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.

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Octahedral Coördination Compounds of Nickel(II) and Cobalt(II) with Ethylenimine[1]

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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$_2$H$_5$)$_6$(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$_2$H$_5$)$_6$(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$_2$H$_5$)$_6$(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$_2$H$_5$)$_6$(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).

with a compensator to give a linear relation between the scale measurements of the instrument and dielectric constant over the range of dielectric constants from 2.0 to 6.0. Benzene (ϵ_{25} = 2.274), diethyl ether (ϵ_{25} = 4.24), chloroform (ϵ_{25} = 4.718), and ethyl acetate (ϵ_{25} = 6.02) were used to calibrate the dielectric scale. All measurements were made at 25.0 ± 0.5° with a cell of approximately 10 ml. volume.

The molar polarization of the solute at infinite dilution ($P_{2\infty}$) was determined by the methods of Hedestrand,[5] Halverstadt and Kumler,[6] and by the simple extrapolation of the curve in a plot of P_2 *vs.* mole fraction of solute. Sugden's method[7] also was used to obtain ($P_{2\infty} - P_D$).

We note that the value ($P_{2\infty} - P_D$) determined by Sugden's method is somewhat lower than the values obtained by the other methods. That is, the solvent effect apparently is in the opposite direction from those reported for the other compounds in the study made by Pilpel.[8]

The distortion polarization (P_D) was calculated using the customary expression

$$P_D = (1.05)[(n_D^2 - 1)/(n_D^2 + 2)](M_2/\rho)$$

where n_D is the refractive index of the solute (1.4100 at 25°) using the sodium-D line (measured with an Abbe refractometer), M_2 is the molecular weight of the ethylenimine (43.07), and ρ is the density of the ethylenimine (0.8318 at 25°). The factor 1.05 is used to take account of an approximately 5% atom polarization. The dipole moment, μ, was calculated from the expression

$$\mu = 0.01281\sqrt{(P_{2\infty} - P_D)T} \times 10^{-18} \text{ e.s.u.}$$

Results

The dipole measurement data are given in Table I. The mean value of the dipole moment calculated from these data by the various methods cited is 1.73 D. We estimate the error in this value to be less than 0.1 D. Although this is a rather large error, it does not seriously affect the calculations in which it is used.

Table I

Experimental Data for the Determination of the Dipole Moment of Ethylenimine[a]

X_2	W_2	$\rho_{1,2}$	$\epsilon_{1,2}$	P_2
0.0000	0.0000	0.8790	(2.274)	
.0490	.0276	.8766	2.505	80.20
.0922	.0530	.8744	2.755	81.89
.1338	.0785	.8727	3.05	83.71
.1706	.1020	.8710	3.40	86.93
.2154	.1315	.8688	3.83	86.53

[a] X_2 = mole fraction of solute; W_2 = weight fraction of solute; $\rho_{1,2}$ = density of solution; $\epsilon_{1,2}$ = dielectric constant of solution.

The absorption spectra of the two complexes, $[Ni(NC_2H_5)_6]^{++}$ and $[Co(NC_2H_5)_6]^{++}$, are shown in Fig. 1 and 2, respectively.

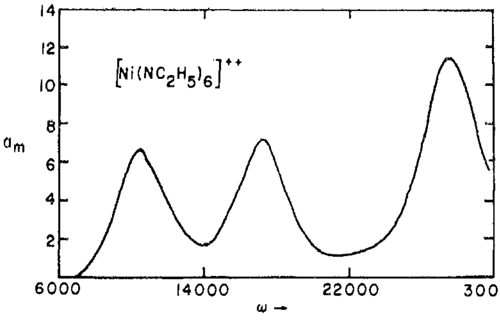

Fig. 1.—Absorption spectrum of $[Ni(NC_2H_5)_6]^{++}$ in aqueous solution, with an excess of ethylenimine present.

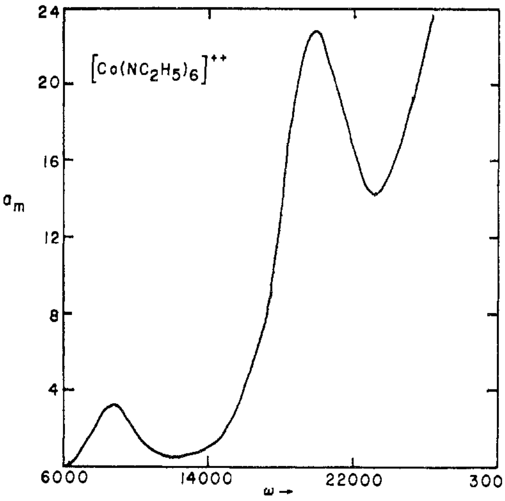

Fig. 2.—Absorption spectrum of $[Co(NC_2H_5)_6]^{++}$ in methanol solution.

