Complex Formation between Manganese(II), Nickel(II), and Zinc(II) Ions and Some Symmetrically Substituted Ethylenediamines: The Use of E_r and δH Values in Assessing Inductive and Steric Effects

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Using the procedures of George and McClure, E_r and δH_{Ni} values have been calculated from the formation constants of manganese(II), nickel(II), and zinc(II) complexes with some symmetrically substituted ethylenediamines. It is shown that C-substitution by alkyl groups appreciably increases the E_r values in the direction expected for an increase in the ligand nucleophilicity. N-Substitution brings about an effect in the same direction but of smaller magnitude. The δH_{Ni} values are lower for the substituted ethylenediamines than for the unsubstituted ligand, indicating that the stabilities of nickel(II) complexes are sensitive to steric influences. The δH_{Ni} values from equilibrium data correlate well with the spectral band positions in the visible and, to some extent, with the activation energies for the dissociation of the complexes. It is proposed that the tendency for nickel(II) to become spin-paired with the C-substituted ligands results in part from the ability of these greater nucleophiles to form stronger bonds in the square-planar complexes. A comparison of the properties of the amine complexes of nickel(II) with those of mercaptide suggests that $d\pi$–$p\pi$ antibonding effects between nickel(II) and sulfur are the cause for the unusually low stabilities of these latter complexes.

The nickel(II) complexes with substituted ethylenediamines have been studied to determine the effects of the substituents on the stabilities of the complexes[1-4] and on their rates of dissociation.[5-8,9] These studies have revealed that with N-substitution steric factors are important. The stepwise formation constants were found to decrease in magnitude, the more so the greater the number of ligands coördinated,[1,2,4] and the dissociation rates of the mono-complexes were shown to increase approximately as their formation constants decrease.[7,10] On the other hand, with the C-substituted ligands no simple relationships were obtained. The effects on the stabilities were found to be small,[3] whereas the dissociation rates were observed to decrease as the degree of substitution was increased.[5,7]

One of the interesting results deriving from these earlier studies has been the observation that with increasing C-alkyl substitution the nickel(II) ion in the bis complex shows an increasing tendency to assume the square planar spin-paired configuration. Indeed, with C,C'-TetraMeen only the bis complex, which is completely in the diamagnetic form, has been observed. This phenomenon has been attributed to steric hindrance[5] and the repulsion of the water molecules coördinated to the perpendicular axis through the hy-

drophobic character of the methyl groups.[3] However, this explanation seems inadequate because to remove two water molecules from the coördination sphere leaving vacant positions, or at least to lengthen their bonds to the metal ion, requires that some dehydration energy be expended. Also, to pair electrons, exchange and repulsion forces must be overcome.[11] These effects both should act to bring about marked decreases in the stability of the spin-paired form so the high formation constant reported for the diamagnetic ion, $Ni(C,C'\text{-TetraMeen})_2^{++}$, (log Q_2 equals 14.68 compared to 14.08 for $Ni(en)_2^{++}$[3]) suggests that, with this ligand at least, other factors also are involved. One possibility is that the C-substituted alkyl groups act through an inductive effect to increase the electron density on the amine nitrogens and thereby provide the opportunity for forming bonds of higher strength.

If a substituent exerts an inductive influence in a ligand it seems reasonable to expect this would be manifested in the E_r values[12,13] derived from the stabilities of the Mn(II) and Zn(II) complexes and also, relative to the present investigation, in the δH_{Ni} values[12,13] for the Ni(II) complexes.

For solution reactions, to the first approximation that the entropies cancel,[13] the E_r value is the negative of the heat for the reaction $Zn^{++}(g) + MnL^{++}(n\text{aq}) \rightarrow ZnL^{++}(n\text{aq}) + Mn^{++}(g)$ and is calculated using the relationship $E_r = -\Delta F_{Zn} + \Delta F_{Mn} - \Delta H_{hZn} + \Delta H_{hMn}$. In this equation ΔF_M is the measured free energy for the reaction $M^{++}(\text{aq}) + nL(\text{aq}) \rightarrow ML^{++}(n\text{aq})$, and ΔH_{hM} is the heat of hydration of M^{++}, $M^{++}(g) \rightarrow M^{++}(\text{aq})$, where M represents Mn or Zn.

