complexes $Ni[PhP(OC_2H_5)_2]_4$ and $Ni[P(OC_2H_5)_3]_4$.[36] It is of some interest that the former complex has considerably more thermal and solution stability. Our tentative conclusion is that both these results suggest that $PhP(OC_2H_5)_2$ is a better π acceptor than $P(OC_2H_5)_3$ and that the structural patterns in the relatively nonhindered systems containing $PhP(OR)_2$ and $P(OR)_3$ ligands are substantially determined by a balance of σ and π electronic effects. We suggest that $PhP(OR)_2$ is a better π acceptor than $P(OR)_3$ (R = alkyl) because the phenyl group provides a low-energy, empty π molecular orbital level which can act in concert with an appropriately situated phosphorus 3d orbital. The -OR groups withdraw electron density from the phosphorus part of the (PhP) π acceptor, which gives stability to the 3d level; thus, according to this model, both Ph and OR groups play a role in the π-acceptor strength, and for his reason $PhP(OR)_2$ is expected to be a better π acceptor than either PPh_3 or $P(OR)_3$. We shall deal with this matter fully in a subsequent paper.[36]

Acknowledgment. The portion of this research carried out by B. B. C. and H. B. G. was supported by the National Science Foundation. We thank Dr. James Hix for checking the electronic spectral measurements on several of the five-coordinate species. We also thank Professor J. G. Verkade and Dr. K. J. Coskran for allowing us to see the results of their work prior to publication and for several stimulating discussions.

Volume Changes in Ion Association Reactions. Inner- and Outer-Sphere Complexes

Thomas G. Spiro, Agnes Revesz, and Judith Lee

Contribution from the Department of Chemistry, Princeton University, Princeton, New Jersey. *Received September 29, 1967*

Abstract: Molar volume changes have been measured dilatometrically for substitution of water in $Co(NH_3)_5H_2O^{3+}$ by various anions. They were found to decrease in the order $OH^- > CH_3CH_2COO^- > SO_4^{2-} > Cl^- > Br^- > NO_3^-$. This order corresponds to the degree of structuring of water by the anions. Volume changes were determined as well for complexing of Ce^{3+} by SO_4^{2-}, $CH_3CH_2COO^-$, Cl^-, and NO_3^-, and of Eu^{3+} by NO_3^-. Comparison of both volume and entropy changes for the lanthanon complexes with the corresponding Co(III) systems support the view that sulfate and propionate complexes of Ce^{3+} are inner sphere while the chloride complex is outer sphere. However, the nitrate complexes of the lanthanons show intermediate behavior. The volume changes for outer-sphere complexing of $Co(NH_3)_6^{3+}$ and $Co(NH_3)_5H_2O^{3+}$ by sulfate were measured in dilute solution ($I = 0.1$) and found, unexpectedly, to be of the same magnitude as for inner-sphere substitution of sulfate in $Co(NH_3)_5H_2O^{3+}$. Again this behavior is paralleled by the entropy changes. Raising the ionic concentration to 1 *M* $NaClO_4$ markedly lowers both the volume and entropy change on outer-sphere binding of SO_4^{2-} to $Co(NH_3)_5H_2O^{3+}$. The wide variability of both inner-sphere and outer-sphere values militates against the establishment of a general criterion for distinguishing between the two structural types based either on volume or entropy changes. Nevertheless, comparisons for related systems under closely similar conditions may be useful.

Ions in solution compress solvent molecules in their vicinity. Molar volumes of ions have been interpreted in terms of this effect, known as electrostriction,[1] by a number of approaches.[2] When oppositely charged ions combine, the solution volume is expected to increase as electrostriction is relieved. Many measurements on Brønsted acid-base systems have documented the expansion accompanying proton transfer from cations to anions.[3,4] The effect is quite large. For example, the reaction $H_{aq}^+ + OH_{aq}^- = H_2O$ has an associated volume increase of 21.9 ml/mole[5] (at infinite dilution and 25°) which is some 4 ml greater than the molar volume of water itself. The expansions associated with other proton-transfer reactions are also substantial. Their magnitudes are of interest with respect to the question of solvent ordering by solutes of various structures and have been used as probes into protein structures.[3,6]

Volume changes accompanying nonprotonic charge neutralization reactions have so far received little attention. Recently Strauss and Leung[7] measured volume changes accompanying the mixing of anionic polyelectrolytes with alkali metal and alkaline earth cations. Some of the molar expansions were of the order of those observed for analogous protonation reactions and were interpreted by the authors as evidence for site binding of the cations to the polyanions, as opposed to ionic atmosphere binding. Volume changes accompanying simple nonprotonic ion association reactions have not previously been determined. Their magnitudes should be of relevance to an understanding of solvent structure and ion hydration, and comparisons with protonic systems should be instructive.

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(1) P. Drude and W. Nernst, *Z. Physik. Chem.*, **15**, 79 (1894).

(2) E. Glueckauf, *Trans. Faraday Soc.*, **61**, 914 (1965), and references cited therein.

(3) W. Kauzmann, A. Bodanszky, and J. Rasper, *J. Am. Chem. Soc.*, **84**, 1777 (1962).

(4) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolyte Solutions," ACS Monograph No. 37, 3rd ed, Reinhold Publishing Corp., New York, N. Y., 1958, p 405.

(5) L. G. Hepler, J. M. Stokes, and R. H. Stokes, *Trans. Faraday Soc.*, **61**, 20 (1965).

(6) J. Rasper and W. Kauzmann, *J. Am. Chem. Soc.*, **84**, 1771 (1962).

(7) U. P. Strauss and Y. P. Leung, *ibid.*, **87**, 1476 (1965).

