The disilicides of Nd–Dy have relatively small c values ($0.750 > R_{Si}/R_M > 0.725$), so that the other two axes must increase, which is achieved by the formation of vacancies in one of the Si chains and by increase of the axis dependent on it. The structure of these silicides is therefore orthorhombic and nonstoichiometric.

In the digermanides of La–Ce, a large metal and a nonmetal are present ($0.750 > R_{Ge}/R_M > 0.725$). The value of c is large, and, in order to maintain the value for the cell volume, one of the other two axes must decrease. This is achieved, as can be seen from the orthorhombic structure, by the incomplete filling of one of the nonmetal chains by Ge atoms, so that these digermanides will be orthorhombic.

In the digermanides of Pr–Sm the length of c is of an intermediate value ($0.760 > R_{Ge}/R_M > 0.750$). The nonmetal chains—depending also on the c axis—are not large enough to accommodate all of the Ge atoms, and vacancies appear in both the a- and b-dependent chains, resulting in nonstoichiometric tetragonal structures.

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A Comparison of the Donor Properties of Dimethylcyanamide and Acetonitrile

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Thermodynamic and spectrochemical data on the donor properties of dimethylcyanamide, $(CH_3)_2NCN$, toward charge-transfer types of acids, conventional Lewis acids, and nickel(II) are reported. Evidence from changes in the infrared and nmr spectra upon coordination is interpreted to indicate that the nitrile nitrogen is the donor atom. The C^{13}–H coupling constants are very informative in elucidating the properties of this donor and the structure of these adducts. The donor properties of N,N-dimethylcyanamide are compared with those of acetonitrile and the differences are discussed.

Introduction

The nitriles as a group have been rather widely investigated as donors toward Lewis acids.[2,3] While classified generally as weak bases, they exhibit several unusual and interesting properties such as an increase in the nitrile stretching frequency ($\Delta\nu_{CN}$) upon coordination[4,5] and very large Dq values in metal complexes.[6] Since it is well known that the substitution of a methyl group in acetone by an N,N-dimethyl group to give N,N-dimethylacetamide (DMA) results in a marked increase in donor strength, it is of interest to examine the donor properties of N,N-dimethylcyanamide (DMCA) which is related to acetonitrile as DMA is to acetone.

Relatively little work has been carried out on N,N-dimethylcyanamide. Augdahl and Klaeboe[7] have reported thermodynamic parameters for the interaction of DMCA with I_2, ICl, and IBr which suggest that DMCA is a better donor toward these acids than is acetonitrile. However the authors were not able to establish the donor site in DMCA. Small increases in $\Delta\nu_{CN}$ were incorrectly taken to be indicative of σ donation from the nitrile lone-pair orbital. Bock[8,9] has prepared a novel series of compounds from nickel carbonyl and various cyanamides. In view of the above considerations, we decided to extend the study of the donor properties of DMCA to a wider range of acids and attempt to elucidate the donor site.

Experimental Section

A. Reagents and Solvents.—Dimethylcyanamide was obtained in a highly purified form (99.9% pure by vapor-phase chromatography) from American Cyanamid Co. A second sample of technical grade, obtained from Matheson Coleman and Bell, was purified by distillation at reduced pressure [bp 48° (10 mm)].

Hydrated nickel(II) perchlorate was obtained from G. F. Smith. Boron trifluoride from Matheson was purified by passing the gas through a drying tower containing concentrated sulfuric acid. Stannic chloride reagent grade from J. T. Baker was used as received. Phenol (Baker and Adamson) was distilled once at reduced pressure. The center fraction was retained and this was sublimed just prior to use. *p*-Chlorophenol from Eastman Organics was distilled at atmospheric pressure just before use.

N,N-Dimethylaniline (Fisher) and N,N-dimethylacetamide (Fisher) were distilled from barium oxide at reduced pressure before use. Trimethylamine, also from Fisher, was used as obtained. Trimethylamine N-oxide (Eastman Organics) was sublimed under vacuum before use. Nitromethane (Eastman Organics), chloroform and carbon tetrachloride (both from Mallinckrodt), methylene chloride (J. T. Baker), and acetonitrile (Fisher) were all stored over Linde V-A Sieves for at least 2 days before being used as solvents.

B. Typical Preparations of Lewis Acid Adducts. 1. BF_3·DMCA.—The boron trifluoride–dimethylcyanamide adduct was prepared in benzene dried over calcium hydride. Boron trifluoride, previously passed through a sulfuric acid tower, was bubbled slowly into the solution of DMCA in benzene at room temperature. The system was vented through a calcium chloride drying tube. A rapid flow of nitrogen was maintained through

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[1] Abstracted in part from the Ph.D. thesis of H. F. Henneike, Jr., University of Illinois, 1967.

[2] (a) M. D. Joesten and R. S. Drago, *J. Am. Chem. Soc.*, **84**, 3819 (1962); (b) A. W. Laubengayer and D. S. Sears, *ibid.*, **67**, 164 (1945).

[3] R. A. Walton, *Quart. Rev.* (London), **59**, 126 (1965).

[4] H. J. Coever and C. Curran, *J. Am. Chem. Soc.*, **80**, 3522 (1958).

[5] K. F. Purcell and R. S. Drago, *ibid.*, **88**, 919 (1966).

[6] C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Addison-Wesley Publishing Co., Reading, Mass., 1962, p 111.

[7] E. Augdahl and P. Klaeboe, *Acta Chem. Scand.*, **19**, 3 (1965).

[8] H. Bock, *Angew. Chem.*, **74**, 695 (1962).

[9] H. Bock and H. T. Dieck, *Chem. Ber.*, **99**, 215 (1966).

the system until the vented vapor fumed indicating an excess of boron trifluoride had been added. Upon cooling the solution to approximately 5°, a white precipitate appeared. This was filtered in a drybox and then the remaining benzene was pulled off under vacuum. The slightly hygroscopic white crystals were stored in a brown bottle. They tend to lose some dimethyl cyanamide under extensive pumping.

Anal. Calcd for $BF_3C_3H_6N_2$: C, 26.16; H, 4.39; N, 20.31. Found: C, 26.57; H, 4.57; N, 20.58.

