vestigated by Perrier and Segré.[2] More recently, Jacobi[27] has reported that manganese sulfide formed by treating Mn(NO₃)₂ with an ammoniacal hydrogen sulfide solution also "carries down" this element. Quantitative measurements of the co-precipitation of technetium with CuS, PdS and Re₂S₇ formed in hydrochloric acid solutions at 95° and digested for 30 minutes (Table IV) were performed. Copper sulfide was of limited value because of its solubility in concentrated hydrochloric acid. The co-precipitation of technetium by palladium sulfide occurred through the entire range of acidity. However, adsorption effects may be important, for when palladium was precipitated at room temperature from 12 N hydrochloric acid little or no technetium was removed from solution. In some instances the failure of trace quantities of technetium to co-precipitate may be of practical value, as for example in the separation of technetium from fission products in the radiochemical analysis for technetium in such mixtures. It has been reported[2,27] that neither zirconium hydroxide precipitated by ammonia nor the hydrous oxides of tantalum and niobium formed by the treatment of alkali tantalates or niobates with sulfuric

(27) E. Jacobi, *Helv. Chim. Acta*, **31**, 2118 (1948).

TABLE IV

CO-PRECIPITATION OF TECHNETIUM WITH VARIOUS ACID-INSOLUBLE SULFIDES AT 95°

| HCl, N | Fraction of technetium co-precipitated (%) | | | |
	CuS	PdS	Re₂S₇	PtS₂[a]
1	100	85	96	100
3	100	83	98	95
6	16	22	58	31
9	..	22	6.5	2
12	..	16; 1[b]	1	2

[a] Data taken from Fig. 3; [b] precipitation at room temperature, no digestion.

acid, nor the 8-hydroxyquinolate of molybdenum co-precipitates pertechnetate ion. We have observed additionally that Tc(VII) is not carried from aqueous solutions by these precipitates: ferric hydroxide, silver or lead molybdate and α-benzoin oxime molybdate.

OAK RIDGE, TENNESSEE

Studies in Coördination Chemistry. VI. The Dielectric Polarization of Some Metal Chelates of N-Alkylsalicylaldimines[1]

BY L. SACCONI, M. CIAMPOLINI, F. MAGGIO AND G. DEL RE

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Measurements have been made of the dielectric polarization at 25° of benzene and dioxane solutions of ten four-coördinated chelates of palladium(II), copper(II) and cobalt(II) with N-alkylsalicylaldimines. The small positive difference between the total polarization and the electronic polarization ($P_{2\infty} - P_E$) for palladium(II) chelates was attributed to atom polarization; these complexes, therefore, must have a *trans*-planar configuration. In the case of copper(II) chelates, the higher $P_{2\infty} - P_E$ values (50–100 cc.) can be considered as due, at least in part, to the existence of unsymmetrical (*cis* or more probably pyramidal) forms. The chelate of cobalt(II) with N-cyclohexylsalicylaldimine, whose magnetic moment (4.4 B.M.) agrees with a tetrahedral structure, shows a $P_{2\infty} - P_E$ value of about 500 cc. This fact corroborates our previous conclusion against a tetrahedral structure for the magnetically anomalous nickel(II) complexes with N-alkylsalicylaldimines.

Introduction

Comparatively few measurements of the dipole moments of metal complexes have been reported. One reason for this is the difficulty of explaining the large difference between the total and electronic polarizations observed for these compounds.[2-4]

In the case of symmetrical complexes, such as the metal acetylacetonates, this difference $P_{2\infty} - P_E$ has been attributed[5] entirely to atom polarization, even though it appears to be very large in comparison with the usual P_A values of organic compounds. In fact $P_{2\infty} - P_E$ values up to 68 cc. have been reported by MacQueen and Smith[6] for eight-coördinated complexes which are believed to be symmetrical or found to be symmetrical as solids.

The atom polarization of a molecule is defined as that part of the total polarization which arises from changes in the geometrical structure of a molecule induced by an external field. It is obvious that its magnitude depends strictly on the various vibrational degrees of freedom of the molecule. Coop and Sutton[5] showed that in the metal acetyl-

(1) Presented at the International Conference on Coördination Chemistry, London, April, 1959.

(2) J. W. Smith, "Electric Dipole Moments," Butterworths, London, 1955, p. 271.

(3) C. C. Meredith, L. Westland and G. F. Wright, THIS JOURNAL, **79**, 2385 (1957).