The polarizability, α, was calculated from

$$\alpha = (3/4\pi N)[(n_D^2 - 1)/(n_D^2 + 2)](M/\rho)$$

Using our experimental value of n^{25}_D 1.4100, $\alpha = 5.10 \times 10^{-24}$ cc.

The molar refraction calculated from n^{25}_D 1.4100 is 12.83. Molar refractions of 12.838, 12.78, and 12.90 were calculated from the atomic refractions given by Fajans,[9] and the bond refractions given by Davidson[10] and by Denbigh,[11] respectively.

Taking the bond distances N–H = 1.000 Å., C–H = 1.083 Å., C–C = 1.480 Å., and C–N = 1.488 Å., with ∠HCH = 116.7°, the angle between the C–C bond and the H–C–H plane as 159.4°, and the angle between the N–H bond

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[5] G. Hedestrand, *Z. physik. Chem.*, **B2**, 428 (1929).

[6] I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2988 (1942).

[7] S. Sugden, *Nature*, **133**, 415 (1934).

[8] N. Pilpel, *J. Am. Chem. Soc.*, **77**, 2949 (1955).

[9] K. Fajans, in "Physical Methods in Organic Chemistry," Vol. I, edited by A. Weissberger, Interscience Publishers, Inc., New York, N. Y., 1945, p. 672.

[10] H. R. Davidson, *J. Chem. Educ.*, **27**, 598 (1950).

[11] K. G. Denbigh, *Trans. Faraday Soc.*, **36**, 936 (1940).

and the C–C–N plane as 112°,[12] we estimate an approximate radius for the ethylenimine molecule of 1.7 Å.

Using the dipole moment of 1.73 D. in conjunction with $r_{\mathrm{Ni}^{++}} = 0.72$ Å. and $r_{\mathrm{Co}^{++}} = 0.74$ Å.,[13] $\alpha = 5.10 \times 10^{-24}$ cc., and the radius of the ethylenimine molecule = 1.7 Å., the dipole moment induced in each ligand of the complex, μ_i, is 3.72 D. for the nickel–ethylenimine complex, and 3.71 D. for the cobalt–ethylenimine complex. Table II summarizes the various attraction and repulsion terms calculated[14] from the electrostatic theory for the two complexes, along with the crystal field stabilization energy (CFSE) calculated from the observed d–d transitions.

TABLE II

CALCULATED BOND ENERGIES FOR THE ETHYLENIMINE COMPLEXES OF COBALT(II) AND NICKEL(II)

(In kcal./mole per bond)

	$[\mathrm{Ni(NC_2H_5)_6}]^{++}$	$[\mathrm{Co(NC_2H_5)_6}]^{++}$
Ion–dipole attractions	−40.9	−40.2
Ion–induced dipole attractions	−68.3	−66.8
Dipole–dipole repulsions	+35.8	+34.8
van der Waals repulsions	+16.7	+16.8
Total attractions	−56.7	−55.4
CFSE	− 6.0	− 3.3
Calculated bond energy	−62.7	−58.7

The CFSE for the two complexes of ethylenimine were determined for weak ligand fields. For $[\mathrm{Ni(NC_2H_5)_6}]^{++}$, $10Dq = 10{,}500$ cm.$^{-1}$ and for $[\mathrm{Co(NC_2H_5)_6}]^{++}$, $10Dq = 10{,}300$ cm.$^{-1}$, as derived from the absorption spectra.

Discussion

Table III compares the experimental results to values calculated from the energy level diagram for nickel(II) given by Liehr and Ballhausen,[3] and for cobalt(II) presented by Orgel.[4] The absorption maxima are very nearly the same as those observed for the hexaammine nickel(II) ion. This suggests that the strength of bonding of ethylenimine (*i.e.*, the relative placement of this ligand in the Fajans–Tsuchida arrangement of ligands) is about the same as that for ammonia in octahedral complexes of nickel(II) and cobalt(II). Jackson and Edwards,[2] from their studies of formation constants, indicate the bonding of ethylenimine to be slightly weaker than that of ammonia.