In an attempt to prepare an adduct of the formula DMCA·$2BF_3$, a solution of DMCA in benzene was saturated with boron trifluoride and left overnight under an atmosphere of boron trifluoride. Twenty hours later a white precipitate had deposited. When filtered and dried, however, it analyzed as above for BF_3·DMCA.

2. **$SnCl_4$·2DMCA.**—A stoichiometric amount of $SnCl_4$ in methylene chloride (or CCl_4) was added to a solution of DMCA in the same solvent. The addition was carried out under a nitrogen atmosphere as above. The adduct is soluble in methylene chloride at room temperature, but can be isolated by cooling the solution to 0°, or below. The adduct precipitates slowly from the CCl_4 solution. The white solid is slightly hygroscopic and must be handled in a drybox or glovebag with exclusion of moisture.

Anal. Calcd for $SnCl_4\cdot 2(C_3H_6N_2)$: C, 17.98; H, 3.02. Found: C, 17.96; H, 3.06.

C. **Preparation of Transition Metal Ion Complexes. Ni(DMCA)$_6$(ClO$_4$)$_2$.**—$Ni(H_2O)_6(ClO_4)_2$ was added to a large excess of dimethoxypropane and stirred for 1 hr. Then approximately a 12:1 ratio of DMCA to $Ni(H_2O)_6(ClO_4)_2$ was added and the solution stirred for 2 hr more. Upon addition of the DMCA there was an immediate color change to a deep blue-green. Upon addition of diethyl ether to this solution, a green-blue oil separated. After repeated washings, a blue or blue-green paste was obtained. (This can be dried under vacuum but does not analyze properly.) This paste was then dissolved in methylene chloride containing an approximately 20:1 excess of DMCA and a 1:3 ratio of dimethoxypropane (both based on initial $Ni(H_2O)_6(ClO_4)_2$). After stirring for 2 hr a light blue solid was precipitated by adding a large excess of dimethyl ether. This last step may have to be repeated in order to obtain good analyses. The light blue solid is very hygroscopic and also loses DMCA slowly even in an inert atmosphere. Attempts to dry it in a desiccator under vacuum gave light yellow or yellow-green solids which were presumably $Ni(DMCA)_x(ClO_4)_2$, where x is less than 6.

Anal. Calcd for $Ni(C_3H_6N_2)_6(ClO_4)_2$: C, 31.79; H, 5.35; Ni, 8.66. Found: C, 30.96; H, 5.36; Ni, 8.54.

D. **Infrared Spectra.**—The basic technique used for obtaining the shifts of the phenol and *p*-chlorophenol O–H stretching frequency upon complexation by DMCA is similar to that previously reported.[2a] However, the high dipole moment of DMCA and probable large dielectric constant make $\Delta\nu_{OH}$ very dependent on the concentration of DMCA employed. An extrapolation of $\Delta\nu_{OH}$ to zero DMCA concentration was, therefore, used.[10]

The shifts in the C≡N and N—C stretching frequencies upon complexation of DMCA by various Lewis acids were measured on a Beckman IR-7 as were the ν_{OH} shifts above. An extrapolation procedure was not used for these frequency shifts since they were obtainable only with fairly large per cent errors in any case. The value of $\nu_{C\equiv N}$ in DMCA was found to be quite insensitive to solvent effects in the absence of a specific interaction. For neat DMCA the vibration was found at 2218 cm^{-1}, and in 0.1 *M* solution in CCl_4, it occurred at 2221 cm^{-1}.

The full spectra of all adducts and complexes were obtained from 4000 to 650 cm^{-1} on a Perkin-Elmer Model 521 recording spectrophotometer. The transition metal ion complexes were run as Nujol mulls prepared in a drybox and protected from atmospheric moisture until spectra were to be run.

E. **Electronic Spectra.**—Solution spectra were run in the 300–1500-mμ region on a Cary Model 14M spectrophotometer. For the electronic spectra of solutions containing an excess of the ligand, the reference solutions contained an equivalent amount of dissolved ligand. The electronic spectrum of DMCA itself in carbon tetrachloride and water was run down to the lower limit of the Cary 14M (200 mμ).

F. **Nuclear Magnetic Resonance Spectra.**—Nuclear magnetic resonance spectra of DMCA and its adducts and metal ion complexes were obtained on a Varian A-60 recording spectrometer using tetramethylsilane as an internal standard. All samples were run at 30 ± 2°. The low solubilities of the BF_3·DMCA and $SnCl_4$·2DMCA adducts in chloroform necessitated the use of a Varian TAC-4300 time-averaging computer for the observation of the $J_{^{13}C-N}$ satellites in their spectra.

Both cyclohexane and tetramethylsilane were used as internal and external standards in the measurement of solution magnetic moments of the metal ion complexes.[11]

Results are given in Tables I–III.[12–20]

TABLE I

SKELETAL STRETCHING FREQUENCIES OF DMCA ACCEPTOR SYSTEMS (CM^{-1})

	$\nu_{C\equiv N}$[a]	Intensity change[c]	ν_{N-C}[a]	Intensity[c]
I_2	2220 ± 2	Increase	1203 ± 3	Little change
C_6H_5OH	2225 ± 1	Increase	1205 ± 3	Increase
ICl	2227 ± 1	Increase	1204 ± 3	Increase
p-ClC_6H_4OH	2227 ± 1	Increase	1201 ± 4	Increase
$(CH_3)_2SnCl$	2226 ± 1	Increase	1206 ± 3	Increase
Ni(II)	2251 ± 8	. . .	1202 ± 8[b]	. . .
$SnCl_4$	2272 ± 5	. . .	1203 ± 10[b]	. . .
BF_3	2307 ± 6	. . .	1200 ± 10[b]	. . .

