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-phenylsalicylaldimine)-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 coordinating 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.

(18) P. Pfeiffer, W. Christeleit, Th. Hesse, H. Pfitzner and H. Thielert, *J. prakt. Chem.*, **150**, 261 (1938).

(19) E. Frasson, R. Zannetti, R. Bardi, S. Bezzi and G. Giacometti, *J. Inorg. Nuclear Chem.*, **8**, 453 (1958).

PALERMO, ITALY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN]

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

BY GORDON ATKINSON

RECEIVED JULY 23, 1959

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.

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-

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(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).

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

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

TABLE I

EQUIVALENT CONDUCTANCES OF RARE EARTH COBALTICYANIDES IN DIOXANE–WATER MIXTURES AT 25°

Salt	% Dioxane	Equivalent conductance at $10^2 \times C^{1/2}$ 0	0.5	1.0	1.5	2.0	2.5	3.0
$LaCo(CN)_6$	0	168.38	155.62	141.88	128.15	116.53	105.70	98.62
	10	137.80	117.05	99.25	85.17	73.77	65.22	58.17
	20	116.63	92.82	72.94	58.18	45.37	37.75	31.15
$NdCo(CN)_6$	0	168.25	140.66	119.47	103.38	90.75	81.72	74.96
	10	137.70	101.42	78.72	65.48	56.18	50.37	45.80
	20	116.54	70.90	51.09	40.48	34.37	30.28	27.38
$SmCo(CN)_6$	0	167.48	124.05	105.30	90.56	79.82	72.43	66.85
	10	137.06	78.98	62.43	51.54	44.52	38.98	34.87
	20	116.01	45.86	32.36	24.98	20.93	16.83	14.08
$YCo(CN)_6$	0	168.08	126.97	108.59	94.45	82.64	74.79	69.40
	10	137.55	91.12	71.37	58.76	51.36	45.63	40.51
	20	116.42	60.37	43.43	34.22	28.50	24.79	21.80

brated as a function of solution resistance and frequency using the Jones and Bradshaw KCl standards.[7]

The electrical apparatus for the conductance measurements consisted of a Leeds and Northrup Jones bridge, a General Radio 1301A low-distortion oscillator, a General Radio 1231B amplifier with a 1231 P-5 filter, and a Dumont 304H oscilloscope to serve as a null indicator. Ground procedures were those recommended by Dike.[8]

The bridge and constant temperature bath were placed on a copper sheet which served as a common ground for the whole measurement apparatus. All measurements were made at 25 ±.005° in a mineral oil-bath. The temperature was measured with a calorimeter thermometer recently checked against a Bureau of Standards calibrated platinum resistance thermometer.

Calculations and Results

After frequency and solvent corrections had been made preliminary Λ_0 values were estimated using Walden's rule,[9] and previously published data on the rare earth ions[10] and the hexacyanocobaltate(III) ion.[11] Viscosity data were obtained from ref. 3. Then the method of Shedlovsky[12] was applied to calculate final Λ_0 and K values. The equivalent conductances at rounded values of the concentration are given in Table I.

Table II gives the dissociation constants and the Λ_0 values for the four salts in each of the three solvent mixtures. The λ_0 values for the rare earth ions agree well with the values previously published.[10]

The Bjerrum model of ion association for a 3–3 electrolyte can be expressed by the equations (see ref. 2, p. 292)

$$-\log K = 8.983 - 3 \log D + \log Q(b)$$
$$-\log b = 4.300 + \log D + \log a$$

In these equations D is the dielectric constant of the solvent mixture, a is the "mean distance of closest approach," K is the dissociation constant and Q(b) is the function

$$Q(b) = \int_2^b e^Y Y^{-4}\, dY$$
$$\text{where } b = \frac{|Z_1Z_2|e^2}{aDKT}$$

