(prepared by addition of 90% nitric acid to acetic anhydride). After stirring for 15 min. at this temperature the reaction mixture is drowned in 2 l. of diethyl ether; the ether layer is decanted, the oily residue is washed twice with 100 ml. of ether, and the ether solution is concentrated to 10 ml. by distilling the ether through a column of *ca.* 20 plates. Gas–liquid chromatography indicates that the sample contains 0.09 mmole of nitrobenzene (read from a reference line prepared from standard solutions). The insoluble semisolid material, 1.630 g., is oxidized with potassium permanganate in water,[3] the acid mixture is esterified with diazomethane, and the resulting esters are dissolved in 10 ml. of chloroform and are analyzed for methyl nitrobenzoates by the liquid–gas chromatographic method described above, indicating the presence of 0.12 mmole of methyl nitrobenzoates.

Exchange Reactions of $KC^{14}N$ with $(p\text{-}XC_6H_4CH_2NC)_5FeCNBr$.—To 0.5 mmole of the isonitrile complex in 45 ml. of absolute methanol was added a solution of 1.0 mmole of $KC^{14}N$ in 5 ml. of water containing a total of 2.7 μcuries. The reaction mixture was stoppered and was stirred with a magnetic stirrer at 23° for 58 hr. The reaction mixture was then poured into 50 ml. of 60% sulfuric acid solution, the methanol was evaporated under reduced pressure, and the remaining solution was heated on a steam bath for 30 min. Subsequently it was extracted three times with 50 ml. of chloroform; the chloroform extracts were dried with magnesium sulfate (anhydrous) and the chloroform removed by evaporation. The resultant complexes were crystallized from methyl ethyl ketone. After drying at 25° (0.1 mm.) the complexes were weighed and analyzed for C^{14} as a solution in methanol by the method of Hayes.[35] The results obtained are summarized in Table V.

Acknowledgments.—The author wishes to thank Miss Lucille E. Williams and Messrs. C. R. Talley and R. S. Blake for polarographic determinations, gas–liquid chromatographies, and radioactive analyses, respectively.

[35] F. N. Hayes, *Intern. J. Appl. Rad. Isotopes*, **1**, 46 (1956).

CONTRIBUTION FROM THE WM. A. NOYES LABORATORY, CHEMISTRY DEPARTMENT,
UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS

Spectrochemical Studies of the Primary Alkylamine Complexes of Nickel(II) and an Evaluation of the Donor Properties of Amines

BY RUSSELL S. DRAGO, DEVON W. MEEK,[1] RAYMOND LONGHI,[1] AND MELVIN D. JOESTEN

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The trends in the donor properties of ammonia and some alkylamines toward the Lewis acids iodine and phenol are qualitatively explained by consideration of the differences in the relative importance of polarization and electrostatic forces in the various adducts. An assignment for the trends in these properties is offered for a series of amines and applied to correlate the magnitude of the interaction in several adducts. Similar considerations can be used to qualitatively explain the positions ammonia and the primary alkylamine donors occupy in the spectrochemical series of the cation nickel(II). Even though the alkylamines are easily displaced from the coordination sphere by water, the amines occupy a higher position in the spectrochemical series than water. The greater stability of ammonia than amine complexes in water is due to several effects, a very important one being the higher heat of hydration of methylamine than ammonia. Water does not appear to form stronger bonds than methylamine with nickel(II).

Introduction

The basicity of amines has long attracted the interest of inorganic and organic chemists. If only the inductive factor were operative in the series NH_3, RNH_2, R_2NH, and R_3N (where R is alkyl), one would predict a regular increase in basicity with increased alkyl substitution. It was found that the pK_B values for a series of methylamines deviated from this order, producing the following sequence of increasing basicity

$$NH_3 < (CH_3)_3N < CH_3NH_2 < (CH_3)_2NH$$

The existence of back strain in trimethylamine was proposed.[2] In an excellent analysis of this problem Pearson and Vogelsong[3,4] have discussed the energetics of this system and have shown clearly that pK_B data cannot be interpreted in terms of the magnitude of the interaction between an acid and a base. It is necessary to consider contributions from solvation terms, ion-pair association, and entropy effects in explaining pK_B data.

