bital singlet. This problem has disturbed us for some time and caused us to consider whether there might not be some assignment for the spectra of all of the compounds which is quite different from the fairly obvious one described above. However, on the evidence at hand we have been unable to invent an acceptable alternative.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASSACHUSETTS]

The Donor–Acceptor Properties of Isonitriles as Estimated by Infrared Study

BY F. ALBERT COTTON AND FRANCO ZINGALES[1]

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A number of complexes of isonitriles with metal atoms and ions have been prepared and their infrared spectra measured. The results provide information about the extent of metal to isonitrile dative pi bonding as a function of the oxidation state of the metal and of the nature of the other ligands, if any, also attached to the metal. In compounds having only isonitrile molecules attached to zero-valent metal atoms, back donation seems to be about as extensive as it is in the corresponding metal carbonyl compounds. Breakdown of the selection rules for the NC stretching modes in $(RNC)_6M$ and $(RNC)_4M$ compounds is believed to indicate that significant back donation causes significant bending of the RNC chains; this in turn spoils what would otherwise be O_h or T_d symmetry in the $(-NC)_6M$ and $(-NC)_4M$ groups. When isonitriles are attached to mono- and dipositive metal ions, however, little or no back donation occurs and the NC stretching frequencies actually rise as a result of the inductive effect of the electrophilic metal ion. The preparation of the new compounds $(RNC)_3M(CO)_3$, where M = Cr, Mo and R = *p*-tolyl and methyl is described.

Introduction

Two extreme types of donor–acceptor behavior are generally recognized in ligands. At one extreme are ligands which are pure donors, such as aliphatic amines and ethers. The first row atoms, N and O, unless incorporated into a molecular system which as a whole can function as π-orbital acceptor (*e.g.*, N in pyridine) are restricted to the single function of being donors by their intrinsic lack of the empty orbitals necessary for them to behave as pi acceptors. In the other direction (which we refrain from calling *an* extreme since there is no sharply defined limit here) are ligands which are only moderately good or even poor donors but which are good π-acceptors. Ligands such as CO and PX_3 are good representatives of this class. These two kinds of ligands, for reasons stemming from the electroneutrality principle taken in a qualitative but not necessarily quantitative sense, generally seek different kinds of acceptors. Considering here only metal atoms as acceptors, pure donor ligands combine well with cations because they can fulfill their single function of transferring electronic charge to the acceptor to a degree sufficient to form a strong ligand-metal bond without causing a net negative charge to appear on the acceptor. Ligands of the second type have little tendency to combine with cationic acceptors since their donor properties alone are insufficient to form strong ligand-metal bonds while their ability to supplement the bonding by pi acceptance is ineffectual when the cation has no significant pi donor properties. Conversely, the second kind of donor combines well with zero-valent or negative-valent (*e.g.*, Co in $Co(CO)_4^-$) metal atoms because it can use synerically its sigma donor and pi acceptor functions, whereas pure donor bonding of which alone the first class of ligands are capable cannot proceed far enough to give stability because of the poor acceptor powers of the zero-valent metal. Ligands of the first type can form reasonably stable bonds to zero-valent metal atoms when ligands of the second type are also present, *e.g.*, in $(amine)_3Mo(CO)_3$ compounds, because the latter can assume the entire burden of draining negative charge from the metal atom.

Examination of the literature on isonitrile complexes[2] indicates that these ligands combine with zero-valent metals both with and without the presence of additional ligands of the second type and also with mono- and dipositive metal ions. This unusual capacity to combine with the entire range of metal atom acceptor types, excepting only the extremes of metal atoms in formally negative oxidation states and those in a tripositive state, suggested to us that isonitriles have the capacity to function as good sigma donors alone, as sigma donors and good pi acceptors simultaneously or to exhibit any intermediate behavior. In order to test this hypothesis, isonitrile complexes representative of all of the basic types known have been prepared and their infrared spectra in the NC stretching region carefully measured using both rock salt and fluorite prisms. The results support the hypothesis.

