ions which could decrease their mutual repulsion. If the apparent acidity constants of the triphosphoric acid, obtained in the same concentrations of alkali metal and other ions, are used in the calculation of the concentrations of the various triphosphate species, and the presence of alkali metal ions in the complex is otherwise neglected, the values calculated for the complexity constants agree closely with those obtained in the tetramethylammonium nitrate supporting electrolyte. The significance and values of these apparent acidity constants are discussed in an earlier series of papers.[3] This result supports the use of con-

stants of this type by Yamane and Davidson[12] in their calculations of the complexity constants of mercury(I) and mercury(II) with pyro- and triphosphate. Although the values obtained may vary slightly with alkali concentration, there is a practical advantage in that the sodium salt is the usual source of polyphosphates. Furthermore, the replacement by the tetramethylammonium ion is time-consuming and expensive.

Complexes of the Ethylamines with the Halides of Calcium, Cobalt(II), and Zinc

BY WILLIAM E. HATFIELD[1] AND JOHN T. YOKE, III

Ethylamine forms stable coördination compounds containing two moles of amine per mole of salt with the chlorides, bromides, and iodides of calcium, cobalt(II), and zinc. Pressure–composition isotherms also indicate the existence of higher complexes with appreciable dissociation pressures at 0°. Such higher complexes of the cobalt-(II) halides have been reported previously by Ephraim and Linn.[2] Diethylamine does not interact with calcium chloride at 25°, and gives only the stable 2:1 complexes with cobalt(II) and zinc. Triethylamine does not react with either calcium or zinc halides at 25°, but gives stable 1:1 complexes with the cobalt(II) halides. Magnetic and spectral data for the cobalt(II) complexes are interpreted as indicating tetrahedral coördination.

Introduction

The Ca, Zn, and Co(II) ions have been chosen as examples of the 8, 18, and incomplete shell electronic configurations in a study of the coördinating tendencies of the primary, secondary, and tertiary ethylamines. The halides of all these metals give a series of complexes with ammonia, with a maximum of six, eight, or ten molecules of ammonia bound per metal ion.[3] It is well known[4] that in general the coördinating abilities of the alkyl amines decrease in the series $NH_3 > RNH_2 > R_2NH > R_3N$.

(1) Abstracted from the Ph.D. Dissertation submitted by W. E. Hatfield to the Graduate College of the University of Arizona, 1962.
(2) F. Ephraim and R. Linn, *Ber.*, **46**, 3742 (1913).
(3) W. Biltz, *Z. anorg. allgem. Chem.*, **130**, 93 (1923); F. Ephraim, *Z. physik. Chem.*, **81**, 513 (1913).
(4) J. C. Bailar and D. H. Busch, "Chemistry of the Coordination Compounds," J. C. Bailar, ed., Reinhold Publishing Co., New York, N. Y., 1956, p. 62.

Ethylamine complexes have not been reported for alkaline earth or subgroup II ions other than Hg(II). Some ethylamine complexes of the fatty acid salts of the divalent first transition series metals have been reported.[5] Nickel cyanide complexes containing one and two molecules of ethylamine are known.[6] Ephraim and Linn[2] have studied Mn(II), Co(II), and Ni(II) halide complexes containing four or six molecules of ethylamine per metal ion. Such compounds have appreciable dissociation pressures at 0°.

Diethylamine complexes have not been reported for halides of Group II elements other than Be and Hg(II). For compounds of the divalent metal ions of the first transition series, only the

(5) S. Fisel, *Acad. rep. populare Romine, Filiala Iasi, Studii cercetari stiint.*, Ser. I, **6**, 295 (1955); *Chem. Abstr.*, **53**, 14928 (1959).
(6) E. Hertel, *Z. anorg. allgem. Chem.*, **178**, 202 (1929).

complex $Ni(CN)_2 \cdot NH(C_2H_5)_2$ is known.[6] Ephraim and Linn[2] report that the anhydrous halides of Mn(II), Co(II), and Ni(II) do not react with liquid diethylamine.

It has been stated that tertiary alkylamines have virtually no tendency to coördinate to metal salts[4,7] unless stabilized by chelation.[8] On the other hand, complexes of trimethylamine and/or triethylamine have been reported with one or more of the halides of the following metals: Li(I),[9,10] Be(II),[11] Al(III) and Ga(III),[12] Ge-(IV),[13-15] Sn(IV),[15-17] Bi(III),[18] Hg(II),[19] Ti-(III),[20] Ti(IV),[15,20-22] Zr(IV),[23] V(III) and V-(IV),[24] Nb(V),[25] Ta(V),[26] Mo(IV),[22] Mo(V),[27] Mn(II),[28] Fe(II),[29] Ni(II).[2,30]

In this work, the reactions of mono-, di-, and triethylamine with anhydrous Ca, Co(II), and Zn halides have been studied. An excess of the pure amine was condensed onto a sample of the anhydrous halide in a tared tube attached to a high vacuum line. Portions of the volatile base then were removed by distillation in the vacuum system. Isothermal measurements of pressure were made as a function of the composition of the system. The ethylamine systems were studied at

