chloride *trans* rather than *cis* to the NH_3 were replaced in the first acid hydrolysis. Only an upper limit for K^* can be given which lies somewhat above the lower line. Further support of this assignment is given by the magnitudes for the second acid hydrolysis constants which have been plotted in Fig. 5 as solid circles. It must be recognized that K_2 cannot be evaluated as accurately as K_1. For *cis*-$[Pt(NH_3)_2(H_2O)Cl]$, with the chloride *trans* to NH_3, the point falls close to the upper line; K_2' for *trans*-$[Pt(NH_3)_2Cl]$ was too small to measure. For $[Pt(H_2O)Cl_3]^-$, in which the chloride must be *trans* to either Cl^- or H_2O, the point falls close to the lower line. Hence, the effect of a *trans* H_2O apparently resembles that of Cl^- rather than NH_3. K_2' for $[Pt(NH_3)Cl_3]^-$ is exceptionally low and it falls somewhat below the lower line, consistent with the contention that the second chloride to be replaced is not *trans* to the NH_3. Furthermore, the high rate constant $k_2' = 13 \times 10^{-5}$ sec.$^{-1}$ for $[Pt(NH_3)(H_2O)Cl_2]$ would characterize the *trans*-isomer, a neutral species closely resembling the *trans*-$[Pt(NH_3)_2Cl_2]$, which also has a high rate constant. The apparent small non-equivalence in the substitution rates for the chloride ligand in solutions of $[Pt(NH_3)(H_2O)Cl_2]$ upon which the original assignment was based might have resulted from the presence of a small amount of the *cis*-isomer present together with the dominant *trans*-isomer. The lines in Fig. 5 predict the presence of 5–10% of the *cis*-isomer with a dominant *trans*-isomer. It will be most interesting, therefore, if some feasible means can be found for identifying unambiguously the predominant isomer formed by the acid hydrolysis of $[Pt(NH_3)Cl_3]^-$.

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The Identification of Some Cobalt(II) Ammine Azides

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X-Ray powder patterns and ammonia absorption studies characterize tbe cobalt(II) compounds formed by the thermal decomposition of $[Co(NH_3)_6](N_3)_3$ and by the reaction of cobalt(II) azide with gaseous ammonia. From the latter a crystalline diammine, an amorphous diammine, and a hexammine have been identified. A labile compound, possibly a diammine, has been recognized in mixtures. Two forms of cobalt(II) azide were found. The decompositions of $[Co(NH_3)_6](N_3)_3$ yield three different compounds, a tetrammine, a diammine, and an unidentified material occasionally observed in mixtures with the diammine.

Introduction

The thermal decomposition of solid $[Co(NH_3)_6](N_3)_3$ may yield cobalt(II) compounds.[1] Thus the products of the room temperature reaction of cobalt(II) azide with gaseous ammonia have been characterized and compared with the ammines yielded by $[Co(NH_3)_6](N_3)_3$.

Experimental

Preparation.—The preparation and decomposition of $[Co(NH_3)_6](N_3)_3$ has been described.[1] Cobalt(II) azide was prepared by the reaction of a 3% solution of hydrogen azide in ether[2] with cobalt(II) carbonate.[3] The very explosive, brown product was prepared in 0.3-g. lots, stored under ethereal HN_3, and protected from light.

Analysis.—The usual preparation yields two crystalline cobalt(II) azides and an unidentified, amorphous contaminant. Efforts to devise better methods of preparation or purification failed, necessitating considerable analytical efforts to establish beyond reasonable doubt the identity of the cobalt(II) azides. These were complicated by the lability of the sample to both hydrolysis and explosion.

The first samples were decomposed explosively in the vacuum line at 120 to 150°. Six runs gave N_2, 57.0 ± 1.8%; calcd. for $Co(N_3)_2$, 58.8%. The accuracy is within the limitations imposed by the small samples (10 to 20 mg.) and the system's volume; however, small quantities of H_2, 0.14 ± 0.04%, and HN_3, 0.3 ± 1%—identified by the approximate melting point, decomposition on sparking, and a red color reaction with aqueous ferric chloride—also were observed. Later efforts to determine cobalt iodometrically[4] or gravimetrically as the anthrani-

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(1) T. B. Joyner and F. H. Verhoek, *J. Am. Chem. Soc.*, **83**, 1069 (1961).