[a] The assignments of these stretching vibrations are those of Fletcher and Brown.[12] The value of $\nu_{C\equiv N}$ for a 0.1 *M* solution of DMCA in CCl_4 occurs at 2221 cm^{-1}. The band which is largely ν_{N-C} occurs at 1204 cm^{-1}. [b] These results are from Nujol mull spectra where this region is not as well resolved. The others in this table are from CCl_4 solution spectra, in all cases with an excess of acid. [c] The change in intensity of this adduct compared to free DMCA consists of mostly a large increase in the band width at half-maximum and a lesser increase in the extinction coefficient at the band center. In the *p*-ClC_6H_4OH–DMCA system the increase in the area of the $\nu_{C\equiv N}$ band is 150%. The increase in the area of ν_{N-C} is much less, on the order of 20%.

Discussion

A. Donor Site in DMCA. 1. Infrared Studies.—Since $\nu_{C\equiv N}$ in DMCA is nearly the same as that for aliphatic nitriles, we would expect to observe much the same behavior as in aliphatic nitriles for coordination at this site. This would mean an increase in the energy of the stretching vibration and an increase in its intensity. Along with this we might expect ν_{N-C} to increase since the nitrile group should now have a greater effective electronegativity and, therefore, draw more of the amino nitrogen lone-pair density into the π-bonding region between these two atoms, increasing its double-bond character.

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TABLE II

NMR MEASUREMENTS ON N-METHYL COMPOUNDS

Compound	Chem shifts,[a]	$J_{^{13}C-H}$,[b] cps	Peak width at half-height, cps
$(CH_3)_2NH$	7.65[13]	132[14]	
$(CH_3)_3N$	7.876[13]	131[14]	
$(CH_3)_2NC_6H_5$	7.21, (7.096)[13]	134.8, (135)[15]	1.8
$(CH_3)_2NC({=}O)CH_3$	7.11, (7.07)[16]	138.4, (138)[16]	
$(CH_3)_2NC({=}S)CH_3$	6.71, (6.62)[16]	139.8, (140)[16]	
$(CH_3)_3NC{\equiv}N$	7.19	140.3	1.7
$(CH_3)_2NN{=}O$	6.52	140.6	1.7
$(CH_3)_4N^+$		144.8, (145)[17]	
$(CH_3)_3NO$	6.94	143.3, (143)[17]	1.8
$(CH_3)_2NH \cdot BF_3$	7.54[18]	140.7[18]	
$(CH_3)_3N \cdot BF_3$	7.40, (7.42)[18]	142 ± 2.0	3.1
$(CH_3)_2C_6H_4N \cdot BF_3$	6.74	140 ± 1.0	2.3
$(CH_3)_2NC{\equiv}N \cdot BF_3$	6.71	140.8	1.7
$(CH_3)_2NC({=}O)CH_3 \cdot BF_3$	6.67	139.2	
$(CH_3)_3NO \cdot BF_3$	6.72	144.7	1.9
CH_3NO_2	5.722[13]	146.7, (147)[14]	

[a] These chemical shifts were all measured on the 250-cps scale, and the error limits are ±0.02 ppm. [b] The coupling constant measurements were done on the 100-cps scale and are thought to be generally accurate to ±0.4 cps for peaks of normal breadth. Error limits for those measurements on broader peaks are indicated in the table.

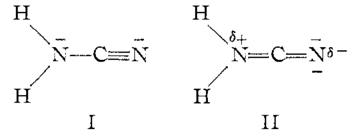
TABLE III

SPECTRAL AND MAGNETIC DATA FOR OCTAHEDRAL COMPLEXES OF ACETONITRILE AND DIMETHYLCYANAMIDE WITH Ni(II)

	$Ni(CH_3CN)_6(ClO_4)_2$[a,b]			$Ni[(CH_3)_2NCN]_6(ClO_4)_2$[g]		
Assignments	Obsd λ_{max}, cm^{-1}	ϵ[c]	Calcd λ_{max}, cm^{-1}	Obsd λ_{max}, cm^{-1}	ϵ[c]	Calcd λ_{max}, cm^{-1}
$^3A_{1g} \rightarrow {}^3T_{2g}$	10,400	6.1		9,490	10.3	
$\rightarrow {}^1E_g$	13,850	1.5		13,679	3.4	
$\rightarrow {}^3T_{1g}(F)$	17,600	4.8	17,200	15,820	9.4	15,580
$\rightarrow {}^3T_{1g}(P)$	28,200	8.4		25,920	22.6	
Dq, cm^{-1}	1040 ± 7			949 ± 5		
β	0.88 ± 0.01			0.88 ± 0.01		
λ,[f] cm^{-1}	−218			−231		
μ_{eff}, BM	3.15[b,d]			3.18[e]		
Nmr contact shift of ligand protons, cps	+712			−238		

[a] Values for this complex listed are within error limits the same as those reported in ref 19. The band positions are very similar to those reported in ref 20, but the extinction coefficients are much smaller. [b] In acetonitrile as solvent. [c] Calculated from $\epsilon = A/lC$, where l, the cell thickness, is 1 cm, C is the molar concentration of complex, and A is the absorbance. [d] Solution moment at 32° same as moment for solid reported in ref 19. [e] Solution moment at 32°. [f] The spin–orbit coupling constant calculated from $X = (8N\beta^2/3kT)[1 - (4\lambda/100q) + (8N\beta^2/100q)$. [g] In dimethylcyanamide as solvent.

Two structures which represent extremes for polarization of the π system can be represented by



I II

If we also postulate that complexation at the nitrile site in DMCA would polarize in the direction represented by structure II, we can qualitatively predict an increase in the intensity of the ν_{C-N} vibration. Structure II would have a large dipole moment and its contribution to the ground state of DMCA would depend upon the amino nitrogen–carbon bond length as well as the effective electronegativity of the nitrile nitrogen. If the electronic structure is polarized toward II in the complex, we would expect a change in the N—C distance to produce a larger change in the dipole moment, and thus ν_{N-C} would increase in intensity. In the absence of normal-coordinate analyses for either DMCA or any of its adducts and without accurate structures for either, these arguments concerning the intensity of ν_{N-C} are not rigorous.