0°, and the di- and triethylamine systems were studied at 25°. The system $CoCl_2-(C_2H_5)_3N$ has been investigated previously[31] in this manner. The vapor pressure of triethylamine, 66 mm. at 25.0°, was observed throughout the composition region above a mole ratio $(C_2H_5)_3N:CoCl_2$ of 1.00, with a sharp break in the isothermal pressure–composition phase diagram at mole ratio 1.00. The compound $CoCl_2 \cdot N(C_2H_5)_3$ has a dissociation pressure too small to be measured with a mercury manometer and loses weight only slowly when maintained at a pressure of less than 1×10^{-4} mm. for several hours at room temperature.[31]

Results

Triethylamine Systems.—The isothermal pressure–composition phase diagrams show that triethylamine does not react with calcium chloride nor with zinc chloride, bromide, or iodide at 25°. In each of these systems the vapor pressure of triethylamine was observed throughout most of the composition region, falling off gradually toward zero at values of the mole ratio amine:salt less than 0.3 to 0.5 due to sorption of the little remaining amine on the powdered solids. Cobalt-(II) bromide and iodide interact with triethylamine in a manner identical to that previously observed for cobalt(II) chloride, and the products, $CoBr_2 \cdot N(C_2H_5)_3$ and $CoI_2 \cdot N(C_2H_5)_3$, exhibit stability of the same degree found for the chloride complex.

Diethylamine Systems.—Diethylamine does not react with calcium chloride at 25°. Zinc and cobalt(II) halides do react; the 25° phase diagrams for the zinc chloride, cobalt(II) chloride, and cobalt(II) bromide systems are shown in Fig. 1. The vapor pressure of diethylamine, 232 mm. at 25°, is observed in the composition region above a mole ratio of amine:salt = 3. With decreasing amounts of amine, the pressure goes to a negligible value at a mole ratio of 2.00, indicating formation of the new compounds dichlorobis-(diethylamine)-zinc(II), dichlorobis-(diethylamine)-cobalt(II), and dibromobis-(diethylamine)-cobalt-(II). No additional amounts of amine could be removed from the systems at this point, *i.e.*, the zinc and cobalt complexes showed no loss in weight when maintained for 12 hr. at a pressure of less than 1×10^{-4} mm. at 25°.

The curvature shown in Fig. 1 in the region mole

(7) L. Tschugaeff, *Ber.*, **40**, 173 (1907); W. Peters, *Z. anorg. allgem. Chem.*, **89**, 192 (1914); J. Chatt and R. G. Wilkins, *J. Chem. Soc.*, 4300 (1952); J. Chatt and G. A. Gamlen, *ibid.*, 2371 (1956); F. Fairbrother, D. Robinson, and J. B. Taylor, *ibid.*, 2074 (1958); F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, New York, N. Y., 1958, pp. 23–24.

(8) F. G. Mann and F. H. C. Stewart, *J. Chem. Soc.*, 1269 (1955); F. G. Mann and H. R. Watson, *ibid.*, 2772 (1958).

(9) J. Bonnefoi, *Ann. chim. phys.*, [7] **23**, 317 (1901).

(10) A. Simon and B. Glauner, *Z. anorg. allgem. Chem.*, **178**, 177 (1929).

(11) S. Prasad and K. P. Srivastava, *J. Indian Chem. Soc.*, **34**, 317 (1957).

(12) R. E. Van Dyke and H. E. Crawford, *J. Am. Chem. Soc.*, **72**, 2823, 2829 (1950).

(13) T. Karantassis and L. Capatos, *Compt. rend.*, **193**, 1187 (1931).

(14) W. C. Johnson and A. E. Sidwell, *J. Am. Chem. Soc.*, **55**, 1884 (1933).

(15) W. R. Trost, *Can. J. Chem.*, **30**, 835 (1952).

(16) A. W. Laubengayer and W. C. Smith, *J. Am. Chem. Soc.*, **76**, 5985 (1954).

(17) H. Böhme and E. Boll, *Z. anorg. allgem. Chem.*, **292**, 61 (1957).

(18) W. R. Trost, *Can. J. Chem.*, **32**, 356 (1954).

(19) K. A. Hoffman and E. C. Marburg, *Ann.*, **305**, 191 (1899).

(20) M. Antler and A. W. Laubengayer, *J. Am. Chem. Soc.*, **77**, 5250 (1955).

(21) S. Prasad and J. B. P. Tripathi, *J. Indian Chem. Soc.*, **34**, 749 (1957).

(22) E. L. Muetterties, *J. Am. Chem. Soc.*, **82**, 1082 (1960).

(23) J. E. Drake and G. W. A. Fowles, *J. Chem. Soc.*, 1498 (1960).

(24) G. W. A. Fowles and C. M. Pleass, *ibid.*, 1674 (1957).

(25) G. W. A. Fowles and C. M. Pleass, *ibid.*, 2078 (1957).

(26) P. J. H. Carnell and G. W. A. Fowles, *ibid.*, 4113 (1959).

(27) D. A. Edwards and G. W. A. Fowles, *ibid.*, 24 (1961).

(28) S. Prasad and K. P. Kacker, *J. Indian Chem. Soc.*, **35**, 719 (1958).

(29) S. Prasad and D. R. Krishnamurty, *ibid.*, **34**, 563 (1957).

(30) S. Prasad and V. Krishnan, *ibid.*, **35**, 352 (1958).