(2) L. F. Audrieth and C. F. Gibbs in H. S. Booth, "Inorganic Syntheses," Vol. 1, McGraw-Hill Book Company, New York, N. Y., 1939, p.77.

(3) L. Wohler and F. Martin, *Ber.*, **50**, 586 (1917).

(4) H. A. Laitinen and L. W. Burdette, *Anal. Chem.*, **23**, 1268 (1951).

late[5] gave considerable variations, even with samples from the same lot. To obtain both cobalt and azide from a single analysis, a *ca.* 25-mg. sample under ether was placed in a vessel attached to a vacuum line by a standard-taper joint. The ether was pumped off, nitrogen was admitted, and the vessel was detached, degreased, capped, and weighed. Treatment with aqueous silver nitrate yielded silver azide. This was separated and dissolved in concentrated ammonia, leaving behind small quantities of a brown material presumed to be the contaminant. Unfortunately it has not been identified. The silver azide was reprecipitated by careful addition of acetic acid to pH 6, filtered, dissolved in nitric acid, and the silver determined gravimetrically as the chloride. The original cobalt-bearing filtrate was treated with hydrochloric acid (to remove excess silver) and the cobalt determined as the anthranilate. While variations in the percentages are noted, the azide-to-silver molar ratios are close to 2.0. (It may be noted that Wohler and Martin[3] also obtained cobalt and nitrogen from a single sample, possibly avoiding the quite hazardous weighing operation. Their reported percentages apparently are based on the analytically determined sum of the two elements and the assumption of an anhydrous compound.)

Anal. Calcd. for $Co(N_3)_2$: Co, 41.22; N, 58.78; N_3/Co, 2.00. Found: Co, 36.23, 38.27, 36.69, 35.07; N, 51.67, 54.79, 53.45, 47.33; N_3/Co, 1.99, 2.01, 2.04, 1.89.

The last value results from a larger sample (81.7 mg.) used for the ammonia absorption studies. This was weighed before and after equilibration and the final solid analyzed. The discrepancy between the analyzed $Co(N_3)_2$ and the observed dry weight indicates about 18% of an unidentified material. The possibility of water of hydration was checked by analyzing the gas after the first equilibration and removal of ammonia (after curve B, Fig. 1). At this point any original water in the solid should have been displaced into the gas phase. Vacuum line manipulation and mass spectrometric analysis did detect a small amount of water. However, this was estimated to be at most 1.0 mg., corresponding to 0.11 mole per $Co(N_3)_2$.

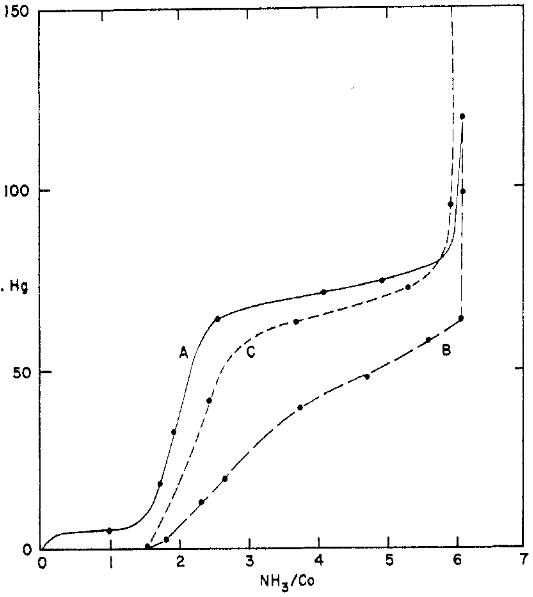

Fig. 1.—Ammonia absorption by cobalt(II) azide: A, initial absorption; B, deammination; C, reabsorption.

The presence of an unidentified material is unfortunate. While it was expected that some analytical inaccuracy would result from the difficulty of obtaining the dry weight (the samples are necessarily small and the vessel bulky and subject to excessive handling), the observed discrepancy is greater than the anticipated weighing errors. However, the contaminant does not affect the azide-to-cobalt ratios and, as will be shown, a stoichiometric quantity of ammonia (based on the cobalt analysis) is absorbed. It also is amorphous since the powder pattern of the hexammine formed from cobalt(II) azide by the absorption of ammonia is identical with that of the hexammine resulting from the decomposition of $[Co(NH_3)_6](N_3)_3$. Consequently, the contaminant should not disturb the points of major interest to this paper, the behavior of cobalt(II) azide with ammonia and the powder patterns of the cobalt(II) ammine azides.