The main concern of this article is with the magnitude of the interaction between acids and amines. The criteria employed are enthalpies of formation of adducts between aliphatic amines and iodine[5] measured in the weakly solvating medium carbon tetrachloride. These reported enthalpies are compared with enthalpies of formation of amine–phenol adducts in carbon tetrachloride. Toward phenol smaller differences in the enthalpies of formation of the adducts are observed for this series of amines than for the iodine adducts. A qualitative proposal is offered to account for the difference in donor properties manifested by these amines toward iodine and phenol.

It is generally accepted[6] that nickel(II) coordinates less readily with monodentate alkyl-substituted amines

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[1] Abstracted in part from the Ph.D. theses of D. W. Meek and R. Longhi, University of Illinois, Urbana, Illinois, 1961 and 1962, respectively.

[2] H. C. Brown and M. D. Taylor, *J. Am. Chem. Soc.*, **69**, 1332 (1947).

[3] R. G. Pearson and D. C. Vogelsong, *ibid.*, **80**, 1038 (1958), and references contained therein.

[4] R. G. Pearson and D. C. Vogelsong, *ibid.*, **80**, 1048 (1958), and references contained therein.

[5] H. Yada, J. Tanaka, and S. Nagakura, *Bull. Chem. Soc. Japan*, **33**, 1660 (1960).

[6] J. C. Bailar, Jr., and D. H. Busch, "The Chemistry of Coordination Compounds," J. C. Bailar, Jr., Ed., Reinhold Publishing Corp., New York, N. Y., 1956, p. 62.

than with ammonia.[6] Solid complexes of monodentate alkylamines have been known for a long time[7] and recently this work has been extended.[8] No conclusions regarding the relative magnitude of the amine–metal ion interaction can be drawn from these studies because of the uncertainties in the lattice energies. This subject has been discussed in detail by Parry and Keller.[9]

The six-coordinate primary alkylamine complexes of nickel cannot be prepared by reactions in water and when prepared under other conditions and dissolved in water, extensive hydration of the metal ion occurs displacing amine from the coordination sphere and precipitating $Ni(OH)_2$. This behavior cannot be used as a measure of how strong the metal ion–amine interaction is relative to the ammonia or water interaction with the metal ion because many other energy terms are operative. Contributions from these same terms make rigorous interpretation of stability constants impossible in most cases. It is proposed that the crystal field parameter Dq, evaluated for Ni(II) complexes, may provide the best information currently available on the relative magnitude of the interaction of alkylamines with nickel(II) to form six-coordinate complexes. For this purpose, the complexes $[Ni(CH_3NH_2)_6](ClO_4)_2$, $[Ni(C_2H_5NH_2)_6](ClO_4)_2$, $[Ni(n\text{-}C_3H_7NH_2)_6](ClO_4)_2$, and $[Ni(i\text{-}C_3H_7NH_2)_6](ClO_4)_2$ were prepared and their spectrochemical properties determined. The differences in the parameters obtained for these amines are discussed and an explanation is proposed to account for the interesting result that the amines have higher Dq values toward Ni(II) than water but water easily replaces the amine in the coordination sphere.

Attempted preparations of six-coordinate nickel(II) complexes of dimethyl- and trimethylamine were unsuccessful even though techniques were employed which yielded complexes of other weak coordinating ligands.[10] The preparative procedures employed by Ephraim and Linn[7] and Hatfield and Yoke[8] are also reported not to yield six-coordinate complexes of these and related amines with transition metal ions.

Experimental

Spectrophotometric Measurements.—Near-infrared and visible absorption spectra were obtained with a recording Cary spectrophotometer, Model 14M. Solutions were prepared by dissolving the complex in an appropriate solvent and adding excess ligand to the solvent. Nonhydroxylic, poorly coordinating solvents were employed whenever possible.

The O–H frequency shifts for adducts of these amines with phenol were obtained by a method which has been previously described.[11] A Beckman Model IR-7 spectrophotometer was employed. A slit width of 0.37 mm. at 3100 cm.$^{-1}$ and sodium chloride cells of 0.2-mm. thickness were employed.

