complex, it seems certain that this quantity must be greater than that of the free amine and that ΔH for the above reaction must be less than -17.6 kcal./mole. Thus it can be said that relative to $B(CH_3)_3$, $CH_3C(CH_2O)_3P$ is a weaker donor than $N(CH_3)_3$ by several kilocalories.

CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORIES
OF BROWN UNIVERSITY, PROVIDENCE 12, RHODE ISLAND

Coördination Compounds of Ethylenimine with Cobalt(III), Chromium(III), Palladium(II), Platinum(II), and Platinum(IV)

BY TATIANA B. JACKSON AND JOHN O. EDWARDS

Received November 14, 1961

The synthesis of inert coördination compounds with ethylenimine (aziridine) as ligand is described. Stable complexes of cobalt(III), chromium(III), palladium(II), platinum(II), and platinum(IV) have been prepared and identified. The properties of the complexes are discussed briefly.

Introduction

In a previous paper[1] the authors described complexes formed by ethylenimine with metal ions whose complexes belong to the "labile" or rapid replacement class. The aim of the present research was to prepare inert complexes with the same ligand. By the use of direct synthesis or of substitution methods, it was possible to prepare such compounds with Co(III), Cr(III), Pt(II), Pt(IV), and Pd(II). Aside from the interest in the complexing properties of this unusual amine, the inert complexes are of importance as potential agents in cancer chemotherapy.

Experimental

Analyses were made by Dr. S. M. Nagy, Massachusetts Institute of Technology, or by Schwarzkopf Microanalytical Laboratory, Woodside 77, New York. The symbol Az for ethylenimine (aziridine) will be used.

Reagents.—The ethylenimine was purchased from the Borden Chemical Co., Leominster, Mass. It was dried over sodium, distilled from potassium hydroxide pellets, and stored in a refrigerator; boiling point, 55.5°. All the salts and solvents were of reagent grade. Distilled water was used through all the preparations.

Infrared Spectra.—It is known that ethylenimine is not a very stable compound, being rather easily hydrolyzed or polymerized with concurrent ring opening. On account of the relatively severe conditions (use of acid media or oxidation with air or chlorine) employed in the preparation of some of the complexes here described, it was necessary to check the presence of the three-membered ring in the products by infrared analysis. A Perkin-Elmer model 137 spectrophotometer was used to obtain spectra of all of the prepared compounds in potassium bromide disks. As a guide on infrared spectra of ethylenimine we used the work of Hoffman, Evans, and Glockler[2]; they observed and assigned the frequencies of infrared bands both in the gas and in the liquid phase. Bands corresponding to those described in that work were found and identified in our compounds, the most useful one for the purpose of qualitative analysis being a strong band occurring at 880–890 cm.$^{-1}$ and assigned to the deformation of the Az-ring. Such a band was found in all of the described compounds, thus confirming the elemental analysis. The infrared spectra will not be reported herein, since a complete study of the infrared spectra of ethylenimine complexes is in progress.

***cis*-Chlorobis-(ethylenediamine)-ethyleniminecobalt-(III) Chloride Hydrate, $[Co(C_2H_8N_2)_2(C_2H_5N)Cl]Cl_2\cdot H_2O$.**—To a slurry of 7 g. of acid-free *trans*-dichloro-bis-(ethylenediamine)-cobalt(III) chloride[3] in 10 ml. of ice-cold water was added 2 g. of Az. The dark red solution thus obtained was left in a refrigerator to crystallize overnight. On the following day the purple-red crystals were filtered by suction, washed with ethanol and ether, and dried over $CaCl_2$. More of the compound was obtained by addition of ethanol to the mother liquor. The complex was recrystallized from water–ethanol.

Anal. Calcd.: C, 20.79; H, 6.69; N, 20.21; Cl, 30.69. Found: C, 21.14; H, 6.83; N, 19.70; Cl, 31.03.