Ammonia Absorption.—The stoichiometry of the reaction of anhydrous ammonia with dry, solid cobalt(II) azide was given by three absorption studies. The room was maintained at 23 ± 2° but the vacuum line was not otherwise thermostated. The solid was exposed to increments of ammonia and the gas absorption followed manometrically. The ammonia absorption per mole of $Co(N_3)_2$—on the basis of the analytically determined $Co(N_3)_2$—is plotted against the ammonia pressure in Fig. 1. The points plotted are from the final experiment using an 81.7-mg. sample. This experiment allowed more time for equilibration than the first two studies, 3 days to 1 week in the case of the initial equilibration (curve A). The removal of increments of ammonia produced curve B. This deammination was slower, and even though 1 to 2 weeks were allowed per point, equilibrium evidently was not obtained. Reammination, curve C, again allowing 1 week per point, approached the original curve.

Powder Patterns.—A 114.6-mm. diameter camera and CoK radiation filtered through an iron filter ($\lambda = 1.7902$ Å.) were used. The samples were rotated. Relative intensities (I/I_1) were measured with a densitometer.

A. Cobalt(II) Azide.—Patterns usually were obtained from ether-wet samples. A slurry was introduced into the wide mouth of a 0.5-mm. diameter "Glaskapillaren," centrifuged to the bottom, and the capillary sealed off with a small flame. A few samples were dried by inserting a glass wool plug above the solid (to prevent bumping), attaching the capillary to a vacuum line with Apiezon W wax, and pumping off the ether. The patterns for wet and dry samples were identical.

The patterns were sharp and with the exception of one line reproducible. This line (at $d = 10.27$ Å.) varied in intensity in different preparations and in one case was absent (Fig. 2, pattern A) although it appeared after a few weeks aging. Since the various samples yielded identical ammines—without the extra line—it seems likely that a second form of cobalt(II) azide was present. A pattern was obtained by forming the hexammine and then deamminating the solid by pumping on it for 5 weeks. The resulting pattern (Fig. 2, pattern B) was moderately intense, the

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[5] P. E. Wenger, C. Cimerman, and A. Corbaz, *Mikrochim. Acta*, **2**, 314 (1938).