Calculations.—A description of the procedure which was followed in making band assignments and in calculating ligand field parameters has been reported.[12]

Preparation of the Complexes.—Hexaamminenickel(II) chloride was prepared in a high state of purity by the standard procedure. The nickel(II) alkylamine complexes were prepared by the following general procedure. The aquated nickel(II) perchlorate was dehydrated with a 50% excess of 2,2-dimethoxypropane[13] by stirring for 2 hr. at room temperature. The solution was diluted with two volumes of absolute methanol and then a stream of nitrogen and amine was bubbled through this solution for 2 hr. When less volatile amines are employed, twofold excess of the liquid amine is added. The resulting solution was stirred for an additional 6 hr. and then filtered. The precipitate was washed with absolute methanol and ether and dried with a stream of dry air.

Anal. Calcd. for $[Ni(CH_3NH_2)_6](ClO_4)_2$: C, 16.23; H, 6.81; N, 18.93; Ni, 13.22. Found: C, 16.38; H, 6.51; N, 18.70; Ni, 12.95.

Anal. Calcd. for $[Ni(C_2H_5NH_2)_6](ClO_4)_2$: C, 27.29; H, 8.02; N, 15.91. Found: C, 27.08; H, 7.99; N, 15.64.

Anal. Calcd. for $[Ni(n\text{-}C_3H_7NH_2)_6](ClO_4)_2$: C, 35.31; H, 8.89; N, 13.73. Found: C, 35.54; H, 8.93; N, 13.72.

The isopropylamine complex was very unstable and lost amine on standing. Good analytical results were not obtained on a solid product but data are presented to substantiate the existence of an octahedral isopropylamine complex in nitromethane solution.

The complexes could also be prepared in a good state of purity by adding the solution which results from dehydrating the nickel perchlorate to excess of the liquid amine at −78°. After warming to room temperature the solid is separated by filtration under nitrogen and dried for 4 hr. under vacuum over P_4O_{10}.

Results

The spectral data for the amine complexes are summarized in Table I. The calculated and experimental values for λ_{max} of the second band are reported in Table II. Agreement of experimental and calculated values supports the existence of octahedral complexes in solution. Table II also contains a summary of the values calculated for Dq and for the ^3P–^3F term splitting. The values reported for β are defined as the percentage lowering of the P–F term splitting in the complex compared to the value for the gaseous ion with no crystalline field.

Evidence for an octahedral configuration for these amine complexes in solution is obtained from the agreement between the calculated and experimental ν_2 band. The constancy of the intensity ratio of $^3A_2 \rightarrow {}^3T_1(P)$ to $^3A_2(P) \rightarrow {}^3T_1(F)$ is also evidence for the existence[14,15] of octahedral nickel(II) in the complexes studied. In this work the ratios 2.0, 1.9, 1.9, and 2.1 were found for the ammonia, methylamine, *n*-propylamine, and isopropylamine complexes of nickel(II).

The frequency shifts, $\Delta\nu_{OH}$, which phenol undergoes upon addition compound formation with the amines are reported in Table III. The enthalpies of formation are calculated from a reported[11] relationship between the frequency shift and enthalpy of adduct formation

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(7) F. Ephrain and R. Linn, *Ber.*, **46**, 3742 (1913).

(8) W. Hatfield and J. Yoke, *Inorg. Chem.*, **1**, 463 (1962), and literature references contained therein.

(9) R. W. Parry and R. N. Keller, "The Chemistry of Coordination Compounds," J. C. Bailar, Jr., Ed., Reinhold Publishing Corp., New York, N. Y., 1956, pp. 137–143.

(10) R. S. Drago, D. W. Meek, M. D. Joesten, and L. LaRoche, *Inorg. Chem.*, **2**, 124 (1963).

(11) M. D. Joesten and R. S. Drago, *J. Am. Chem. Soc.*, **84**, 3817 (1962).

(12) D. W. Meek, R. S. Drago, and T. S. Piper, *Inorg. Chem.*, **1**, 285 (1962).

(13) K. Starke, *J. Inorg. Nucl. Chem.*, **11**, 77 (1959).

(14) C. K. Jørgenson, *Acta Chim. Scand.*, **9**, 1362 (1955).

(15) W. Low, *Phys. Rev.*, **109**, 247 (1958).