Bis-(ethylenediamine)-diethyleniminecobalt(III) Bromide, $[Co(C_2H_8N_2)_2(C_2H_5N)_2]Br_3$.—To 3 g. of ice-cold Az was added in very small portions 1 g. of *trans*-dibromobis-(ethylenediamine)-cobalt(III) bromide,[4] taking care that each portion had dissolved before adding the next one. The yellow solution was left at ice-temperature for a few hours, then by addition of ethanol and ether a yellow powdery compound was obtained. The complex was recrystallized from water–ethanol, filtered by suction, washed with

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[1] T. B. Jackson and J. O. Edwards, *J. Am. Chem. Soc.*, **83**, 355 (1961).

[2] H. T. Hoffman, Jr., G. E. Evans, and G. Glockler, *ibid.*, **73**, 3028 (1951).

[3] A. Werner, *Ber.*, **34**, 1733 (1901); *Inorg. Syntheses*, **2**, 222 (1946).

[4] A. Werner, *Ber.*, **44**, 111 (1911).

ethanol and ether, and dried over KOH. It is soluble in water and methanol and insoluble in ethanol, acetone, and ether. In water it slowly releases the Az to give red aquo-complexes.

Anal. Calcd.: C, 19.03; H, 5.19; N, 16.64. Found: C, 19.27; H, 5.53; N, 16.10.

***cis*-Chloro-(triethylenetetramine)-ethyleniminecobalt(III) Chloride,** $[Co(C_6H_{18}N_4)(C_2H_5N)Cl]Cl_2 \cdot H_2O$.—For the preparation of the *cis*-dichloro-(triethylenetetramine)-cobalt(III) chloride see Basolo.[5] Eight-tenths of a gram of *cis*-$[Co(C_6H_{18}N_4)Cl_2]Cl$ was added to 2.5 g. of ice-cold Az. Within 20 min. the complex dissolved and a brownish-red solution was obtained. By addition of ethanol and ether a brick-red solid was formed; it was filtered by suction, washed with ether, and dried. The complex was recrystallized from methanol–ether; the purple-red crystalline powder was filtered by suction, washed with ether, and dried *in vacuo* over $CaCl_2$. This compound is soluble in water, methanol, and ethanol and insoluble in ether.

Anal. Calcd.: C, 25.74; H, 6.77; N, 18.80; Cl, 28.60. Found: C, 26.11; H, 6.53; N, 18.87; Cl, 28.40.

Dinitrotetraethyleniminecobalt(III) Bromide, $[Co(C_2H_5N)_4(NO_2)_2]Br$.—A mixture of 2 g. of sodium hexanitrocobaltate(III) and 3 g. of Az was kept well stoppered in a refrigerator for 2–3 days, with occasional shaking. The complex dissolved slowly and crystals of sodium nitrite separated from the brown solution. After the addition of 20 ml. of absolute ethanol, the solution was filtered. The filtrate was collected and the solid on the filter was washed with absolute ethanol and ether. The yield of $NaNO_2$ was 0.88 g. (average) or 2.6 moles. By addition of ether to the filtrate a yellow powder was obtained which was recrystallized from ethanol–ether several times, until completely free from residual traces of sodium nitrite. Analyses of this yellow product did not clarify its constitution, as the results varied somewhat from sample to sample. It was found by conductance measurement to be an electrolyte; the anion was the nitrite ion and it could be replaced easily by addition of $NaClO_4$, KI, NaBr, and $NaNO_3$ to aqueous solutions of the powder, giving yellow-orange crystalline precipitates. All of these derivatives as well as the original compound showed identical infrared absorptions (besides those due to the anions), which were ascribed to the presence of ethylenimine and of nitro-groups. As simple recrystallizations did not improve the purity of the original product, the complex finally was isolated as the bromide salt which was recrystallized from methanol–ether. The bromide forms nice orange-colored needles, soluble in water, methanol, and ethanol and insoluble in acetone and ether. It is less soluble than the starting compound and quite stable toward aquation.