(4) P. J. McCarty and A. E. Martell, *ibid.*, **78**, 2106 (1956).

(5) J. W. Smith and W. R. Angus, *Proc. Roy. Soc. (London)*, **A131**, 372 (1932); A. Finn, G. Hamps and L. E. Sutton, *J. Chem. Soc.*, 1254 (1938); I. E. Coop and L. E. Sutton, *ibid.*, 1269 (1938).

(6) J. MacQueen and J. W. Smith, *ibid.*, 1821 (1956).

acetonates the bending vibrations of the chelate groups, considered as rigid units, were sufficient to account for the P_A values of such complexes.

In a previous paper[7] the dielectric polarization of bis-(N-alkylsalicylaldimine)–nickel(II) complexes was studied in an attempt to elucidate the behavior of these complexes, which, while diamagnetic in the solid state, become paramagnetic in solutions[8] and melts.[9] Furthermore, these nickel complexes have high $P_{2\infty} - P_E$ values. We felt that a similar study of analogous complexes containing other metals was needed to check our interpretation of the results and to determine the effect of the metal on the dielectric polarization. In this work, therefore, the dielectric behavior of bis-(N-alkylsalicylaldimine) complexes of palladium(II), copper(II) and cobalt(II), with the general formula
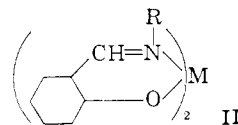
where R = Me, Et, *n*-Pr, *n*-Bu or *n*-Am, was investigated.

Experimental

Preparation of the Metal Complexes. Palladium(II).— A cold solution containing 1.1 g. (0.006 mole) of palladium

(7) L. Sacconi, P. Paoletti and G. Del Re, THIS JOURNAL, **79**, 4062 (1957). (Part I of this series.)

(8) J. B. Willis and D. P. Mellor, *ibid.*, **69**, 1237 (1947).

(9) L. Sacconi, R. Cini and F. Maggio, *ibid.*, **79**, 3933 (1957).

dichloride in 0.5 ml. of concd. hydrochloric acid and 30 ml. of water was adjusted to pH 5–6 by the addition of 20% aqueous sodium acetate. A solution of 1.46 g. (0.012 mole) of salicylaldehyde in 20 ml. of 95% ethanol was added. The yellow-orange product was filtered, washed with alcohol and ether and recrystallized from chloroform. The analytical results correspond to the compound bis-salicylaldehyde–palladium(II). As the crude product decomposed easily with separation of a black palladium powder, it was used directly for the preparation of the complexes according to the following general method: 1.06 g. of the crude product suspended in 30 ml. of 0.2 M solution of the alkylamine in chloroform was refluxed on a water-bath until solution was complete. After separation of some black powdery palladium, the excess solvent was evaporated and the yellow precipitate recrystallized from chloroform and petroleum ether.

The bis-(N-alkylsalicylaldimine)–palladium(II) complexes so prepared are stable yellow-gold crystalline products soluble in alcohol, ether, dioxane, chloroform and benzene. Palladium was determined as the metal by digestion of the sample in a Kjeldahl flask with fuming sulfuric acid and then precipitation of the palladium with ammonium formiate.

Bis-salicylaldehyde–palladium(II): yellow sheets, sparingly soluble in benzene and chloroform. *Anal.* Calcd. for $C_{14}H_{10}O_4Pd$: C, 48.19; H, 2.89; Pd, 30.58. Found: C, 48.03; H, 2.92; Pd, 30.74.

Bis-(N-methylsalicylaldimine)–palladium(II): m.p. 265–266°. *Anal.* Calcd. for $C_{16}H_{16}O_2N_2Pd$: N, 7.47; Pd, 28.45. Found: N, 7.66; Pd, 28.36.

Bis-(N-ethylsalicylaldimine)–palladium(II): m.p. 217–218°. *Anal.* Calcd. for $C_{18}H_{20}O_2N_2Pd$: N, 6.95; Pd, 26.47. Found: N, 7.12; Pd, 26.56.

Bis-(N-propylsalicylaldimine)–palladium(II): m.p. 187–188°. *Anal.* Calcd. for $C_{20}H_{24}O_2N_2Pd$: N, 6.49; Pd, 24.75. Found: N, 6.54; Pd, 24.90.

Bis-(N-butylsalicylaldimine)–palladium(II): m.p. 183–184°. *Anal.* Calcd. for $C_{22}H_{28}O_2N_2Pd$: N, 6.10; Pd, 23.24. Found: N, 6.14; Pd, 23.58.