The δH_{Ni} value represents the ligand field stabilization energy of the corresponding Ni(II) complex and is obtained from stability data using the relationship

(1) F. Basolo and R. K. Murmann, *J. Am. Chem. Soc.*, **74**, 5243 (1952).
(2) F. Basolo and R. K. Murmann, *ibid.*, **76**, 211 (1954).
(3) F. Basolo, Y. T. Chen, and R. K. Murmann, *ibid.*, **76**, 956 (1954).
(4) H. Irving and J. M. M. Griffiths, *J. Chem. Soc.*, 213 (1954).
(5) R. G. Wilkins, *ibid.*, 4521 (1957).
(6) A. K. Shamsuddin Ahmed and R. G. Wilkins, *ibid.*, 3700 (1959).
(7) A. K. Shamsuddin Ahmed and R. G. Wilkins, *ibid.*, 2895 (1960).
(8) A. K. Shamsuddin Ahmed and R. G. Wilkins, *ibid.*, 2901 (1960).
(9) To be consistent with the earlier workers, we shall use these abbreviations for the ligands: en = ethylenediamine; N,N'-DiMeen = N,N'-dimethylethylenediamine; N,N'-DiEten = N,N-diethylethylenediamine; N,N'-TetraMeen = N,N,N',N'-tetramethylethylenediamine; *m*-bn = *meso*-C,C'-dimethylethylenediamine (*m*-2,3-diaminobutane); C,C'-TetraMeen = C,C,C',C'-tetramethylethylenediamine; *t*-chx = *trans*-1,2-diaminocyclohexane.
(10) The order is not rigid and an exception is found with the mono-(N,N'-dimethylethylenediamine) complex, which has both a lower dissociation rate constant and a lower formation constant than the mono-(ethylenediamine) complex (ref. 7).

(11) J. S. Griffith and L. E. Orgel, *Quart. Rev.* (London), **11**, 381 (1957).
(12) P. George, *Rec. trav. chim.*, **75**, 671 (1956).
(13) P. George and D. S. McClure, *Progr. Inorg. Chem.*, **1**, 381 (1959).

$$\delta H_{Ni} = \Delta F_{Mn} - (3/5)E_r - \Delta F_{Ni} + \Delta H_{hMn} - \Delta H_{hNi}.$$

To obtain this equation, the assumption is made that in the absence of ligand field stabilization the Ni(II) complex has a relative stability $(3/5)E_r$ after a correction is made for the hydration energy of the aqua Ni(II) ions.[12,13]

The E_r value is a measure of the influence upon the ligand of the greater effective ionic charge of Zn(II)[14] relative to Mn(II). With different donor atoms the E_r values are found to increase in the order oxygen of water and carboxylate < amine nitrogen < mercaptide sulfur,[13,15] which is also in the order of increasing polarizability of these atoms. In substitution reactions where coördinated water molecules are replaced by amine or mercaptide groups the increase in E_r is observed to be almost linear with the number of water molecules replaced, at least up to four.[13,15,16]

The δH_{Ni} values also are observed to increase when amine groups replace water molecules, the increase in δH_{Ni} usually being proportional to that in E_r.[12,13]

Those substituents which serve to increase the strength of the metal–donor atom bond through polarizability (inductive) effects should also bring about an increase in E_r and δH_{Ni}, and conversely for those effects which serve to weaken the bond. Furthermore, any steric hindrance between two coördinated groups should be more noticeably in the order Mn(II) < Zn(II) < Ni(II), partly because the ionic radii decrease slightly in this order,[17] and partly because this is the order in which ligands are more tightly bound. This latter effect would result in greater energy expenditures when metal–ligand bonds are lengthened.

The present investigation was undertaken to determine the E_r and δH_{Ni} values for various substituted ethylenediamines in order to ascertain what information can be obtained from these regarding the forces within the complexes. The spectra of the Ni(II) complexes also were determined as a check for consistency since the position of the band corresponding to the first d–d transition is also a function of δH_{Ni}.

The results obtained in this work regarding the diamagnetic Ni(II) complexes of the diamines also made it possible to draw some conclusions regarding the nature of the bonding in the diamagnetic Ni(II) mercaptides. These conclusions are discussed below.