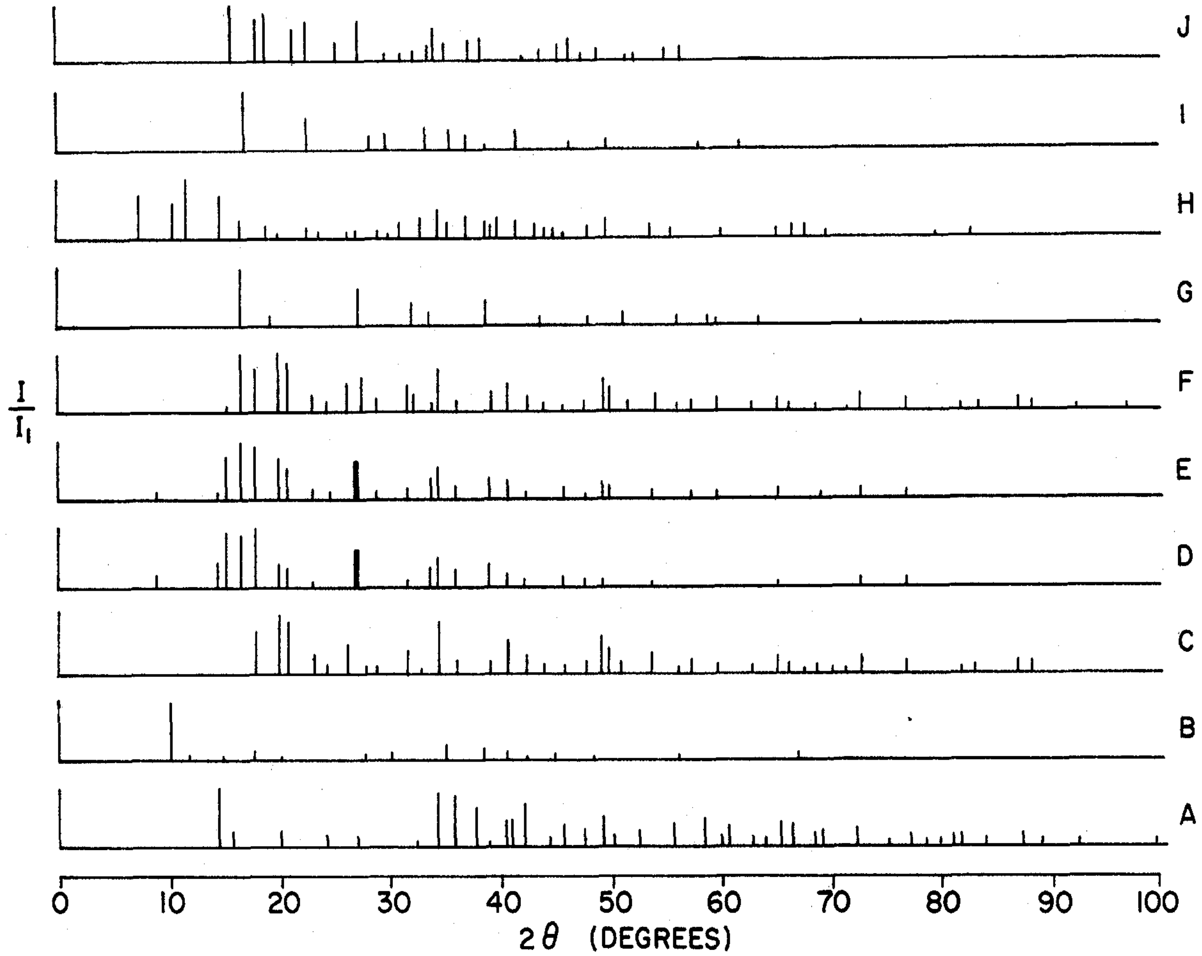

Fig. 2.—Powder patterns of cobalt(II) ammine azides: A, $Co(N_3)_2$, form I; B, $Co(N_3)_2$, form II; C, $Co(NH_3)_2(N_3)_2$; D, E, F, mixture, successive 6-hr. irradiations; G, $[Co(NH_3)_6](N_3)_2$; H, $Co(NH_3)_2(N_3)_2$ from $[Co(NH_3)_6](N_3)_3$; I, unknown from $[Co(NH_3)_6](N_3)_3$; J, $Co(NH_3)_4(N_3)_2$ from $[Co(NH_3)_6](N_3)_3$.

line at d = 10.27 Å. was clear, and the remaining lines were rather faint. (The relatively low intensity of the latter prevents their observation when the azide responsible is present as a minor portion of a mixture.) Control experiments showed no extra lines in the hexammine formed by the first ammonia absorption or by reabsorption following deammination.

B. Ammines Derived from Cobalt(II) Azide.—Lability to explosion, hydrolysis, and oxidation forced the preparation of individual samples directly in the X-ray capillaries. The capillaries were loaded, attached to the vacuum line, and dried as described above. They then were exposed to ammonia pressures of 1 to 700 mm. About 20% of the capillaries imploded on evacuation. Among the survivers only one case of leakage was found.

More than sixty patterns were taken in order to investigate the curves of Fig. 1 and identify the components of the mixtures produced under most conditions. Equilibration times ranged from 12 hours to 2 weeks. Samples were converted to the hexammine and deamminated (corresponding to curve B), and after various periods of pumping reëxposed to ammonia (curve C.) Representative samples were X-rayed twice so as to detect changes caused by radiation or aging. Such changes were noted only in samples exposed to low ammonia pressures (10 to 40 mm.).

C. Ammines Derived from Powdered $[Co(NH_3)_6](N_3)_3$.—At temperatures of 110 to 150° and, usually, under a pressure of 100 to 200 mm. of ammonia, powdered $[Co(NH_3)_6](N_3)_3$ decomposes to cobalt(II) compounds. The apparatus and procedures have been described. Figure 3 presents typical runs with the moles of gas evolved per mole of complex (n/n_0) plotted against time. If allowed to cool in the presence of ammonia, the cobalt(II) compounds will absorb ammonia to yield the hexammine. To avoid this absorption, the reaction vessel was removed from the hot bath, cooled for 20 sec. (immediate evacuation often causes explosions), and the gases pumped off. The solids were sampled by two methods. Initially, capillaries sealed onto the reaction vessel's cap could be loaded by inverting the vessel and sealed off under vacuum. Explosions were frequent, hence in later studies the solid was handled under ether. After evacuation an atmosphere of nitrogen was admitted, the vessel was detached from the vacuum line and filled with ether, and the capillaries were loaded as in A.