Of further interest is the possibility that volume changes might be of aid in the resolution of a recurrent and troublesome structural question about ion association: namely, whether a given pair of associated ions is in contact or separated by one or more solvent molecules or, in the language of coordination chemistry, whether a given complex ion is inner or outer sphere.[8] *A priori* one would expect the two products to have quite different volume changes associated with their formation. On the assumption that the electrostriction volume loss of an ion is mainly carried by the first solvent layer, one anticipates that the expansion should be much larger for inner- than for outer-sphere complex formation. In that event the volume changes might serve as a criterion for structural type in ion association reactions.

If such a criterion is to be evaluated, data are required on known inner- and outer-sphere systems. The two structural types are clearly distinguishable at present only for cations whose coordination sphere is substitution inert. We have accordingly measured inner-sphere volume changes in the substitution of water in $Co(NH_3)_5H_3O^{3+}$ by a number of anions: hydroxide, propionate, sulfate, chloride, bromide, and nitrate. For comparison we explored some cerium(III) and europium(III) complex systems, for which thermodynamic arguments for inner- *vs.* outer-sphere complexes have been advanced.[9-11] We also attempted to measure volume changes for outer-sphere complexation of $Co(NH_3)_6^{3+}$ and $Co(NH_3)_5H_2O^{3+}$ with sulfate and chloride.

Experimental Section

Chemicals. $[Co(NH_3)_6]Cl_3$ was prepared by air oxidation of $CoCl_2$ in ammonia.[12a] $Co(NH_3)_5X^{3-z}$ species were prepared from $[Co(NH_3)_5CO_3]NO_3$[12b] by reaction with the appropriate acid, H_zX ($HClO_4$ for X = H_2O). For X = NO_3^-, a sample of commercial salt (Alfa Inorganics) was dried at 100° for 18 hr[12c] to ensure elimination of any coordinated water. The salts were converted to perchlorates by repeated recrystallization from dilute $HClO_4$, except for X = $CH_3CH_2COO^-$ and NO_3^-, whose complexes were retained as the nitrates. The final products were tested for purity by cation-exchange chromatography and analyzed for cobalt spectrophotometrically.[13]

A europium perchlorate stock solution was prepared from europium chloride (Alfa) by precipitation with ammonia and dissolution of the hydroxide in perchloric acid, the final pH being adjusted to 4. Reagent grade cerous perchlorate (Alfa) was used to make a stock solution. Both rare earths were standardized by EDTA titration. Reagent grade sodium sulfate, sodium nitrate, and sodium chloride were weighed out directly. A sodium perchlorate stock solution was prepared from perchloric acid and sodium carbonate and analyzed by weighing a residue dried at 180°.

Dilatometry. Volume changes were measured in Carlsberg dilatometers using the technique of Linderström-Lang and Lanz[14] as described by Rasper and Kauzmann.[6] All measurements were at 30.0° in a water bath regulated to ±0.0001°. They were in duplicate, and agreement to within 0.02 μl was obtained in almost all cases.

Results

1. Cobalt(III) Substitution Reactions. The reaction of interest in establishing a scale of volume changes for inner-sphere complex formation is

$$Co(NH_3)_5H_2O^{3+} + X^{z-} = Co(NH_3)_5X^{3-z} + H_2O \qquad (1)$$

However, the rates of this reaction, either in the forward or reverse direction, are inconveniently low at 30°. Consequently volume changes were measured instead for

$$Co(NH_3)_5X^{3-z} + OH^- = Co(NH_3)_5OH^{2+} + X^{z-} \qquad (2)$$

Substitution reactions for acidopentaamminecobalt(III) complexes being base catalyzed, reaction 2 proceeds rapidly, and equilibrium was reached within 30 min for all X^{z-}. Furthermore, the equilibrium lies substantially to the right in all cases so that the reaction goes to completion even when equivalent quantities of the reactants are employed. The volume change of the reaction

$$Co(NH_3)_5H_2O^{3+} + OH^- = Co(NH_3)_5OH^{2+} + H_2O \qquad (3)$$

was also measured. Then

$$\Delta V_1 = \Delta V_3 - \Delta V_2$$

where the ΔV's are the volume changes per mole of product, and the subscripts refer to the reaction numbers above.

The results are given in Table I. For calculation of the molar volume changes, the measured volume changes, Δv, were first corrected for the contribution attributable to electrolyte mixing. This contribution was taken to be the sum of the volume changes found when each reactant solution was in turn mixed with a volume of the ionic medium, 1 *M* $NaClO_4$, equal to that of the other reactant solution. For mixing of the cobalt solutions with 1 *M* $NaClO_4$, Δv was found to be zero, while for the NaOH solution it was found to be −0.03 μl, which value was therefore taken as the mixing contribution in each case. Based on an estimated uncertainty of ±0.02 μl in the dilatometric measurements, the uncertainty in the calculated molar volume changes is ±0.4 ml.