Anal. Calcd.: C, 23.83; H, 5.00; N, 20.85; Br, 19.82; Co, 14.64. Found: C, 23.78; H, 4.85; N, 20.44; Br, 19.64; Co, 14.25.

On these bases, the first reaction product was identified as impure dinitrotetraethyleniminecobalt(III) nitrite. The nature of the impurity could not be ascertained. However a sample of the powder was found by Dr. A. P. Ginsberg of Bell Telephone Laboratories to have a small paramagnetism. At 1.4 and 4.2°K., the calculated values for μ_{eff} (B.M.) were 0.20 and 0.26, respectively. This might suggest the presence of a cobalt(II) complex as an impurity.

Bis-(dimethylglyoximato)-diethyleniminecobalt(III) Chloride, $[Co(C_4H_7N_2O_2)_2(C_2H_5N)_2]Cl$.—A mixture of 2 g. of cobalt(II) chloride hexahydrate and 2 g. of dimethylglyoxime was dissolved in 95% ethanol. To this solution was added an ice-cold solution of 3.5 g. of Az in the same solvent. The total volume was 55 ml. A stream of air was passed for 40 min. through the dark brown solution. The brownish-orange crystals thus formed were filtered by suction, washed with a little absolute ethanol and ether, and dried; yield, 2.60 g. The complex was recrystallized from methanol–ether and dried *in vacuo* over $CaCl_2$. It is soluble in water, methanol, and ethanol and insoluble in acetone and ether.

Anal. Calcd.: C, 35.09; H, 5.89; N, 20.46; Cl, 8.63; Co, 14.35. Found: C, 35.23; H, 5.91; N, 20.64; Cl, 8.53; Co, 14.29.

***trans*-Dichlorotetraethyleniminechromium(III) Chloride,** $[Cr(C_2H_5N)_4Cl_2]Cl$.—In a flask equipped with a mechanical stirrer and cooled in an ice-bath was placed 6 g. of Az, then 3 g. of violet chromium(III) chloride was added in small portions with good stirring. Within 3 hr. the $CrCl_3$ dissolved yielding a violet solution and a green precipitate. (If this solution process should not occur rapidly, the addition of a trace of zinc metal helps to start the reaction.) Ice-cold chloroform was added to the reaction mixture, which then was filtered by suction. The violet filtrate was collected and set aside (see next preparation). The dark green solid on the filter was washed with chloroform and ether, dried, dissolved in methanol and quickly filtered to remove traces of unreacted $CrCl_3$, then recrystallized by addition of ether. This complex, which is presumably the *trans*-chloride judging from its green color and solubility properties, is soluble in water and methanol, slightly soluble in ethanol, and insoluble in acetone, chloroform, and ether. In water it undergoes a fairly rapid aquation. The anion can be replaced readily, giving the bromide, perchlorate, nitrate, and iodide.

Anal. Calcd.: C, 29.06; H, 6.10; N, 16.94. Found: C, 29.06; H, 6.18; N, 16.92.

Aquopentaethyleniminechromium(III) Chloride, $[Cr(C_2H_5N)_5H_2O]Cl_3$.—By addition of ether to the filtrate of the above preparation was obtained a relatively small quantity of a reddish-violet powdery compound, which was recrystallized from ethanol–ether, washed with ether, and dried *in vacuo* over $CaCl_2$. This compound could not be prepared by an independent method and its formation as a by-product of the previous preparation must be due to the influence of humidity from the $CrCl_3$ and the atmosphere. Its yield can be increased by addition of traces of water up to a point, after which hydrolysis takes place and the products are not crystallizable.

Anal. Calcd.: C, 30.66; H, 6.95; N, 17.88. Found: C, 30.37; H, 6.81; N, 17.65.