(31) J. T. Yoke, Dissertation, University of Michigan, 1954; J. T. Yoke, G. Kodama, and R. W. Parry, unpublished work.
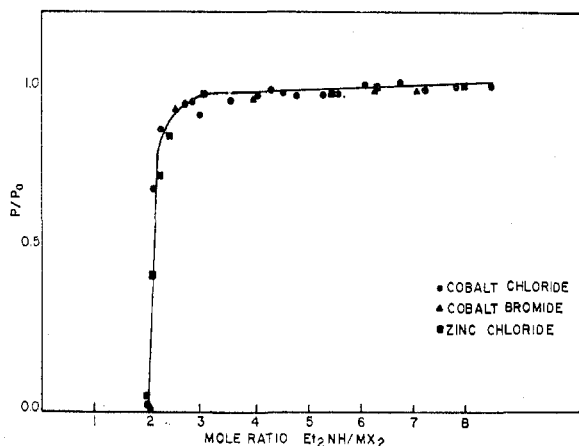
Fig. 1.—25° isotherm for the diethylamine–ZnCl₂, CoCl₂, and CoBr₂ systems.

Fig. 2.—0° isotherm for the ethylamine–zinc and calcium halide systems.

ratio 2 to 3 might be attributed to a decrease in the vapor pressure of the amine due to partial solubility of the complexes, to sorption of amine by the solids, or to the extreme slowness of attainment of equilibrium in these systems. At each point, a time period of one-half to two days was allowed for attainment of equilibrium. Individual points in this portion of the composition region also were determined in a special one-piece all glass evacuated system to eliminate the possibility of sorption of amine by stopcock grease, but the curvature was not eliminated.

Ethylamine Systems.—Ethylamine reacts with the halides of all three metals. The more complicated phase relations in these systems are shown in Fig. 2. These studies at 0° show that in all cases complexes containing more than two molecules of amine per metal ion are formed. In general these higher complexes have appreciable dissociation pressures. Such higher complexes have been reported for the ethylamine–cobalt(II) halide systems by Ephraim and Linn.[2] The stoichiometries and instability constants P/P_0 of these compounds are shown in Table I.

In cases of equivalent stoichiometry, a general trend for the stability series I > Br > Cl and Co > Zn > Ca is observed.

In each system, ethylamine is removed in a short time by distillation at 0° *in vacuo* to give a stable complex of the formula MX₂·2NH₂C₂H₅. Stability of these dihalobis-(ethylamine)-calcium, cobalt(II), and zinc complexes is indicated by their lack of a measurable dissociation pressure at 0°, and by their small loss in weight when kept for several hours at a pressure of less than 1 × 10⁻⁴ mm. The thermal stabilities of the dichlo-

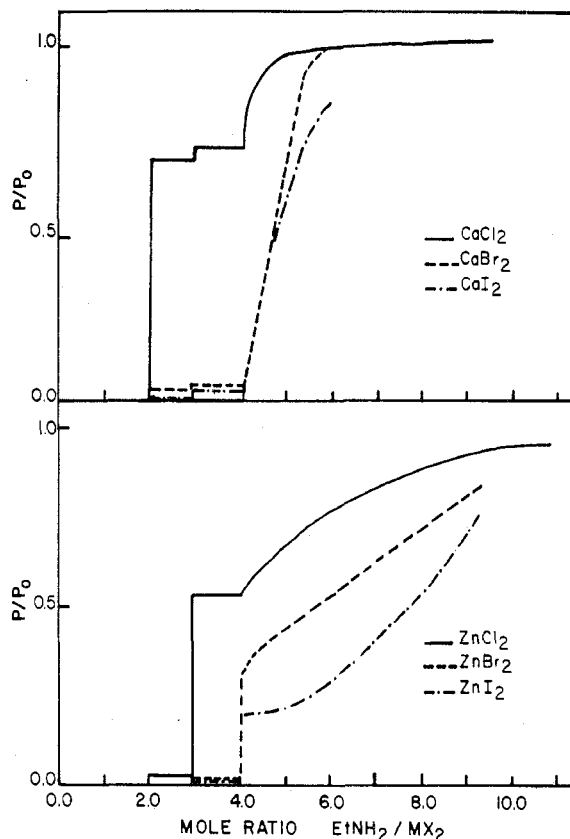robis-(ethylamine)-metal complexes were investigated in a qualitative experiment. The compounds were heated to 150° without formation of sufficient pressure to cause condensation of vapor in another part of the apparatus held at 0°, *i.e.*, in no case did the dissociation pressure at 150° exceed 370 mm. It has been reported[32] that under these conditions ZnCl₂·2NH₃ begins to lose one-half its content of ammonia, with the formation of a linear polymer.

In an investigation of the possibility that solvolysis reactions of the type

ZnI₂ + 2C₂H₅NH₂ = ZnI(HNC₂H₅) + C₂H₅NH₃I
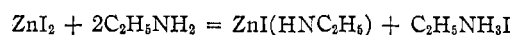
might occur, chips of sodium metal were added to a solution of ZnI₂·2NH₂C₂H₅ in excess ethylamine. Only a very slow and limited evolution of hydrogen occurred, like the evolution from pure ethylamine, whereas a solution of ethylammonium iodide in ethylamine gave a vigorous evolution of hydrogen. This indicates that no appreciable concentration of the ethylammonium ion was present in the zinc iodide–ethylamine reaction mixture.