TABLE II

DISSOCIATION CONSTANTS AND EQUIVALENT CONDUCTANCES AT INFINITE DILUTION

Salt	% Dioxane	$K \times 10^{-4}$	Λ_0
$LaCo(CN)_6$	0.0	3.835	168.36
	10.0	1.891	137.82
	20.0	0.7672	116.60
$NdCo(CN)_6$	0.0	2.092	168.23
	10.0	1.122	137.72
	20.0	0.4929	116.53
$SmCo(CN)_6$	0.0	1.770	167.47
	10.0	0.9185	137.05
	20.0	0.4363	116.03
$YCo(CN)_6$	0.0	1.488	168.09
	10.0	0.8642	137.56
	20.0	0.3738	116.45

TABLE III

WALDEN'S RULE PARAMETER AND "a" PARAMETERS

Salt	$\Lambda_0\eta_0$	D(solv.)	"a"
$LaCo(CN)_6$	1.510	78.54	9.44
	1.508	69.69	9.22
	1.507	60.79	9.07
$NdCo(CN)_6$	1.506	78.54	7.51
	1.502	69.69	7.85
	1.505	60.79	8.15
$SmCo(CN)_6$	1.500	78.54	7.17
	1.495	69.69	7.45
	1.498	60.79	7.93
$YCo(CN)_6$	1.503	78.54	6.82
	1.505	69.69	7.35
	1.504	60.79	7.70

The a parameter was calculated by these equations and is listed in Table III with the D of the mixture and the Walden's rule parameter $\Lambda_0\eta_0$. As can be seen, Walden's rule is obeyed extremely well but a changes with D for each of the salts, decreasing with decreasing D for lanthanum and increasing for the other three. This difference between lanthanum and the other three rare earths is most probably an artifact of the Bjerrum approach due to the functional form of $Q(b)$ and the slightly different shape of the lanthanum phoreograms.

The constancy of $\Lambda_0\eta_0$ implies that there is little change in effective ion radius as D is changed. In all four cases we are dealing with hydrated rare earth ions and hydrated cobalticyanide ions. This viewpoint is supported by an examination of the visible spectra of the Nd and Sm solutions. The spectra do not change with the addition of dioxane in the range used here. By Bjerrum's

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(7) G. Jones and B. C. Bradshaw, THIS JOURNAL, **55**, 1780 (1933).

(8) P. H. Dike, *Rev. Sci. Instr.*, **2**, 379 (1931).

(9) Ref. 2, pp. 283–285.

(10) F. H. Spedding and G. Atkinson, "The Structure of Electrolytic Solutions," ed. W. J. Hamer, John Wiley and Sons, Inc., New York, N. Y., 1959, Chapter 22.

(11) J. C. James, *Trans. Faraday Soc.*, **46**, 1041 (1950).

(12) T. Shedlovsky, *J. Franklin Inst.*, **225**, 739 (1938).

theorem of corresponding solutions[13] this can only mean essentially no change in the immediate surroundings of the rare earth ions. Therefore the change of the a parameter with dielectric constant indicates that the purely electrostatic approach of Bjerrum is inadequate for these systems. We are faced again with the difficulty of naming an electrolyte that does not obey the criteria of the Onsager–Fuoss or Bjerrum approaches. At the present time I can only call these hexacyanocobaltates of the rare earths incompletely dissociated electrolytes, with no solid operational definition to clarify this title.

As more data accumulate it seems more and more apparent that different experimental approaches are giving us different association parameters for the same salts. These differences seem partially inherent in the methods and theories involved and not merely experimental artifacts. It would be of great value if the "association" of some symmetrical electrolyte, preferably of the 2–2 variety, could be measured by a coöperating group of researchers using four or five of the most important methods and a very exhaustive study made of the results.

A plot of $-\log K$ *versus* $1/D$ is a straight line for all four of these salts. However, the slope is less than that predicted by the Bjerrum equation. To obtain the Bjerrum line for this comparison a was assumed constant and equal to the pure water value. A plot of $-\log K$ *versus* cation radius is also a straight line within experimental error for lanthanum, neodymium and samarium. It is not possible to say much about the off-line position of yttrium without association data for some of the yttrium-group rare earths. Although yttrium is not a true rare earth its ionic radius lies between those of dysprosium and holmium. This leads to a strong similarity to the heavy rare earths both in its solution chemistry[14] and in complex formation.[15] It should be noted also that although the K and a values change in the order La, Nd, Sm, Y; the Λ_0 values and phoreograms fall in the order La, Nd, Y, Sm.

