Refractometric Study of Some Cyano and Oxalato Complex Anions

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The molar refraction of simple salts, particularly in the dissolved state, has been studied extensively by Fajans and others; however, little attention has been paid to that of complex salts. It seemed of great interest to examine the following two effects based on this physical quantity;

(1) polarization effect; the decrease of mobility of electrons in ligands due to the field of a central metal ion, and

(2) delocalization effect; the increase of mobility of electrons by the formation of π-bonds.

The former effect is expected to contribute to the decrease of molar refraction and the latter to the increase. With this hope we studied the molar refraction of some cyano and oxalato complex salts. Because of the high polarizability and the great ability for π-bond formation of ligand, cyano complex anions of the inner orbital type were chosen to demonstrate the above-mentioned two effects. On the other hand, oxalato complex anions are of the outer orbital type and the interaction between the constituents may not be very strong.

Experimental

Materials.—They were prepared by the methods described in the references cited. $K_3Cu(CN)_4$, prepared from cupric sulfate and potassium cyanide, and dried at 150°C[1]. $K_2Zn(CN)_4$, prepared from zinc sulfate and potassium cyanide, and dried at

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1) W. Biltz, *Z. anorg. u. allgem. Chem.*, **170**, 161 (1928).

105°C[2]. $K_2Cd(CN)_4$, prepared from cadmium sulfate and potassium cyanide, and dried at 105°C[1]. $K_2Hg(CN)_4$, prepared from mercuric cyanide and potassium cyanide, and dried at 80°C[1]. $K_3Cr(CN)_6$, prepared from potassium dichromate and potassium cyanide, and dried at 100°C[3]. $K_3Mn(CN)_6$, prepared from potassium cyanide and manganese(III) phosphate[3]. $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$, Dog brand guaranteed reagents supplied by Koso Chemical Co., Ltd. Tokyo. $K_3Co(CN)_6$, prepared from cobalt chloride and potassium cyanide[3]. $K_2Ni(CN)_4$, prepared from nickel sulfate and potassium cyanide, and dried at 105°C[3]. $K_3Al(C_2O_4)_3 \cdot 3H_2O$, prepared from aluminum sulfate, potassium oxalate and oxalic acid[4]. $K_3Fe(C_2O_4)_3 \cdot 3H_2O$, prepared from ferric sulfate, barium oxalate, and potassium oxalate[4]. $K_2C_2O_4 \cdot H_2O$, prepared from oxalic acid and potassium carbonate.

Measurements.—The refractive index n of aqueous solutions was measured with a Pulfrich refractometer using the NaD line. The density d of the same solution was determined with Ostwald's pycnometers of about 10 cc. Most salts involved in this study are easily soluble in water, so that a concentration higher than three per cent by weight was applied. The specific refraction r of the respective solution was calculated from these data using the Lorentz-Lorenz formula,

$$r=(n^2-1)/(n^2+2)\times 1/d$$

The molar refraction R of the dissolved salt was derived from this specific refraction by the application of the additivity rule,

$$R=MW[r(\text{soln.})-(100-w)\times r(\text{water})]/w$$

where w is the concentration of salt and MW is the molecular weight. The value R was found to be independent of concentration in the measured range.

TABLE I. MOLAR REFRACTION OF COMPLEX SALTS

	Molar refraction, cc.		
	Solution		Crystal[c]
Salt	Obs.	Lit.	
$K_3Cu(CN)_4$	46.8	—	44.9[d]
$K_2Zn(CN)_4$	37.8	—	37.5
$K_2Cd(CN)_4$	39.9	—	40.5
$K_2Hg(CN)_4$	43.1	—	43.2
$K_3Cr(CN)_6$	55.5	—	56.2
$K_3Mn(CN)_6$	61.0	—	—
$K_3Fe(CN)_6$	61.2	61.44[a], 60.91[b]	58.4
$K_4Fe(CN)_6$	67.4	67.8[a], 69.06[b]	—
$K_3Co(CN)_6$	59.2	—	—
$K_2Ni(CN)_4$	42.1	—	—
$K_2Al(C_2O_4)_3$	59.5	—	—
$K_2Fe(C_2O_4)_3$	66.4	—	—
$K_2C_2O_4$	22.5	—	—

a See Ref. 5.
b See Ref. 6.
c The values of density were taken from Ref. 1, and those of refractive index from Ref. 7 except that for $K_3Cu(CN)_4$.
d Refractive indices were taken from Ref. 8.