Experimental

N,N'-Dimethylethylenediamine and N,N'-diethylethylenediamine were Matheson, Coleman and Bell products. N,N'-

(14) F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," John Wiley and Sons, New York, N. Y., 1958, p. 72.

(15) D. L. Leussing and T. N. Tischer, *J. Am. Chem. Soc.*, **83**, 65 (1961).

(16) Another advantage favoring comparisons of E_r when it is desired to assess substituent effects is that E_r is a property of the actual quantity of interest: the effect of the metal ion on the ligand *in the complex*. Since the absolute value of the formation constant of a complex has a term in the free ligand concentration, any effect of a substituent which changes the degree of solvation, the conformation, or the primary activity of the free ligand will cause the formation constant to change accordingly, even if the substituent has no effect on the metal–ligand bond. In calculating E_r values the terms involving the concentrations of the free ligands cancel out, so comparisons can more safely be made between complexes with different ligands.

(17) N. S. Hush and M. H. L. Pryce, *J. Chem. Phys.*, **26**, 143 (1957).

Tetramethylethylenediamine was obtained from Rohm and Haas and was fractionally distilled through a 60-plate column. Only those fractions which gas chromatography showed to consist of one component were taken.

2,3-Diaminobutane was prepared following the procedure of Dickey, Fickett, and Lucas.[18] The dihydrochloride of that portion determined to be the *meso* form was fractionally recrystallized five times from methanol–water mixtures. The solubilities in methanol of the first and last fractions were found to be the same, indicating that the sample was reasonably pure and free of contamination by the racemic mixtures.

C,C'-Tetramethylethylenediamine was prepared according to the method of Siegle and Hass.[19] *trans*-Cyclohexanediamine was very kindly supplied by the Geigy Chemical Co.

In order to obviate contamination by CO_2 and H_2O and to minimize storage problems, the amines were converted to the dihydrochlorides. These were twice recrystallized from CH_3OH–H_2O solutions and were air-dried after rinsing with ether. The chloride content of the dried salts was determined by potentiometric titration with standard $AgNO_3$. The purities were found to lie in the range 98.5 to 100%.

The 0.1 M $ZnCl_2$ solution was prepared by dissolving an accurately known weight of reagent grade Zn in a slight excess of 12 N HCl. $BaCl_2$, $MnCl_2$, and $NiCl_2$ solutions were prepared from the salts. The latter two also were made about 0.001 M in HCl to minimize hydrolysis. The metal ion concentrations of these two were determined by titration with a standard sodium EDTA solution.[20] The total cation content was determined by passing the MCl_2 aliquots through a Dowex IR50 cation-exchange column in the acid form and determining the total H^+ concentration by titration with 1.005 N NaOH. The amount of acid initially present was obtained by subtracting twice the initial divalent cation concentration from the total cation found.

The usual pH titration technique was used at 25° to determine the degree of complexing.[21] The pH values of the solutions were measured during the titrations with a Radiometer PHM22 pH meter equipped with a pHA630 scale expander. Each pH value was read to the nearest 0.005 unit. The solutions were deaerated before each titration was begun and were maintained under a nitrogen atmosphere during the titration. Manganese-(II) complexes oxidize easily above pH 7.

A relatively high concentration (0.368 M) of amine dihydrochloride was used in order to minimize the precipitation of manganese hydroxide. The initial metal chloride concentration was 0.030 M. The pK_a values of the amine hydrochlorides were determined under the same conditions but with $BaCl_2$ present instead of a transition metal chloride.

Even under the conditions used it was found that $Mn(OH)_2$ precipitation interfered in the experiments with the N-substituted ethylenediamines. Only relatively few significant points were obtained and these were in the region of $n < 1.00$.[22] With N,N'-TetraMeen only a slight degree of complexing was indicated before precipitation occurred so that it is possible to give only an upper limit for the formation constant of the mono-complex.