TABLE I

SPECTRAL BANDS FOR THE COMPLEXES OF NICKEL(II) WITH AMINES AND AMMONIA[a]

Compound	Solvent	λ_{max}, cm.$^{-1}$	ϵ_{max}, l. mole^{-1} cm.$^{-1}$
$Ni(NH_3)_6Cl_3$	10% aq. NH_3	10,526	6.31
		17,241	6.35
		28,011	12.2
$Ni(CH_3NH_2)_6(ClO_4)_2$	CH_3NO_2	9,930	...
		16,233	...
		...[b]	...
$Ni(CH_3NH_2)_6(ClO_4)_2$	DMF	10,000	6.25
		12,987 (sh)	
		16,779	8.50
		27,322	15.3
$Ni(C_2H_5NH_2)_6(ClO_4)_2$	CH_3NO_2	9,872	...
		16,313	
		...[b]	
$Ni(C_2H_5NH_2)_6(ClO_4)_2$	DMF	9,662	...
		16,666	...
		27,027	...
Ni(*n*-$C_3H_7NH_2)_6(ClO_4)_2$	*n*-$C_3H_7NH_2$	9,920	
		16,447	
		27,174	
Ni(*n*-$C_3H_7NH_2)_6(ClO_4)_2$	CH_2Cl_2	9,823	6.4
		16,502	5.2
		26,809	14.0
Ni(*i*-$C_3H_7NH_2)_6(ClO_4)_2$	CH_3NO_2 + 10% excess *i*-$C_3H_7NH_2$	9,480	
		15,267	
		26,042	

[a] The band assignments are ${}^3A_{2g} \rightarrow {}^3T_{2g}$, ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$, and ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ for the low, middle, and high energy bands, respectively. [b] In CH_3NO_2 solvent, this band cannot be detected because of intense solvent absorption.

for a large number of addition compounds. The empirically derived[11] relation is

$$-\Delta H(\text{kcal. mole}^{-1}) = 0.016\Delta\nu_{O-H} + 0.63$$

Data which will be employed in an evaluation of the donor properties of the amines are summarized in Table III.

Discussion

In earlier articles[12,16,17] the magnitude of the interaction between several different Lewis acids and bases has been qualitatively explained by employing the classical model considering the contributions to the interaction from polarization and dipole forces. This is a crude approach but is reasonably successful for correlating the data. One of the problems with this approach arises from the fact that attempts are being made to explain donor and acceptor ability in terms of ground state properties of the donor (or acceptor) molecule when what is needed is a correlation with some property of the donor (or acceptor) measured in a configuration similar to that in the adduct; *i.e.*, the donor and acceptor molecule rehybridized. For example, BCl_3 is planar and has no dipole moment but the configuration in the adduct is polar. A second complication is introduced by attempting to employ ground state polarizabilities or dipole moments of the entire molecule for correlations. Problems are encountered in accurately resolving the lone pair components to the polarizability and dipole moment. Even an accurate resolution does not eliminate the first objection listed.

In order to rationalize all of the amine data we propose that in a bonding configuration, lone pair polarization follows the inductive order $NH_3 < CH_3NH_2 < (CH_3)_2NH < (CH_3)_3N$. This is the order manifested toward the easily polarized acid iodine where lone pair donor polarization should be significant in determining the donor order (for example diethyl sulfide is a better donor toward iodine than diethyl ether). The cumbersome phrase lone pair donor polarization will be indicated by the term distortability. Toward phenol, the electrostatic interaction (dipole–dipole effects) makes a very large contribution to the heats of interaction. It is proposed that the activated donor dipoles decrease in the order $NH_3 > CH_3NH_2 > (CH_3)_2NH > (CH_3)_3N$. In the interaction with phenol the *differences* between ammonia and the alkylamines are due to distortability differences but since the total contribution to the heat from the polarizability term is less for phenol than for iodine, smaller differences are obtained for the phenol heats. The activated donor dipole and distortability terms go in the opposite direction for the amines and for an acid where both effects are important this will result in only small differences in the donor properties of the amines. The relative ordering for the donor ability of the amines toward a given acid will depend upon the relative importance of the polarizability (covalent) or electrostatic nature of the interaction.