Table I. Volume Changes for Co(III) Substitution Reactions[a]

X^{z-}	Δv, μl	ΔV,[b] ml	ΔV_1,[c] ml
H_2O	0.94	19.4	...
H_2O[d]	1.08	20.6	...
$CH_3CH_2COO^-$ [e]	0.07	2.0	17.4
$CH_3CH_2COO^-$ [d,e]	0.05	1.0	19.6
SO_4^{2-}	0.18	4.2	15.2
SO_4^{2-} [d]	−0.01	1.4	19.2
Cl^-	0.42	9.0	10.4
Br^-	0.46	9.8	9.6
NO_3^- [e]	0.64	13.4	6.0

[a] 5 ml of 0.01 *M* $[Co(NH_3)_5X](ClO_4)_{3-z}$ in (0.97 + 0.01*z*) *M* $NaClO_4$ mixed with 2 ml of 0.025 *M* NaOH in 0.975 *M* $NaClO_4$. [b] Calculated molar volume change for the reaction $Co(NH_3)_5X^{3-z} + OH^- = Co(NH_3)_5OH^{2+} + X^{z-}$. [c] Calculated molar volume change for the reaction $Co(NH_3)_5H_2O^{3+} + X^{z-} = Co(NH_3)_5X^{3-z} + H_2O$. [d] $NaClO_4$ absent. [e] Presents as $[Co(NH_3)_5X](NO_3)_2$.

The reactions were run in 1 *M* $NaClO_4$ for later comparison with the results obtained in the Ce(III) and Eu(III) systems. High ionic concentrations re-

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(8) This is related to the question of site binding on polyelectrolytes, addressed by Strauss and Leung.[7]

(9) F. A. Posey and H. Taube, *J. Am. Chem. Soc.*, **78**, 15 (1956).

(10) G. R. Choppin and W. I. Strazik, *Inorg. Chem.*, **4**, 1250 (1965).

(11) G. R. Choppin and A. J. Graffeo, *ibid.*, **4**, 1254 (1965).

(12) (a) *Inorg. Syn.*, **2**, 217 (1950); (b) *ibid.*, **4**, 171 (1953); (c) *ibid.*, **4**, 174 (1953).

(13) E. S. Gould and H. Taube, *J. Am. Chem. Soc.*, **86**, 1318 (1964).

(14) K. Linderström-Lang and H. Lanz, *Compt. Rend. Trav. Lab. Carlsberg, Ser. Chim.*, **21**, 315 (1938).

duce somewhat the volume changes of ionic reactions[4] because the partial molar volumes of the ions increase with increasing electrolyte concentration. To gauge this effect, and also to help connect the present results with those on protonic systems, reaction 3 and reaction 2, with X = propionate and sulfate, were also run in the absence of supporting electrolyte. These results are likewise given in Table I. In the absence of supporting electrolyte, the contribution from electrolyte mixing cannot readily be determined experimentally. It can, however, be estimated on the assumption of Debye–Hückel limiting behavior of the ions, with the aid of Redlich's equation[15]

$$\Phi_i = \Phi_{i0} + 0.93 z_i^2 \sqrt{I} \qquad (4)$$

Here Φ_{i0} and Φ_i are the apparent molar volumes at infinite dilution and at ionic strength I, respectively, for ion i, whose charge is z_i. The difference in volume between final and initial solutions predicted from the last term in eq 4 is +0.05, 0.00, and −0.08 μl for X = H_2O, $CH_3CH_2COO^-$, and SO_4^{2-}, respectively. These values were used as corrections in calculating the molar volume changes. The corrections may be too large, since the electrolyte concentrations exceed the Debye–Hückel limiting region for polyvalent ions, but the results cannot be greatly affected.

It should be noted that the formation of outer-sphere complexes is probably negligible for the reactions run in 1 *M* $NaClO_4$, the high salt concentration serving to reduce the relevant ion-pairing equilibrium quotients to insignificant values. The interaction of perchlorate itself with cobalt(III) complexes has always been found to be negligible on spectral criteria, but in any case this is a constant factor in these experiments, 1 *M* $NaClO_4$ serving as the "solvent" or reference state.

On the other hand, outer-sphere complex formation may have some influence on the volume changes for the reactions run in the absence of $NaClO_4$, insofar as the products are incompletely dissociated. The most important interaction (based on charge type) is expected to be between SO_4^{2-} and $Co(NH_3)_5OH^{2+}$. This equilibrium has not been measured, but equilibrium constants are available[16,17] for association of SO_4^{2-} with the analogous $Co(NH_3)_5Cl^{2+}$. Application of these constants to the ionic strength and product concentrations present in our solution leads to the estimate that some 28–34% of the $Co(NH_3)_5OH^{2+}$ may be associated with SO_4^{2-}. This interaction should produce a volume expansion relative to the separate ions, leading to an overestimate of the volume increase associated with reaction 2. In turn this would produce an underestimate for ΔV associated with reaction 1; *i.e.*, the increase in molar expansion for sulfate substitution of water in $Co(NH_3)_5H_2O^{3+}$ on removing the supporting electrolyte may be somewhat greater than indicated in Table I. Ion pairing for $Co(NH_3)_5OH^{2+}$ with $CH_3CH_2COO^-$, or with ClO_4^-, the other products of the experiments run without 1 *M* $NaClO_4$, should be less significant.

2. **Ce(III) and Eu(III) Complexes**. Complexing of Ce(III) by sulfate, propionate, nitrate, and chloride and of Eu(III) by nitrate was measured dilatometrically. The stabilities of these complexes range from moderate to weak, and it was therefore felt desirable to vary the concentrations over a substantial range in order to shift the equilibrium significantly and provide a reliable extrapolation to the molar volume change. Consequently, the ionic medium was maintained approximately constant by addition of 1 *M* $NaClO_4$. Before mixing, the lanthanon solutions were all 1 *M* in ClO_4^- while the solutions containing the anionic reactants were all 1 *M* in Na^+. The aim of this device is to minimize the variation with concentration of both the ionic activity coefficient quotients and the volume change due to electrolyte mixing. In all cases the cationic reactant was kept in excess to minimize the formation of higher complexes.

