than one higher complex. Our data do not show what the composition of these species is, but there seems little reason not to infer the formation of $PdCl_5^{\equiv}$ and $PdCl_6^{\overline{\equiv}}$. Hexacovalency of palladium (II) is thus indicated. It may be noted that nickel, the vertical neighbor of palladium in the periodic system, appears to give a complex chloride of the hexacovalent type, namely, $Li_4NiCl_6 \cdot 10H_2O$.[3] Tricovalent nickel chloride complexes (M^INiCl_3) are well known in the solid state.

The rather rapid decline in absorbance for $Cl/Pd > 4 < \sim 10$ points to a moderate stability of $PdCl_5^{\equiv}$, but not comparable to the stability of the lower complexes. From Fig. 3 it may be seen that in a 0.0044 *M* palladium solution the absorbance at 410 mμ decreases from 0.82 at $Cl/Pd = 4$ to 0.60 at $Cl/Pd = 10$ ($[Cl^-] = 0.04$ *M*). This means that at least 25% of $PdCl_4^{=}$ has been converted into higher complexes under the latter conditions. In 0.1 *M* chloride solution probably less than half of the palladium is present as $PdCl_4^{=}$ when the total palladium concentration is small compared to the chloride concentration.

Complexing with Nitrate.—Addition of chloride-free nitric acid to a palladium(II) perchlorate solution alters the absorption curve of palladium(II) ion (Fig. 5). The absorbance increases (in the 360–500 mμ range investigated) and the absorption maximum is shifted to longer wave lengths with increasing nitrate ion concentration. The species formed are markedly dissociated at low nitrate concentrations.

MINNEAPOLIS, MINN.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

The Methylamine Complexes of the Rare Earth (III) Chlorides[1]

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The addition of methylamine to lanthanum, cerium(III), praseodymium, neodymium, samarium and gadolinium chlorides was followed at 700 mm. pressure from room temperature to 300°. Methylamine readily combines with the rare earth chlorides forming a series of complexes of the type $MCl_3 \cdot nCH_3NH_2$ where n varies from 5 to 1. Fractional compounds with $n = 4.5, 3.25, \ldots$ down to 0.75 were observed in several cases.

Introduction

Methylamine complexes of metallic salts were first mentioned by Simon and Glauner[3] who investigated the reaction of methyl, dimethyl and trimethylamine with the lithium halides. They reported that methylamine forms a series of addition compounds with the halides of the type, $LiX \cdot nMeNH_2$. For lithium chloride, n is 1, 2, 3 and 4; lithium bromide, n is 1, 2, 3, 4 and 5; and lithium iodide, n is 1, 2, 2.5, 3, 3.5, and there was some evidence for n being 0.25, 0.50 and 1.5. In a pressure–composition study, Maillard[4] investigated the reaction between methylamine and calcium chloride. The compounds, $CaCl_2 \cdot nMeNH_2$, where n is 2, 4, 6 and 8 were reported. The above two studies seem to complete all the previous work done on the addition of methylamine to anhydrous inorganic salts.

Since the ammonia complexes of the rare earth chlorides are well known[5] it was of interest to study the corresponding compounds formed between the anhydrous rare-earth chlorides and methylamine. The salts involved in this investigation were lanthanum, cerium(III), praseodymium, neodymium, samarium and gadolinium chlorides. The addition of methylamine was followed by observing the change in composition with temperature at a constant pressure of the gaseous amine. This method was found to be preferable to the isothermal study since in the latter case the equilibrium was obtained considerably more slowly.

Experimental

Reagents.—The methylamine hydrochloride was obtained from Eastman Organic Chemicals Co., Rochester, N. Y. The source and the purity of the rare earth oxides used for this study were described in a previous publication.[6]

Preparation of Methylamine.—Anhydrous methylamine was prepared by the method of Kenner and Felsing[7] by treating the hydrochloride with a 40–50% solution of sodium hydroxide in the presence of mercuric oxide. The evolved gas was dried by passing through a four-foot column, 2 inches in diameter filled with barium oxide, and then condensing over metallic sodium chips at Dry Ice temperatures. Contrary to the observation reported by Kenner and Felsing, no blue color was observed in the sodium–methylamine mixture. The methylamine was distilled into the storage system of the apparatus prior to use.