***cis*-Dichlorodiethylenimineplatinum(II),** $[Pt(C_2H_5N)_2Cl_2]$.—To an ice-cold, filtered solution of 2 g. of K_2PtCl_4 in 20 ml. of H_2O was added 1 g. of Az. The flask was stoppered and kept in a refrigerator. On the following day the pale yellow precipitate that had formed was collected on a filter, washed with water, ethanol, and ether, and dried *in vacuo* over $CaCl_2$. This complex is almost insoluble in water and is insoluble in the common organic solvents. From the mother liquor (without the washings) is obtained

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(5) F. Basolo, *J. Am. Chem. Soc.*, **70**, 2636 (1948).

by longer standing first a mixture of the diamino complex and the red $[Pt(C_2H_5N)_4]PtCl_4$, then the latter compound crystallizes alone in the form of beautiful rose-colored needles (see next preparations).

Anal. Calcd.: C, 13.64; H, 2.86; N, 7.95; Cl, 20.13. Found: C, 13.71; H, 2.90; N, 8.04; Cl, 20.32.

Tetraethylenimineplatinum(II) Chloride, $[Pt(C_2H_5N)_4]Cl_2$.—By dissolving $[Pt(C_2H_5N)_2Cl_2]$, $[Pt(C_2H_5N)_4]PtCl_4$, or a mixture of the two in ice-cold anhydrous Az, a colorless solution was obtained. On addition of ether after a few hours of standing a white crystalline powder was obtained, which was filtered, recrystallized from ethanol–ether, filtered by suction, washed with ether, and dried *in vacuo* over $CaCl_2$. This complex is soluble in water, methanol, and ethanol and insoluble in ether.

Anal. Calcd.: C, 21.92; H, 4.60; N, 12.78; Cl, 16.17. Found: C, 21.73; H, 4.86; N, 12.70; Cl, 15.64.

Tetraethylenimineplatinum(II) Tetrachloroplatinate, $[Pt(C_2H_5N)_4]PtCl_4$.—This compound was obtained by addition of an aqueous solution of potassium tetrachloroplatinate to a solution of tetraethylenimineplatinum(II) chloride, in the form of a rose-colored crystalline powder. It also is formed as a by-product in the preparation of the dichlorodiethylenimineplatinum(II), as reported above. This complex is insoluble in water, alcohols, acetone, chloroform, and ether and soluble in Az and dilute HCl.

Anal. Calcd.: C, 13.64; H, 2.86; N, 7.95. Found: C, 13.63; H, 2.80; N, 7.95.

Dichlorotetraethylenimineplatinum(IV) Chloride, $[Pt(C_2H_5N)_4Cl_2]Cl_2$.—The method employed was similar to the one used by Grinberg and Gil'dengershel'[6] in the preparation of the analogous ethylamine complex. Through an ice-cold, concentrated solution of 0.7 g. of pure $[Pt(C_2H_5N)_4]Cl_2$, to which had been added 1.5 ml. of cold concentrated HCl, was led for 20 min. a stream of chlorine gas, with occasional shaking. The cream-colored crystalline precipitate was filtered by suction and washed with acetone and ether. By addition of acetone to the mother liquor (without the washings) more of the compound was obtained; total yield, 0.60 g. The compound was recrystallized from water–acetone, washed as above, and dried *in vacuo* over KOH. It is soluble in water, methanol, and ethanol and insoluble in acetone and ether. The compound was presumed to be in the *trans* form, on the basis of the method of preparation.

Anal. Calcd.: C, 18.86; H, 3.96; N, 11.01; Cl, 27.84. Found: C, 18.73; H, 3.90; N, 10.98; Cl, 28.00.