Experimental

Tri-(*p*-tolyl isonitrile)-molybdenum Tricarbonyl-(p-CH_3-$C_6H_4NC)_3Mo(CO)_3$.—1.4 g. (0.012 mole) of p-$CH_3C_6H_4NC$ (see below for preparation of the isonitriles) was added to a solution of $C_7H_8Mo(CO)_3$[3,4] (0.82 g., 0.003 mole) in benzene (5 ml.). After a few minutes, the red color of the cycloheptatriene complex had completely disappeared. The

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benzene was then taken off in vacuum and the dry residue crystallized from a chloroform–ethanol mixture. The yellow crystals, m.p. 148°, were soluble in chloroform, methylene chloride, carbon tetrachloride, carbon disulfide, benzene and acetone but insoluble in ethyl alcohol and petroleum ether.

Anal. Calcd. for $C_{27}H_{21}MoN_3O_3$: C, 61.02; H, 3.98; N, 7.91. Found: C, 61.29; H, 4.01; N, 7.93.

Tri-(methyl isonitrile)-molybdenum Tricarbonyl-$(CH_3NC)_3Mo(CO)_3$.—This compound was prepared in the same manner as its *p*-tolyl isonitrile analog from 0.49 g. (0.012 mole) of methyl isonitrile[2] and 0.82 g. (0.003 mole) of $C_7H_8Mo(CO)_3$[3,4] and recrystallized from a methylene chloride–petroleum ether mixture. It was obtained as white crystals, m.p. 177°, soluble in chloroform, methylene chloride benzene and acetone, insoluble in carbon tetrachloride, carbon disulfide, ethyl alcohol and petroleum ether.

Anal. Calcd. for $C_9H_9MoN_3O_3$: C, 35.66; H, 2.99; N, 13.86. Found: C, 35.90; H, 3.05; N, 13.92.

Tri-(*p*-tolyl isonitrile)-chromium Tricarbonyl-$(p\text{-}CH_3C_6H_4NC)_3Cr(CO)_3$.—0.24 g. (0.002 mole) of $p\text{-}CH_3C_6H_4NC$[2] was added to a solution of $C_7H_8Cr(CO)_3$[3,4] (0.12 g., 0.0005 mole) in benzene (2 ml.). The solution was heated under reflux until the red color of the cycloheptatriene complex had completely disappeared (10 min.). Benzene was then removed in vacuum and the dry residue crystallized from chloroform–ethanol. The compound was obtained as yellow crystals, m.p. 145°, soluble in chloroform and methylene chloride, insoluble in ethanol.

Anal. Calcd. for $C_{27}H_{21}CrN_3O_3$: C, 66.52; H, 4.34; N, 8.62. Found: C, 66.49; H, 4.21; N, 8.90.

Tris-(methyl isonitrile)-chromium Tricarbonyl-$(CH_3NC)_3Cr(CO)_3$.—This compound was prepared in the same way as its *p*-tolyl analog from 0.085 g. (0.002 mole) of methyl isonitrile (preparation described below) and 0.12 g. (0.0005 mole) of $C_7H_8Cr(CO)_3$ and recrystallized from methylene chloride–petroleum ether as white crystals which begin to decompose without melting at ~157°.

Anal. Calcd. for $C_9H_9CrN_3O_3$: C, 41.70; H, 3.50; N, 16.21. Found: C, 41.85; H, 3.56; N, 16.21.

Other Complexes.—All of the other compounds studied in this work were already known and were prepared by methods in the literature. Carbon and hydrogen analyses were performed on all samples to be certain of identity and purity.

Chromium(II) acetate was prepared in good yield following Hatfield.[5] (Phenyl isonitrile)$_6$Cr, (*p*-tolyl isonitrile)$_6$Cr and (*p*-chlorophenyl isonitrile)$_6$Cr were prepared according to Malatesta, *et al.*,[6] by adding, under nitrogen, an excess of aryl isonitrile to a methyl alcohol suspension of chromium (II) acetate. (*p*-Anisyl isonitrile)Mo(CO)$_5$ was prepared according to Hieber and von Pigenot[7] by heating Mo(CO)$_6$ and *p*-anisyl isonitrile together in a sealed tube.