Preparation of the Anhydrous Rare Earth Chlorides.—The anhydrous rare earth chlorides were prepared by the method of Kleinheksel and Kremers.[8] The hydrogen chloride was prepared and dried as described elsewhere.[9] Commercial tank hydrogen chloride was found unsuitable for the

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(1) Abstracted in part from the Ph.D. thesis of Wesley W. Wendlandt, State University of Iowa, June, 1954.

(2) Du Pont Teaching Fellow 1953–1954.

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

(4) A. Maillard, *Compt. rend.*, **203**, 187 (1936).

(5) (a) C. Matignon, *Ann.*, Ser. VIII, **8**, 284, 402, 464 (1906); (b) W. Klemm and J. Rockstroh, *Z. anorg. allgem. Chem.*, **176**, 181 (1928); (c) M. Barre, *Compt. rend.*, **156**, 1017 (1913); (d) F. Ephraim and P. Ray, *Ber.*, **62**, 1639 (1929); (e) G. Beck and A. Gasser, *Anal. Chem. Acta*, **3**, 41 (1949); (f) F. Ephraim and R. Block, *Ber.*, **59**, 2692 (1926); (g) F. W. Bergstrom, *J. Phys. Chem.*, **29**, 160 (1925).

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(7) C. T. Kenner and W. A. Felsing, *ibid.*, **61**, 2457 (1939).

(8) J. H. Kleinheksel and H. C. Kremers, *ibid.*, **50**, 954 (1928).

(9) L. F. Audrieth, "Inorganic Syntheses," McGraw-Hill Book Co., New York, N. Y., Vol. III, p. 14, and Vol. II, p. 72.

dehydration process because of the presence of 1–2% of hydrocarbons.[10] The purity of the dehydrated salts was established by analysis and ranged from 99.10–100% of the anhydrous salt.

Apparatus.—The absorption system is shown in Fig. 1. It consists of a 50-ml. water jacketed gas buret, H, connected to the absorption tube D by a 2-mm. bore Pyrex glass tubing. A sealed-end mercury manometer, E, is used to indicate the pressure in the system. The pressure can be adjusted by means of the leveling bulb K. The liquid methylamine is stored in tube A and distilled before use into the four-liter storage bulb, C. The gas storage system is connected to the absorption system through stopcock 6. Calibration of the system consisted of determining the volume and the effect of temperature changes in the 0–300° range on the absorption tube D. The choice of lubricant was important. Preliminary experiments have indicated that most lubricants have a pronounced tendency to absorb methylamine; however, it was found that with the "Apiezon N," the absorption was exceedingly small.

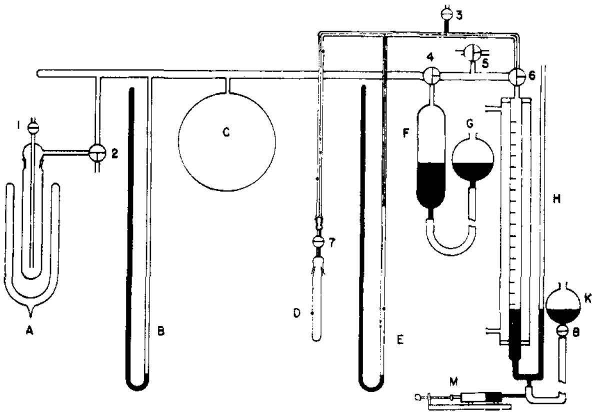

Fig. 1.—The absorption apparatus.

The procedure for carrying out a run was as follows: the anhydrous rare earth chloride was loaded, in a dry-box, into the weighed absorption tube, D. After reweighing to determine the amount of the salt, it was attached to the system by means of a standard taper joint. The entire system was then evacuated for 2 hours with a Hy-vac vacuum pump connected to stopcock 3. The gas buret was filled with methylamine by means of the mercury pump F. Then, with stopcock 7 closed, stopcock 6 is opened to the absorption system and by means of the leveling bulb K, the pressure is adjusted to a fixed point on the manometer. The fine adjustment of the mercury level can be brought about by closing stopcock 8 and adjusting the screw on the 10 ml. syringe M. The buret level is then recorded. An ice-bath was placed around the absorption tube D and stopcock 7 was opened, allowing the methylamine to come in contact with the salt. There was an immediate absorption of the gas by the rare earth chloride. Additional methylamine was added until the reading on the buret became constant. From the volume of the methylamine absorbed, the composition of the solid phase was calculated. From 4 to 12 hours were required to obtain a constant reading on the gas buret. During the reaction, the volume of the addition compound increased 3- to 4-fold.