Bis-(N-amylsalicylaldimine)–palladium(II): m.p. 178–179°. *Anal.* Calcd. for $C_{24}H_{32}O_2N_2Pd$: N, 5.75; Pd, 21.89. Found: N, 5.92; Pd, 21.78.

Copper(II).—The copper chelates of this series have been prepared by Charles.[10] We have found this method more suitable: one mole of the complex bis-salicylaldehyde–copper(II)[11] was refluxed with an alcohol or water–alcohol solution of the appropriate primary amine (2 moles) until solution was complete. On cooling crystals separated which were recrystallized from a mixture of chloroform and alcohol. The crystals, which range from a green-brown to brown with lengthening of the amine-alkyl chain, are soluble in alcohol, dioxane, chloroform and benzene, and insoluble in petroleum ether.

Bis-(N-methylsalicylaldimine)–copper(II): m.p. 154°. *Anal.* Calcd. for $C_{16}H_{16}O_2N_2Cu$: N, 8.61; Cu, 19.15. Found: N, 8.61; Cu, 18.97.

Bis-(N-ethylsalicylaldimine)–copper(II): m.p. 145°. *Anal.* Calcd. for $C_{18}H_{20}O_2N_2Cu$: N, 7.78; Cu, 17.66. Found: N, 8.15; Cu, 17.77.

Bis-(N-propylsalicylaldimine)–copper(II): m.p. 127°. *Anal.* Calcd. for $C_{20}H_{24}O N_2Cu$: N, 7.22; Cu, 16.38. Found: N, 7.63; Cu, 16.50.

Bis-(N-butylsalicylaldimine)–copper(II): m.p. 80°. *Anal.* Calcd. for $C_{22}H_{28}O_2N_2Cu$: N, 6.73; Cu, 15.28. Found: N, 7.02; Cu, 15.57.

Bis-(N-amylsalicylaldimine)–copper(II): m.p. 96°. *Anal.* Calcd. for $C_{24}H_{32}O_2N_2Cu$: N, 6.31; Cu, 14.31. Found: N, 6.63; Cu, 14.26.

Bis-(N-cyclohexylsalicylaldimine)–cobalt(II).—A mixture of 6.74 g. (0.02 mole) of bis-salicylaldehyde—cobalt(II) dihydrate[11] and 3.97 g. (0.04 mole) of cyclohexylamine in 50 ml. of alcohol was refluxed for 1 hr. on a water-bath. The crude product was crystallized from chloroform and petroleum ether to yield 7.1 g. of red crystals, m.p. 182–184°. *Anal.* Calcd. for $C_{26}H_{32}O_2N_2Co$: C, 67.37; H, 6.96; N, 6.04; Co, 12.72. Found: C, 67.36; H, 6.95; N, 6.08; Co, 12.60.

Measurements.—The dielectric constants of the solutions relative to those of the solvents were determined with a

heterodyne oscillator and a cell previously described.[12] The solvents, benzene and dioxane, were purified by the standard procedures required for dipole moment measurements. For each compound, measurements were made on at least four solutions. The refractive indices were determined with a Pulfrich refractometer, and the densities with a pycnometer. The main source of error in the determinations was the low solubility of the first members of the series; in one case, bis-(N-methylsalicylaldimine)–palladium(II), the solubility was so low that it was impossible to obtain reasonable accuracy. All measurements were carried out at 25°.

The molar polarizations of the solutes at infinite dilution were determined by the method of Halverstadt and Kumler.[13] Plots of the dielectric constants ϵ_{12} and the densities d_{12} vs. the molar fractions of the solute f_2 gave straight lines, over the concentration range studied, with the slopes α and β, respectively. The extrapolated values ϵ_1 and d_1 for $f_2 = 0$ were in most cases very close to the experimental values for the pure solvents. The P_E values, which were determined experimentally, varied according to the additivity rule of molar refractions.

Results and Discussion

All the chelates which were sufficiently soluble to permit a cryoscopic determination of the molecular weight were found to be monomeric in benzene and dioxane.

Table I contains the dielectric polarization data for the complexes investigated. It should be noted that a cobalt complex has been included, whose $P_{2\infty} - P_E$ value is 503 cc. This complex was selected because, unlike its analogs in the alkyl series, it is not readily oxidized. The value of μ_{eff} for the complex, both as a solid and in benzene solution, was found to be 4.4 B.M., which corresponds to three unpaired electrons. This complex, therefore, has a tetrahedral structure.[14] Accordingly, one would expect the tetrahedral configuration of a bis-salicylaldimine–metal(II) complex to have a $P_{2\infty} - P_E$ value of the order of 500 cc. and obviously a larger value should be attributed to the *cis*-planar configuration.