(Phenyl isonitrile)$_4$Ni and (*p*-tolyl isonitrile)$_4$Ni were prepared by the method of Malatesta and Sacco.[8] (*p*-Chlorophenyl isonitrile)$_4$Ni was prepared in the same manner as the phenyl isonitrile compound by reduction of nickel (II) acetate by hydrazine in presence of the isonitrile. $(CH_3NH)_3NiCO$ was prepared in a manner similar to that described by Hieber and Böckly.[9]

[(*p*-Tolyl isonitrile)$_4$Ag]ClO$_4$ was prepared by Sacco's method[10]; [(*p*-tolyl isonitrile)$_2$Ag]NO$_3$ was prepared according to Klages, *et al.*[11]

The manganese(I) compounds were prepared by Sacco's methods.[12,13] The manganese (II) compounds were prepared by treating an alcoholic solution of [(RNC)$_6$Mn]Br with bromine in the presence of $CdBr_2$ according to a procedure soon to be published by Naldini.[14]

The iron(0) compounds were prepared according to Hieber and von Pigenot[15] and Cotton and Parish.[16]

Isonitriles.—Phenyl, *p*-tolyl, *p*-chlorophenyl and *p*-anisyl isocyanides were all prepared and purified as described by Malatesta.[17]

Methyl isocyanide was prepared by the modification of the method of Gautier[18] reported by Lindemann and Wiegrebe.[19] *t*-Butylisocyanide was prepared in a manner similar to that described by Nef.[20]

Discussion

Free Isonitriles.—In Table I are listed the NC stretching frequencies of the five isonitriles occurring in the various complexes which have been studied. These data are presented primarily to provide points of reference in interpreting the NC frequencies of the coördinated isonitriles. Measurements were made using several solvents in order to assure that no anomalously solvent-dependent values were used. It may be seen that the frequencies are, in fact, not greatly sensitive to solvent.

TABLE I

CN STRETCHING FREQUENCIES OF FREE ISONITRILES IN VARIOUS SOLVENTS[a]

Isonitrile	Frequencies[b] in solvents, cm.$^{-1}$			
	$CHCl_3$	CCl_4	$n\text{-}C_7H_{16}$	CS_2[c]
C_6H_5NC	2136	2133	2134	2130
$p\text{-}CH_3C_6H_4NC$	2136	2131	2132	2129
$p\text{-}ClC_6H_4NC$	2136	2133	2132	2129
$p\text{-}CH_3OC_6H_4NC$	2140	2128	2126	2124
CH_3NC	2142	2169	2168	..[c]

[a] These data were obtained using a Perkin–Elmer Spectrophotometer, Model 21, equipped with a rock salt prism. [b] Frequencies are believed to be accurate to ± 3 cm.$^{-1}$; each spectrum was calibrated using polystyrene film. [c] All of the isonitriles appeared to decompose, at varying rates, in CS_2. This results in broad absorption in the 1900–2100 cm.$^{-1}$ region, but if the solutions are run immediately, the true isonitrile band is easily discerned. CH_3NC reacts very rapidly, and it was impossible to obtain a spectrum showing a genuine isonitrile band unambiguously.

$(RNC)_{4\,or\,6}M(0)$ Compounds.—The first compounds listed in Table II are some of the most stable representatives of the class in which isonitrile molecules are the only ligands bound to zerovalent metal atoms. In such cases we should expect the greatest amount of metal-carbon pi bonding to be found in any isonitrile complexes presently known. This in turn should result in the largest observed depressions of the CN stretching frequencies by the favoring of structure I over II.[21] The depressions of the CN stretching

$$\mathrm{M::C::\ddot{N}:R} \qquad \mathrm{\overset{-}{M}:C:::\overset{+}{N}:R}$$

I II

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TABLE II

CN AND CO STRETCHING FREQUENCIES IN VARIOUS ISONITRILE COMPLEXES[a,b]