For coordination at the amino nitrogen, the changes in the infrared spectrum of DMCA should be both more pronounced and more widely distributed than for coordination at the nitrile site. Not only must the symmetry of the molecule change from essentially C_{2v} to C_s, but any double-bond character of the NC bond must decrease. This reduction of CN double-bond character should lead to a noticeable reduction in the energy of the ν_{C-N} band. However, Bellamy[21] lists $\nu_{C=N}$ as *1650–1680 cm*$^{-1}$ and ν_{C-N} as *1020–1220 cm*$^{-1}$ which suggests that either double-bond character in this bond is already quite low or the observed band also contains contributions from other vibrations of lower energy.

With coordination at the amino nitrogen, the lone pair is less effective in undergoing the conjugative-type interaction shown in structure II. This would lead to greater triple-bond character in the nitrile bond and, therefore, an increase in the energy of the $\nu_{C\equiv N}$ stretching vibration invalidating previous[7] conclusions regarding the donor site. It seems probable that for coordination at the amino nitrogen, the component of the molecular dipole moment along the C≡N and N—C bonds would be reduced, and it would be changed less by stretching these bonds. Thus, it would seem to be difficult to rationalize an increase in the intensity of either $\nu_{C\equiv N}$ or ν_{N-C} for coordination at the amino nitrogen. These predictions are substantiated by a comparison of the infrared spectra of acetonitrile and benzonitrile. π-Electron density is delocalized into the C≡N group in benzonitrile but this effect is absent in acetonitrile. The frequency is lower and the intensity higher in benzonitrile.[22]

In examining Table I we see that the observed behavior is consistent with the behavior expected for nitrile coordination although the absence of an increase in ν_{N-C} is a little surprising. The fact that this band does not shift to lower energy coupled with the intensity increases for both bands makes coordination at the nitrile nitrogen seem more likely.

The assignment of the band at 2218 cm^{-1} in uncomplexed DMCA is certain since there are no other fundamentals within 300 cm^{-1}. The assignment of ν_{N-C} (ν_6 in ref 12) to the band at 1204 cm^{-1} is not as certain since in this region there are two other fundamentals of species A, which the authors cannot positively assign. These bands occur at 1456 and 1057 cm^{-1} and are

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(21) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958.

(22) H. W. Thompson and G. Steele, *Trans. Faraday Soc.*, **52**, 1451 (1956).

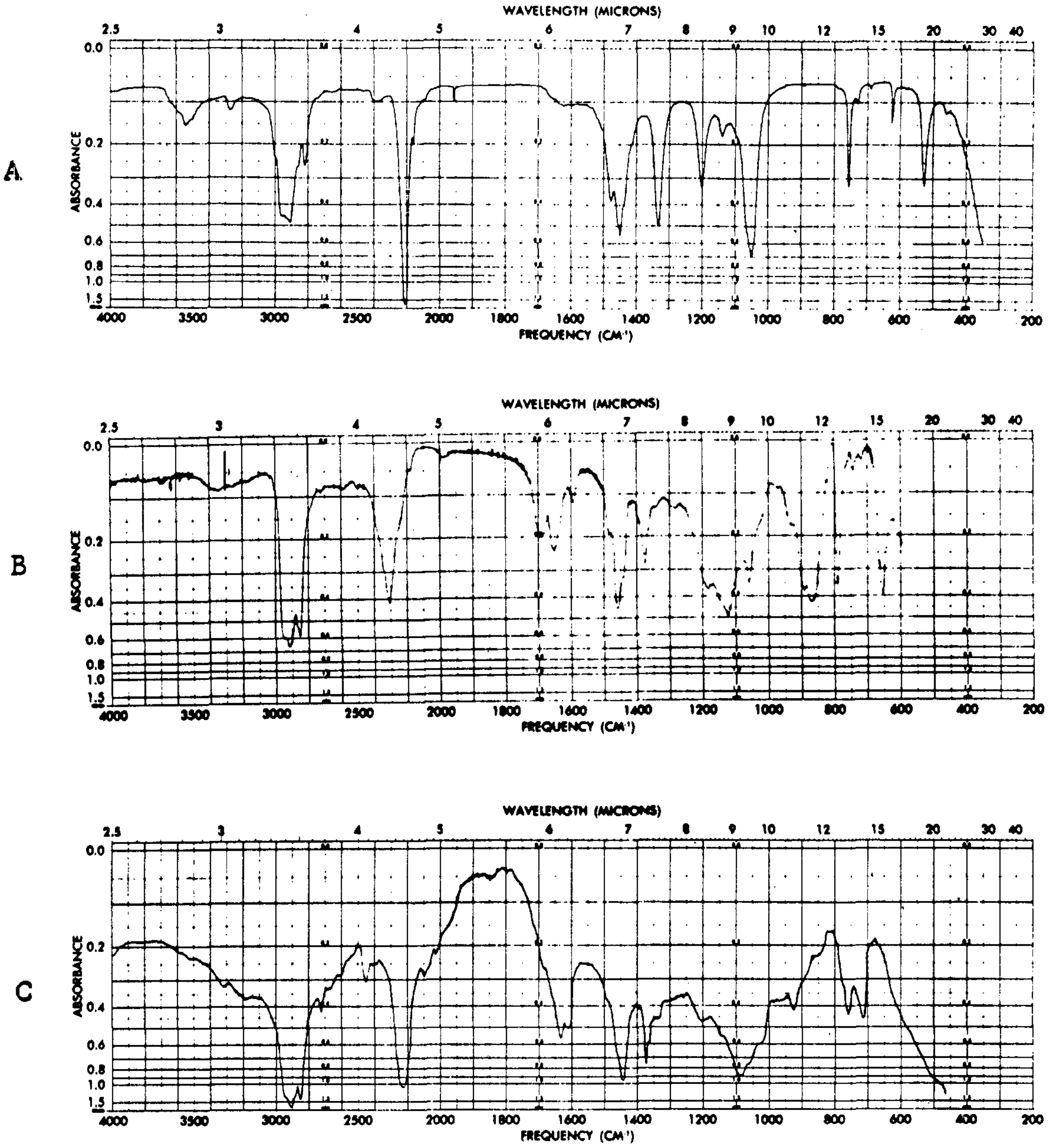

Figure 1.—(A) Infrared spectrum of liquid DMCA; (B) Nujol mull spectrum of $BF_3 \cdot$DMCA adduct; (C) Nujol mull spectrum of $Ni(DMCA)_6(ClO_4)_2$.

tentatively assigned as CH_3 deformation and rock modes.