The donor properties of ammonia, methylamine, and dimethylamine toward $B(CH_3)_3$ parallel the order based on distortability although there are certainly electrostatic contributions to the bonding. Trimethylamine is out of line for it is a weaker donor than dimethylamine but there is very good evidence for the existence of F-strain[18] in this adduct.

In considering the *Dq* values for the amine complexes, it is informative to compare the amine data with the following *Dq* values obtained for other ligands in octahedral nickel(II) complexes: NH_3 (1060); $(CH_2)_2NH$ (1050); CH_3NH_2 (993); H_2O (860); DMA (769); $(CH_3)_2SO$ (773).

In accounting for the observed *Dq* values for ammonia and amines in these nickel(II) complexes it appears as if the activated donor dipole moment is the most important parameter. Charge–dipole interaction appears to be very important. The slightly larger moment of ammonia compared to methylamine results in the higher position of ammonia in the spectrochemical series (Table II). The similarity in the *Dq* values for CH_3NH_2, $C_2H_5NH_2$, and *n*-$C_3H_7NH_2$ correlates with the similarity of the reported dipole moments of these molecules and with the similarity in distortability, for it is found that the gas phase heats of association of the

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(16) R. S. Drago and D. A. Wenz, *J. Am. Chem. Soc.*, **84**, 526 (1962).

(17) M. D. Joesten and R. S. Drago, *ibid.*, **84**, 2037 (1962).

(18) H. C. Brown, *J. Chem. Soc.*, 1248 (1956), and the references contained therein.

TABLE II

SPECTROCHEMICAL PARAMETERS CALCULATED FROM THE DATA[a] IN TABLE I

Compound	Solvent	Position of ν_2 ($\rightarrow {}^3T_{1g}F$)		$E(P) - E(F)$	Dq	β
		Calcd., cm.$^{-1}$	Obsd., cm.$^{-1}$			
$Ni(NH_3)_6Cl_2$	NH_4OH	16,996	17,241	13,412	1060	15.3
$Ni(CH_3NH_2)_6(ClO_4)_2$	CH_3NO_2	16,156	16,233	13,388	993	15.5
$Ni(C_2H_5NH_2)_6(ClO_4)_2$	CH_3NO_2	16,083	16,313	13,499	987	14.8
$Ni(n\text{-}C_3H_7NH_2)_6(ClO_4)_2$	$n\text{-}C_3H_7NH_2$	16,274	16,447	13,577	992	14.3
$Ni(i\text{-}C_3H_7NH_2)_6(ClO_4)_2$	CH_3NO_2 + $i\text{-}C_3H_7NH_2$	15,466	15,265	13,060	948	17.6

[a] The best results are obtained from calculations made on spectra measured in the pure ligand as solvent. The solvents CH_2Cl_2 CH_3NO_2, and DMF are listed in the order of increased coordinating ability and hence decreasing suitability as solvents. Calculations of spectral data obtained in CH_3NO_2 solution are made by employing the wave length for the ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ absorption found in other solvents. Any error introduced by this procedure would only affect the β-value and would be indicated by the lack of agreement in the calculated and experimental frequencies of the middle band. The error limits of Dq are ±10 cm.$^{-1}$ and errors of ±1.2 are encountered in the β-values.

TABLE III

DONOR PROPERTIES OF AMINES TOWARD PHENOL AND IODINE

Amine	$\Delta\nu_{O\text{-}H}$, cm.$^{-1}$	$-\Delta H$ from $\Delta\nu_{O\text{-}H}$, kcal./mole	$-\Delta H$ for I_2 adduct,[5] kcal./mole	$-\Delta H$ for[3] $B(CH_3)_3$ adduct, kcal./mole	Dipole moment[a] (vapor), D.	Ionization potential,[c] e.v.
NH_3	462 ± 20	8.0	4.8	13.8	1.45	10.15 ± 0.01
CH_3NH_2	540 ± 15	9.3	7.1	17.6	1.28	8.97 ± .02
$C_2H_5NH_2$	540 ± 15	9.3	7.4	18.0	1.3[b]	8.86 ± .02
$(CH_3)_2NH$	540 ± 15	9.3	9.8	19.3	1.02	8.24 ± .02
$(CH_3)_3N$	553 ± 15	9.5	12.1	17.6	0.64	7.82 ± .02

