

earlier studies.^{5,6,8} The values of k at atmospheric pressure were in satisfactory accord with earlier measurements when allowance was made for differences in ionic strengths. Values of ΔV^* were computed from slopes of plots of $\log k$ vs. pressure (which were generally linear up to at least 2 kbars) using the relation $\Delta V^* = -RT(d \ln k/dP)$, and are summarized in Table II.

TABLE II
VOLUMES OF ACTIVATION FOR THE REDUCTION OF COBALT(III)
COMPLEXES BY IRON(II)^a

Oxidant	ΔV^* , cm. ³ /mole ^b
Co(NH ₃) ₅ F ²⁺	+11
Co(NH ₃) ₅ Cl ²⁺	+8
Co(NH ₃) ₅ Br ²⁺	+8
Co(NH ₃) ₅ N ₃ ²⁺	+14
<i>cis</i> -Co(NH ₃) ₄ (N ₃) ₂ ⁺	+14
<i>trans</i> -Co(NH ₃) ₄ (N ₃) ₂ ^{+c}	+2.2
<i>trans</i> -Co(NH ₃) ₄ (N ₃) ₂ ^{+d}	+2.8
Co(HY)Cl ⁻	+3

^a Conditions are given in Table I. ^b Estimated uncertainty ± 1 cm.³/mole. ^c 0.001 *M* HClO₄. ^d 0.02 *M* HClO₄.

Unfortunately the mechanisms of these reactions are not known with certainty although indirect arguments for inner-sphere mechanisms have been advanced in each case.^{5,6,8} The present findings of positive values of ΔV^* for all the reactions are also most readily reconciled with this interpretation, in line with the expectation noted earlier of a positive contribution to ΔV^* from the liberation of a coordinated water molecule in forming the inner-sphere bridged transition state. Positive values of ΔV^* are otherwise difficult to understand, particularly in the reactions between two cations, *e.g.*, Fe²⁺ + Co(NH₃)₅X²⁺, where, in the absence of the specific effect in question, the increase in electrostriction accompanying formation of the transition state would be expected to result in a negative ΔV^* . Also in accord with this are the results of some preliminary measurements¹⁰ which have yielded positive values of ΔV^* for several metal ion catalyzed halide solvolysis reactions whose mechanisms almost certainly involve

(10) J. P. Candlin and J. Halpern, unpublished results.

inner-sphere halide bridged transition states, *i.e.*, Co(NH₃)₅Cl²⁺ + Hg²⁺, $\Delta V^* = +2$; Co(NH₃)₅Br²⁺ + Hg²⁺, $\Delta V^* = +3$; Co(HY)Cl⁻ + Cu²⁺, $\Delta V^* = +9$; and Co(HY)Cl⁻ + Cd²⁺, $\Delta V^* = +6$ cm.³/mole.

The origin for the variation in the magnitude of the ΔV^* values in Table II is far from clear. In particular the small value of ΔV^* for *trans*-Co(NH₃)₄(N₃)₂⁺, in contrast to Co(NH₃)₅N₃²⁺ and *cis*-Co(NH₃)₄(N₃)₂⁺, is puzzling. The reaction of *trans*-Co(NH₃)₄(N₃)₂⁺ with Fe²⁺ is also unusual in that it exhibits an acid-catalyzed (in addition to the acid-independent) path which has been attributed to protonation of the nonbridging N₃⁻ ligand. Although it was not possible in the present studies to increase the H⁺ concentration to the point of predominance of the acid-catalyzed path, comparison of the results for 0.001 and 0.02 *M* H⁺ suggests that the ΔV^* values for the two paths are of the same order. One possible interpretation of this behavior is that general acid catalysis, involving binding of a water molecule to the nonbridging N₃⁻ ligand, and resulting in a negative contribution to ΔV^* , contributes to the H⁺-independent path.