After a constant reading was obtained, the thermal decomposition of the compound was begun. The ice-bath was replaced with a constant temperature bath, by means of which temperatures could be maintained to within ±1° in the range from 25 to 300°. The temperature of the absorption tube was slowly increased with readings taken on the buret at every 2 to 3° intervals. As the temperature increased, a point would be reached where the methylamine would come off quite rapidly. This would indicate a transition to a lower methylammoniate. The temperature was then maintained at this point until the readings on the buret became constant. Usually the transition interval would require 3 to 4 hours, occasionally, it took up to 12 hours. After recording the constant volume reading, the temperature was increased again and the process repeated at the next transition.

The decomposition was tested for reversibility by allowing the temperature to drop and noting the amount of methylamine re-absorbed. The curves were reproducible but it was found that a longer time, up to 24 hours, was required for each transition in order for the composition to become constant. The usual pressure of the decomposition was 700 mm. but in the case of neodymium chloride, a decomposition curve was also carried out at 305 mm.

Results

The results of the thermal decompositions are shown in Table I. It can be seen that besides the stoichiometric compounds of $M(MeNH_2)_nCl_3$, where M is La, Ce(III), Pr, Nd, Sm and Gd, and *n* is 1, 2, 3, 4 and 5, there are also fractional compounds in which *n* is 0.75, 1.25, 1.5, 2.25, 2.33, 3.33 and 4.5. The decomposition temperatures in all cases were sharp and reproducible.

TABLE I

DECOMPOSITION TEMPERATURES FOR THE METHYLAMINE COMPLEXES WITH THE RARE EARTH CHLORIDES AT 700 MM. PRESSURE

	Decomposition temp., °C.					
n	$LaCl_3$	$CeCl_3$	$PrCl_3$	$NdCl_3$	$SmCl_3$	$GdCl_3$
5	15[a]	38	49	50	41	20[a]
4.5	..	..	..	..	..	30
4	29	55	78	65	73	76
3.33	..	..	92	..	..	..
3	115	109	118	105	150	165
2.33	..	..	145	..	..	..
2.25	..	..	..	145	185	..
2	160	154	187	164	205	198
1.5	..	194	240	200	237	..
1.25	202	..	..	..	..	242
1	236	..	..	255	..	..
0.75	..	205	..	..	..	..

[a] Approximately.

Discussion

The existence of fractional compounds in such systems is not surprising since such were reported by Simon and Glauner[3] in the lithium iodide–methylamine system. It is possible that these fractional compounds are actually polynuclear complexes with amino-type bridge linkages.

Since the bonding between the cation, M^{+3}, and methylamine is presumably due to ion–dipole forces, it was thought that the decomposition temperatures for a series of methylamine complexes of like composition would increase with decreasing ionic radius of the cation. However, this was not the case. As seen from Table I there is no strict regularity in the variation of the decomposition temperature with the ionic size of the rare earth for any of the complexes.

With ammonia, the rare earth chlorides form an octaammoniate at 0° and 760 mm. However, with the methyl substituted ammoniates, only a pentamethylamine complex is stable at this temperature. It is quite likely that at lower temperatures higher methylammoniates can be prepared. The rare earth chlorides also form a pentaammoniate which is stable to about 120°. The effect of a methyl group thus seems to lower the decomposition temperatures by a considerable amount. Preliminary experiments indicated that

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[10] F. H. Spedding and J. M. Wright, USAEC Document ISC-143, March, 1951.

the corresponding dimethylamine compounds would be stable only at lower temperatures than the methylamine compounds.

Compounds having a fractional composition are also known in the case of the ammoniates of the rare earth halides. With samarium chloride, the compound, $SmCl_3 \cdot 2.66NH_3$ was shown to exist.[5b] The tendency to form this type of complex seems to be greater in the methylamine complexes. These fractional compounds are stable phases as they are reproducible on different samples and can be obtained reversibly either from the lower or from the higher compound. The decomposition curve of the neodymium chloride–methylamine system at 305 mm. pressure gave the same compounds as at 700 mm., but with somewhat lower decomposition temperatures.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUQUESNE UNIVERSITY]

Association of Imidazole with Nickel(II) and Alkaline Earth Ions[1,2]

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RECEIVED AUGUST 19, 1954

The interaction of imidazole with nickel(II) ion was determined by means of polarographic and *p*H measurements at ionic strength 0.15. The coördination number of nickel ion for imidazole is 6. The successive logarithmic formation constants at 25° are: 3.27, 2.68, 2.15, 1.65, 1.12 and 0.52. The structure of the complex is that of an octahedron and the bonds are essentially ionic. From the absorption spectra of nickel imidazole complexes, the molar extinction coefficient of $NiIm^{++}$ is calculated to be approximately 3.3 l. mole^{-1} cm.$^{-1}$ at 650 mμ, the same as the corresponding value for $NiNH_3^{++}$. Barium and calcium ions have slight tendency to enter into complex formation with imidazole at 25 and 35°.