Compound	Solvent or medium	CN stretching frequencies, cm.$^{-1}$			CO stretching frequencies, cm.$^{-1}$		
1. (RNC)$_{4 \text{ or } 6}$ M^0 compounds							
(*p*-Tolyl isonitrile)$_6$Cr	CHCl$_3$	2062	1972	1934			
(Phenyl isonitrile)$_6$Cr	CHCl$_3$	2070	2012	1965			
(*p*-Chlorophenyl isonitrile)$_6$Cr	CHCl$_3$	2070	2024	1969			
(*p*-Tolyl isonitrile)$_4$Ni	CHCl$_3$	2065	2033				
(Phenyl isonitrile)$_4$Ni	CHCl$_3$	2050	1990				
(*p*-Chlorophenyl isonitrile)$_4$Ni	CHCl$_3$	2049	2008				
2. (RNC)$_{4, 6 \text{ or } 6}$ M$^{\text{I or II}}$ compounds							
(*p*-Tolyl isonitrile)$_2$AgNO$_3$	CHCl$_3$	2195					
(*p*-Tolyl isonitrile)$_4$AgClO$_4$	CHCl$_3$	2186(sh)	2177	2136(w)			
(*p*-Tolyl isonitrile)$_6$MnI	CHCl$_3$	2090	2035(w)				
(CH$_3$NC)$_6$MnI	Nujol	2114 ± 15					
(CH$_3$NC)$_6$MnI	CH$_2$Cl$_2$	2129					
(*p*-Tolyl isonitrile)$_6$Mn(CdBr$_4$)	Nujol	2161					
(*p*-Anisyl isonitrile)$_6$Mn(CdBr$_4$)	Nujol	2161					
3. (RNC)$_n$M(CO)$_{6-n}$ compounds, M = Cr, Mo							
(*p*-Anisyl isonitrile)Mo(CO)$_5$	CHCl$_3$	2145			2062	1953	
(*p*-Tolyl isonitrile)$_3$Mo(CO)$_3$	CHCl$_3$	2142	2083	2040(sh)	1950	1894	
(CH$_3$NC)$_3$Mo(CO)$_3$	CH$_2$Cl$_2$	2186	2150		1944	1860	
(*p*-Tolyl isonitrile)$_3$Cr(CO)$_3$	CHCl$_3$	2150	2085	2047(sh)	1950	1902	
(CH$_3$NC)$_3$Cr(CO)$_3$	CH$_2$Cl$_2$	2185	2147		1942	1860	
4. (RNC)$_n$Fe(CO)$_{5-n}$ compounds							
(C$_6$H$_5$NC)Fe(CO)$_4$	CHCl$_3$	2165			2054	1994	1970
(CH$_3$NC)Fe(CO)$_4$	CHCl$_3$	2213			2059	1993	1961
[(CH$_3$)$_3$CNC]Fe(CO)$_4$	CHCl$_3$	2183			2057	1992	1964
[(CH$_3$)$_3$CNC]$_2$Fe(CO)$_3$	CHCl$_3$	2129	2090(vw)		1994(w)	1919	
5. (RNC)$_n$Ni(CO)$_{4-n}$ compound							
(CH$_3$NC)$_3$Ni(CO)	Nujol	2183	2128	2016(w)	1923		

[a] All data in this table were obtained using a Baird Infrared Spectrophotometer equipped with a calcium fluoride prism.
[b] Frequencies are believed accurate to within ±3 cm.$^{-1}$ except as noted to the contrary, each spectrum was calibrated using polystyrene film.

frequencies in these compounds, which range from 60 to 200 cm.$^{-1}$ with an average value of about 110 cm.$^{-1}$, are indeed very significant and by far the largest observed. They are in fact quite comparable to those found in the corresponding carbonyls: $\nu_{CO} = 2170$; ν_{a_1} of Ni(CO)$_4$ = 2040; ν_{t_2} of Ni(CO)$_4$ = 2050; $\nu_{a_{1g}}$ in Cr(CO)$_6$ = 2063; ν_{e_g} in Cr(CO)$_6$ = 2020; $\nu_{t_{1u}}$ in Cr(CO)$_6$ = 2000.

There is an additional feature of the data in section 1 of Table II which is of considerable interest. For the (RNC)$_6$Cr compounds three NC stretching bands are observed and for the (RNC)$_4$Ni compounds two NC stretching bands are observed. It is to be emphasized that all of the bands listed in Table II are strong unless the contrary is explicitly stated and that the data for the (RNC)$_6$Cr and (RNC)$_4$Ni compounds were obtained on solutions using a CaF$_2$ prism. It may also be noted that the substituted phenyl isonitriles, *p*-tolyl and *p*-chloro, were so chosen that the substituent and its placement in the ring are such as not to lower the symmetry of the isonitrile molecule. Now, if the M-C-N-C$_6$H$_4$-X (X = H, CH$_3$, Cl) groupings were strictly linear, the (RNC)$_6$Cr and (RNC)$_4$Ni molecules would have, respectively, *effective* O$_h$ and T$_d$ symmetries in the (>CNC)$_6$Cr and (>CNC)$_4$Ni portions of the molecules. This would then mean that only *one* infrared active CN stretching mode should occur in each case. The fact that more than one strong band is observed in each compound must mean that the effective symmetries of the (>CNC)$_6$Cr and (>CNC)$_4$Ni groupings are less than O$_h$ and T$_d$. This may be most reasonably attributed to the fact that a significant contribution by I to the resonance hybrid causes a significant bending of each C-N-C< grouping.