This conclusion is supported by the measurements of McCarty and Martell,[4] who found $P_{2\infty} - P_E$ values of 400–500 cc. for *cis*-planar chelates of Cu(II), Co(II), Ni(II) and Pd(II) with bisacetylacetoneëthylendiimine; the Co(II) complexes gave the lowest values.

According to the magnetic measurements,[7,15] a benzene solution of bis-(N-methylsalicylaldimine)–nickel(II) at 25° contains about 40% of the complex in the paramagnetic form. Assuming the tetrahedral nickel(II) complex to have a $P_{2\infty} - P_E$ value equal to that of bis-(N-cyclohexylsalicylaldimine)–cobalt(II), *i.e.* about 500 cc. ($\mu = 4.9$ D), we would expect the $P_{2\infty} - P_E$ value of the above nickel complex in benzene solution to be about 200 cc. Instead we found a value of 27 cc., or 17 cc. if allowance is made for P_A which is assumed to be equal to 10% P_E. This is additional evidence against a tetrahedral structure for the paramagnetic form of bis-(N-methylsalicylaldimine)–nickel(II).

The $P_{2\infty} - P_E$ values for the bis-(N-alkylsalicylaldimine)–Pd(II) complexes range from 8 to 24 cc., *i.e.*, 8–16% of P_E. These are the lowest

(10) R. G. Charles, *J. Org. Chem.*, **22**, 677 (1957).

(11) P. Pfeiffer, E. Breith, E. Lübbe and T. Tsumaki, *Ann.*, **503**, 84 (1933).

(12) G. Speroni, G. Del Re and C. Caselli, *Ricerca Sci.*, **26**, 3115 (1956).

(13) I. Halverstadt and W. Kumler, This Journal, **64**, 2988 (1942).

(14) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 12 (1954).

(15) H. C. Clark and A. L. Odell, *ibid.*, 3431 (1955).

TABLE I

DIELECTRIC POLARIZATION DATA FOR BIS-(N-ALKYLSALICYLALDIMINE)-PALLADIUM(II), COPPER(II) AND COBALT(II) COMPLEXES AT 25°

Bis-N-alkylsalic. complex	Solvent	ϵ_1	α	d_1	β	R_D (cc.)	$P_{2\infty}$ (cc.)	$P_{2\infty} - R_D$ (cc.)	$K_b \times 10^{12}$ (erg/ radian²)
N-Ethyl–Pd	Bzn	2.2739	2.58	0.8720	2.00	109	126	17	2.8
	Diox	2.2162	3.03	1.0273	1.57	109	118	9	5.3
N-Propyl–Pd	Bzn	2.2731	2.63	0.8725	1.71	118	142	24	2.0
	Diox	2.2197	3.09	1.0274	1.41	118	131	13	3.6
N-Butyl–Pd	Bzn	2.2736	2.63	0.8725	1.88	128	145	17	2.9
	Diox	2.2209	2.61	1.0274	1.25	128	136	8	5.9
N-Amyl–Pd	Bzn	2.2732	2.41	0.8725	1.83	137	153	16	3.0
	Diox	2.2202	3.30	1.0272	1.28	137	153	16	3.0
N-Methyl–Cu	Bzn	2.2780	5.28	0.8732	1.31	94	156	60	..
	Diox	2.2194	5.40	1.0276	1.01	94	146	52	..
N-Ethyl–Cu	Bzn	2.2752	7.27	0.8725	1.41	105	192	97	..
	Diox	2.2222	6.66	1.0272	0.95	105	174	67	..
N-Propyl–Cu	Bzn	2.2764	7.17	0.8727	1.36	115	202	87	..
	Diox	2.2207	7.30	1.0270	0.84	115	194	79	..
N-Butyl–Cu	Bzn	2.2756	7.65	0.8729	1.31	124	220	96	..
	Diox	2.2209	7.39	1.0271	0.74	124	206	82	..
N-Amyl–Cu	Bzn	2.2742	7.83	0.8730	1.30	133	232	99	..
	Diox	2.2144	7.92	1.0273	0.66	133	223	90	..
N-Cyclohexyl–Co	Bzn	2.2702	36.59	0.8725	1.63	144	647	503	..
N-Methyl–Ni	Bzn					99	125	26	1.5
	Diox					99	143	44	0.9
N-Ethyl–Ni	Bzn					108	128	20	2.1
	Diox					108	130	22	1.8
N-Propyl–Ni	Bzn					117	140	23	1.7
	Diox					117	148	31	1.3
N-Butyl–Ni	Bzn					127	149	22	1.8
	Diox					127	154	27	1.5
N-Amyl–Ni	Bzn					138	165	27	1.5
	Diox					138	179	41	1.0