Results and Discussion

In Table I are presented our observed values of molar refraction of the complex salts in the dissolved state together with a few recorded values and also some estimated values for the crystalline salts. The molar refraction of aqueous complex anion was estimated, assuming that the contributions of cation and anion are additive. The value for aqueous K^+ ion was taken as 2.255 cc.[9] The molar refraction of aqueous ions is generally smaller than that of gaseous ions. For example the values: 0.20, 0.50 and 0.28 cc. were given by Fajans and Joos for gaseous Li^+, Na^+ and Mg^{2+} ions, respectively[10]. On the other hand, they gave −0.42, +0.200 and −1.57 cc. for the above-mentioned ions in the dissolved state. The difference between the values in the two states can be ascribed to the polarization, or the decrease of mobility of electrons in water molecules by the electrostatic force due to the cation concerned. Great polarizing power is expected from small ions of high valency. The negative values assigned to aqueous Li^+ and Mg^{2+} ions arise from the large polarization effect on the water molecules in the hydration sphere. However, the magnitude of this effect in hydrated ions seems to be too small and inaccurate to be discussed quantitatively. The size of complex anions is much larger than that of simple ions, therefore we may consider that the molar refraction of aqueous complex anion is approximately equal to that of gaseous complex anion.

We assume that the molar refraction of complex anions is given by the sum of the following three terms:

(1) The sum of the molar refractions of the constituents in the gaseous state. The term A in Table II gives the molar refraction of the imaginary complex anion in which there is neither metal-ligand nor ligand-ligand interaction.

2) G. Bauer, "Handbuch der Präparativen Anorgachen Chemie", F. Enke, Stuttgart (1954), pp. 807, 819.
3) W. C. Fernelius, "Inorganic Syntheses", vol. 2, McGraw-Hill Book Co., New York (1946), pp. 203, 213, 225, 227.
4) H. S. Booth, ibid., Vol. 1., Mc Graw-Hill Book Co., New York (1939), p. 35.
5) A. Heydweiller, *Physik. Z.*, **26**, 526 (1925).
6) M. T. Rogers and J. G. Malik, *J. Am. Chem. Soc.*, **77**, 6515 (1955).
7) A. N. Winchell and R. C. Emmons, "The Microscopic Characters of Artificial Inorganic Solid Substances or Artificial Minerals", John Wiley & Sons, Inc., New York (1931), pp. 173, 177, 178.
8) E. G. Cox, W. Wardlaw and K. C. Webster, *J. Chem. Soc.*, **1936**, 775.
9) K. Fajans and R. Lühdemann, *Z. physik. Chem.*, **B29**, 150 (1935).
10) K. Fajans and G. Joos, *Z. Physik*, **23**, 1 (1924).

(2) The contribution of polarization of ligands: the term P in Table II. The ligand-ligand interaction may be ignored because of the rather large size of cyanide and oxalate ions. Therefore, the magnitude of this term may be assumed to be proportional to the polarizing power of central metal ion; namely to the valency of metal ion and to the reciprocal of the square of metal-ligand distance.

(3) The contribution of delocalization of electrons by the formation of π-bonds: the term D in Table II. The magnitude of this term may depend on the configuration of complex ion and the number of available electrons.

TABLE II. MOLAR REFERACTION OF COMPLEX ANIONS

Anion	R for anion cc.	A, cc. (additive)	P, cc. (polarization)	D, cc. (delocalization)
$Cu(CN)_4^{3-}$	40.1	34.7	− 6.4	11.8
$Zn(CN)_4^{2-}$	33.3	34.3	−12.8	11.8
$Cd(CN)_4^{2-}$	35.4	36.3	−12.8	11.9
$Hg(CN)_4^{2-}$	38.6	36.7	−12.8	14.7
$Cr(CN)_6^{3-}$	48.8	50.9	−16.5	15.4
$Mn(CN)_6^{3-}$	54.3	50.9	−16.5	20.9
$Fe(CN)_6^{3-}$	54.4	50.9	−16.5	21.0
$Fe(CN)_6^{4-}$	58.2	51.1	−11.0	19.1
$Co(CN)_6^{3-}$	52.5	50.9	−16.5	19.1
$Ni(CN)_4^{2-}$	37.6	34.3	− 8.7	(12)
$Al(C_2O_4)_3^{3-}$	52.8	54.1	− 1.3	0
$Fe(C_2O_4)_3^{3-}$	59.7	54.5	− 1.3	6.5