Thus, in the (RNC)$_6$Cr and (RNC)$_4$Ni compounds, where extensive back donation of dπ electrons from the zero-valent metal to the isonitrile ligands is to be expected, its consequences, namely, large decreases in the CN stretching frequencies (comparable to decreases in CO frequencies in corresponding metal carbonyls) and multiple infrared active CN frequencies as a result of nonlinearity of the M-C-N-C< groupings, are strikingly evident. Therefore, the present results show that, when necessary, isonitriles can exhibit π-acceptor properties and engage in extensive synergic sigma donor-pi acceptor bonding.

(RNC)$_n$M(I or II) Compounds.—We consider next some compounds representative of the class in which isonitrile molecules are coördinated to metal atoms in the (I) and (II) oxidation states. In the two Ag(I) complexes and the Mn(II) complexes the NC frequencies are actually higher than those for the free ligand molecules. Two consequences of attaching the isonitrile molecules to the metal atom would, unless overwhelmed by some opposing action, such as back donation, lead to this rise in frequency. It has already been noted[21] that coupling the CN oscillator to an M–C oscillator will cause a small upward shift. Of more importance however, is the effect of coördinating the isonitrile carbon to a cation, if we assume that the electronic structure of the free isonitrile is a resonance hybrid of III and IV, with the contribution of III being significant. The positive charge adjacent to the carbon atom will enhance the importance of IV in the hybrid thus increasing the NC bond order and raising the NC stretching frequency. If the degree of back donation by the metal is sufficiently small, this electrostatic effect will predominate and a net rise in the NC stretching frequency will be observed, as in the Ag complexes.

$$\underset{\text{III}}{\mathrm{R{:}\ddot{N}{:}{:}C{:}}} \qquad \underset{\text{IV}}{\mathrm{R{:}\overset{+}{N}{:}{:}{:}\bar{C}{:}}}$$

The complete infrared spectrum of bis-(*p*-tolyl isonitrilo)-silver (I) nitrate shows that it is correctly formulated as $[(p\text{-}CH_3C_6H_4NC)_2Ag]NO_3$, that is, with the nitrate ion outside the coördination sphere. The only absorption bands attributable to the nitrate ion are two very broad and strong ones at ~1310 and ~1390 cm.$^{-1}$. Thus there is close resemblance to the spectra of ionic nitrates,[22] but the features characteristic of coördinated nitrate ions[23,24] are completely lacking. In this compound, with only two ligands coördinated to the Ag(I) cation, there should be little if any electrostatic driving force for back donation. As a result, there is so little, if any, cancellation of the inductive effect operating to raise the NC frequency that there is a fairly substantial net rise (~60 cm.$^{-1}$). In $[(p\text{-}CH_3C_6H_4NC)_4Ag]ClO_4$ where simple dative bonding tends to put approximately twice as much negative charge on the silver as in the *bis* complex, there is more electrostatic driving force for back donation. Consequently the NC frequency, 2177 cm.$^{-1}$ is lower than in the *bis* compound. In the manganese(I) compounds, where there are six isonitriles bound to a unipositive ion, there is still greater electrostatic driving force for donation, and it occurs to such an extent that in the *p*-tolyl compound there is a net lowering of the NC frequency by some 40 cm.$^{-1}$. In the methyl isonitrile complex the net lowering is less, suggesting that CH_3NC is a poorer pi acceptor than the aryl isonitriles, an observation we will find confirmed later. On changing the manganese cation from unipositive to dipositive we should expect a substantial decrease in the amount of back donation. This is evidently just what occurs for the NC frequency rises by about 70 cm.$^{-1}$.

$(RNC)_nMo(CO)_{6-n}$ and $(RNC)_nCr(CO)_{6-n}$ Compounds.—The compounds in section 3 of Table II illustrate the behavior of isonitrile ligands when they are, as it were, in competition with CO groups for dπ electrons. It appears that the readiness of the CO groups to serve as pi acceptors is greater than that of the isonitriles. In (*p*-anisyl isonitrile) $Mo(CO)_5$ the NC frequency suggests that the isonitrile does very little back-accepting but allows the five CO groups to shoulder most of the burden. This of course may be partly due to the great excess of CO's over isonitriles. In the $(RNC)_3M(CO)_3$ compounds, the average frequencies of the NC bands shows that some back donation to isonitriles is occurring, but it seems evident that the CO's are again bearing the greater burden. Thus, the data presented for compounds in sections 1 and 3 of Table II would appear to suggest that while isonitriles can function effectively as pi acceptors, they will give way on this function to CO's when the latter are also present.