reported for four-coördinated symmetrical chelates which usually have $P_{2\infty} - P_E$ values between 20 and 30 cc. In fact this range is about the same as that of organic molecules (5–15% of P_E). In this case therefore, the $P_{2\infty} - P_E$ differences must be due to atom polarization, and a trans-planar configuration can be assigned to these complexes. It should be remembered that the same conclusion was reached for the analogous nickel complexes.[7] In the latter case, however, larger values of $P_{2\infty} - P_E$ (19 to 44 cc.) were found. This discrepancy can be accounted for by using the treatment of MacQueen and Smith,[6] according to whom the behavior of a planar complex with respect to atom polarization corresponds practically to that of a single unidimensional vibrator.

If only bending vibrations are taken into account

$$P_A = 4\pi N\mu^2/k_b \qquad (1)$$

where k_b is the force constant relative to the bending vibration of the vector μ which represents the dipole moment of one vibrating entity. Now, palladium is more electrophilic, and therefore less basic than nickel, as the sum of the first and second ionization potentials shows[16]: Pd, 27.8; Ni, 25.85 e.v. The palladium–ligands bonds should therefore be more homopolar in character than the nickel–ligands bonds and, according to Coop and Sutton,[5] should have higher force constants. On the other hand, the electric moment μ of the vibrating units depends both on the polar character

of the coördinated bonds and on the molecular parameters of the complexes. As the values for the covalent radii of the two metal atoms are[17] Pd, 1.278 Å. and Ni, 1.149 Å., the substitution of nickel for palladium should change the molecular parameters, but the extent of this change cannot be predicted. The coördinated bonds of palladium complexes may, however, have a higher charge separation and a smaller ionic character than those of nickel complexes. As these two effects are in a way opposite to each other, it appears safe to assume that the value of μ does not change as one proceeds from the complexes of palladium to those of nickel. Coop and Sutton,[5] and subsequently MacQueen and Smith,[6] made a similar assumption, and the results of MacCarty and Martell[4] are consistent with this view. Accordingly, P_A should be an inverse function of k_b, and it will be larger for the nickel complexes which have lower k_b values.

The k_b values in Table I were calculated from eq. 1 with $\mu = 7.2$ D, the value used by MacQueen and Smith for bis-(N-methysalicylaldimine)–copper(II).

In the case of palladium and the homologous nickel–salicylaldimine complexes, $P_{2\infty} - P_E$ shows a "zig-zag" dependence upon the number n of carbon atoms in the alkyl side chain. The ligands deriving from amines with an even n will be stronger donors and favor the establishment of

(16) W. Latimer, "Oxidation Potentials," 2nd Ed., Prentice–Hall, Inc., New York, N. Y., 1952, pp. 15 f.

(17) T. Moeller, "Inorganic Chemistry," John Wiley and Sons, New York, N. Y., 1952, p. 135.

bonds of lower polarity and hence of less flexible structures, i.e., with a lower atom polarization.

The $P_{2\infty} - P_E$ values of the copper complexes are larger than those of the nickel and palladium complexes of the same series, and much larger than those reported for four-coördinated complexes which are considered to be symmetrical. We, therefore, believe that this difference should be attributed in part to an orientation polarization.

These high $P_{2\infty} - P_E$ values might be due to an equilibrium existing in solution between cis- and trans-planar forms, an hypothesis suggested by MacQueen and Smith[6] to explain the large values of $P_{2\infty}$ and $P_{2\infty} - P_E$ found for bis-(N-phenyl-salicylaldimine)–copper(II). Our results appear to indicate that the proportion of the cis-planar form should increase with the length of the alkyl chain. This is not easy to understand, because one would expect in the cis-form a tendency toward

"crowding," and therefore a repulsion of the alkyl chains with increasing chain length.