The molar refraction of gaseous cyanide ion was estimated to be 8.40 cc. based on the value observed for potassium cyanide in the dissolved state[11] and that of gaseous oxalate ion 18.0 cc. similarly. Pauling has given the following values for gaseous cations; Cu^+ 1.08, Zn^{2+} 0.72, Cd^{2+} 2.74, Hg^{2+} 3.14 and Al^{3+} 0.136 cc.[12] We assumed 0.7 cc. for Ni^{2+} and Fe^{2+} ions and 0.5 cc. for trivalent ions of the first transition metals. The terms A given in Table II were calculated using these values. It must be noted that the values of tetrahedral complex anions are in good agreement with the observed molar refractions except in the case of $Cu(CN)_4^{3-}$ ion, However, as is shown in the following paragraph, this agreement arises from the compensation between the terms P and D.

For the estimation of the term P we must know the distance between ligand and central metal ion. Only the following values are available; Zn–CN (center) 2.61, Cd–CN 2.67 and Hg–CN 2.65 Å[13]. We may assume that the required distances are the same in the series of tetrahedral cyano complex anions including $Cu(CN)_4^{3-}$. The maximum error arising from this assumption may not be more than 10 per cent of the term P or about 1 cc., as seen in Table II. The positive charge on central metal ion is mostly neutralized as a result of polarization of ligands. The magnitude of the term D for the isoelectronic $Cu(CN)_4^{3-}$ and $Zn(CN)_4^{2-}$ ions may be assumed to be roughly the same. Therefore, the chief difference between the two is that of the valency of the central metal ions, and the term P for $Cu(CN)_4^{3-}$ ion may be about one half of that for $Zn(CN)_4^{2-}$ ion. Consequently the difference between $(A-R)$ for $Zn(CN)_4^{2-}$ ion and that for $Cu(CN)_4^{3-}$ ion gives the magnitude of the term P for the latter. The term P estimated for $Zn(CN)_4^{2-}$ ion was assumed to be applicable to the other two tetrahedral complex anions. The $Cu(CN)_4^{3-}$ ion has been known to dissociate appreciably in dilute solution[14]. However, we ignored this fact in our treatment of molar refraction because rather concentrated solutions were used for our measurements.

For octahedral cyano complex anions the isoelectronic ions $Fe(CN)_6^{4-}$ and $Co(CN)_6^{3-}$ were used for the basis of discussion. We assumed again that the distance between metal ion and ligand is nearly constant in these five complex anions, therefore the term P for $Fe(CN)_6^{4-}$ ion may be about two thirds of that for $Co(CN)_6^{3-}$ ion and the term D for this pair may be roughly the same. The term P estimated for $Co(CN)_6^{3-}$ ion was applied to the other trivalent cyano complex anions.

The contribution of polarization effect on a cyanide ion was found to be about 1.6 cc. per unit charge on central metal ion for tetrahedral anions and about 0.9 cc. per unit charge for octahedral ones. The similar polarization found in the reaction,

$$H^+ + CN^- \rightarrow \text{gaseous HCN } (6.47\text{ cc.})^{15}$$

1.93 cc. may be compared with the above two estimations. As the mutual repulsion of cyanide ions in a complex anion must be weaker in a tetrahedral configuration than in an octahedral one, the cyanide ions in the former are closer to the central metal ion than those in the latter. Therefore, the observed order of polarization of a cyanide ion; HCN > tetrahedral complex anion > octahedral complex anion seems to be reasonable. The contribution of electron-delocalization to molar refraction was estimated to be around 3 cc. per cyanide ion for both tetrahedral and octahedral complex