In amides (R(C═O)NR′R″), nitrosamines (RR′N-(N═O)), and thioamides (R(C═S)NR′R″) there exists an analogous situation where a trigonal nitrogen is bonded to an unsaturated system. In amides a band in the region of 1200–1300 cm^{-1} has been assigned[21] as largely a C═N stretching vibration. In thioamides,[21] this band is stationary near 1290 cm^{-1} while in nitrosamines a band near 1060 cm^{-1} [22] has been assigned as largely due to a N═N stretching mode. Since a frequency range for N—N vibrations of 100 cm^{-1} below the range for C═C vibrations is quoted[21] all of these arguments favor the present assignments for DMCA over either alternative.

The position of the 1456-cm^{-1} band is insensitive to coordination. The band at 1057 cm^{-1} appears also to remain largely stationary although, since it cannot always be resolved from the intense peaks in the 1100–1200-cm^{-1} region, this is tentative. In the $BF_3 \cdot$DMCA adduct this band can be clearly resolved, and it occurs at 1071 cm^{-1}.

The increase in intensity noticed for the 1100–1200-cm^{-1} region seems to be centered around 1130–1150 cm^{-1}. It would seem possible that the arbitrary assignment of the band at 1150 cm^{-1} to species B_1 may be in error and that it also is of A_1 symmetry and contains some contribution from the C—N stretching mode. This would explain[23] why the intensity increase seems to be associated largely with this band. If the ν_{C-N} character is distributed among several of the bands in this region, the failure to observe a significant trend in the position of any one band as a function of acid

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[23] E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., Inc., New York, N. Y., 1955.

strength becomes more understandable. (See Figure 1 for the ir spectrum of DMCA.)

2. **Nmr Studies.**—It was decided to investigate by nmr a number of BF_3 adducts of compounds containing N-methyl groups to substantiate the conclusions of the infrared study. Heitsch[18] and Coyle, *et al.*,[24] reported studies on amine complexes with various boron acids, in which they generally concluded that the chemical shifts of groups on boron or groups in the ligand give shifts that can be correlated with enthalpies of formation for the complexes where these are available.

Of more interest for this study is the observation that in the BF_3–amine complexes the proton spectra show evidences of coupling to the B^{11} nucleus of the acid and in some cases even to the F^{19} nuclei of the acid. Such couplings are not observed in the proton spectra of BF_3 adducts of acetonitrile,[25] dimethylformamide (DMF),[26] DMCA, dimethylacetamide (DMA), or trimethylamine N-oxide. In all of these complexes, the proton resonances for the complexed ligands are merely shifted downfield from those of the free ligands by various amounts as shown in Table II. The resonances are not split or even noticeably broadened by coordination to BF_3.

In the DMA complex, the magnetic nonequivalence of the two N-methyl groups is slightly increased, and the coupling constants with the CCH_3 protons are still evident in the spectrum. This was also observed for the $DMF \cdot BF_3$ complex[26] and serves to identify the coordination site in these complexes as the carbonyl oxygen rather than the amino nitrogen.

The amine–BF_3 complexes are distinct in that they all show evidence of coupling of the amine protons to nuclei in the acid. Heitsch[18] succeeded in resolving this coupling for the three methyl amine–BF_3 complexes and found the coupling of the ligand protons to the B^{11} nucleus in BF_3 (J_{H-B}) to be between 1.5 and 2.1 cps. In this study the resolution was not so great, and the evidence for coupling consists of a marked broadening of the N-methyl resonances for the complexed ligand.

Further evidence for coordination at the nitrile nitrogen of DMCA comes from a comparison of the increase in $J_{^{13}C-H}$ for DMCA and the other ligands in Table II when they are coordinated to BF_3. All of the amines, including dimethylaniline, show a large increase in $J_{^{13}C-H}$. This increase is probably the net result of at least two effects. The coordination to BF_3 would drain electron density from the amine leading to an increase in Z_{eff}[27] for both the carbon and the hydrogen atoms as well as the nitrogen. The reduction of electron density on the nitrogen would make it more electronegative with respect to carbon, which according to Bent's isovalent hybridization[28] scheme, should require the methyl carbon to rehybridize, placing more p character in its orbital directed to nitrogen and leaving more s character for its three C–H bonds. This increase in s character for the C–H bonds would lead to a larger value of $J_{^{13}C-H}$.[29]

These amines form strong coordinate bonds to BF_3 as evidenced by the available thermochemical data,[30,31] and the large changes are not unreasonable in view of this. Trimethylamine N-oxide has been shown to be a somewhat better donor toward iodine[32] and phenol[33] than is dimethylacetamide, but it is a weaker donor than the amines. The small increase in $J_{^{13}C-H}$ in this complex is probably largely due to the fact that the inductive process must go through one more bond to affect the CH_3 group. Another factor which could account for the small increase might be called a "saturation" effect. That is, in the free ligand $J_{^{13}C-H}$ is already large in this case and may have reached nearly a maximum value above which further perturbation would not affect it as much. That this is not true is demonstrated by the much larger coupling constant of 147 cps which the N-methyl in nitromethane exhibits.

The very small increases noted upon coordination for $J_{^{13}C-H}$ in the dimethylacetamide and DMCA adducts are easily understood if coordination takes place at a position three atoms removed from the methyl groups in DMCA as well as in dimethylacetamide. The coupling constants for the methyl groups in the free ligands DMCA, DMNA, DMA, and TDMA suggest that the N-dimethyl groups in this series are quite similar in nature.

Taking the above evidence as a whole, coordination at the nitrile nitrogen in DMCA is indicated with a high degree of certainty. While this is not too surprising in view of the known coordination tendencies of the amides and thioamides, it is a point of some importance due to the unusual $Ni(CO)_4$ adducts formed by the cyanamides.