Although the conclusions reached above are necessarily tentative and subject to further verification, the results are considered as encouraging from the standpoint of pointing to the potential usefulness of ΔV^* as a criterion for distinguishing between inner- and outer-sphere electron-transfer mechanisms. It would obviously be desirable to calibrate the method by examining some reactions of known mechanism (including both inner- and outer-sphere examples) such as the Cr²⁺¹ and Ru(NH₃)₆²⁺³ reductions of pentaamminecobalt(III) complexes. This will require some modifications of the experimental procedures, which are presently being attempted.

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Correspondence

Spectral and Magnetic Properties of Hydroxo Complexes. The Position of the Hydroxide Ion in the Spectrochemical Series

Sir:

The spectrochemical series has been very valuable in the characterization of coordination compounds. However, there exist in the series several apparently anomalous arrangements. An extremely puzzling one is the arrangement of hydroxide ion below water, since hydroxide ion has both a higher charge and a greater polarizability than water. This arrangement has been

rationalized on the basis of the π -bonding behavior of the two ligands.¹ In order to gain information about this conundrum we have undertaken a study of the spectral properties of compounds in which the transition metal ion is coordinated only by hydroxide groups. Jørgensen² in his compendium lists the spectral properties of only Co(OH)₄²⁻, Pd(OH)₄²⁻, and Rh(OH)₆³⁻, and a search of the literature has failed to yield further

(1) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 54.

(2) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford, 1962, p. 284 ff.

examples. Scholder and his co-workers³ have reported the preparation of two series of compounds which have been formulated as $M_2[M'(OH)_6]$ and $Na_2[M'(OH)_4]$ where M is either barium or strontium and M' is divalent Mn, Fe, Co, Ni, Cu, or Zn. We have prepared several compounds from the two series and have studied their spectral and magnetic properties. We wish to communicate the results of our measurements since they support Scholder's formulation but *more remarkably* show that water and hydroxide ion give rise to essentially the same d-orbital splitting in their six-coordinate complexes with cobalt(II) and nickel(II). This indicates that in a one-dimensional spectrochemical series hydroxide ion and water should be assigned nearly equivalent positions.

Although Scholder and his co-workers³ have carefully characterized their compounds, there was little evidence⁴ which would permit structural assignments. For this reason we have prepared $Ba_2[Co(OH)_6]$ by the directions given by Scholder and Weber⁵ and have carefully measured its diffuse reflectance spectrum, its infrared spectrum, and its magnetic moment at room temperature. The analytical data for the compound were used for identification and as a criterion for purity. The infrared spectrum of a sample pressed in a potassium bromide pellet was recorded with a Perkin-Elmer Infracord spectrophotometer, and the reflectance spectrum of a finely ground sample was measured with a Beckman DU spectrophotometer equipped with a standard reflectance attachment using a block of $MgCO_3$ as a reflectance standard. The magnetic moment was determined by the Faraday method using equipment and procedures which have been described previously.⁶

The infrared spectrum consists of a sharp intense band at about 3600 cm^{-1} and a broad intense band centered at about 780 cm^{-1} . These bands are assigned to the O-H stretching vibration and the Co-O-H bending motion, respectively.⁷ The absence of the water bending mode near 1630 cm^{-1} substantiates the formulation of the compound as a hydroxo complex. For instance, $Na_2[Sn(OH)_6]$ exhibits no infrared absorption in the region where the water bending mode is found.⁸ The corrected molar magnetic susceptibility was measured to be $10,500 \times 10^{-6}$ c.g.s unit at 296°K ., which yields a magnetic moment of 5.0 B.M., a value which is well within the range expected for a spin-free cobalt(II) ion in an octahedral field. These data (along with the spectral data presented below) are strong evidence for the assignment of a structure which contains $Co(OH)_6^{4-}$ as structural units. The results of our measurements will permit a structural assignment for the other compounds in the series which are known to be isomorphous

(3) R. Scholder and E. Giesler, *Z. anorg. allgem. Chem.*, **316**, 237 (1962), and references therein.

(4) V. Lorenzelli, T. Dupius, and J. Lecomte, *Compt. rend.*, **259**, 1057 (1964).

(5) R. Scholder and H. Weber, *Z. anorg. allgem. Chem.*, **216**, 159 (1933).