TABLE III

EXPERIMENTAL AND CALCULATED SPECTRA OF THE STUDIED OCTAHEDRAL COMPLEXES

		Absorption energies, cm.$^{-1}$		
Ion	Transition[a]	Calcd.[a]	Obsd.	a_m
$[\mathrm{Ni(NC_2H_5)_6}]^{++}$	$^3A_{2g} \rightarrow {}^3T_{2g}$	10,500	10,500	6.7
	$^3A_{2g} \rightarrow {}^1E_g$	12,400		
	$^3A_{2g} \rightarrow {}^3T_{1g}$	16,500 17,250	17,100	7.2
	$^3A_{2g} \rightarrow {}^1A_{1g}$	21,250	*ca.* 22,000	*ca.* 1
	$^3A_{2g} \rightarrow {}^1T_{2g}$	22,600		
	$^3A_{2g} \rightarrow {}^3T_{1g}$	27,250	27,500	11.5
	$^3A_{2g} \rightarrow {}^1E_g, {}^1T_{2g}$	35,000	33,500	
$[\mathrm{Co(NC_2H_5)_6}]^{++}$	$^4T_{1g} \rightarrow {}^4T_{2g}$	8,900	8,900	3.3
	$^4T_{1g} \rightarrow {}^4A_{2g}$	19,200	19,800	22.7
	$^4T_{1g} \rightarrow {}^4T_{1g}$ (P)	22,400		

[a] See Liehr and Ballhausen[3] for Ni(II) and Orgel[4] for Co(II).

The octahedral $[\mathrm{Ni(NC_2H_5)_6}]^{++}$ ion exhibits a number of absorption bands, with the centers of the bands located at 10,500; 17,100; 22,000; 27,500; and 33,500 cm.$^{-1}$. These absorption bands all are rather broad, since they are vibronic in origin, and have been shown in Fig. 1. Although the 33,500 cm.$^{-1}$ band is not shown, it was resolved in methanol solution. From Liehr and Ballhausen's energy level diagram[3] for nickel(II), a consistent assignment of the experimental spectrum is possible taking $10Dq = 10{,}500$ cm.$^{-1}$, $\lambda = 275$ cm.$^{-1}$, and $F_4 = 90$ cm.$^{-1}$ (*i.e.*, $B = 810$ cm.$^{-1}$). The observed absorptions are correlated with these computed energy level transitions: (i) $\Gamma_5 \rightarrow \Gamma_j$ ($j = 2,3,4,5$), 10,500 cm.$^{-1}$; (ii) $\Gamma_5 \rightarrow \Gamma_j$ ($j = 1,4$), 16,500 cm.$^{-1}$; (iii) $\Gamma_5 \rightarrow \Gamma_j$ ($j = 3,5$) 17,200 cm.$^{-1}$; and (iv) $\Gamma_5 \rightarrow \Gamma_j$ ($j = 1,3,4,5$), 27,250 cm.$^{-1}$. These transitions are nearly pure triplet–triplet transitions among the perturbed ^{3}F and ^{3}P states of the free ion.[3] One can see from the above that the (ii) and (iii) transitions lie quite close in energy, *i.e.*, *ca.* 17,000 cm.$^{-1}$. From Fig. 1, these appear as a single peak. From the methanol solution spectrum of $[\mathrm{Ni(NC_2H_5)_6}]^{++}$, however, we observed two very close-lying peaks, centered about 16,600 and 17,300 cm.$^{-1}$. In addition, we see from Fig. 1 an apparent small absorption at about 22,000 cm.$^{-1}$, which would agree with the calculated "spin-forbidden" transitions: (v) $\Gamma_5 \rightarrow \Gamma_1$, 21,250 cm.$^{-1}$; and (vi) $\Gamma_5 \rightarrow \Gamma_5$, 22,600 cm.$^{-1}$. Because the "spin-forbidden" transition $\Gamma_5 \rightarrow \Gamma_4$ at 26,750 cm.$^{-1}$ lies so close to the $\Gamma_5 \rightarrow \Gamma_j$ ($j = 1,3,4,5$) transition at 27,250 cm.$^{-1}$, we would not expect to observe it experimentally in the absorption

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[12] "Interatomic Distances," Special Publication No. 11, The Chemical Society, London, 1958, p. M134.

[13] L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, p. 518.