(32) J. Simkin and B. P. Block, Abstracts, 136th National Meeting of the American Chemical Society, Atlantic City, September, 1959.

TABLE I

FORMULAS AND DISSOCIATION PRESSURES OF THE HIGHER
ETHYLAMINE COMPLEXES

Salt	Mole ratio amine:salt	P/P_0 (0°)
$CaCl_2$	4:1	0.734
$CaCl_2$	3:1 (?)	.715
$CaBr_2$	4:1	.043
$CaBr_2$	3:1	.024
CaI_2	4:1	.01
CaI_2	3:1	.002
$ZnCl_2$	4:1	.549
$ZnCl_2$	3:1	.032
$ZnBr_2$	4:1	.024
$ZnBr_2$	3:1	.002
ZnI_2	5:1	.215
ZnI_2	4:1	.016
ZnI_2	3:1	.002
$CoCl_2$	4:1 (2)	.108[a]
$CoBr_2$	4:1 (2)	.026[a]
CoI_2	6:1 (2)	(>1)[a]
CoI_2	4:1 (2)	0.005[a]

[a] Extrapolation of the data in ref. 2 to 0°.

Magnetic Moments and Spectra of the Cobalt Complexes.

—The room temperature magnetic susceptibilities of the 2:1 complexes of mono- and diethylamine with the cobalt halides, and of the 1:1 complexes of triethylamine with the cobalt halides, were determined by the Gouy technique. Calculated values of μ_{eff} are shown in Table II.

TABLE II

MAGNETIC MOMENTS AND WAVE LENGTHS OF ABSORPTION
IN THE VISIBLE REGION OF COBALT(II) HALIDE
COMPLEXES WITH THE ETHYLAMINES

	$CoX_2 \cdot 2NH_2C_2H_5$	$CoX_2 \cdot 2NH(C_2H_5)_2$	$CoX_2 \cdot N(C_2H_5)_3$
$CoCl_2$	4.53 B.M. 600 mμ	4.66 B.M. 620 mμ	4.52 B.M. 625 mμ
$CoBr_2$	4.70 B.M. 605 mμ	4.70 B.M. 640 mμ	4.62 B.M. 665 mμ
CoI_2	4.69 B.M. 590 mμ	. . .	4.80 B.M. 700 mμ

The reflectance spectra of these cobalt complexes were determined in the visible region. In each case a single broad peak appeared, with partial resolution of a shoulder on the high energy side appearing in some cases. The results are shown in Fig. 3. Values of the centers of gravity of the absorption bands, estimated graphically from the spectra, are given in Table II.

Discussion

The importance of the progressive weakening of Lewis base strength in the series $RNH_2 > R_2NH > R_3N$ has been overemphasized,[7,8] as is seen by
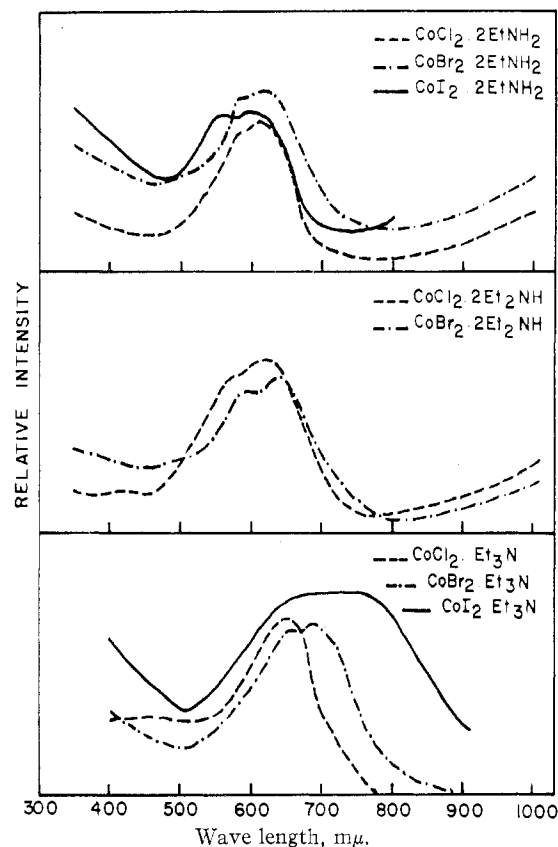

Fig. 3.—Reflectance spectra of the complexes of the ethyl-amines with cobalt(II) halides.

the existence of a variety of previously known trialkylamine complexes[9-31] as well as those prepared in this work. However, the maximum coördination numbers shown by metal ions toward the ethylamines do decrease with increasing degree of alkyl substitution on nitrogen. Ethylamine forms higher complexes with appreciable dissociation pressures, as well as stable 2:1 complexes, with the halides of all three metals. Diethylamine forms only 2:1 complexes with cobalt(II) and zinc, but not with calcium. Triethylamine forms only 1:1 complexes with cobalt(II) halides, and does not interact with calcium or zinc halides. Each amine does form some complexes which are stable in the sense of very low dissociation pressures. The stoichiometries of coördination reflect a decreasing coördinating tendency with increasing degree of alkyl substitution on nitrogen.