(6) W. E. Hatfield, Y. Muto, H. B. Jonassen, and J. S. Paschal, *Inorg. Chem.*, **4**, 97 (1965).

(7) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, pp. 76, 159.

(8) R. L. Williams and R. J. Page, *J. Chem. Soc.*, 4143 (1957).

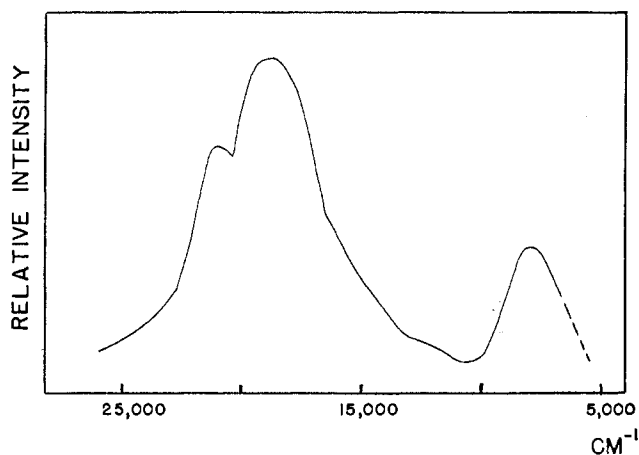


Figure 1.—The reflectance spectrum of $Ba_2[Co(OH)_6]$.

with this compound. However, the data for the series $Na_2[M'(OH)_4]$ are not easily interpretable in terms of simple structures. Extensive studies of the properties of these compounds are under way in our laboratory.

The reflectance spectrum of $Ba_2[Co(OH)_6]$ is presented in Figure 1. The centers of gravity of the absorption bands were estimated visually and are compared in Table I with the data for the $Co(H_2O)_6^{2+}$ ion. The

TABLE I
SPECTRAL DATA

Species	Band maxima, cm^{-1}	Spectral assignment
$Co(OH)_6^{4-}$	8,200	${}^4T_{1g} \rightarrow {}^4T_{2g}$
	11,700	$\rightarrow {}^2E_g$
	15,000 sh (?)	$\rightarrow {}^4A_{2g}$
	19,200	$\rightarrow {}^4T_{1g}$
	21,200	$\rightarrow {}^2T_{2g}, {}^2T_{1g}$
$Co(H_2O)_6^{2+}$	8,200 ^a	${}^4T_{1g} \rightarrow {}^4T_{2g}$
	11,300	$\rightarrow {}^2E_g$
	16,000	$\rightarrow {}^4A_{2g}$
	19,400	$\rightarrow {}^4T_{2g}$
	21,600	$\rightarrow {}^2T_{2g}, {}^2T_{1g}$
$Ni(OH)_6^{4-}$	9,100	${}^3A_{2g} \rightarrow {}^3T_{2g}$
	14,100 } 15,300 }	$\rightarrow {}^3T_{1g}$
	8,500 ^b } 13,500 } 15,400 }	${}^3A_{2g} \rightarrow {}^3T_{2g}$ $\rightarrow {}^3T_{1g}$

^a Reference 2, p. 285. ^b C. K. Jørgensen, *Acta Chem. Scand.*, **10**, 887 (1956).

data for $Ba_2[Ni(OH)_6]$ are also compared in Table I with the spectral data for the $Ni(H_2O)_6^{2+}$ ion. The spectral assignments given in the table were made with the aid of the Sugano-Tanabe diagrams and agree with recent assignments.

The relative intensity of the band at $11,700\text{ cm}^{-1}$ in the spectrum of $Ba_2[Co(OH)_6]$ agrees with what would be expected for a spin-forbidden transition. The shoulder at $15,000\text{ cm}^{-1}$ assigned to the ${}^4T_{1g} \rightarrow {}^4A_{2g}$ transition is comparable to the absorption exhibited by $Co(H_2O)_6^{2+}$. Theoretically, the band is predicted to have a very small intensity.⁹ Although these cobalt(II) complexes have triply degenerate ground states and

(9) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 256.