Introduction

As part of a general program on studies of complex formation between different metallic ions and the imidazoles,[3] this paper presents the results on the nickel(II) complexes of imidazole, using the polarographic, potentiometric, magnetic and spectrophotometric methods. Nickel(II) was chosen because the configuration of the complex formed can be determined from the coördination number and magnetic moment. Thus if the complex is paramagnetic then the bonds are essentially ionic and the complex has a tetrahedral or octahedral configuration, depending on whether the coördination number is four or six, respectively.

Cohn, *et al.*,[4] have shown that barium and calcium ions appear not to form association complexes with human serum albumin. In view of the accumulating evidence that in the combination of some other metals, namely, zinc, cadmium and copper, with serum albumin the principal binding sites are the imidazole groups of the histidine residues of the protein molecule, it was thought worthwhile to determine whether these alkaline earth ions enter into complex formation with imidazole or not. The results obtained at 25 and 35° are included in this paper.

Experimental

Material.—Imidazole purchased from Eastman Kodak Co. was treated and analyzed as previously described.[3] Stock solutions of $NiCl_2$ and $Ni(NO_3)_2$ were prepared and analyzed by precipitation wih dimethylglyoxime. All other compounds were of reagent grade and were used without further purification or analysis.

Magnetic Susceptibility Measurements.—The magnetic susceptibilities of a series of nickel(II) chloride solutions containing varying amounts of imidazole were measured at room temperature (approx. 18°) by the Gouy method. The apparatus has been described elsewhere.[5] It was calibrated with distilled water and with a standard $NiCl_2$ solution. Densities required for calculation of the magnetic susceptibilities were determined by the usual pycnometer method.

Other Measurements.—The polarographic and potentiometric *p*H measurements were as previously described.[3] Spectrophotometric measurements were made with a Beckman quartz spectrophotometer, Model DU.

Results

Table IA and B summarize the polarographic results obtained for imidazole solutions containing nickel(II) and barium ions, respectively, at 25° in aqueous medium. A plot of $-E_{1/2}$ *vs.* log C_{Im} for the nickel(II) complexes yields a line of slope 0.18. Since the theoretical slope corresponding to $p = 6$, where p is the number of groups coördinated to each metal ion (see equation 1, ref. 3), is 0.178, the complex is $NiIm_6^{++}$.

TABLE I

(A) POLAROGRAPHIC RESULT FOR SOLUTIONS CONTAINING 5×10^{-4} *M* $Ni(NO_3)_2$, 0.05% GELATIN, 0.15 *M* KNO_3 AND VARYING CONCENTRATIONS OF IMIDAZOLE

C_{Im}	log C_{Im}	$-E_{1/2}$	$E_{3/4} - E_{1/4}$
1.2363	0 09213	1.053	0.038
1.1288	.05262	1.046	.037
1.0384	.0164	1.038	.038
1.0326[a]	.01393	1.037	.037
0.9616	−0.01701	1.033	
.0000		1.106	.091 ($i_d = 2.18$ μa.)
.000[a]		1.101	.11 ($i_d = 2.64$ μa.)

[a] 0.022% gelatin.

(B) POLAROGRAPHIC RESULT FOR SOLUTIONS CONTAINING 5×10^{-4} *M* $Ba(NO_3)_2$, 0.15 *M* $(C_2H_5)_4NBr$ AND VARYING CONCENTRATIONS OF IMIDAZOLE

C_{Im}	$-E_{1/2}$	$E_{3/4} - E_{1/4}$
0.9856	1.925	0.030
.7885	1.922	.030
.0000	1.924	.028

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(1) Taken in part from the M.S. theses of C. T. Fujii and J. M. White, Duquesne University.

(2) This investigation was supported in part by a research grant from the National Science Foundation, Grant No. G510.

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(4) E. J. Cohn, D. M. Surgenor, K. Schmid, W. H. Batchelor, H. C. Isliker and E. H. Alameri, *Faraday Soc. Disc.*, 176 (1953).

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