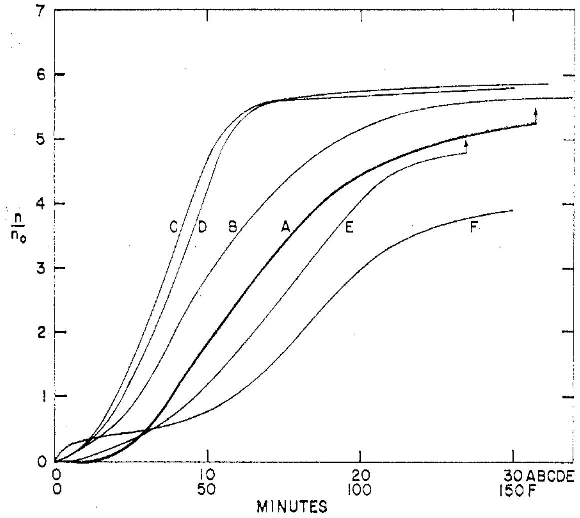

Fig. 3.—Thermal decomposition of powdered $[Co(NH_3)_6](N_3)_3$. Moles of gas evolved per mole of complex (n/n_0) *vs.* time: A, 140°, initially evacuated; B, 140°, 11 mm. NH_3 initially present; C, 140°, 50 mm. NH_3; D, 140°, 106 mm. NH_3; E, 140°, 406 mm. NH_3; F, 120°, 201 mm. NH_3.

Results

The Ammonia–Cobalt(II) Azide System.—The powder patterns of the two cobalt(II) azides are reported in Fig. 2, patterns A and B.[6] Pattern A is the more common.

The first equilibration of cobalt(II) azide with ammonia (Fig. 1, curve A) shows two plateaus corresponding to a diammine and hexammine (Fig. 2, patterns C and G, respectively). At low pressures a metastable compound sometimes appears in mixtures with the diammine and cobalt(II) azide or the hexammine. A 94-hr. exposure to 4.31 mm. of ammonia produced such a mixture. Figure 2, patterns D, E, and F, report successive 6-hr. irradiations. The decrease in cobalt(II) azide and the metastable material to leave the diammine and hexammine is clear.

The hexammine loses ammonia fairly readily to the approximate composition of a diammine. Powder patterns show this to be amorphous. No further gas evolution occurs during a 2-week exposure to a manometrically measured pressure of 0 mm. Prolonged pumping (5 weeks) yields the second form of cobalt(II) azide. Either the cobalt(II) azide or the amorphous diammine will reabsorb ammonia to give the hexammine.

Decomposition Products.—The thermal decomposition of powdered $[Co(NH_3)_6](N_3)_3$ at moderate ammonia pressures (Fig. 3) produces a diammine according to the stoichiometry

$$[Co(NH_3)_6](N_3)_3 \longrightarrow Co(NH_3)_2(N_3)_2 + 4NH_3 + 1.5N_2{}^1 \qquad (1)$$

This compound (Fig. 2, pattern H) is distinct from the diammine formed from cobalt(II) azide. Upon cooling in the presence of ammonia the diammine absorbs four ammonias to produce a hexammine identical with that prepared from cobalt(II) azide.

Decompositions with higher ammonia pressures (Fig. 3, curve E) show an apparent reduction in rate most readily explained by a retention of more than two molecules of ammonia in the solid. Runs at 120 and 130° and 200 mm. of ammonia and 110° and 100 mm. of ammonia evolve 3.7 to 3.9 moles of gas and leave a dark green solid. The stoichiometry approximates a tetrammine. While five experiments have confirmed the powder pattern (pattern J), the green solid has not been studied further. A third compound (pattern I) occasionally is observed mixed with the diammine. In one experiment the pattern of the latter was diffuse while that of the unknown was sharp, permitting the measurement of the major lines with some assurance. The material is otherwise unidentified.

Thermal Behavior of the Ammines.—The diammine produced according to eq. 1 is quite inert at the decomposition temperature and may persist for over an hour. A slow decomposition does occur and will result in an explosion. The nature of the solid depends somewhat on the conditions of the decomposition. With lower ammonia pressures it is a loose brown powder with a rather diffuse powder pattern. At higher pressures it is dark red, caked, and shows a sharp pattern.