B. σ-Donor Strengths of DMCA.—The use of the double-scale enthalpy equation of Drago and Wayland[34] provides a quantitative framework for comparing the donor properties of a series of bases or the acceptor properties of a series of acids. A real advantage of this method is that it allows a quantitative estimate of the enthalpy of interaction for a base with a wide variety of acids with only a minimum of information. A minimum of two measured heats for the interaction of a base with two acids of widely differing nature will suffice.

In this case we will use this equation in a different manner. There exist a number of correlations between an easily measured physical parameter of an acid and its enthalpy of interaction with a base. Using several of these correlations and reported enthalpy data[7] we can compile a list of enthalpies for interaction of DMCA with several acids. The coherency of these values can

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(26) S. J. Kuhn and J. S. McIntyre, *ibid.*, **43**, 375 (1956).
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(30) D. P. Eyman, Doctoral Dissertation, University of Illinois, 1964.
(31) T. D. Coyle and F. G. A. Stone, *Progr. Boron Chem.*, **1**, 83 (1964).
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then be checked by determining how well they are reproduced by a single set of E and C parameters for DMCA.

Klaeboe[7] reports a $\Delta\nu_{OH}$ value for the phenol–DMCA system, although no details were given of the procedure used for the measurement. Since it is known that the value of $\Delta\nu_{OH}$ for systems involving highly polar bases can be quite dependent on the concentration of the bases employed in the measurement, it was decided to redetermine this value. The extrapolated $\Delta\nu_{OH}$ value of 226 ± 8 cm^{-1} is considered to be more reliable than the value of 215 cm^{-1} obtained without this correction for concentration effects. Using the former in the equation[35]

$$-\Delta H = 0.0103\Delta\nu_{OH} + 3.08$$

gives −5.4 kcal/mol for the enthalpy of interaction of phenol with DMCA.

Employing the same procedure and the proper equation for *p*-chlorophenol, a value of 245 ± 5 cm^{-1} for $\Delta\nu_{OH}$ and −5.6 kcal/mol for ΔH are obtained for this interaction. Although the errors in $\Delta\nu_{OH}$ correspond to errors of only 0.1 kcal/mol in ΔH, these correlations are only thought to be good to ±0.3 kcal/mol.

Bolles and Drago have reported a correlation between $J_{^{119}Sn-H}$ and the enthalpy of formation of 1:1 complexes between trimethyltin chloride and a series of bases.[36] For this relationship to hold, the steric requirements of the base must be small. For coordination to the nitrile nitrogen of DMCA, this requirement should be met. A solution of trimethyltin chloride in DMCA at 35° gives $J_{^{119}Sn-H} = 66.8$ cps. This converts to an enthalpy of −6.4 kcal/mol.

Table IV presents a comparison of the enthalpies available for DMCA and those for acetonitrile with the same acids. It appears that DMCA is a stronger σ donor than acetonitrile as would be expected by analogy with the acetone–dimethylacetamide pair. The increase in donor strength, however, appears to be somewhat smaller here. This may be due to the lower electronegativity of the nitrile nitrogen compared to a carbonyl oxygen.

The agreement between the corresponding values of columns 2 and 3 suggests that a single averaged set of E and C parameters will adequately reproduce the experimental data. Changing either E or C by 0.2 or more disrupts this agreement. Since the C and E values for acetonitrile are 1.01 and 0.917, respectively, it appears that E and C are both increased by substitution of CH_3 by $N(CH_3)_2$ but C is increased more than E. The increase in C probably corresponds to an increase in the ease of polarization of the donor by the Lewis acid because of the increased size of the π system in DMCA compared to CH_3CN. The increase in E parallels the observed increase in dielectric constant and arises from a polarization of the ground state in the direction of structure II compared to acetonitrile.

TABLE IV

THERMODYNAMIC DATA FOR DMCA AND ACETONITRILE (KCAL/MOL)

Acid (C_A, E_A)[d]	$-\Delta H$ (DMCA)	$-\Delta H$ (calcd)[a]	$-\Delta H$ (CH_3CN)[b]
I_2 (1.00, 1.00)	2.8[c]	2.8	1.9
ICl (1.06, 4.58)	7.3[c]	6.9	4.9
C_6H_5OH (0.528, 4.16)	5.4	5.5	4.6
p-ClC_6H_4OH (0.549, 4.24)	5.6	5.6	...
$(CH_3)_3SnCl$ (0.449, 4.96)	6.4	6.3	4.8

[a] ΔH(calcd) values are for DMCA and are calculated using the equation $\Delta H = E_AE_B + C_AC_B$ with E_A and C_A values in Table IV and $C_B = 1.66$, $E_B = 1.12$. [b] Values are from R. S. Drago and B. B. Wayland, *J. Am. Chem. Soc.*, **87**, 3571 (1965). [c] Reference 7. [d] These E and C numbers are improved over those previously reported. These represent the best computer fit of 164 simultaneous equations in 86 unknowns: R. S. Drago, G. Vogel, and W. Partenheimer, in press.

C. Transition Metal Ion Complexes.—The synthesis of a transition metal ion complex containing DMCA as a ligand was undertaken in order to study its donor characteristics toward this type of acceptor. The parameters which are at once measurable and indicative of the type of the metal–ligand interaction are Dq ($\Delta = 10Dq$) and β. The system from which this is most readily and accurately obtained is the octahedral nickel(II) complex containing six molecules of DMCA. The infrared spectrum of this complex, which is shown in Figure 1, is quite similar and in many ways resembles that of the $DMCA \cdot BF_3$ adduct. In particular, the absence of a band at 2220 cm^{-1} indicates that there is no uncoordinated DMCA in the complex. The increase in the stretching frequency of the $\nu_{C\equiv N}$ band by about 30 cm^{-1} is indicative of coordination through the nitrile nitrogen as in the previous cases.

Actually, for coordination at the amino nitrogen site, the steric hindrance between six DMCA molecules around the nickel ion would be at least as great as that between six trimethylamine molecules due to the greater degree of planarity of DMCA. In fact, it proves impossible to make a molecular model with six planar DMCA's around a nickel ion when coordination is through the amino nitrogen. The fact then that the infrared spectrum of this complex closely resembles that of the $DMCA \cdot BF_3$ adduct offers added evidence that coordination in both adducts is actually at the nitrile nitrogen site.