[a] R. S. W. Le Févre and P. Russell, *Trans. Faraday Soc.*, **43**, 374 (1947). [b] C. P. Smyth, "Dielectric Constant and Molecular Structure," Reinhold Publishing Corp., New York, N. Y., 1931. [c] K. Watanabe and J. R. Mottle, *J. Chem. Phys.*, **26**, 1773 (1957).

boron trimethyl adducts are similar. This discussion is not intended to imply that there is no polarization of the ligands in the metal ion–amine interaction. Evidence for polarization is indicated by the higher position of ammonia (μ = 1.47 D.) than water (μ = 1.84 D.) in the series. The point is that the differences in the distortability of the amines and ammonia do not appreciably affect the relative positions in the spectrochemical series. This result is in contrast to the importance of this property in the iodine interaction.

The above conclusion also receives support from the higher position of ethylenimine than methylamine in the spectrochemical series.[19] Toward $B(CH_3)_3$, methylamine and ethylenimine are of equal basicity, indicating that the distortability of ethylenimine is about the same as or less than methylamine (possibly less because the electrostatic interaction is greater for ethylenimine). It is reported[20] that ethylenimine has a dipole moment of 1.7 D. and assignment of a large activated lone pair dipole accounts for its higher position in the spectrochemical series than methylamine.

For the amines, the assignment of the activated dipole order correlates with the measured moments for the free amines. As can be seen from Table III, the assignment of the distortability order correlates with the ionization potentials of the amines. This is interesting for in the Mulliken charge-transfer formulation[21] of donor–acceptor interaction the "covalency" or polarization term is $\psi_{B^+A^-}$. This involves transfer of an electron from the donor to the acid and for adducts in which the acid is constant and the bases are a series of amine nitrogens a correlation of distortability with ionization potential might be expected.

Having correlated the spectrochemical positions of the amines with the activated donor dipoles and distortability of the amines and ammonia it is interesting to speculate on the magnitude of the amine–metal ion interaction. Since neither gas phase data nor equilibrium constants in nonpolar solvents can be obtained for these nickel–amine complexes, it is impossible to evaluate these heats of formation. It is proposed that the ligand field parameter Dq can be employed under certain conditions as an indicator to provide a measure of this interaction. If the complex were treated as a point dipole–charge interaction this would be a rigorous assumption. Since β is a measure of deviation from the purely ionic model, Dq is a reasonable qualitative approximation to the magnitude of the interaction for complexes with small and similar β-values. This is the case for the ammonia, amine, and water complexes, where β values of 16, 14 to 16, and 11 are reported for the per cent lowering of the P–F term.

Although the primary aliphatic amine complexes studied dissociate readily in water, these amines occupy a higher position in the spectrochemical series than water. There are probably several causes for the instability of these complexes in water. Entropy considerations may be important. Thermodynamic data[22] indicate that a very important effect is the greater

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(19) R. W. Kiser and T. W. Lapp, *Inorg. Chem.*, **1**, 401 (1962).

(20) K. Watanabe and J. R. Mottle, *J. Chem. Phys.*, **26**, 1773 (1957).

(21) S. P. McGlynn, *Chem. Rev.*, **58**, 1149 (1958), and references contained therein.

(22) U. S. Bureau of Standards, "Selected Values of Chemical Thermodynamic Properties," Circular 500, 1949.

solvation of methylamine than ammonia. The heat of hydration of gaseous methylamine is -11.2 kcal. mole^{-1} compared to -8.3 kcal. mole^{-1} for ammonia. Enthalpy differences of this order of magnitude have an appreciable effect on the stability constants and must play an important role in affecting the instability of the alkylamine complexes. One might also expect that another factor contributing to the stability difference is the larger solvation of the ammonia complex than the alkylamine complexes. The spectrochemical data indicate the instability is not attributed to the relative strength of the metal ion–ligand interaction of water and the alkylamines.

