[CONTRIBUTION OF THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

The Non-Exchange of Cobalt in Certain Complex Salts

BY JOHN F. FLAGG

Exchange reactions involving elements in various states of valency have been widely investigated. Arsenic, bromine, carbon, chlorine, iodine, manganese, mercury, phosphorus, silver, sulfur, and zinc are among the elements which have been studied.[1] This paper presents the results of an investigation of exchange reactions between radioactive cobaltous ions and certain complex salts of trivalent cobalt.

The instability of the simple cobaltic ion in water makes it difficult to study exchange in the system: $Co^{++} \rightleftarrows Co^{+++}$. Favorable forms for stabilizing trivalent cobalt are available in the cobalt ammines, and in the cobalticyanide ion. The compounds chosen for study were: hexammine cobaltic nitrate, chloropentammine cobaltic chloride, dichlorodipropylenediamine cobaltic chloride, trinitrotriammine cobalt, chlorodinitrotriammine cobalt, and potassium cobalticyanide.

In an aqueous solution of any such complex salt, a certain small concentration of cobaltic ion is in equilibrium with the complex ion.[2] Exchange between cobaltous ions and the cobalt in the complex would be conditioned by two factors: (1) the exchange $Co^{++} \rightleftarrows Co^{+++}$ must be operative, and (2) the exchange reaction must be more rapid than the reduction of the cobaltic ion by water. As the concentration of cobaltic ion derived from the complex ion is extremely small, the exchange might proceed slowly, but should lead eventually to the appearance of radioactive cobalt in the complex.

Experimental Part

Hexammine Cobaltic Nitrate, $[Co(NH_3)_6][NO_3]_3$ (1); Chloropentammine Cobaltic Chloride, $[Co(Cl)(NH_3)_5][Cl]_2$ (2); Dichlorodipropylenediamine Cobaltic Chloride, $[Co(Pn)_2Cl_2][Cl]$ (3).—Samples of these salts were supplied by Professor Willard R. Line of this Department. Each was analyzed electrolytically for cobalt, and the results were as follows: (1) found, 17.20%; calcd. 16.98%; (2) found, 23.68%; calcd., 23.53%; (3) found, 18.68%; calcd., 18.80%.

Trinitrotriammine Cobalt, $[Co(NH_3)_3(NO_2)_3]$.—This compound was prepared by the method of Jörgensen.[3] The result of analysis for cobalt by the electrolytic method was: found 23.83%, calcd. 23.76%.

Chlorodinitrotriammine Cobalt, $[Co(Cl)(NO_2)_2(NH_3)_3]$.—This compound was prepared as directed by Gmelin.[4] Analysis for cobalt by the electrolytic method gave: 24.93% found, calcd. 24.82%.

Potassium Cobalticyanide, $K_3Co(CN)_6$.—This compound was prepared by the method of Benedetti-Pichler.[5] Analysis for cobalt by the electrolytic method gave: 17.70% found, calcd. 17.74%.

Radioactive Cobalt.—The radioactive cobalt used in the investigation was obtained from proton bombardment of iron telluride in the University of Rochester cyclotron. The radio-iodine produced from the tellurium was removed at the Strong Memorial Hospital, and radio-cobalt was recovered from the residue. Care was taken to avoid contamination of the cobalt by Zn^{65}. Using inactive zinc as a carrier, zinc sulfide was precipitated by the method of Fales and Ware,[6] and an appreciable activity was removed. A second precipitation removed only slight activity. As several months elapsed between preparation and use of the sample, most of the short period activities were absent. The principal radiation remaining was assumed to be derived in the most part from Co^{56} and Co^{58}.

The other chemicals used were of the reagent grade. The ether and isoamyl alcohol used for the extraction of cobalt thiocyanate were of good commercial grade.

Procedure.—To ten ml. of a solution of the ammine, 0.00806 *M* in cobalt, was added an equivalent amount of radioactive cobaltous sulfate in 6.00 ml. of water. After various time intervals, 13 g. of ammonium thiocyanate was dissolved in this solution. The cobaltous ion was thereby converted into the thiocyanate complex, in which form it was extracted with a mixture consisting of four parts ether and one part isoamyl alcohol. Blanks were run to make certain that no cobalt was extracted from the ammines, and that the ammines themselves were not extracted by the solvent. Exactly 10.00 ml. of the solvent was used for the extraction, which was carried out in a 60-ml separatory funnel. The activity of both water and "solvent" layer was measured in a Geiger-Müller counter of the type described by Bale.[7] Correction for radioactive decay was always made.

Every effort was made to keep the extraction procedure as uniform as possible. As indicated by the data, however, variations in supposedly identical measurements were found. These variations nevertheless do not exceed those normally to be expected. If the actual deviations between pairs of figures given in Table I are added and averaged, they come to approximately 6. This value agrees reasonably well with the average probable errors as given in the table.

Most of the experiments were run in duplicate. All were run in the dark, as the ammines in solution decomposed

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[1] For review, see G. T. Seaborg, *Chem. Rev.*, **27**, 199 (1940).