The graphical method of King and Gallagher[23] was used to evaluate the formation constants shown in Table I. The application of the graphical method was straightforward except in two cases which merit special discussion. In the Ni+2–N,N'-Tetra-Meen system only a one-to-one complex was formed. The points at higher $\bar{n}$ values in the King–Gallagher plot behaved normally and fell along a straight line which passed through the origin but the points at the lower $\bar{n}$ values deviated from this line and described a curve. The formation constant was ob-

(18) F. H. Dickey, W. Fickett, and H. J. Lucas, *J. Am. Chem. Soc.*, **74**, 944 (1952).

(19) L. W. Siegle and H. B. Hass, *J. Org. Chem.*, **5**, 100 (1940).

(20) G. Schwarzenbach, "Die Komplexometrische Titrationen," Ferdinand Enke, Stuttgart, 1955.

(21) A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, New York, N. Y., 1952.

(22) The quantity $\bar{n}$ is the average number of diamine molecules complexed per divalent metal ion.

(23) E. L. King and P. K. Gallagher, *J. Phys. Chem.*, **63**, 1073 (1959).

TABLE I

THE FORMATION CONSTANTS OF THE SYMMETRICALLY SUBSTI-
TUTED ETHYLENEDIAMINE COMPLEXES AT 25°

pK_a	Metal ion	log Q_1	log Q_2	log Q_3	
		Ethylenediamine			
pK_{1a} = 7.47	Mn$^{++a,b}$	2.73	4.79	5.66	30°, 1.0 M KCl
pK_{2a} = 10.18	Ni^{++c}	7.60	14.08	19.11	25°, 0.5 M KNO$_3$
	Zn$^{++a,b}$	5.92	11.07	12.93	25°, 1 M KNO$_3$
		N,N′-Dimethylethylenediamine			
pK_{1a} = 7.39	Mn^{++d}	2.48	...	...	
pK_{2a} = 10.23	Ni^{++c}	7.11	11.84	13.84	25°, 0.50 M KNO$_3$
	Ni^{++e}	6.65	10.50	...	25°, 0.10 M KCl
	Zn^{++}	5.51	9.73	...	
		meso-C,C′-Dimethylethylenediamine			
pK_{1a} = 6.95	Mn^{++}	2.72	4.32	...	
pK_{2a} = 9.95	Ni^{++}	7.04	12.74	15.63	25°, 0.5 M KNO$_3$
	Zn^{++}	6.06	11.15	V. wk.	
		N,N′-Diethylethylenediamine			
pK_{1a} = 7.62	Mn^{++}	2.3	...	...	
pK_{2a} = 10.38	Ni^{++c}	5.62	8.92	...	25°, 0.5 M KNO$_3$
	Zn^{++}	5.47	9.0	...	
		N,N-Tetramethylethylenediamine			
pK_{1a} = 6.26	Mn^{++}	<0.9	...	...	
pK_{2a} = 9.34	Ni$^{+'+}$	4.1	...	...	
	Zn^{++}	3.62	5.5	...	
		C,C′-Tetramethylethylenediamine			
pK_{1a} = 6.43	Mn^{++}	2.09	3.78	...	
pK_{2a} = 10.03	Ni^{++}	<6	14.56	...	
	Ni^{++f}	..	14.68	...	25°, 0.5 M KNO$_3$
	Zn^{++}	6.32	11.92	...	
		trans-1,2-Diaminocyclohexane			
pK_{1a} = 6.81	Mn^{++}	2.94	5.33		
pK_{2a} = 9.88	Ni^{++g}	7.99	14.98	20.07	20°, 0.10 M KCl
	Ni^{++h}	7.93	14.77	19.67	20°, $\mu \rightarrow 0$
	Zn^{++}	6.65	12.12	14.1	
	Zn^{++g}	6.37	11.98	...	20°, 0.10 M KCl
	Zn^{++h}	6.24	11.56		20°, $\mu \rightarrow 0$

[a] Taken from "Stability Constants," Part I, J. Bjerrum, G. Schwarzenbach, and L. G. Sillén, The Chemical Society, London, 1957. [b] Results of J. Bjerrum. [c] Reference 2. [d] Results of J. Bjerrum and P. Andersen. [f] Reference 4. [e] Reference 3. [g] G. Schwarzenbach and R. Baur, *Helv. Chim. Acta*, **39**, 722 (1956). [h] C. R. Bertsch, W. C. Fernelius, and B. P. Block, *J. Phys. Chem.*, **62**, 444 (1958).