The electrolyte mixing contribution, $\Delta\nu_{mix}$, was evaluated as before by assuming it to be the sum of the volume changes experienced by the individual reactants on mixing with the ionic medium. This assumption perforce ignores the possibility that the contribution from nonspecific mutual interaction of the reactant ions is different from the contribution of their interaction with an equivalent number of medium counterions. There does not appear to be any way to test this approximation. However, the measured mixing volume changes were all relatively small, and the error introduced by this approximation should not materially affect the results.

The dilatometric data are presented in Table II. They were treated by extrapolation procedures analogous to those in common use in spectrophotometry.[18]

If for a reaction

$$M + A = MA$$

the molar volume change, ΔV, is treated as an intrinsic property of MA, then one can write

$$\Delta v_{cor} = \Delta V(\text{moles of MA}) = \Delta V(MA)v_t \qquad (5)$$

where Δv_{cor} is the volume change, corrected for the effect of electrolyte mixing, in an experiment giving rise to a concentration of product (MA) in a total volume v_t.

From this point the treatment depends on the magnitude of the stoichiometric equilibrium constant, K, for the reaction. If K is small, then $(MA)^2 \ll C_M C_A$, whence[18a]

$$(MA) = \frac{C_M C_A}{K^{-1} + C_M + C_A} \qquad (6)$$

where C_M and C_A are the analytical concentrations of M and A, respectively. Combination of eq 5 and 6 gives, upon rearrangement

$$V_A(C_M + C_A)/C_M = \Delta V - K^{-1}V_A/C_M \qquad (7)$$

where $V_A = \Delta v_{cor}/C_A v_t$, *i.e.*, the volume change per mole of A. A plot of the left side of eq 7 against V_A/C_M should give a straight line with ΔV as intercept and $-K^{-1}$ as slope. Such plots were made for $CeNO_3^{2+}$, $EuNO_3^{2+}$, and $CeCl^{2+}$ for all of which K is quite small, and are shown in Figure 1. Here the indicated uncertainties in the quantities plotted correspond

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[15] O. Redlich and D. M. Meyer, *Chem. Rev.*, 64, 226 (1964).

[16] F. A. Posey and H. Taube, *J. Am. Chem. Soc.*, 79, 255 (1957).

[17] C. W. Davies and I. W. Williams, *Trans. Faraday Soc.*, 54, 1547 (1958).

[18] (a) F. J. C. Rossotti and H. Rossotti, "The Determination of Stability Constants," McGraw-Hill Book Co., Inc., New York, N. Y., 1961, p 276; (b) *ibid.*, p 274.

Table II. Volum e Changes for Ce(III) or Eu(III) Complex Formati on[a]

x	y	Δv_{mix},[b] μl	Δv_{cor},[c] μl	V_A,[d] ml
1. $Ce^{3+} + NO_3^- = CeNO_3^{2+}$ ($\Delta V^e = 3.4 \pm 0.5$ ml)				
0.333	0.500	−0.19	1.13	1.13 (0.03)
0.333	0.350	−0.18	0.83	1.19 (0.05)
0.333	0.250	−0.17	0.62	1.24 (0.07)
0.333	0.150	−0.17	0.35	1.17 (0.11)
0.150	0.350	−0.08	0.46	0.66 (0.05)
0.150	0.210	−0.07	0.30	0.71 (0.08)
0.150	0.105	−0.07	0.17	0.81 (0.16)
2. $Eu^{3+} + NO_3^- = EuNO_3^{2+}$ ($\Delta V^e = 4.2 \pm 0.5$ ml)				
0.333	0.500	−0.14	1.30	1.30 (0.03)
0.333	0.250	−0.13	0.65	1.30 (0.07)
0.200	0.500	−0.09	0.86	0.86 (0.03)
0.200	0.350	−0.08	0.66	0.94 (0.05)
0.120	0.250	−0.04	0.32	0.64 (0.07)
3. $Ce^{3+} + Cl^- = CeCl^{2+}$ ($\Delta V^e = 0.8 \pm 0.5$ ml)				
0.333	0.500	−0.16	0.33	0.33 (0.03)
0.200	0.500	−0.09	0.23	0.23 (0.03)
0.200	0.250	−0.09	0.14	0.28 (0.07)
4. $Ce^{3+} + SO_4^{2-} = CeSO_4^+$ ($\Delta v^f = 15.1 \pm 0.3$ ml)				
0.333	0.100	−0.13	2.78	13.9 (0.2)
0.333	0.050	−0.16	1.44	14.4 (0.3)
0.150	0.100	−0.03	2.58	12.9 (0.2)
0.150	0.050	−0.06	1.31	13.1 (0.3)
0.100	0.100	0.00	2.30	11.5 (0.2)
0.050	0.100	+0.03	1.68	8.4 (0.2)
0.050	0.050	0.00	0.87	8.7 (0.3)
5. $Ce^{3+} + CH_3CH_2COO^- = CeOOCCH_2CH_3^{2+}$ ($\Delta v^f = 23.6 \pm 0.2$ ml)				
0.333	0.150	−0.16	7.09	23.6 (0.1)
0.333	0.050	−0.16	2.37	23.7 (0.3)
0.150	0.150	−0.06	7.08	23.6 (0.1)
0.150	0.100	−0.06	4.73	23.6 (0.2)
0.150	0.050	−0.06	2.36	23.6 (0.3)
0.100	0.050	−0.03	2.37	23.7 (0.3)
0.050	0.030	−0.01	1.42	23.4 (0.6)

[a] 5 ml of x M $M(ClO_4)_3$ in $(1 - 3x)$ M $NaClO_4$ mixed with 2 ml of y M Na_zA in $(1 - zy)$ M $NaClO_4$. [b] Volume change attributable to electrolyte mixing (see text). [c] $\Delta v_{cor} = \Delta v - \Delta v_{mix}$. [d] Volume change per mole of A^{z-}; estimated uncertainties, which correspond to an uncertainty of 0.02 μl in the dilatometric measurements, are given in parentheses. [e] Extrapolated molar volume; see Figure 1. [f] Extrapolated molar volume; see Figure 2.