[2] A. B. Lamb and A. T. Larson, THIS JOURNAL, **42**, 2024 (1920).

[3] S. M. Jörgensen, *Z. anorg. Chem.*, **17**, 475 (1896).

[4] L. Gmelin, "Handbuch der anorganischen Chemie," Syst. No. 58 (B), Verlag Chemie, Berlin, 1932, p. 307.

[5] A. Benedetti-Pichler, *Z. anal. Chem.*, **70**, 258 (1927).

[6] H. A. Fales and G. M. Ware, THIS JOURNAL, **41**, 487 (1919).

[7] W. F. Bale, *Radiology*, **35**, 184 (1940).

photochemically. With each experiment, a blank consisting of the proper amount of ammine dissolved in 16.00 ml. of water was run simultaneously. At the end of the run, the blank was checked for decomposition by adding 13 g. of ammonium thiocyanate and extracting with 10.00 ml. of the solvent. The results are given in Table I.

The procedure for determining exchange in the cobalticyanide complexes was as follows: 17.0 mg. of $K_3Co(CN)_6$ was dissolved in 10.00 ml. of water, and to this solution was added 11.00 ml. of radioactive cobaltous nitrate, containing an equal number of mols of Co^{++}. The precipitated cobaltous cobalticyanide was converted into silver cobalticyanide after any desired time by shaking with 10.00 ml. of silver nitrate solution containing an equivalent amount of silver. The silver cobalticyanide was centrifuged off, and the activity of the supernatant liquid determined as above. The silver cobalticyanide was collected on a filter paper, washed thoroughly with water, and dissolved in 5 ml. of 8 *N* ammonia. This solution was made up to 10.00 ml. and its activity determined. The results are given in Table II.

TABLE I

Time, min.	Temp., °C.	Counts/min., "solvent"[a]	Counts/min., water[a]
		$[Co(NH_3)_6][NO_3]_3$	
2	23	226.0 ± 6.2	6.0 ± 1.4
2	23	213.3 ± 6.0	1.4 ± 1.2
60	23	235.3 ± 6.3	3.0 ± 1.3
60	23	221.3 ± 6.1	....
300	23	231.3 ± 7.7	1.6 ± 1.2
300	23	227.6 ± 6.2	2.1 ± 1.3
60	99	Cpd. dec.; exchange not measd.	
		$[Co(NH_3)_5Cl][Cl]_2$	
2	23	233.0 ± 6.1	6.4 ± 1.2
2	23	228.6 ± 6.0	8.4 ± 1.3
60	23	225.0 ± 6.0	8.4 ± 1.3
60	23	224.2 ± 6.0	9.0 ± 1.3
780[b]	23	229.4 ± 6.0	11.2 ± 1.4
780	23	232.7 ± 6.1	10.5 ± 1.4
60	99	Cpd. dec.; exchange not measd.	
		$[CoPn_2Cl_2][Cl]$	
2	24	229.9 ± 5.3	6.1 ± 1.4
2	24	226.3 ± 5.3	2.5 ± 1.2
70	24	210.3 ± 5.9	6.8 ± 1.4
70	24	222.5 ± 5.2	8.2 ± 1.4
300	24	224.5 ± 5.3	5.9 ± 1.4
300	24	230.0 ± 5.3	7.9 ± 1.4
		$[Co(NH_3)_3(NO_2)_3]$	
2	23	233.9 ± 6.2	3.9 ± 1.3
2	23	224.2 ± 6.1	0.2 ± 1.1
60	23	214.2 ± 6.0	5.2 ± 1.4
60	23	210.5 ± 5.9	8.2 ± 1.4
300	23	224.2 ± 6.1	3.7 ± 1.3
300	23	226.2 ± 6.1	6.6 ± 1.4
60[b]	99	224.5 ± 6.1	4.6 ± 1.4
60	99	229.2 ± 6.2	6.2 ± 1.4
		$[Co(NH_3)_3(NO_2)_2Cl]$	
2	23	228.8 ± 6.1	5.3 ± 1.3
2	23	231.2 ± 6.2	6.7 ± 1.4
60	23	221.6 ± 6.1	8.2 ± 1.4
60	23	225.0 ± 6.1	6.7 ± 1.4
300[b]	23	210.6 ± 5.9	8.5 ± 1.4
300	23	220.9 ± 6.1	....

[a] Net activity; background subtracted. [b] Partial decomposition of compound indicated by blank.

TABLE II

NON-EXCHANGE OF $K_3Co(CN)_6$

Time, min.	Temp., °C.	Counts/min., solution[a]	Counts/min., dissolved ppt.[a]
2	23	48.3 ± 3.0	....
2	23	53.1 ± 2.9	....
2	23	53.8 ± 2.9	0.0 ± 0.8
1560	23	55.1 ± 2.9	− .7 ± .8
1560	23	55.6 ± 2.9	− .5 ± .8
3660	23	52.1 ± 2.9	.8 ± .8
3660	23	51.6 ± 2.9	− .9 ± .8

[a] Net activity; background subtracted.