It therefore appears more reasonable to assume that the unsymmetrical form is pyramidal. In this connection it may be remembered that Pfeiffer and co-workers,[18] on the basis of measurements of the Cotton effect in salicylaldimine–copper(II) chelates, suggested that the coördinating bonds of these complexes are not co-planar; also a pyramidal configuration of the four coördinating bonds has been found in another copper-(II) complex, bis-(dimethylglyoxime)–copper(II), in the solid state.[19]

Acknowledgment.—We are indebted to the Italian "Consiglio Nazionale delle Ricerche" (C.N.-R.) for the financial support of this work.

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PALERMO, ITALY

Ionic Association in Polyvalent Symmetrical Electrolytes. I. Conductances of Several Rare Earth Hexacyanocobaltates(III) in Dioxane–Water Mixtures[1]

BY GORDON ATKINSON

The conductances of lanthanum, neodymium, samarium and yttrium hexacyanocobaltates(III) have been measured in dioxane–water mixtures at 25°. All measurements were made in the concentration range below 0.002 molar. Dissociation constants for these 3–3 electrolytes are calculated by the method of Shedlovsky (K is approximately 10^{-4}). Ion-pair size parameters are calculated by Bjerrum's method. Although Walden's rule is obeyed, the Bjerrum "a" parameter varies with the dielectric constant of the solvent mixture for a given salt, indicating lack of adherence to the electrostatic Bjerrum model. Yttrium cobalticyanide gives results somewhat at odds with the other three salts.

Recent advances in electrolyte conductance theory[2] have demonstrated the need for further data on polyvalent salts for testing the range of validity of the theory. A large number of 1–1 salts have been investigated in a great variety of solvent mixtures.[3] The theory has been proven valid for many of these salts over the predicted concentration range ($\kappa a < 0.2$).[4] Unfortunately, few, if any, strong electrolytes of higher valence types have been found. This problem is intensified by the fact that the theoretical extensions have been made only for symmetrical salts.

This investigation is the first of a series on polyvalent salts and ionic association. Since highly dissociated electrolytes of the 3–3 type have not yet been found, it was decided to explore further some weak electrolytes, the rare earth hexacyanocobaltates(III). By using the rare earths with their very similar chemical properties but different ionic radii it should be possible to relate the association constants and ion-pair size parameters to the dielectric constant of the solvent and the ionic radius.

(1) Presented at the 134th national meeting of the American Chemical Society, Chicago, Illinois, September 10-16, 1958.

(2) (a) R. M. Fuoss and L. Onsager, J. Phys. Chem., **61**, 668 (1957); (b) R. M. Fuoss, THIS JOURNAL, **79**, 3301 (1957).

(3) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd Ed., Reinhold Publ. Co., New York, N. Y., 1958, Chapter 6.

(4) R. M. Fuoss and C. A. Kraus, THIS JOURNAL, **79**, 3304 (1957).

Procedure

The rare earths were Lindsay Chemical Co. 99.9% pure grade. The dioxane was purified by the method of Kraus and Vingee.[5] The water used was double-distilled and had a specific conductance of less than 1.5×10^{-6} mho. The $K_3Co(CN)_6$ for the preparation of the rare earth salts was obtained from Amend and Co. and recrystallized from water to remove HCN traces.

The rare earth hexacyanocobaltates(III) were prepared by the method of James and Willard.[6] Since they are of low solubility they were not recrystallized but were washed extensively with water and alcohol to remove the more soluble impurities. On desiccation over concentrated H_2SO_4 they all reached the composition $RCo(CN)_6 \cdot 5H_2O$ after 1–2 weeks and were weighed in this form. They were analyzed for rare earth by the method of James[6] and for cobalt by a wet oxidation destruction of the $Co(CN)_6^{\equiv}$ and subsequent electrodeposition of the cobalt. The water analyses were obtained by Karl Fischer titration using the dead-stop end point method.

All conductance measurements were made in flask type cells with the various concentrations being prepared in the cell by the addition of rare earth stock solution to the solvent. The solvent was always the first material measured so as to obtain the correct solvent correction for that particular run. No measurements on solutions were made until a steady solvent specific conductance of less than 1.5×10^{-6} mho was obtained. Since smooth platinum electrodes were used resistance measurements were made at four audiofrequencies (400, 1000, 2000, 4000 c.p.s.) and an extrapolation to "infinite frequency" made by an R versus $1/\sqrt{f}$ plot. Corrections to the cell constants for solution conductance (Parker effect) also were made. The cells were cali-

(5) C. A. Kraus and R. A. Vingee, ibid., **56**, 513 (1934).

(6) C. James and P. S. Willard, ibid., **38**, 1497 (1916).