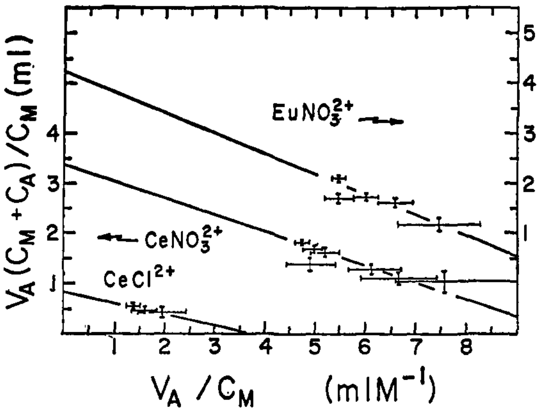

Figure 1. Plot of eq 7 for $CeCl^{2+}$, $CeNO_3^{2+}$ (left-hand ordinate), and $EuNO_3^{2+}$ (right-hand ordinate) formation. The lengths of the crossed lines indicate the uncertainties in the quantities plotted corresponding to an uncertainty of ±0.02 μl in the dilatometric measurements.

to an uncertainty in the dilatometric measurements of ±0.02 μl. The extrapolations to the intercepts are rather long (a result of the weakness of the complexes). Least-squares linear fits to the data give $\Delta V = 3.4 \pm 0.5$ ml for $CeNO_3^{2+}$, and 4.2 ± 0.5 ml for $EuNO_3^{2+}$. The corresponding K's are 2.9 and 2.4, respectively. These are somewhat larger than the values, 1.63 and 2.04, found by Choppin and Strazik[10] in 1 M $HClO_4$ at 25°. The discrepancies may be attributable to the difference in medium. In order to obtain reliable measurements, we were forced to use quite high concentrations of the lanthanons. In fact, our medium was essentially 0.333 lanthanon perchlorate (*i.e.*, a "self-medium"[19]) with a degree of substitution by Na^+ and NO_3^-. The volume changes on mixing cerous and chloride ions are very small, not much larger than Δv_{mix}. From the three points shown in Figure 1, we estimate ΔV for $CeCl^{2+}$ as 0.8 ± 0.5 ml/mole.

For the cerium sulfate and propionate systems, where K is considerably larger, the approximation on which eq 6 is based is no longer valid, and another approach[18b] was used. Division of eq 5 by C_A and v_t gives

$$V_A = \Delta V(\mathrm{MA})/C_A = \frac{K(\mathrm{M})\Delta V}{1 + K(\mathrm{M})}$$

Rearrangement produces

$$V_A = \Delta V - K^{-1}V_A/(\mathrm{M}) \qquad (8)$$

so that a plot of V_A against $V_A/(\mathrm{M})$ should again give a straight line with intercept ΔV_M and slope $-K^{-1}$. The concentration of unbound M can be obtained using

$$(\mathrm{M}) = C_M - C_A\left[\frac{K(\mathrm{M})}{1 + K(\mathrm{M})}\right] \qquad (9)$$

A preliminary value of K is chosen for the calculation of (M) by iteration at each point, then a new value of K is obtained from the best straight line representing eq 8, and the cycle is repeated. Convergence is rapidly obtained if the concentration range is wide.

The plot of eq 8 for $CeSO_4^+$ is shown in Figure 2. A good straight line is obtained, and a least-squares fit gives an intercept, $\Delta V = 15.1 \pm 0.3$ ml. The slope corresponds to $K = 57$. Newton and Arcand,[20] in a spectrophotometric study, found $K = 17$ in 1 M $NaClO_4$ at 25°. On the other hand, cation-exchange measurements in the same medium at 20° were evaluated by Fronaeus[21] to give $K = 43$. (The difference in temperature only increases the discrepancy on the basis of Newton and Arcand's enthalpy value, $\Delta H = 3.64$). Our value for K is probably within experimental error of Fronaeus' estimate.

The corresponding plot for $CeOOCCH_2CH_3^{2+}$ is also shown in Figure 2. Here $\Delta V = 23.6 \pm 0.2$ ml by least-squares fit. However, the very low slope implies a value of K two orders of magnitude larger than the value, 47, reported by Choppin and Graffeo[11] in a 2 M $NaClO_4$ medium at 25°. This difference is much too large to ascribe to medium changes. An explanation might be sought in the influence of higher complex formation. Using Choppin and Graffeo's[11] equilibrium constants, we estimate that the ratio $(MA_2)/(MA)$

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(19) S. Hietanen and L. G. Sillén, *Acta Chem. Scand.*, **13**, 533 (1959).

(20) T. W. Newton and G. M. Arcand, *J. Am. Chem. Soc.*, **75**, 2449 (1953).

(21) S. Fronaeus, *Svensk Kem. Tidskr.*, **64**, 500 (1952).