Reasons for the effects of alkyl substitution, of the halide ion, and of the metal ion on the formulas and stabilities of the complexes may be given in terms of the energy factors involved in the coördination reaction. Two major energy terms are the change in lattice energy in passing

from the simple to the complex salts, and the coördinate bond energy. Qualitative considerations of these terms may be based on the sizes of the halide ions and the amine molecules, and on the metal ion–amine dipole interaction.

The stability series I > Br > Cl observed for the higher ethylamine complexes with appreciable dissociation pressures may be attributed to the relative degree of expansion of the crystal lattice needed in order to accommodate the amine ligands. Similarly, one reason for the variation in the maximum number of amine molecules bound per metal ion, decreasing in the series RNH_2 > R_2NH > R_3N, is the steric factor involved in expansion of the lattice. The extreme slowness of reaction and of attainment of equilibrium at low values of the mole ratio suggest that diffusion of the amine and expansion of the lattice may be rate limiting steps. The failure of Ephraim and Linn[2] to observe reaction in the cobalt(II) halide–diethylamine systems presumably is due to the slowness of reaction. Similar behavior of the indium trihalide–ether systems has been attributed by Fairbrother, *et al.*,[33] to a reorganization of the lattice from a polymeric ionic to a molecular form. At high values of the mole ratio, *i.e.*, in the presence of an excess of liquid amine, the rate would depend on the solubility of the salt or complex. The solubility ranged from a negligible value in the calcium systems to complete solubility in the zinc systems. The cobalt halides were greatly puffed up when treated with the primary and secondary amines; the triethylamine cobalt complexes were so slightly soluble in excess amine as to give only a faint coloration to the liquid.

Using a polarized ion–dipole model, Parry and Keller have attributed the general trend for decrease in basicity with increasing alkyl substitution on ammonia to the decreasing contributions of both permanent and induced dipoles to the dipole moment.[34] Brown[35] has shown that the relative basicities of the alkylamines are variable in going from one Lewis acid to another, and has interpreted this in terms of the *B* and *F* strains. However, Taft found that $\Sigma\sigma^*$ values give a single linear correlation of dipole moments of primary, secondary, and tertiary amines.[36]

Hall[37] has shown that the Brönsted–Lowry base strengths of the alkylamines are correlated by Taft's $\Sigma\sigma^*$ values, but that primary, secondary, and tertiary amines are separated as classes, giving three different linear correlations. If account is made of the contributions of the induced moments to the total dipoles by adding to the permanent moments αF, the products of some arbitrary field strength and the polarizations based on the electron group refractions for nitrogen in the primary, secondary, and tertiary amine classes,[38] then the $\Sigma\sigma^*$ correlation with dipole moments splits into three lines. A similar division of the alkylamines into three classes corresponding to the degree of alkyl substitution was observed by Bruehlman and Verhoek in a comparison of the Brönsted–Lowry base strengths with Lewis base strengths toward silver ion.[39] A plot of pK_a against $pK_{instability}$ gave three lines, one each for primary, secondary, and tertiary amines. An explanation of this can be based[31] on the consideration that the induced dipole contribution occurs as a nearly constant amount within each class of amine, but differs between the primary, secondary, and tertiary classes.

This point of view is supported by the finding that the primary, secondary, and tertiary alkylphosphines give three linear correlations of pK_a with $\Sigma\sigma^*$, reversed in order from the amine sequence so that for a given value of $\Sigma\sigma^*$, basicity varies in the order R_3P > R_2PH > RPH_2.[40] The variation in the total dipole moments of alkylphosphines with the degree of alkyl substitution is opposite in order to that of the amines.[34] The effect of this on the coördinating abilities of primary, secondary, and tertiary alkylphosphines will be discussed in forthcoming papers.[41]

In considering the ion–total dipole interaction energy, the importance of shielding of the nuclear charge is clearly reflected in the influence of the electronic configuration of the metal ion on the coördinating abilities of the amines. The smallest and most polar monoethylamine forms complexes with all three metals, diethylamine only with d^7 cobalt and d^{10} zinc but not the calcium ion, and the largest and least polar triethylamine only with d^7 cobalt(II) halides. In the last case,

(33) F. Fairbrother, N. Flitcroft, and H. Prophet, *J. Less-Common Metals*, **2**, 49 (1960).

(34) R. W. Parry and R. N. Keller, ref. 4, pp. 128–129.

(35) H. C. Brown, *J. Chem. Soc.*, 1248 (1956).

(36) R. W. Taft, "Steric Effects in Organic Chemistry," M. S. Newman, ed., John Wiley and Sons, New York, N. Y., 1956, pp. 614–615.

(37) H. K. Hall, *J. Am. Chem. Soc.*, **79**, 5441 (1957).

(38) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., New York, N. Y., 1955, p. 409.

(39) R. J. Bruehlman and F. H. Verhoek, *J. Am. Chem. Soc.*, **70**, 1401 (1948).

(40) W. A. Henderson and C. A. Streuli, *ibid.*, **82**, 5791 (1960).

(41) W. E. Hatfield and J. T. Yoke, *Inorg. Chem.*, **1**, 470,475 (1962).

cation polarization (crystal field stabilization energy) is also important.