If the cooled diammine is allowed to absorb ammonia and the resulting hexammine reheated, a rapid deammination results. At 140° three to four ammonias are lost within a minute and an explosion occurs within five minutes. Thus the deammination product (an amorphous diammine if the reaction is analogous to the room temperature studies) is more labile than the diammine yielded by the original decomposition.

Discussion

The existence of two forms of cobalt(II) azide is indicated by the presence of two crystalline compounds in most samples; the preparation, in one case, of a single compound which in time

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[6] The data have been submitted to the American Documentation Institute.

yielded the usual mixture; the identity of ammines prepared from either the pure compound or mixtures; and the deammination of the ammines to the less common of the original compounds.

The absorption of ammonia is typical of cobalt(II) compounds.[7] The metastable compound observed in the low pressure region—possibly a second form of the diammine—probably is responsible for the lack of sharpness in the break between the diammine and hexammine in Fig. 1. Its disappearance (patterns D, E, and F) may be simple aging or an irradiation-accelerated process. The hexammine is formulated as $[Co(NH_3)_6](N_3)_2$ (instead of, for instance, $Co(NH_3)_4(N_3)_2\cdot 2NH_3$) on the basis of the ammonia absorption studies and the known structure of the hexamminecobalt(II) halides.[8]

The products of the thermal decomposition of $[Co(NH_3)_6](N_3)_3$ are clearly linked to the cobalt(II) azide system by the ability of the diammine to absorb ammonia and form the customary hexammine. The relation of the sharpness of the powder pattern and the physical appearance of the diammine to ammonia pressure suggests that the reaction initially produces a finely divided compound with higher pressures favoring the growth of crystals. The tetrammine formed by decomposition persists at room temperature; however, the absence of a corresponding plateau in Fig. 1 or X-ray evidence from the cobalt(II) azide preparations indicates instability at the lower temperatures. It probably is more sensitive than the diammine since decompositions at 140° producing the tetrammine exploded (Fig. 3), while the diammine was formed without difficulty. The unknown compound appears in runs with the stoichiometry of eq. 1 and thus may be still another form of the diammine. However, since it is observed in mixtures, usually in small amounts judging by powder pattern intensities, a certain identification is not now possible.

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[7] "Gmelins Handbuch der anorganischem Chemie, System Number 58: Kobalt, Teil B: Die Ammine des Kobalts," Verlag Chemie, Berlin, 1930, p. 9f.

[8] R. W. Parry, *Chem. Rev.*, **46**, 507 (1950).

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A Potentiometric Study of the Reaction between Halides and Divalent Zinc, Cadmium, Mercury, and Lead in Glacial Acetic Acid

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Bivalent zinc, cadmium, mercury, and lead acetates react with potassium halides in glacial acetic acid to form MX_2 as the predominant species in solution. Only in the reaction between cadmium(II) and potassium bromide is there evidence of fourfold coördination of the metal. The potential difference of the glass–calomel electrode pair as a function of concentration of solution was used to determine the dissociation constants for the soluble reactant metal acetates. The order of decreasing dissociation of the acetates is Cd > Pb ≫ Hg. The molar solubilities of the slightly soluble halides of cadmium and lead follow an order of increasing solubility in acetic acid with increasing molecular weight.

The divalent metals of periodic group IIB, possessing complete electronic d-levels, exhibit coördination numbers of two, three, four, and six with ligands in aqueous solutions, and covalently bonded weak electrolytes may be formed. The polarographic behavior of divalent zinc, cadmium, and mercury in acetonitrile as a solvent indicates that the most stable metal halide complexes are identical to those found in aqueous solutions.[1] (The dielectric constant of acetonitrile is 38 at 25°.) However, in glacial acetic acid as the solvent, the reaction of mercury(II) with halides forms non-ionic HgX_2 as the predominant species.[2] No clear potentiometric evidence has been found for tetrahedral complexes with halides, although the solvate, $HgCl_2\cdot 2HOAc$, reported by Davidson and Chappell may have such a structure.[3] Sol-

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[1] I. M. Kolthoff and J. Coetzee, *J. Am. Chem. Soc.*, **79**, 870 (1957).

[2] O. W. Kolling, *ibid.*, **79**, 2717 (1957).

[3] A. W. Davidson and W. Chappell, *ibid.*, **60**, 2043 (1938).