11) M. Le Blanc and P. Rohland, *Z. physik. Chem.*, **19**, 261 (1896).
12) L. Pauling, *Proc. Roy. Soc.*, **A114**, 181 (1927).
13) R. G. Dickinson, *J. Am. Chem. Soc.*, **44**, 774 (1922).
14) J. H. Baxendale and D. T. Westcott, *J. Chem. Soc.*, **1959**, 2347.
15) K. Fajans, *Z. physik. Chem.*, **B24**, 103 (1934).

anions. The term P for the square planar $Ni(CN)_4^{2-}$ ion was obtained using a value of 4×3 cc. for its term D, and the polarization of a cyanide in per unit charge in this anion seems to be nearly the same as that for octahedral complex anions.

In the case of oxalato complex anions, the observed molar refraction of $Al(C_2O_4)_3^{3-}$ ion, in which the aluminum ion has no d-electron for π-bonding, is only slightly smaller than its term A or we may say in agreement with its term A within the limit of estimations. This agreement suggests that the polarization of the oxalate ions by the field of the aluminum ion is very small. The term D for $Fe(C_2O_4)_3^{3-}$ ion was found to be about 6.5 cc. This value is much less than that for cyano complex anions of the inner orbital type.

TABLE III. COMPARISON BETWEEN MOLAR REFRACTION AND MOLAR VOLUME OF CYANO COMPLEX ANIONS

Anion	Molar refraction cc.	Molar volume[a] cc.
$Cu(CN)_4^{3-}$	40.1	93
$Zn(CN)_4^{2-}$	33.3	118
$Cd(CN)_4^{2-}$	35.4	128
$Hg(CN)_4^{2-}$	38.6	126
$Cr(CN)_6^{3-}$	48.8	135
$Mn(CN)_6^{3-}$	54.3	—
$Fe(CN)_6^{3-}$	54.4	129
$Fe(CN)_6^{4-}$	58.2	126
$Co(CN)_6^{3-}$	52.5	129
$Ni(CN)_4^{2-}$	37.6	98

a These values were taken from Ref. 1.

Recently Hieber and his collaborators have discussed the molar volumes of some complex cyano anions[16,17]. They have observed the following series of molar volumes for the isoelectronic anions with the configuration of rare gas type,

$$Zn(CN)_4^{2-} > Cu(CN)_4^{3-} > Ni(CN)_4^{4-}$$

and $$Co(CN)_6^{3-} > Fe(CN)_6^{4-} > Mn(CN)_6^{5-}$$

and concluded that the decrease of molar volume can be correlated with the increasing double bond character of metal-carbon bonds. The importance of polar structures as the determining factor was also pointed out for the molar volume of anions of non-rare gas type. Although molar refraction is a measure of size of complex anion, these two physical quantities have no simple correlation as seen in Table III. For the pairs of isoelectronic complex anions; $Cu(CN)_4^{3-}$ and $Zn(CN)_4^{2-}$, and $Fe(CN)_6^{4-}$ and $Co(CN)_6^{3-}$, the molar refractions were found in the reverse order to the molar volumes.

16) W. Hieber, R. Nast and J. G. Floss, *Z. anorg. u. allgem. Chem.*, **283**, 188 (1956).
17) W. Hieber and O. Vohler, ibid., **294**, 219 (1958).

Summary

The molar refractions of ten cyano and two oxalato complex salts were measured in the dissolved state using the NaD line. The molar refractions of complex anions were assumed to be given by the sum of (1) the molar refractions of the ligands and the central metal ion in the gaseous state, (2) the polarization of the ligands due to the field of the central metal ion, and (3) the delocalization of electrons by the metal-ligand π-bonding. The estimation of each term was attempted on the assumption that the chief difference between isoelectronic anions, for example $Cu(CN)_4^{3-}$ and $Zn(CN)_4^{2-}$, is that of the valency of the central metal ions and the contribution of delocalization is roughly the same in such a pair. The polarization of a cyanide ion was found to be about 1.6 cc. per unit charge of metal ion for tetrahedral anions and about 0.9 cc. for octahedral ones. The contribution of π-bonding was estimated to be around 3 cc. per metal-ligand bond for both of the above-mentioned cyano complex anions. The small polarization and delocalization effects were observed in the case of oxalato complex anions.

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