The absence of a noticeable absorption near 3500 cm^{-1} is good evidence that very little, if any, water from the starting materials remains since the water absorption band in this region has a large extinction coefficient. The 800–1000-cm^{-1} region also seems to be free of bands assignable to water vibrations.[37]

The complex of Ni(II) is only negligibly soluble in chloroform or methylene chloride and then the spectral peaks are shifted to lower energy; for instance the Dq band for the Ni(II) complex in chloroform with no added DMCA occurs at 9000 cm^{-1} rather than at 9500 cm^{-1} as in the solid state or in DMCA as solvent.

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(35) T. D. Epley, Ph.D. Thesis, University of Illinois, 1968.

(36) T. F. Bolles and R. S. Drago, *J. Am. Chem. Soc.*, **88**, 5730 (1966).

(37) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963.

It appears that here the perchlorate anions may well be entering the coordination sphere to some degree resulting in a lower average *Dq*. This would be in agreement with the low ionizing ability of these solvents and their inability to act as donors. Spectral changes also take place upon dissolution of the complex in acetone, acetonitrile, and nitromethane. In these solvents the nickel complex is somewhat more soluble; however, it is not until the solutions are at least 0.5 *M* in added DMCA that the spectrum again approaches that of the solid. Although there is no definitive evidence against perchlorate ion coordination in the nickel complex, the weight of evidence seems to indicate we must look elsewhere for the reason for the apparently lower value of *Dq* exhibited by DMCA than by CH_3CN in octahedral Ni(II) complexes.

The electronic spectra and magnetic moments of these complexes are given in Figure 2 and in Table III along with data for the analogous acetonitrile complexes for the sake of comparison. The electronic spectrum of the nickel(II) complex (Figure 2) in the presence of excess DMCA is seen to be quite consistent with the assignment of octahedral symmetry for the ligand field in this complex. In particular, when the energies of the high-energy band and the low-energy or *Dq* band are used to calculate the unknown quantities *Dq* and β, the agreement between the observed energy for the middle band and the energy calculated for this band using *Dq* and β agrees to better than 2%. Furthermore, the ratio of the extinction coefficient for the high-energy band and the *Dq* band is seen to be 2.19 which is within the range 2.1–2.2 expected for an octahedral Ni(II) complex.[38] The dashed line at the left of Figure 2 represents the tail of a very intense band which has $\epsilon > 10^3$ and its center somewhere below 300 mμ. The spectrum of dimethyl cyanamide itself in carbon tetrachloride consists of only a shoulder which begins at about 250 mμ[39] and by 200 mμ has reached $\epsilon > 10^3$. It appears then that the shoulder visible in the electronic spectrum of $Ni(DMCA)_6(ClO_4)_2$ is due either to a charge-transfer band or to a shift toward lower energy (~150 mμ) of the DMCA spectrum. If it were the latter, one would expect that the magnitude of the shift should increase with acid strength; however, the spectrum of $BF_3 \cdot$DMCA is indistinguishable from that of DMCA alone between 200 and 100 mμ. It would appear then that this is a new charge-transfer band. The low-intensity shoulder near 13,679 cm^{-1} is assigned to the forbidden $^3A_{1g} \rightarrow {}^1E_g$ transition as is usually done. This transition should be independent of *Dq*, yet it is found throughout the range 13,750 ± 1000 cm^{-1}.[40]

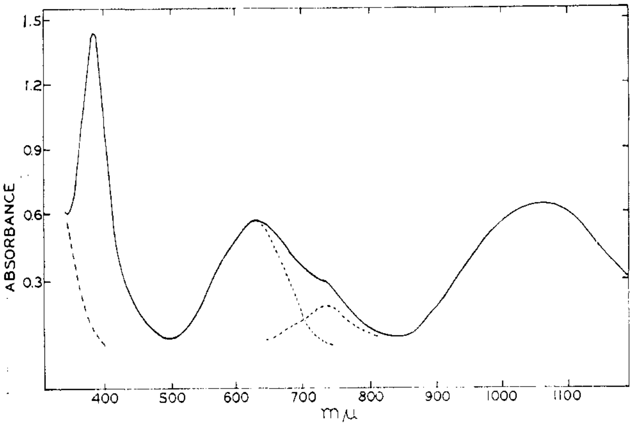

Figure 2.—The electronic spectrum of $Ni(DMCA)_6(ClO_4)_2$ in $CHCl_3$ with added DMCA. The concentration of DMCA is approximately 0.213 *M*.

Comparison of the parameters *Dq* and β for the DMCA complex with those for the analogous acetonitrile complex shows one somewhat surprising result. The *Dq* produced by DMCA is smaller than that produced by acetonitrile. Since we have already shown DMCA to be a better σ donor than acetonitrile, we might have expected the opposite. However, there are several factors which contribute to the magnitude of *Dq*. According to Jørgensen[41] these contributions can be broken down into four terms: (a) electrostatic first-order perturbation; (b) σ bonding, ligand to metal; (c) π bonding, ligand to metal; and (d) π bonding, metal to ligand. Of the above factors, the presence of (a), (b), and (d) tend to increase *Dq* while the presence of (c) will lead to a smaller value for *Dq*. It seems unlikely that there is any appreciable contribution from (c) in these complexes. The stronger σ-donor strength of DMCA relative to acetonitrile should lead to a larger *Dq* through (b). Since the dipole moment for cyanamide is larger than that for acetonitrile, it would appear that the increased σ-donor strength is connected with delocalization of the amino nitrogen lone pair into the C≡N bond. This should then lead to a larger fractional charge on the nitrile nitrogen which in turn should produce a larger *Dq* through effect (a). This would suggest then that π back-bonding from the metal to the ligand is less effective in increasing *Dq* in the case of DMCA than it is in the case of acetonitrile.