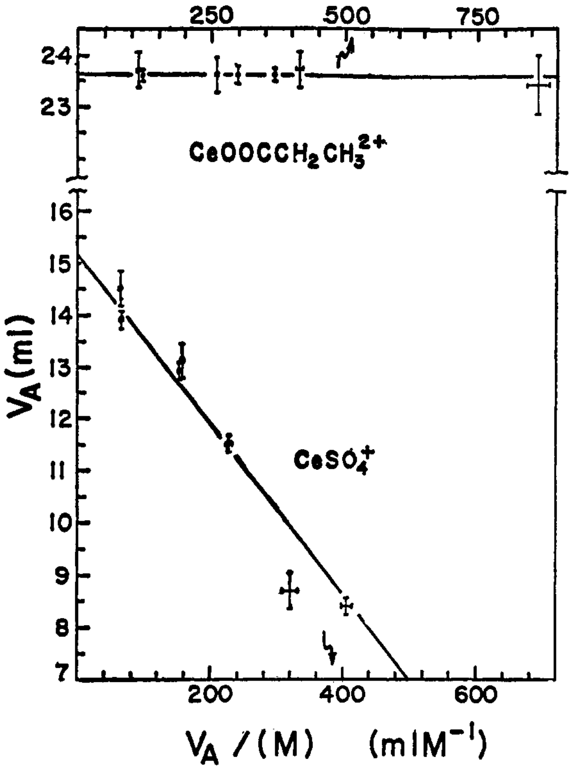

Figure 2. Plot of eq 8 for $CeOOCH_2CH_3^{2+}$ (upper abscissa) and $CeSO_4^+$ (lower abscissa) formation. The lengths of the crossed lines indicate the uncertainties in the quantities plotted corresponding to an uncertainty of ±0.02 μl in the dilatometric measurements.

ranges up to 0.1 in our propionate solutions. (For the sulfate solutions this ratio attains 0.07 using Fronaeus' constants,[21] but is negligibly small if Newton and Arcand's constants are used.) The ratio increases with increasing values of the abscissa in Figure 2. Consequently, if formation of MA_2 adds an increment of expansion to the volume change, the effect would be to decrease (numerically) the slope of the plot and to increase the estimated K. However, examination of the data reveals that, in order to remove the discrepancy in K, the molar expansion associated with formation of $Ce(OOCH_2CH_3)_2^+$ would have to be on the order of 100 ml which seems an unreasonable value.

It is possible that the substantial ionic medium changes required in our measurements produce sufficient changes in either the stoichiometric equilibrium constants or the molar expansions, or both, that the over-all trends in the data fortuitously produce a high apparent equilibrium constant. At present, however, there is no convincing explanation of the observation that the volume changes do not decrease with dilution to the extent predicted by the published equilibrium constants. Nevertheless, the intercept of the plot in Figure 2 is probably a reliable estimate of the molar volume change for $Ce(OOCH_2CH_3)^{2+}$ formation in 0.333 M cerous perchlorate medium. This is because, whatever the corrections which should be applied to eq 8 for this system, it seems likely that the dilution-independent term will remain ΔV, and the extrapolation required is sufficiently short that it should be fairly accurate for any reasonable modification of eq 8.

3. **Cobalt(III) Outer-Sphere Complexes.** Unambiguous characterization of outer-sphere complexes is difficult by any experimental method and dilatometry is no exception. There is much evidence that the phenomenon occurs in a wide variety of systems. However, even for complexes, such as those of Co(III), which are substitution inert, and therefore provide a clear distinction between inner- and outer-sphere reaction products, quantitative data are scanty.

For the labile complexes of Ce(III) and Eu(III) we were able, as described in the previous section, to obtain reliable estimates of ΔV by varying the reactant concentrations widely in a relatively constant ionic medium. This approach is ruled out for Co(III) outer-sphere complexes because of the low solubility of the Co(III) salts, especially in $NaClO_4$ solutions. For these species, we must therefore rely on external equilibrium data and correct the observed volume changes for the calculated degree of dissociation.

Posey and Taube[9] have made a thorough equilibrium study of outer-sphere sulfate complexing with $Co(NH_3)_6^{3+}$ and $Co(NH_3)_5H_2O^{3+}$, and report both equilibrium quotients as functions of ionic strength at 25°. (These are equally well applicable to the temperature of our experiments, 30°, ΔH of association being close to zero.[9]) The dilatometric results for mixing 5 ml of a solution 0.0167 M in the appropriate Co(III) perchlorate with 2 ml of 0.0333 M Na_2SO_4 are shown in Table III. Using Posey and Taube's equilibrium quotient functions, and allowing, by successive approximations, for the decrease in ionic strength due to ion association, we calculate that the fraction of the limiting reactant, sulfate, bound in the final mixture is 49.7% for $Co(NH_3)_5H_2O^{3+}$ and 56.3% for $Co(NH_3)_6^{3+}$. The molar volume changes calculated on this basis have the surprisingly high values of 18.9 ± 0.6 and 16.0 ± 0.5 ml, respectively.

Table III. Volume Changes on Outer-Sphere Complexing of Co(III) Species[a]

Solution 1:	0.0167 M $[Co(NH_3)_5H_2O](ClO_4)_3$	
Solution 2:	0.0333 M Na_2SO_4	$\Delta v = 0.62\ \mu l$
Solution 1:	0.0167 M $[Co(NH_3)_6](ClO_4)_3$	
Solution 2:	0.0333 M Na_2SO_4	$\Delta v = 0.60\ \mu l$
Solution 1:	0.010 M $[Co(NH_3)_5H_2O](ClO_4)_3$ in 1 M $NaClO_4$	
Solution 2:	0.50 M Na_2SO_4 $\Delta v_{mix} = 0.50\ \mu l$	$\Delta v_{cor} = 0.43\ \mu l$
Solution 1:	0.0167 M $[Co(NH_3)_5H_2O](ClO_4)_3$	
Solution 2:	0.100 M NaCl	$\Delta v = 0.05\ \mu l$
Solution 1:	0.0167 M $[Co(NH_3)_6](ClO_4)_3$	
Solution 2:	0.100 M NaCl	$\Delta v = 0.06\ \mu l$

[a] 5 ml of solution 1 mixed with 2 ml of solution 2.