From the data given, there appears to be no exchange of the radioactive cobaltous ion either with the cobalt ammines, or with the cobalticyanide ion. Exchange reactions involving simple electron transfer generally occur readily. If such were true of cobaltous and cobaltic ions, then failure to observe exchange under the conditions used must result from decomposition of the ammines. Presumably the cobaltic ion in equilibrium with the ammine is reduced by water before measurable exchange can occur.

The activity observed in the water layer (Table I) results from imperfect separation of the radioactive cobaltous ion during the extraction procedure. The activities in the solvent layer are constant within experimental error, but would have decreased if exchange had occurred.

In the case of chloropentammine cobaltic chloride, an equilibrium exists between this salt and aquopentammine cobaltic chloride, $[Co(NH_3)_5Cl][Cl]_2 + H_2O \rightleftharpoons [Co(NH_3)_5(H_2O)][Cl]_3$. Apparently the establishment of this equilibrium does not make the cobalt atoms more available for exchange.

The non-exchange of cobalt atoms in cobaltous cobalticyanide is similar to the reported[1] non-exchange of iron atoms in Turnbull's blue.

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Summary

1. No exchange between radioactive cobaltous ion and hexammine cobaltic nitrate, chloropentammine cobaltic chloride, dichlorodipropylenediamine cobaltic chloride, trinitrotriammine cobalt, and chlorodinitrotriammine cobalt was found to occur within the limits of experimental error.

2. Probably the reduction of cobaltic ion by water is a more rapid reaction than the exchange reaction.

3. No exchange of cobalt atoms in cobaltous cobalticyanide was found to occur within the limits of experimental error.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY]

The Densities, Surface Tensions and Parachors of Diborane, Boron Triethyl and Boron Tribromide. The Atomic Parachor of Boron

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The suggestion made by Sugden[3] that the parachor is a measure of molecular volume at constant surface tension has been supported by Bayliss.[4] Using atomic parachor data, Bayliss was able to calculate bond radii for quadrivalent atoms and packing radii for univalent atoms which are in good agreement with the values secured by other methods. Moreover, Bayliss showed that the increase in bond radius for a quadrivalent atom, observed when its tetrachloride is converted to the tetraethyl, is paralleled by a corresponding increase in its atomic parachor. It is desirable that additional information concerning the correlation between bond radii and atomic parachors be available.

In the compounds of boron there is considerable variety in the environment of the boron atom and the bond distances in many of these compounds have been determined. In the present investigation the parachors of diborane, boron triethyl and boron tribromide have been determined. These parachors, together with those recorded in the literature for boron trifluoride, boron trichloride, methyl borate and ethyl borate, are compared with the data available on the bond distances. It is shown that a close correlation exists between the effect of bond type on the parachor and the effect on the bond radius of boron.

Experimental

Materials.—Boron trichloride and boron tribromide were made by the action of the halogens on powdered "Moissan" boron at 650°. The compounds were freed of excess halogen by allowing them to stand over mercurous chloride, and then were purified by fractional distillation.

Diborane was prepared by the reaction of boron tribromide with hydrogen, according to the method described by Stock and Sütterlin.[5] Its high purity was demonstrated by comparing its vapor tension at several temperatures with the values given by Stock and Kuss.[6]

Boron triethyl was prepared by the action of zinc diethyl on boron trichloride and was purified by fractional distillation. Its purity was demonstrated by analysis and by determination of its physical constants.

Density, Surface Tension and Parachor of Diborane.—The density of liquid diborane was determined pycnometrically at −105.1, −112.5 and −129.5°, employing a pycnometer calibrated with ethylene at the same temperatures, and using the values for the density of ethylene given by Maass and Wright.[7] The values for duplicate runs checked closely and were plotted to give a straight line corresponding to the equation

$$d = 0.3140 - 0.001296t\text{°C.}$$

from which the density values given in Table I were calculated.

The surface tension of diborane was measured by the maximum bubble pressure method, using the cell previously described.[8] The cell was placed in a thermostat containing pentane cooled with liquid air, and the temperature was measured by an ethylene vapor pressure thermometer.[9] The surface tension cell was calibrated with ethylene, using the data for surface tension and density of ethylene given by Maass and Wright.[7]

Determinations of the surface tension of seven samples of diborane were made over the temperature range −129.5 to −108.2° and were found to agree well. These data are summarized in Table I, together with the parachor values calculated by the usual methods. The mean value found for

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[1] Present address: Standard Oil Development Co., Linden, N. J.

[2] Present address: E. I. du Pont de Nemours and Co., Newark, N. J.

[3] Sugden, "The Parachor and Valency," G. Routledge and Sons, London, 1930.

[4] Bayliss, THIS JOURNAL, **59**, 444 (1937).

[5] Stock and Sütterlin, *Ber.*, **67B**, 407 (1934).

[6] Stock and Kuss, *ibid.*, **56**, 789 (1923).

[7] Maass and Wright, THIS JOURNAL, **43**, 1098 (1921).

[8] Sidgwick and Laubengayer, *ibid.*, **54**, 984 (1932).

[9] Stock, *Z. Elektrochem.*, **29**, 354 (1923).