For complexes of cobalt(II) containing mixed ligands, Cotton and his co-workers[42] have found it convenient to consider an average ligand field in interpreting the magnetic and spectral properties of the compounds. In terms of the considerations put forward by these workers, it seems clear that the cobalt(II) complexes reported here are examples of pseudo-tetrahedral coördination. The magnetic moments indicate spin-free cobalt with a significant orbital contribution. The visible absorption is attributed to the transition ν_3 from a $^4A_2$ to a $^4T_1$ state, these arising from the ^4F ground state and ^4P first excited state of a Co(II) ion in an average tetrahedral ligand field. No major distinction between the positions of primary, secondary, and tertiary amines in the spectrochemical series can be made on the basis of our results on the spectra or orbital contributions to the magnetic moments.

Thus, in the 2:1 cobalt(II) complexes of ethylamine and diethylamine, the halide ions are coördinated to give pseudo-tetrahedral geometry. To account for a similar tetracoördinated cobalt-(II) in the 1:1 complexes of triethylamine, doubly halogen bridged dimers or singly halogen bridged linear polymers may be postulated. Unfortunately, lack of sufficient solubility in non-complexing solvents precluded determination of the molecular weight of these complexes. The diammine zinc halides have been found to be tetrahedrally coördinated,[43] and there is no reason to suppose that the 2:1 mono- and diethylamine zinc complexes are different. We have no basis for assigning any structure to the calcium complexes.

Experimental

Reagents.—Potassium iodide, phosphoric acid, iodine, calcium carbonate, and cobalt(II) carbonate were Reagent Grade chemicals and were used without further purification. Anhydrous Reagent Grade diethyl ether was used directly from freshly opened cans, or was stored over sodium before used. Zinc powder, Reagent Grade, was washed thoroughly with ether before use. Oil-pumped nitrogen was passed through a train of towers containing (a) an acidic solution of $CrCl_2$ in contact with mossy zinc, (b) concentrated H_2SO_4, (c) soda lime, (d) glass wool. Anhydrous hydrogen chloride (Matheson) was passed through (a) concentrated H_2SO_4, (b) glass wool, (c) a cold trap

packed with glass beads. Anhydrous hydrogen bromide (Matheson) was passed through a glass wool-packed trap and a cold trap. Hydrogen iodide, prepared from KI and 85% phosphoric acid, was swept from the generator in a stream of warm nitrogen and used at once.

Amines.—The three amines were Eastman Kodak Anhydrous Grade. Mono- and diethylamine each were purified by trap-to-trap distillation in the high vacuum line. The vapor pressures determined at several temperatures agreed with the values given in the literature.[44] Triethylamine was distilled twice from barium oxide and then purified in the vacuum line. We observed a pressure of 66 mm. at 25.0° for this sample and for other samples dried over sodium before fractionation in the vacuum line, and distilled through a Todd column. This vapor pressure is some 6 mm. lower than is calculated from the equation of Thompson and Linnett.[45] At 0.0°, we observed a pressure of 18.1 mm., in good agreement with the value of 18.3 mm. at this temperature reported by Holmes and Bertaut,[46] but some 3 mm. lower than is calculated from the equation of Thompson and Linnett. No impurity in our sample could be detected using a Wilkens Aerograph gas chromatographic instrument. All the amine samples used in this research were tensiometrically homogeneous.

Anhydrous Metal Salts.—Anhydrous Reagent Grade calcium chloride was heated at 400° in a stream of HCl. Calcium bromide, prepared from $CaCO_3$ and HBr, was similarly heated in a steam of HBr. Calcium iodide was prepared from $CaCO_3$ and freshly generated HI, and heated in a stream of HI and nitrogen. Zinc chloride was prepared from zinc powder and HCl by the method of Hamilton and Butler.[47] The metal was covered with ether in a flask, HCl was bubbled through the ether, and the mixture was set aside for several hours until all the zinc dissolved. Ether and HCl were removed and the product was heated *in vacuo* at 170° for 1 day. Zinc bromide was prepared similarly and dried *in vacuo* at 100° for 1 day. Zinc iodide was prepared from the elements in ether. A mixture of zinc powder (5 g.) and iodide (20 g.) in 75 cc. of ether was maintained at reflux overnight, leading to disappearance of the iodine color. The excess of zinc was removed by filtration. Ether was removed from the filtrate *in vacuo*. The product was heated at 125° overnight and then sublimed *in vacuo*. Cobalt(II) chloride was prepared from the Reagent Grade hexahydrate by heating at 400° in a stream of HCl for several hours. Cobalt(II) bromide, prepared from $CoCO_3$ and HBr, was similarly dehydrated in a stream of HBr. Cobalt(II) iodide was prepared similarly and heated at 200° in a stream of HI and nitrogen. The composition of each anhydrous metal halide was confirmed by halide analysis.

Procedure for Pressure–Composition Studies.—A 0.2 to 0.5-g. sample of an anhydrous metal halide was transferred in a drybox to a tared reaction assembly consisting of a reaction tube containing a magnetic stirrer and fitted

(42) F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *J. Am. Chem. Soc.*, **83**, 4690 (1961), and references therein.

(43) C. H. MacGillavry and J. M. Bijvoet, *Z. Krist.*, **94**, 249 (1936).

(44) (a) A. Berthoud, *J. chim. phys.*, **15**, 3 (1917); (b) J. L. Copp and D. H. Everett, *Discussions Faraday Soc.*, **15**, 174 (1953).

(45) H. W. Thompson and J. W. Linnett, *Trans. Faraday Soc.*, **32**, 681 (1936).

