhat loose usage of that term. It does not seem likely that there will be large deviations from the tetrahedral angle in view of the dimensions and configuration of the ligands. $Zn(DPM)_2$ is isomorphous with $Co(DPM)_2$ and mixed crystals may be grown. An e.s.r. study of $Co(DPM)_2$ in a dilute mixed crystal is in progress and will be reported later.

This result was surprising since $Co(DPM)_2$ has a reddish color reminiscent of the colors of non-tetrahedral Co(II) complexes[2] but not at all like the deep blue and green hues of the previously known tetrahedral ones.[3] Moreover, the visible absorption band of $Co(DPM)_2$ has an ϵ_{max} of only 40 and this is much closer to those ($\sim$10) found in octahedral complexes and others not previously thought to be tetrahedral than to those (400–1700) of previously known tetrahedral complexes.

Rigorous theoretical treatment of the oscillator strengths $f(\nu_i)$ of electronic transitions in tetrahedral complexes is a very formidable task which has not yet been accomplished, but Ballhausen and Liehr,[4] in semiquantitative calculations, have provided convincing evidence that the intensities are direct functions of the degree of mixing of ligand orbitals and metal *d* orbitals and, considering only MO's of σ type, they produced an expression for this relationship. Moreover, it is well-known that the Racah parameter B is decreased from the free ion value in tetrahedral Co(II) complexes[3] and in complexes generally[5,6,7] and one[8] likely cause for this is mixing of ligand and metal orbitals resulting in delocalization of metal *d* electrons. From these considerations one might expect a correlation between absorption band intensities and the amount of lowering, ΔB, of the B value from the free ion value (967 cm.$^{-1}$ for Co(II)).

The spectrum of $Co(DPM)_2$ therefore was measured and from the positions of the ν_3 and ν_2 bands a B value of 880 cm.$^{-1}$ was calculated.[3] Thus ΔB = 87 cm.$^{-1}$, which is very much smaller than ΔB values (200–300 cm.$^{-1}$) previously[3] found in tetrahedral Co(II) complexes.

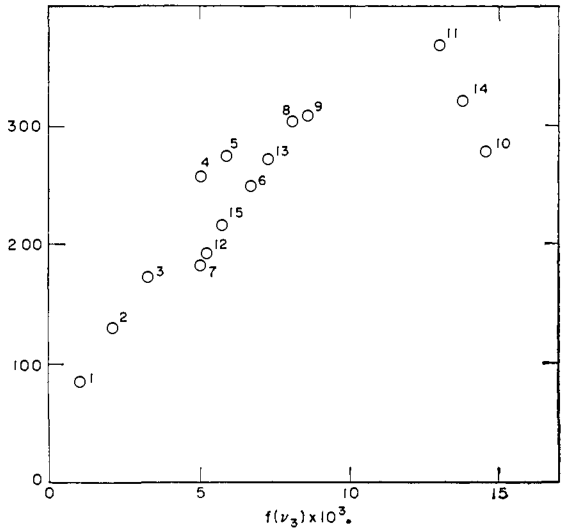

Fig. 1.—A plot of $f(\nu_3)$ *vs.* ΔB for all tetrahedral Co(II) complexes on which the necessary data are currently available. The compounds and, where appropriate, sources of data are: 1, $Co(DPM)_2$; 2,3, $Co(Ph_3PO)_2(ONO_2)_2$ and $Co(Ph_3AsO)_2(ONO_2)_2$, data from D. M. L. Goodgame, R. H. Soderberg and F. A. Cotton, *J. Chem. Soc.*, in press; 4, 5, 6, 7, 8, 9, 10, $[CoCl_4]^{2-}$, $[CoBr_4]^{2-}$, $[Co(NCO)_4]^{2-}$, $[Co(Ph_3PO)_4]^{2-}$, $[CoI_4]^{2-}$, $[Co(N_3)_4]^{2-}$, $[Co(NCS)_4]^{2-}$, data from ref. 3; 11, 12, Co in ZnS and ZnO, data from H. A. Weakliem, RCA Laboratories, private communication; 13, $[Co(benzimidazole)_4]^{2+}$, data from M. Goodgame and F. A. Cotton, *J. Am. Chem. Soc.*, in press; 14, $[Co(NCSe)_4]^{2-}$, data from F. A. Cotton, D. M. L. Goodgame and H. E. Haas, *Inorg. Chem.*, in press; 15, $[Co(Ph_3AsO)_4]^{+}$, data from D. M. L. Goodgame, M. Goodgame and F. A. Cotton, *Inorg. Chem.*, in press.

In order to test further the expected relationship between ΔB and $f(\nu_3)$, previously published and newly obtained data for a number of other tetrahedral Co(II) complexes have been collected and plotted as shown in Fig. 1. It can be seen that there is a generally good correlation of the kind anticipated. Work along these lines is being continued and detailed reports will be submitted as soon as possible.

Financial support from the U. S. Atomic Energy Commission is gratefully acknowledged.

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[2] F. A. Cotton and R. H. Holm, *J. Am. Chem. Soc.*, **82**, 2979 (1960).

[3] F. A. Cotton, D. M. L. Goodgame and M. Goodgame, *ibid.*, **83**, 4690 (1961), and other references cited here.

[4] C. J. Ballhausen and A. D. Liehr, *J. Mol. Spect.*, **2**, 342 (1958); errata, *ibid.*, **4**, 190 (1960).

[5] C. K. Jørgensen, *Acta Chem. Scand.*, **11**, 53 (1957).

[6] O. Bostrup and C. K. Jørgensen, *ibid.*, **11**, 1223 (1957).

[7] T. M. Dunn, *J. Chem. Soc.*, 623 (1959).

[8] As Dunn[7] points out, the situation actually is somewhat more complicated. Also it has been suggested[9] recently that configuration interaction under the influence of the ligand field may make some contribution to the lowering of the B values.

[9] H. B. Gray and C. J. Ballhausen, *Acta Chem.*, **15**, 1327 (1961).

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RECEIVED JANUARY 22, 1962

HYDROGEN ION DEPENDENCE OF THE RATE OF REDUCTION OF ACETONE BY BOROHYDRIDE

Sir:

Recently H. C. Brown[1] has published additional data on the reduction of acetone by borohydrides in

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[1] H. C. Brown and K. Ichikawa, *J. Am. Chem. Soc.*, **83**, 4372 (1961).