We considered the possibility that some of the volume change was due to electrolyte mixing and change in ionic strength due to complex formation. However, the contribution from these effects calculated with Redlich's equation[15] is −0.01 μl compared to the actual volume changes of greater than +0.6 μl. Again, the Debye–Hückel limiting region is exceeded for polyvalent ions at $I = 0.1$, but the calculation is not likely to be in error by a large amount. In control experiments we found that mixing of the cobalt solutions with 2 ml of 0.1 M $NaClO_4$ gave volume changes of −0.02 to −0.03 ml, while mixing of the sulfate solution with 5 ml of 0.1 M $NaClO_4$ gave a volume change of −0.02 ml.

For comparison with the volume change produced by inner-sphere substitution of SO_4^{2-} in $Co(NH_3)_5H_2O^{3+}$, it would clearly be valuable to have the outer-sphere ΔV in 1 *M* $NaClO_4$. Unfortunately this aim is frustrated by the low solubility of the cobalt salt and the low association constant, 11.2,[9] in this medium. We did measure the volume change for the mixing of 5 ml of 0.01 *M* $Co(NH_3)_5H_2O^{3+}$ in 1 *M* $NaClO_4$ with 2 ml of 0.50 *M* Na_2SO_4, which is also reported in Table III. We calculate 61% of the cobalt present as outer-sphere complex in the final mixture and a resulting ΔV (after correction for the substantial volume change of mixing sulfate and perchlorate at these high concentrations) of 12.9 ml, or 68% of its value at $\mu = 0.1$. However, there is good evidence[9,22] that more than one sulfate can bind to the cobalt complex, and, at the high sulfate concentrations perforce used here (a deficiency of sulfate results in a concentration of product much too low to be detected in the dilatometer), this effect will certainly contribute to the volume change. Consequently, ΔV in 1 *M* $NaClO_4$ is probably substantially less than 68% of its value at $I = 0.1$.

We measured volume changes of only 0.05 and 0.06 μl for mixing 2 ml of 0.1 *M* NaCl with 5 ml of 0.0167 *M* $Co(NH_3)_5H_2O(ClO_4)_3$ and $Co(NH_3)_6(ClO_4)_3$, respectively, indicating that volume changes for outer-sphere complexing are substantially less for chloride than for sulfate. However, in view of the considerable uncertainty about the equilibrium constants involved,[23–26] no quantitative comparison can be made.

Discussion

It is of interest to compare the present data on cobalt(III) substitution reactions with analogous protonation reactions. We note first that the molar expansion for

$$Co(NH_3)_5H_2O^{3+} + OH^- = Co(NH_3)_5OH^{2+} + H_2O$$

in dilute solution, 20.6 ml, is close to that for

$$H^+ + OH^- = H_2O$$

at infinite dilution, 21.9 ml.[5] One might have thought that the electrostriction change between a trivalent and a divalent cation would be greater than for neutralization of a monovalent cation. However, the inner coordination sphere of Co^{3+} is undoubtedly subject to dielectric saturation, so that a simple electrostatic model is inadequate. Similarly inner-sphere substitution of sulfate in $Co(NH_3)_5H_2O^{3+}$ in dilute solution produces a molar expansion of at least (*cf.* Results) 19.2 ml, close to that for protonation of sulfate, 20.2 ml at infinite dilution.[27] On the other hand, for propionate, reaction with Co(III) produces a much larger molar volume change, 19.6 ml, in dilute solution (17.4 ml at $I = 1.0$) than does reaction with H^+, for which $\Delta V = 12.6$ at $I \sim 0.2$.[3] A possible explanation is that the hydrocarbon tail of the propionate disrupts the outer hydration sphere of $Co(NH_3)_5H_2O^{3+}$ more than that of H^+.

The cobalt(III) scale of ΔV values is significantly broader than that for hydrogen ion, because anions can be included whose proton acids are too strong for measurement of volume changes associated with their formation. Thus we find a substantial reduction in volume change for Co(III) substitution on progressing from propionate and sulfate to chloride and bromide and finally to nitrate, for which ΔV is only about one-third that for propionate. This order corresponds quite well to the degree of structuring of water by these ions,[28] and it may be that the variation in volume change largely reflects the alteration of water structure around the anions on complexation.

The cerium and europium complexes were chosen for study because they had previously been characterized as primarily inner or outer sphere on the basis of the entropy changes accompanying their formation.[9–11] It seemed of interest to determine whether volume changes parallel the entropy changes. Certainly the two quantities are related. Hepler[29] has shown that they correlate quite well for protonation reactions.

For $CeSO_4^+$ formation, Posey and Taube[9] pointed out that the entropy change, 17 eu, was close to that for sulfate substitution in $Co(NH_3)_5H_2O^{3+}$, 16.3 eu, both measured in 1 *M* $NaClO_4$, and inferred that $CeSO_4^+$ is mainly an inner-sphere complex. The corresponding volume changes, 15.1 and 15.2 ml/mole, likewise, support the inference. Choppin and Graffeo[11] interpreted the large entropy increase on formation of propionate (15–21 eu) and isobutyrate (19–26 eu) complexes of the lanthanons (measured in 2 *M* $NaClO_4$) in terms of inner-sphere association. No entropy data for corresponding substitution inert species are available for comparison. The molar volume change on propionate complexing of cerium(III), in 1 *M* perchlorate, is also large, 23.6 ml; in fact, it is larger by 6 ml than that found for propionate substitution in $Co(NH_3)_5H_2O^{3+}$. Presumably Ce^{3+} suffers an even greater disruption of its associated water structure than does the cobalt complex. Possibly the outer hydration sphere is more highly structured for Ce^{3+}, where it surrounds an inner sphere of waters, than for $Co(NH_3)_5H_2O^{3+}$, where the inner sphere is mostly ammonia. The disruptive influence of the propionate hydrocarbon tail might then be greater for the former cation.