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[13] J. Bjerrum and C. K. Jørgensen, *Acta Chem. Scand.*, **7**, 951 (1953).

[14] Ref. 9, pp. 327, 330.

[15] (a) E. J. Wheelwright, F. H. Spedding and G. Schwarzenbach, THIS JOURNAL, **75**, 4196 (1953); (b) F. H. Spedding, J. E. Powell and E. J. Wheelwright, *ibid.*, **76**, 2557 (1954).

ANN ARBOR, MICH.

[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORIES OF THE OHIO STATE UNIVERSITY]

Complexes of Iron(II), Cobalt(II) and Nickel(II) with Biacetyl-bis-methylimine, 2-Pyridinal-methylimine and 2,6-Pyridindial-bis-methylimine

BY PAUL E. FIGGINS AND DARYLE H. BUSCH

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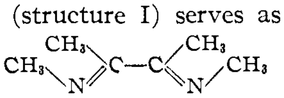
The synthesis of the series of octahedral complexes formed by iron(II), cobalt(II) and nickel(II) with biacetyl-bis-methylimine (BMI), 2-pyridinal-methylimine (PMI) and 2,6-pyridindial-bis-methylimine (PdMI) has been completed, and seven of the complexes are reported for the first time. The magnetic moments have been determined at room temperature. The values observed for the nickel(II) complexes are typical of spin-free, regular octahedral structures. The iron(II) complexes are essentially diamagnetic, exhibiting small residual paramagnetisms as is commonly found for spin-paired octahedral species involving d^6 ions. The moments for the cobalt(II) complexes are unusually low in value (2.31, 2.98 and 4.39 Bohr magnetons). It is suggested that these compounds exist as equilibrium mixtures of isomeric spin-free and spin-paired ions.

Introduction

In 1953, Krumholz[1] prepared the iron(II) complexes with α-diimines, of which biacetyl-bis-methylimine (structure I) serves as an example.[2]



I

The spectra of these complexes were compared with those of tris-(*o*-phenanthroline)-iron(II) and tris-(2,2′-bipyridine)-iron(II), and it was concluded that these α-diimine complexes were of the same type as the more familiar species. Krumholz found that only the N,N′-bis-methylimines formed this type of complex; *i.e.*, biacetyl-bis-anil, biacetyl-bis-benzilimine and biacetyl-bis-ethylimine do not form the permanganate colored iron(II) complexes. This observation is explained readily in terms of the great steric requirements of the relatively large alkyl or aryl groups. The interpretations of Krumholz were confirmed in later studies[3,4] in which it was shown that $[Fe(BMI)_3]\ I_2$ is spin-paired (essentially diamagnetic). Although a number of complexes have been reported for the benzil and phenyl analogs of BMI,[5] no metal ion other than iron(II) previously has been incorporated in complexes with simple aliphatic α-diimines. Further, the cobalt(II) and nickel(II) complexes reported here represent the only examples of octahedral complexes formed by α-diimines, other than those prepared by Krumholz.

During the course of investigations directed toward the verification of the nature of the complexes of iron(II) with α-diimines,[3] the iron(II) complex of 2-pyridinal-methylimine (structure II) was prepared. This ligand provides a simple structural link between 2,2′-bipyridine (structure III) and the α-diimines (structure I), being constituted of one functional group of each type. The results of studies of the visible, ultraviolet and infrared spectra, together with the diamagnetism of this complex, completed the synthesis and characterization of the series of octahedral, diamagnetic iron(II) complexes which were labeled, because of

[1] P. Krumholz, THIS JOURNAL, **75**, 2163 (1953).

[2] These abbreviations will be used extensively: BMI, biacetyl-bis-methylimine; PMI, 2-pyridinal-methylimine; PdMI, 2,6-pyridindial-bis-methylimine.

[3] D. H. Busch and J. C. Bailar, Jr., THIS JOURNAL, **78**, 1137 (1956).

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[5] G. Bähr, *Z. anorg. allgem. Chem.*, **267**, 137, 161 (1951).