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Notes

Contribution from the Department of Chemistry,
Kansas State University, Manhattan, Kansas

Polarographic Determination of the Cadmium Complexes of Pyrazole[1]

By A. C. Andrews and J. Kirk Romary[2]

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Pyrazole (1,2-diazole), like its isomer imidazole, is a monodentate ligand. Furthermore, pyrazole is an extremely weak Lewis base ($pK_a = 2.53$ at 25°) and would not be expected to form strong coordination compounds. This could explain the absence of pyrazole complex data in the literature. The complex-forming tendency of pyrazole with cadmium(II) has been investigated. It was of interest to determine the stability of the complexes and to determine the extent of reaction as indicated by the highest ordered complex formed. In addition to the stability constants and stoichiometry of the complexes, it was desirable to evaluate the enthalpy changes associated with the complex formation reaction. Accordingly, the investigations described herein were conducted at three temperatures, namely, 0, 25, and 45°. In view of the excellent characteristics of cadmium(II) at the dropping mercury electrode (d.m.e.), the polarographic method was used throughout this investigation.

Experimental

Reagent grade cadmium nitrate and potassium nitrate were used without further purification. Stock solutions of cadmium nitrate were analyzed gravimetrically by conversion to cadmium sulfate. Pyrazole was obtained from K & K Laboratories and the stock solutions were freshly prepared before each investigation.

Polarographic current–voltage curves were obtained with a Sargent Model XXI polarograph. Potential measurements were made *vs.* a saturated calomel electrode (s.c.e.), using a saturated potassium nitrate salt bridge, by means of a Rubicon potentiometer, No. 2730. A Leeds and Northrup pH meter, No. 7663AL, was used for pH measurements. A No. 1199–30 glass electrode was used at 25 and 45°, while measurements at 0° were obtained with electrode No. 1194–44.

All solutions to be analyzed were made up to 5×10^{-4} *M* in cadmium nitrate and 0.1 *M* in potassium nitrate. The concentration of pyrazole varied from 0.05 to 2.0 *M*. Cylinder nitrogen, purified of any traces of oxygen by an alkaline pyrogallol train, was used to remove oxygen from the cell solution. During electrolysis a nitrogen atmosphere was maintained over the solution. Maximum suppressors were not necessary since none of the pyrazole complexes produced maxima.

A constant and reproducible mercury drop time was obtained by means of a capillary standtube affixed to a centimeter scale. In 0.1 *M* potassium nitrate at 25° and at an applied potential of -1.000 volt the capillary characteristics were: $m = 2.44$ mg. sec.$^{-1}$ and $m^{2/3}t^{1/6} = 2.28$ mg.$^{2/3}$ sec.$^{-1/2}$.

Results and Discussion

The proof of reversibility of the electrode reactions and the determination of half-wave potentials was accomplished in the conventional manner as described by Lingane.[3]

The number of pyrazole ligands coordinated to a central cadmium(II) ion was calculated from the slope of plots of $E_{1/2}$ *vs.* the logarithm of the pyrazole concentration according to the equation[3,4]

$$\Delta E_{1/2}/\Delta \log [\mathrm{Py}] = -p(2.303RT)/nF \qquad (1)$$

where p is the number of ligands coordinated.

The stability constants were calculated by application of the relation

$$(E_{1/2})_c - (E_{1/2})_s = -(2.303RT/nF) \log (K_{st} f_s k_c/f_c k_s) - p(2.303RT/nF) \log [\mathrm{Py}] \qquad (2)$$

which is a modification of the usual form[3] for the purpose of placing emphasis upon the stability constant (formation constant) rather than the dissociation constant. In eq. 2, f is the activity coefficient and k is a constant which is proportional to the square root of the diffusion coefficient of the ion. The subscripts c and s refer to the complex and simple ions, respectively. The ratio $f_s k_c/f_c k_s$ is often assumed to be unity. However, in this investigation, at constant ionic strength, only the activity coefficient ratio was assumed to be unity. The ratio k_c/k_s was determined experimentally from the ratio of the observed diffusion cur-

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[1] This investigation was carried out during the tenure of Predoctoral Fellowship No. GF-10,095, United States Public Health Service.

[2] Abstracted in part from the Ph.D. dissertation of J. K. Romary, Kansas State University, 1961.

[3] J. J. Lingane, *Chem. Rev.*, **29**, 1 (1941).

[4] N. C. Li and M. Chen, *J. Am. Chem. Soc.*, **80**, 5678 (1958).