Dichlorotetraethylenimineplatinum(IV) Hexachloroplatinate, $[Pt(C_2H_5N)_4Cl_2]PtCl_6$.—A solution of 0.3 g. of K_2PtCl_6 in 60 ml. of water was added little by little to an aqueous solution of $[Pt(Az)_4Cl_2]Cl_2$. The yellow precipitate was allowed to settle for 1 hr., then it was filtered by suction, washed with water, ethanol, and ether, and dried *in vacuo* over $CaCl_2$; yield, 0.34 g. It is very slightly soluble in water and insoluble in acetone, alcohols, and ether.

Anal. Calcd.: C, 11.35; H, 2.38; Cl, 33.51. Found: C, 11.21; H, 2.28; Cl, 33.44.

***trans*-Dichlorodiethyleniminepalladium(II),** $[Pd(C_2H_5N)_2Cl_2]$.—A solution of 1 g. of palladium chloride in water acidified with HCl was filtered and cooled in ice. By addition of an aqueous solution of Az a brownish precipitate was formed at first, probably a mixture of $[Pd(Az)_2Cl_2]$ and $[Pd(Az)_4]PdCl_4$, which redissolved with an excess of Az to give a very pale yellow solution. By addition of an ice-cold 50% solution of HCl, the desired complex precipitated as a yellow crystalline powder which was filtered by suction, washed with water, ethanol, and ether, and dried *in vacuo* over $CaCl_2$; yield, 1.2 g. The complex was recrystallized from acetone–ether. It is soluble in Az, aqueous Az-solutions, and acetone and insoluble in water, alcohols, and ether.

Anal. Calcd.: C, 18.22; H, 3.82; N, 10.62; Cl, 26.89. Found: C, 18.10; H, 3.95; N, 10.43; Cl, 27.01.

Discussion

The results of this work confirm the conclusions made in the previous paper[1] regarding the bonding ability of ethylenimine with metal ions. The colors of the compounds here described are very similar to those of the corresponding ammine complexes.

The visible and ultraviolet spectra of one of the Co(III) compounds, $[Co(C_2H_5N)_4(NO_2)_2]Br$, showed three bands, at 455, 352, and 257 mμ. A paper by Kiss and Czeglédy[7] reports bands for $[Co(NH_3)_3(NO_2)_3]$ at 433, 342, and 251 mμ and for $[Co(NH_3)_2(NO_2)_4]^-$ at 428, 346, and 253 mμ (the compound $[Co(NH_3)_4(NO_2)_2]^+$ was not reported). The fact that the absorption pattern is so remarkably similar to that of the ammine complexes suggests that the crystal field splitting parameter Dq of ethylenimine must be closely similar to that of ammonia.

It was found that these complexes are all inert. Their rates of aquation, although not studied in detail, correlated well with our expectations for typical amino complexes.

Many attempts to synthesize complexes which are well known with other amines and with pyridine did not lead to analogous ethylenimine complexes; it was possible to show in these cases by infrared that the ethylenimine ring had cleaved. The methods successfully employed include both substitution and direct synthesis. The latter method was the one found most useful in working with chromium, platinum, and palladium. In the case of cobalt it was impossible to apply the normal oxidation methods, except in the presence of dimethylglyoxime, and pre-formed Co(III) compounds had to be used as starting compounds. It is worth noting that the $[Co(en)_2(Az)Cl]Cl_2$

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[6] A. A. Grinberg and Kh. I. Gil'dengershel', *Zhur. Priklad. Khim.*, **22**, 1056 (1949); *Chem. Abstr.*, **44**, 474 (1950).

[7] A. v. Kiss and D. v. Czeglédy, *Z. anorg. u. allgem. Chem.*, **235**, 407 (1938).

[8] J. C. Bailar, Jr., and L. B. Clapp, *J. Am. Chem. Soc.*, **67**, 171 (1945).

represents the first case to our knowledge[8] where a secondary amine was used successfully in this type of displacement. Also, in the case of the *trans*-[Co(en)$_2$Br$_2$]Br, reaction with ethylenimine in aqueous solution led only to disproportionation to give the trisethylenediamine complex, while the use of anhydrous ethylenimine gave displacement of two halogen ligands and resulted in the described complex.