(46) R. R. Holmes and E. F. Bertaut, *J. Am. Chem. Soc.*, **80**, 2980 (1958).

(47) R. T. Hamilton and J. A. V. Butler, *J. Chem. Soc.*, 2283 (1932).

through ground glass joints with a connecting tube having a stopcock, permitting attachment to and removal from the vacuum system. The assembly was weighed before and after evacuation. An excess of the amine was transferred through the vacuum system and condensed onto the metal halide. The assembly was removed from the vacuum system and reweighed. It then was reattached to the vacuum line and maintained at 25.0 ± 0.1° by means of water circulated from a constant temperature bath. The contents were stirred magnetically. Systems involving ethylamine were studied at 0.0° (ice bath). To weigh the assembly during study of the ethylamine systems, a special tared insulated vessel with crushed ice was used to contain the reaction tube.

After a period of from 6 to 48 hr., the pressure was measured on a mercury manometer adjacent to the reaction assembly on the vacuum line. The amine was removed by portions by distillation in the vacuum system. The reaction assembly was reweighed each time, and an additional 6 to 48-hr. time period was allowed for reestablishment of equilibrium at each point. Additional measurements of pressure as a function of composition were made by adding new increments of amine after a number of portions had been removed. Thus, the equilibrium condition within the various composition regions was approached from each direction.

Finally, all readily removable amine was distilled off to give the various stable complexes of negligible dissociation pressure. The assembly was taken from the vacuum line to the drybox and the coördination complexes were removed for analysis and further study.

Analysis of Stable Compounds.—Values of the mole ratio amine:salt for complexes with negligible dissociation pressures were determined by weighing the reaction assembly at the composition corresponding to the point where all easily removable amine had been taken off. Halide analyses were by the Volhard method. The results are shown in Table III.

Magnetic Susceptibility Measurements.—A Gouy balance of the type described by Ihrig and Caldwell[48] was used. The sample tube was suspended from a semimicro analytical balance by means of a Nylon thread. Two permanent magnets of field strengths 2800 and 5200 gauss were available. The weaker magnet was used only to check for dependence of susceptibility on field strength. The calibrants, mercury(II) tetrathiocyanatocobaltate(II) and diquinolinium tetrachloro- and tetrabromocobaltate-(II) were prepared by methods described in the literature.[49] The tube calibration constant was obtained using powdered mercury(II) tetrathiocyanatocobaltate(II) following the method of Figgis and Lewis.[50] Reproducibility of replicate determinations using separate packings of the tube and two different preparations of the calibrant was ±1%. Determinations of the susceptibilities of diquinolinium tetrachloro- and tetrabromocobaltate(II) gave values agreeing within 2% of those of Holm and Cotton.[51]

(48) J. L. Ihrig and R. C. Caldwell, *J. Chem. Educ.*, **32**, 320 (1955).

(49) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958); E. G. Percival and W. Wardlaw, *ibid.*, 1505 (1929).

(50) B. N. Figgis and J. Lewis, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, ed., Interscience Publishers Inc., New York, N. Y., 1960, chapter 6.

(51) R. H. Holm and F. A. Cotton, *J. Chem. Phys.*, **31**, 788 (1959).

TABLE III

ANALYTICAL DATA

Compound	Mole ratio found amine:salt	% Halide Found	% Halide Calcd.
$CoCl_2 \cdot N(C_2H_5)_3$	0.98	30.8	30.7
$CoBr_2 \cdot N(C_2H_5)_3$	.97	49.8	49.9
$CoI_2 \cdot N(C_2H_5)_3$	.99	61.6	61.4
$CoCl_2 \cdot 2N(C_2H_5)_2H$	1.93	25.1	25.6
$CoBr_2 \cdot 2N(C_2H_5)_2H$	1.99	43.2	43.4
$ZnCl_2 \cdot 2N(C_2H_5)_2H$	1.99	25.4	25.2
$CaCl_2 \cdot 2N(C_2H_5)H_2$	2.00	34.8	35.3
$CaBr_2 \cdot 2N(C_2H_5)H_2$	a	a	a
$CaI_2 \cdot 2N(C_2H_5)H_2$	2.08	66.8	66.2
$CoCl_2 \cdot 2N(C_2H_5)H_2$	2.04	31.8	32.3
$CoBr_2 \cdot 2N(C_2H_5)H_2$	2.05	51.1	51.7
$CoI_2 \cdot 2N(C_2H_5)H_2$	1.96	63.8	63.1
$ZnCl_2 \cdot 2N(C_2H_5)H_2$	1.90	31.3	31.3
$ZnBr_2 \cdot 2N(C_2H_5)H_2$	b	b	b
$ZnI_2 \cdot 2N(C_2H_5)H_2$	2.00	61.9	62.1

[a] The 2:1 complex lost amine slowly *in vacuo* at room temperature to give a sample of composition $CaBr_2 \cdot 1.51$ $N(C_2H_5)H_2$; % Br found 59.4, calcd. 59.6. [b] Similarly, a sample of composition $ZnBr_2 \cdot 1.76$ $N(C_2H_5)H_2$ was obtained; % Br found 51.8, calcd. 52.4.