[14] See, for example, F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 46-58.

spectrum of the $[Ni(NC_2H_5)_6]^{++}$ ion. The 33,500 cm.$^{-1}$ absorption band observed in the methanol solution spectrum of $[Ni(NC_2H_5)_6]^{++}$ apparently is to be correlated with the "spin-forbidden" transition $\Gamma_5 \rightarrow \Gamma_j$ ($j = 3,5$), which has a calculated energy of 35,000 cm.$^{-1}$. Although we are unable to resolve accurately the 10,500 cm.$^{-1}$ band from a weak, "spin-forbidden" transition $\Gamma_5 \rightarrow \Gamma_3$ expected at 12,400 cm.$^{-1}$, the slightly non-Gaussian shape on the high-energy side of the 10,500 cm.$^{-1}$ band suggests that this $\Gamma_5 \rightarrow \Gamma_3$ transition is present in the experimental spectrum.

In the absorption spectra of octahedral $[Co(NC_2H_5)_6]^{++}$ ion only two absorption bands, with the centers of the bands located at 8900 and 19,800 cm.$^{-1}$, were observed. These absorption bands, like those of Ni(II), are rather broad. This may be seen from Fig. 2. Using the Orgel energy level diagram[4] for cobalt(II), a consistent assignment of the experimental spectrum is possible taking $10Dq = 10{,}300$ cm.$^{-1}$. The observed absorptions are correlated with the energy level transitions: (i) $^4T_{1g} \rightarrow {}^4T_{2g}$, 8,900 cm.$^{-1}$; (ii) $^4T_{1g} \rightarrow {}^4A_{2g}$, 19,200 cm.$^{-1}$; (iii) $^4T_{1g} \rightarrow {}^4T_{1g}(P)$, 22,400 cm.$^{-1}$. From Fig. 2, transitions (ii) and (iii) apparently appear as a single peak. Although we are unable to resolve accurately the 19,800 cm.$^{-1}$ band, the slightly non-Gaussian shape on the high-energy side of this peak suggests that the $^4T_{1g} \rightarrow {}^4T_{1g}(P)$ transition is present in the experimental spectrum. A complete resolution of this peak occurring at 19,800 cm.$^{-1}$ was quite difficult. However, we estimate the higher-energy transition to occur at approximately 21,000 cm.$^{-1}$.

The electrostatic theory calculations presented in Table II, with the crystal field stabilization energy taken into account, give the calculated bond energies for the two complexes we have considered. Although the "experimental" bond energies were not calculated for the two complexes, the calculated bond energies of the ethylenimine complexes of nickel(II) and cobalt(II) appear to agree with calculated bond energies of comparable[15] complexes (*e.g.*, $M(OH_2)_6^{++}$, $M(NH_3)_6^{++}$, and $M(en)_3^{++}$).

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[15] Reference 14, p. 65.

CONTRIBUTION FROM THE WILLIAM ALBERT NOYES LABORATORY,
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A Consideration of Steric Effects in the Chelating Tendencies of Some Methylene-Substituted β-Diketones

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Three series of compounds were prepared and chelating tendencies determined: I, $CH_3COCH(R)COCH_3$; II. $CH_3OCH_2COCH(R)COCH_3$; III, $C_6H_5COCH(R)COC_6H_5$. A linear pK_D–log K relationship was observed for uranyl chelates of series II and III and for beryllium chelates of series II, but such a relationship was not observed for copper and other divalent metal chelates of series I, II, and III. Several possible steric effects are considered, and rationalizations of these are presented. An alternate interpretation, *viz.*, that of solvation effects, is favored.

Introduction

The effect of a methylene-substituent, R′, upon the chelating tendency of a β-diketone, RCOCHR′COR″, has been examined by previous workers[1,2]: An alkyl substituent lowers the acidity, as would be expected, and, generally, the stability of the copper chelates is less than that expected on the basis of a pK_D–log K relationship. This effect has been attributed to steric interaction (R and R″ with R′) and concomitant deformation of the planar ring structure which seems to be necessary for maximum stability.[1] However, it has been suggested[3] that steric *or solvation* factors may be involved in anomalous

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[1] M. Calvin and K. W. Wilson, *J. Am. Chem. Soc.*, **67**, 2003 (1945).

[2] B. B. Martin and W. C. Fernelius, *ibid.*, **81**, 2342 (1959).

[3] R. N. Keller and R. W. Parry in J. C. Bailar, Jr., "The Chemistry of the Coördination Compounds," Reinhold Publishing Corp., New York, N. Y., 1956, p. 183.