Two other conclusions seem evident from the data so far considered. First, analogous substituted chromium and molybdenum carbonyls do not differ significantly in their CO stretching frequencies. This same conclusion follows from the observations of Wilkinson, *et al.*[4] Second, methyl isonitrile appears to be a significantly poorer pi acceptor than are the several aryl isonitriles used in this work. The data in section 2 of Table II also support this conclusion, which is of course not surprising in view of the known inductive effects of methyl and phenyl groups. The fact that varying the *para* substituent of the aryl isonitriles from H to CH_3, CH_3O and Cl, has little effect on the NC frequencies either in the free isonitriles or in the complexes suggests that resonance coupling of the —N≡C and —C_6H_4— electrons is not of much importance here.

Data for the compounds in section 4 of Table II are reported here to verify the previous infrared studies[16] of these and similar compounds. Previously, the spectra were taken using a rock salt prism. In view of recent reports[25,26] showing that the resolution obtainable in the CO stretching region with a rock salt prism is sometimes inadequate, the re-examination of some of the previously studied compounds using a fluorite prism seemed desirable. Comparison of the data in Table II with those previously reported for the same compounds shows that, aside from small differences in the frequencies, the previous data are correct, and all of the conclusions previously drawn as to the stereochemistry of the molecules remain valid.[27]

The compound $(CH_3NC)_3Ni(CO)$ is the only reported member of the group containing nickel compounds with partial substitution of CO by isonitriles. It is rather difficult to prepare in a state of high purity and it appears to rearrange, disproportionate or otherwise decompose in solution, for spectra of solutions always contained a large number of bands in the NC and CO stretching region. Therefore, only the spectrum of the solid compound can be of use in this study. The appearance of

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two strong NC bands is in accord with the expected C_{3v} symmetry of the molecule. The relatively high mean frequency (2156 cm.$^{-1}$) suggests that back acceptance by the isonitriles is not great. This then would require that the CO engage in considerable back acceptance, and the rather low CO frequency (1923 cm.$^{-1}$) is in accord with this view.

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

Coördination Compounds of Labile Metals with Ethylenimine

BY TATIANA B. JACKSON AND JOHN O. EDWARDS

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Ethylenimine (aziridine) forms coördination compounds with labile metal ions similar to those formed by ammonia and primary amines. Complexes with divalent copper, nickel, cobalt, manganese and mercury have been isolated and identified. The formation constants of complexes with copper, zinc, silver and mercury ions in aqueous solution have been measured by the Bjerrum method. The temperature dependence of ethylenimine ionization is expressed by the equation: $pK_a = 2438\left(\frac{1}{T}\right) - 0.244$, whence $\Delta H^0 = 11.6$ kcal./mole.

Introduction

No data have been found in the literature to indicate that work on coordination compounds containing ethylenimine as a ligand has been carried out. This is presumably a result of the well-known instability of the ethylenimine ring. It is only with the advent of the kinetic data on ring opening[1,2] that stability conditions have become sufficiently defined to encourage synthetic work on such unusual reactions of the ethylenimines.

The aim of this research was to find out: (1) what types of complexes are possible, (2) the stability of the ethylenimine ring when bonded to a metal and (3) the strength of the resulting metal-to-nitrogen bond. With the use of special precautions, complexes of ethylenimine with several transition metals have been prepared and identified, and the Bjerrum method has been applied in four cases to determine the formation constants of these complexes. Definite conclusions on these research aims have been reached.

Experimental and Results[3]

A. **Reagents.**—The ethylenimine was prepared either by the method of Wenker[4] or was a commercial product. It was dried over sodium and distilled from this metal just before use; boiling point, 55.5°.

All the salts and solvents used in the preparation of complexes were of reagent grade. The solution of mercuric nitrate was prepared from mercuric oxide plus the equivalent amount of nitric acid in 2*N* sodium nitrate. The mercury concentration was determined by titration with thiocyanate. The stock solution of 5*N* sodium nitrate was prepared from reagent grade salt and tested for neutrality. The nitric acid solutions were standardized with a solution of sodium hydroxide of known normality. Distilled water was used through all the preparations.