On the other hand, the very small entropy change found for $EuNO_3^{2+}$ and $EuCl^{2+}$ formation in 1.0 *M* $HClO_4$, −0.5 and −0.4 eu, respectively, led Choppin and Strazik[10] to suggest that nitrate and chloride complexes of the lanthanons were mainly outer sphere. For the chlorides, this view gains some support from Taube's determination[30] of the entropy of inner-sphere chloride substitution in $Co(NH_3)_5H_2O^{3+}$, 13 eu in 0.30 *M* NaCl. Although this value would probably decrease somewhat in 1 *M* $NaClO_4$, it should still be much higher than the $EuCl^{2+}$ value. The large difference between the molar volume change in 1 *M* perchlorate for chloride substitution in $Co(NH_3)_5H_2O^{3+}$, 10.4 ml, and for formation of $CeCl^{2+}$, 0.8 ml, also suggest a difference in structure.

For the nitrates, the situation is more ambiguous. The molar volume changes on formation of $EuNO_3^{2+}$ and $CeNO_3^{2+}$, 4.2 and 3.4 ml in 1 *M* perchlorate, are substantially higher than the $CeCl^{2+}$ value. At the

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same time, they are not much lower than the 6.0 ml/mole increase associated with inner-sphere nitrate substitution in $Co(NH_3)_5H_2O^{3+}$. Thus the volume changes provide no clear evidence that the lanthanon nitrate complexes are outer sphere. In fact, their intermediate values suggest that an equilibrium mixture containing comparable fractions of both structural types may be present. The entropy change for $Co(NH_3)_5NO_3^{2+}$ formation has not been determined. If it turned out to be small, the entropy argument for outer-sphere nitrate complexing of the lanthanons would be vitiated. It is relevant to note that Raman spectra provide evidence[31] for distortion of nitrate in cerium(III) solutions. Hester and Plane concluded[32] that in zinc(II) solutions similar distortion of nitrate is due to inner-sphere complexing. It has not been established whether the same conclusion applies to cerium. Very recently Abrahamer and Marcus[33] have demonstrated that most of the nitrate bound to erbium(III) in concentrated lithium nitrate solutions is in the primary coordination sphere.

The present findings on volume changes due to outer-sphere complexing were unexpected. The conclusion seems inescapable that, in dilute solution, the expansion accompanying outer-sphere association of sulfate to $Co(NH_3)_6^{3+}$ or $Co(NH_3)_5H_2O^{3+}$ is nearly as large as that accompanying inner-sphere substitution by sulfate in the latter complex. Both values decrease substantially on raising the ionic medium to 1 M $NaClO_4$, but the effect is apparently greater for the outer-sphere volume change. Significantly, the entropy change for sulfate outer-sphere association to $Co(NH_3)_6^{3+}$ or $Co(NH_3)_5H_2O^{3+}$ is also quite large,[9] 16 eu, and decreases markedly, to 3.3 eu, in 1 M $NaClO_4$.

We tentatively conclude that volume and entropy changes parallel one another for complex formation in aqueous solution and probably measure essentially the same structural changes. It appears that, contrary to expectations based on simple models, both quantities may have substantial positive values for outer- as well as inner-sphere complex formation, and the former is especially sensitive to the ionic medium used. Furthermore, inner-sphere volume changes, and quite probably entropy changes as well, can vary widely for a given cation, depending on the nature of the anion. Evidently there can be no general criterion for distinguishing between inner- and outer-sphere complexing based either on volume or on entropy changes. Nevertheless, comparison of volume or entropy data with corresponding data for complexes of known structure under closely similar conditions may provide a basis for judgment of structural type. Such comparisons should preferably be carried out at high electrolyte concentrations, where the differences in ΔV and ΔS between inner- and outer-sphere complexes appear to be most pronounced.

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Ionization Potentials of Tris(β-diketonate)metal(III) Complexes and Koopmans' Theorem[1]

Steven M. Schildcrout,[2] Ralph G. Pearson, and Fred E. Stafford

Contribution from the Department of Chemistry and The Materials Research Center, Northwestern University, Evanston, Illinois 60201. *Received November 15, 1967*

Abstract: Electron-impact ionization potentials have been determined for 11 complexes of acetylacetone, trifluoroacetylacetone, and hexafluoroacetylacetone with various trivalent metals, as well as for the two fluorinated uncomplexed diketones. Each of the metal(III) complexes has an ionization potential which is close to that of the corresponding free diketone and which depends only slightly on the metal. This conflicts with predictions based on the application of Koopmans' theorem to the usual molecular orbital theory of these complexes. It is concluded that Koopmans' theorem is not valid for these complexes. There is evidence that the Fe and Co complexes decompose thermally in the mass spectrometer, showing the need for mass analysis in ionization-potential measurements.

According to Koopmans' theorem[3,4] the energy eigenvalue of the highest occupied molecular orbital (MO) has physical significance in that it approximates the negative of the molecular ionization potential (IP). There has been much recent interest in the application of MO, or ligand field, theory to metal complexes.[5] The energy separations among the calculated MO's are often compared with visible–ultraviolet spectroscopic results, but only rarely are attempts made

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