All measurements were made at room temperature. The susceptibilities calculated according to Figgis and Lewis[50] were corrected for the diamagnetic contribution using Pascal's constants as given by Selwood.[52] No dependence of susceptibility on field strength was observed in any case within an experimental error of ±0.1 B.M. Magnetic moments were calculated by the formula

$$\mu_{eff} = 2.84 \, (\chi_{corr} \times T)^{1/2}$$

Reflectance Spectra.—The standard reflectance attachment to the Beckman DU spectrophotometer was used. The reflectance standard was magnesium oxide. Powdered samples of standard and complex were given temporary protection from dust and moisture with a plastic bag.

Thermal Stability Studies.—Samples of the dichlorobis-(ethylamine) complexes of calcium, cobalt(II), and zinc were placed in one arm of a small inverted U tube. The tube was evacuated and sealed off. The arm containing the complex was heated in an oil bath; the other arm was placed in an ice bath. The temperature of the oil bath was raised slowly to 150°. In no case did liquid ethylamine condense in the cold portion of the tube. The cobalt compound melted at about 110°; the other two compounds did not melt.

Insolubility of $CoX_2 \cdot N(C_2H_5)_3$ Complexes.—Attempts were made to find a solvent for the 1:1 triethylamine complexes of the cobalt(II) halides suitable for molecular weight determinations. No significant concentration could be obtained of the chloride or the iodide in benzene, nitrobenzene, or acetonitrile.

(52) P. W. Selwood, "Magnetochemistry," Interscience Publishers Inc., New York, N. Y., 1956, p. 78.

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Complexes of Ethylphosphine and Diethylphosphine with the Halides of Cobalt(II) and Zinc

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Calcium chloride does not react with ethylphosphine at $0°$ nor with diethylphosphine at $20°$, but cobalt(II) and zinc halides give complexes of the types $CoX_2 \cdot C_2H_5PH_2$, $CoX_2 \cdot 2C_2H_5PH_2$, $CoX_2 \cdot 2(C_2H_5)_2PH$, $CoX_2 \cdot 4(C_2H_5)_2PH$, $ZnX_2 \cdot C_2H_5PH_2$, and $ZnX_2 \cdot 2(C_2H_5)_2PH$. These compounds are compared with the previously reported primary, secondary, and tertiary ethylamine complexes[2] and the triethylphosphine complexes.[3] The coördinating sequence $R_2PH > R_3P > RPH_2$ is observed, and interpreted in terms of a competition between polarized ion–dipole coördinate bonding and the energy required for expansion of the crystal lattice on coördination. Some spectral and magnetic data for the cobalt(II) complexes are presented.

Introduction

It has long been known that alkylation of phosphine by reaction of alkyl halides with phosphonium iodide in a sealed tube gives only tertiary phosphines and quaternary phosphonium salts unless zinc oxide is incorporated in the reaction mixture. Zinc oxide is converted into zinc iodide during the reaction, and in some manner the zinc iodide binds the primary and secondary alkylphosphine intermediates so that they subsequently can be obtained on hydrolysis of the reaction product.[4] This preparative method has been superseded in practice.[5] It was suggested that the primary and secondary phosphines were removed from the reaction zone by formation of double salts of their phosphonium iodides with zinc iodide. Another possibility could be formation of primary and secondary phosphine–zinc coördination compounds.

While tertiary phosphines are common ligands in coördination chemistry, very little work has been done with primary and secondary phosphines. Satisfactory preparative methods for these bases have been developed recently.[5]

The compounds are toxic–probably very much so although no information seems to be available[6]—and have the foul odor and property of spontaneous inflammability characteristic of volatile organic phosphines.[7] They are strong reducing agents and have more protonic acidic character than amines, so that it may be expected that coördination reactions might be complicated by oxidation–reduction or dehydrohalogenation reactions.

Brown[8] has compared the base strengths toward trimethylborane of primary, secondary, and tertiary amines and phosphines in developing his well known theories of steric strain, and similar studies with other Group III alkyl reference acids have been reported. The compounds $AlCl_3 \cdot C_2H_5PH_2$[5,9] and $BF_3 \cdot (CH_3)_2PH$[10] have been described. There have been two reports on transition metal complexes. The compound $CoCl_2 \cdot C_2H_5PH_2$ was prepared[5,9] by treating anhydrous cobalt(II) chloride with an excess of ethylphosphine and then pumping off the unreacted base *in vacuo*. The compounds $CoCl_2 \cdot 4(C_2H_5)_2PH$

(1) Abstracted from the Ph.D. Dissertation submitted by W. E. Hatfield to the Graduate College, University of Arizona, 1962.

(2) W. E. Hatfield and J. T. Yoke, *Inorg. Chem.*, **1**, 463 (1962).

(3) W. E. Hatfield and J. T. Yoke, *ibid.*, **1**, 475 (1962).

(4) A. W. Hofmann, *Ber.*, **4**, 430, 605 (1871).

(5) J. T. Yoke, G. Kodama, and R. W. Parry, to be published.

(6) T. W. Hale, Medical Advisory Committee, Manufacturing Chemists' Association, private communication.

(7) G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, New York, N. Y., 1950, Chapter 2.

(8) H. C. Brown, *J. Chem. Soc.*, 1250 (1956).

(9) J. T. Yoke, Dissertation, University of Michigan, 1954.

(10) E. Fletcher, Dissertation, Purdue University, 1952.