Acknowledgment.—We are grateful to Drs. L. B. Clapp and R. L. Carlin for helpful discussion, to Dr. A. P. Ginsberg for some special measurements, and to the U. S. Public Health Service for financial aid.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Octahedral Coördination Compounds of Nickel(II) and Cobalt(II) with Ethylenimine[1]

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Received September 18, 1961

Ethylenimine is known to form coördination compounds with nickel and cobalt similar to those formed by ammonia. The absorption spectra of the ethylenimine coördination compounds of nickel and cobalt are reported from 6000 to 30,000 cm.$^{-1}$; extinction coefficients are reported and d–d transition assignments are made. Based on measurements of the dipole moment and polarizability of ethylenimine, calculations of bond energies are made using the electrostatic theory.

Introduction

The recent report by Jackson and Edwards[2] of the preparation of coördination compounds of labile (transition) metals with ethylenimine prompted us to investigate the absorption spectra of some of these complexes and to attempt to apply the ligand field theory to the results. The octahedral complexes of nickel(II) and cobalt(II) were chosen for study. Using the Liehr and Ballhausen[3] energy level diagram for nickel(II) and the Orgel diagram[4] for cobalt(II), assignments of the observed absorptions of the ethylenimine coordination compounds of nickel(II) and cobalt(II) were made.

It also was desired to make an electrostatic calculation of the bond energy for each of the complexes. To make these calculations, it was necessary to determine the dipole moment of ethylenimine. By combination of the electrostatic calculations and the crystal field stabilization energy (CFSE), the bond energies were determined.

Experimental

Hexaethylenimine Nickel(II) and Cobalt(II) Nitrate.—The compound $Ni(NC_2H_5)_6(NO_3)_2$ was prepared by the methods of Jackson and Edwards.[2] The cobalt complex was conveniently prepared by the addition of an aqueous solution of cobalt(II) nitrate hexahydrate to a solution of ethylenimine in a small amount of water, cooled in ice. The complex precipitated from solution, upon addition of a saturated solution of potassium nitrate, as orange-to-pink crystals. The $Co(NC_2H_5)_6(NO_3)_2$ complex was removed by filtration and washed with a cold solution of ethylenimine in water. All of the salts used in the preparations of the complexes were of reagent grade. The ethylenimine (98–100%) was obtained from Matheson Coleman & Bell, and was used as received. A 0.018 *M* solution of $Ni(NC_2H_5)_6(NO_3)_2$ in methanol produced an azure-blue color; a 0.05 *M* solution of this same complex in water gave a lavender-violet color. A 0.02 *M* methanol solution of $Co(NC_2H_5)_6(NO_3)_2$ was pink in color.

Spectral Measurements.—The solution spectra of the various complexes in the near infrared region were obtained with a Perkin–Elmer Model 4000A Spectracord recording spectrophotometer, using 1.00-cm. matched quartz cells. The solution spectra in the visible and near-ultraviolet were obtained with a Beckman Model DB spectrophotometer, using 1.00-cm. matched quartz cells. Both methanol solutions and aqueous solutions containing a slight excess of ethylenimine of known concentrations of the complexes were prepared and used in determining the molar absorbance indices (extinction coefficients), a_m.

Dipole Moment of Ethylenimine.—Dielectric constants of dilute solutions of ethylenimine (aziridine) in benzene were determined using a Sargent Model V oscillometer

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(1) This work was supported in part by the U. S. Atomic Energy Commission under Contract No. AT(111)-751 with Kansas State University.

(2) T. B. Jackson and J. O. Edwards, *J. Am. Chem. Soc.*, **83**, 355 (1961).

(3) A. D. Liehr and C. J. Ballhausen, *Ann. Phys.* (N. Y.), **6**, 134 (1959).

(4) L. E. Orgel, *J. Chem. Phys.*, **23**, 1004 (1955).