In addition to these, there is another factor which can affect the magnitude of *Dq*. This is steric interaction between the ligands. It has been suggested[42] that steric hindrance between ligand molecules when coordinated to a metal ion is in part responsible for the fact that the increasing order of *Dq* for a series of amide molecules toward Ni(II) does not correlate with the relative basicities toward the reference acids phenol and iodine. It would be expected that the steric interactions between DMCA molecules would be larger than those between acetonitrile molecules. While this increased steric interaction may contribute to the lower effective *Dq* value for DMCA, it does not seem likely that it is the only factor involved. The observed difference in *Dq* values is greater than 90 cm^{-1}. When

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(38) R. S. Drago, D. W. Meek, R. Longhi, and M. D. Joesten, *Inorg. Chem.*, **2**, 1056 (1963).

(39) The authors of ref 7 report two small peaks (ϵ 1.0) above 265 mμ, but these were never observed in this work.

(40) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Addison-Wesley Publishing Co., Reading, Mass., 1962, p 296.

(41) See ref 40, p 133.

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

the greater σ-donor strength of DMCA is taken into account, the actual lowering must be considerably larger. This apparent steric effect then would be larger in the case of DMCA and acetonitrile than it is in the case of DMA and DMF although in the first case the increase in steric bulk takes place 1.4 Å further from the metal ion center. Consequently, it seems improbable to relate the smaller Dq in DMCA to a steric effect and leaves less effective metal to ligand back-bonding as the most likely explanation.

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Linear Free Energy Relationships for the Aquation of Acidopentaaquochromium(III) and Related Complexes. The "Stability Constant" of Iodopentaaquochromium(III) Ion

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For the reaction $Cr(H_2O)_6^{3+} + I^- = Cr(H_2O)_5I^{2+} + H_2O$, the equilibrium quotient $Q_I = [CrI^{2+}]/[Cr^{3+}][I^-]$ has the value 7.0×10^{-5} M^{-1} at 25°, in a KI–HI medium of ionic strength 4.2 M and $[H^+] = 0.26$ M. The corresponding values of $\Delta H°$ and $\Delta S°$ are +7.6 kcal mol^{-1} and +6.6 cal mol^{-1} deg^{-1}, respectively. The dependence of Q_I on acidity and ionic strength is analyzed. A linear relationship exists between the logarithms of the rate coefficients for aquation of $Cr(H_2O)_5X^{2+}$ and the negative logarithms of the corresponding equilibrium quotients Q_X; the slope is 0.56. The significance of this for the $(H_2O)_5CrX^{2+}$ and $(NH_3)_5CoX^{2+}$ systems is discussed.

Langford[1] has demonstrated that the free energy ΔF^* of activation for the aquation of acidopentaamminecobalt(III) ions is linearly related to the standard free energy change $\Delta F°$ for the over-all reaction

$$Co(NH_3)_5X^{2+} + H_2O \rightleftharpoons Co(NH_3)_5OH_2^{3+} + X^- \qquad (1)$$

The slope of the straight line is fully 1.0, which yields the useful information that, in the transition state of the aquation reaction, the role of the departing ligand X is strongly similar to its role in the product, *viz.*, that of a solvated ion. Langford[1] further argued, after Hammond,[2] that the incoming aqua ligand will be no more than very weakly bound in the transition state of the aquation reaction, since reactions such as (1) are not highly endothermic. Thus, *bond breaking* is the major characteristic of the aquation reaction. Basolo and Pearson[3] have shown that the same is true for the analogous reaction of the ions $Ir(NH_3)_5X^{2+}$; in this instance, the slope of the linear free energy plot is about 0.9.

The object of the present study was to collect sufficient data for the investigation of free energy relationships in the systems

$$Cr(H_2O)_6^{3+} + X^- \underset{k_0}{\overset{K_X}{\rightleftharpoons}} (H_2O)_5CrX^{2+} + H_2O \qquad (2)$$

where k_0 is the pseudo-first-order rate coefficient for the acid-independent aquation of the acidopentaaquochromium(III) ion (hereafter referred to as acidochromium(III), or CrX^{2+}) and K_X is the thermodynamic formation quotient ("stability constant") of CrX^{2+}, defined as

$$K_X = \frac{a_{CrX^{2+}}a_{H_2O}}{a_{Cr^{3+}}a_{X^-}} = \frac{[CrX^{2+}]}{[Cr^{3+}][X^-]}a_{H_2O}\frac{y_{CrX^{2+}}}{y_{Cr^{3+}}y_{X^-}} \qquad (3)$$

in which a_i represents the activity and y_i the activity coefficient of species i. According to the ionic strength principle, it may be assumed that the activity coefficient quotient is constant at a given ionic strength $I = {}^1/_2\Sigma_iC_iZ_i^2$, and, since the water activity a_{H_2O} is often not accurately known for the reaction conditions necessary to obtain satisfactory measurements of $[CrX^{2+}]$, we shall use in place of K_X the quotient Q_X

$$Q_X = \frac{[CrX^{2+}]}{[Cr^{3+}][X^-]} = \frac{K_Xy_{Cr^{3+}}y_{X^-}}{a_{H_2O}y_{CrX^{2+}}} \qquad (4)$$

While k_0 and Q_X values are available in the literature for several simple anionic ligands X^-, equilibrium data for the system for which $X^- = I^-$ are conspicuously lacking, despite considerable current interest[4-6] in the behavior of the ion CrI^{2+}, and we now report our data on this system in connection with a linear free energy relationship between log k_0 and log Q_X for reactions of the type (2).

Experimental Section

Materials.—Baker Analyzed reagents were used throughout this work. All materials were checked for the absence of chloride ion. Chromium(III) perchlorate solutions were made by reduction of chromium(VI) oxide in aqueous perchloric acid with hydrogen peroxide. Dowex 50W-X8 ion-exchange resin (50–100 mesh, H^+ form) was prepared for use by flushing it with 3 M hydrochloric acid until the eluate was completely transparent in

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[1] C. H. Langford, *Inorg. Chem.*, **4**, 265 (1965).

[2] G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

[3] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1967, p 167.

[4] See, for example, ref 3, pp 201, 202.

[5] D. E. Pennington and A. Haim, *Inorg. Chem.*, **6**, 2138 (1967).

[6] A. Adin, J. Doyle, and A. G. Sykes, *J. Chem. Soc.*, *A*, 1504 (1967).