B. **Preparation and Properties of Cu(II) Complexes.** 1. **Tetraethylenimine Copper(II) Nitrate.** $[Cu(C_2H_5N)_4](NO_3)_2$.—*Prep.* 1.4 g. of Az were dissolved in 1.5 ml. of ethanol and cooled in ice. A solution of 0.5 g. of cupric nitrate trihydrate in the same solvent was then added drop by drop. The flask was left in ice for half an hour. The violet, crystalline precipitate thus formed was filtered by suction, washed once with cold ethanol and redissolved at R.T. in ethanol containing a few drops of Az. The complex was recrystallized by adding ether and cooling in ice. The precipitate was filtered and washed successively with a cold dilute solution of Az in ethanol, cold ethanol and finally with anhydrous ether. It was dried in a vacuum desiccator over KOH pellets.

Anal. Calcd.: C, 26,70; H, 5.60; N, 23.34. Found: C, 26.27; H, 5.45; N, 23.28.

Properties.—M.p., 142°(d). The compound is soluble in water and polar solvents, insoluble in ethyl ether and benzene. Aqueous solutions of this and of the following copper-complexes are decomposed by boiling or by the addition of mineral acids.

II. **Tetraethylenimine Copper(II) Sulfate Hydrate.** $[Cu(C_2H_5N)_4]\ SO_4 \cdot 1.5\ H_2O$.—*Prep.* 3 g. of finely powdered cupric sulfate pentahydrate were dissolved in a solution of 3.5 g. of Az in 4 ml. of water cooled in ice. The solution was filtered, ethanol added until precipitation began and precipitation completed by cooling in ice for 1 hr. The deep blue crystals were collected on a filter and redissolved in the minimum amount of water at R.T. After addition of a few drops of Az, the complex was recrystallized by addition of ethanol and cooling, filtered by suction and washed successively with a solution of Az in ethanol, ethanol and ether. It was dried in a vacuum desiccator over KOH.

Anal. Calcd.: C, 26.77; H, 6.46; N, 15.61; S, 8.93. Found: C, 26.81; H, 6.88; N, 15.31; S, 8.79.

Properties.—M.p., 132°(d). The compound is very soluble in water and methanol, slightly soluble in ethanol and acetone, insoluble in ether and benzene.

III. **Tetraethylenimine Copper(II) Iodide.**[5] $[Cu(C_2H_5N)_4]I_2$.—*Prep.* 0.3 g. of finely powdered cupric acetate was dissolved in a mixture of 1.2 g. of Az in 2 ml. of water. By addition of a saturated solution of 1 g. of potassium iodide in water, a violet crystalline precipitate was formed at once. This was filtered by suction, dissolved in a concentrated solution of Az in water and recrystallized by addition of a concentrated solution of potassium iodide in water. The precipitate was filtered and washed with a cold dilute solution of Az in water, taking care not to pass air through the solid, and dried "*in vacuo*" over KOH.

Anal. Calcd.: C, 19.61; H, 4.11; I, 51.80. Found: C, 19.60; H, 4.21; I, 51.58.

Properties.—M.p., 120°(d). Treatment with ethanol or ether decomposes the compound, leaving a brown solid or solution. The solid complex can be kept unchanged for a long time in a closed container, if protected from air and humidity.

IV. **Tetraethylenimine Copper(II) Bromide.** $[Cu(C_2H_5N)_4]Br_2$.—The preparation is similar to the one used for

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[1] W. G. Barb, *J. Chem. Soc.*, 2564, 2577 (1955).

[2] J. E. Earley, C. E. O'Rourke, L. B. Clapp, J. O. Edwards and B. C. Lawes, THIS JOURNAL, **80**, 3458 (1958).

[3] Analyses were performed by the Microchemical Laboratory, Massachusetts Institute of Technology. The symbol Az for ethylenimine (azridine) will be used. R.T. Stands for room temperature (about 23°).

[4] H. Wenker, THIS JOURNAL, **56**, 2328 (1936).

[5] See F. Ephraim and R. Linn, *Ber.*, **46**, 3746 (1913–1914) for $[Cu(CH_3NH_2)_4]I_2$.