tained from the slope of the linear portion. Since only a weak complex was indicated it is likely that one end of the diamine easily dissociates and therefore the behavior at the lower $\bar{n}$ values (where the solutions are more acid) possibly is due to the formation of protonated species. The other system of interest is that with Ni^{++} and C,C′-TetraMeen. Basolo and co-workers[3] determined the formation constant of this species by spectrophotometric methods. In the present potentiometric study this system was reinvestigated. Earlier results were confirmed. Within the experimental error, it was not possible to detect a 1:1 complex. The upper limit of its formation constant can be set at about 10^{+6}.

The constants for the zinc complexes in Table I have been corrected for the formation of chloro complexes using the constants of Sillén and Liljeqvist.[24,25] Dilution of the solutions occurred during the titrations, causing a corresponding decrease in the chloride concentrations. The fraction of Zn not complexed by chloride, f_{Zn}, was calculated to vary from 0.57 at the beginning of each titration to 0.42 at the end. An average value of 0.49 was used. This does not influence the results appreciably, since the maximum error of 0.08 unit in log f_{Zn} produces less than 0.1 of a unit error in E_r. The actual error is even less since the intermediate regions of the titration curve are of greatest interest.

(24) L. G. Sillén and B. Liljeqvist, *Svensk Kem. Tidskr.*, **56**, 85 (1944), as reported in ref. 20, part II.

(25) J. Bjerrum, G. Schwarzenbach, and L. G. Sillén, "Stability Constants," The Chemical Society, London, Part I, 1957, Part II, 1958.
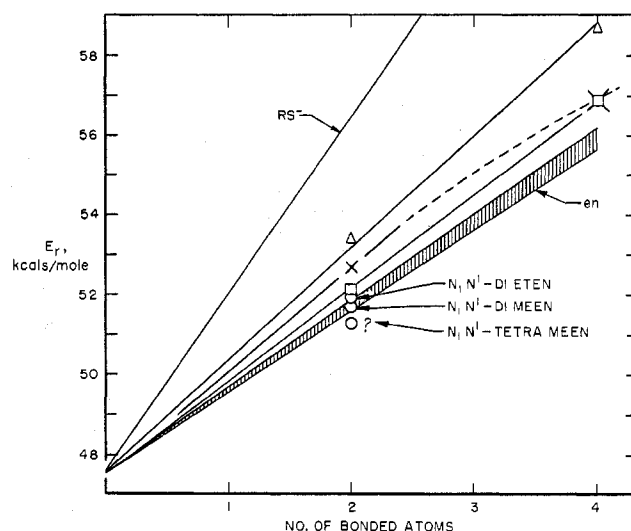

Fig. 1.—The variation in E_r with the number of coördinated ligand atoms: △, C,C′-TetraMeen; ✕, *t*-chx; □, *m*-bn.

The absorption spectra of the nickel(II) mono-complexes were obtained using a Cary Model 14 spectrophotometer. Except with N,N′-TetraMeen, the spectra were determined in 5.00-cm. cells on solutions which were made up to contain initially 0.15 M diamine dihydrochloride, 0.050 M sodium hydroxide, and 0.090 M nickel chloride. A 0.062 M nickel chloride solution in a 5.00-cm. cell was placed in the reference beam to compensate for the absorption of the uncomplexed nickel(II) ions. Because fairly strong complexes are formed, the assumption that the hydroxide is completely consumed in the reaction

$$AH_2^{++} + 2OH^- + Ni^{++} \longrightarrow + 2H_2O$$
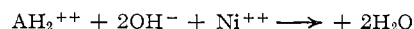
is reasonably good. The spectrum of the N,N′-TetraMeen complex was obtained using a solution made up to contain initially 0.301 M diamine dihydrochloride, 0.25 M sodium hydroxide, and 0.050 M nickel chloride. Water was used in the reference cell.

The positions of the absorption maxima of the mono-complexes are given in Table II together with the calculated δH_{Ni} values. With one exception it is seen that the positions of the absorption maxima generally follow the changes in the δH_{Ni} values within the uncertainty of about 100 cm.$^{-1}$. The deviation of ν_1 with *m*-bn is about 200–300 cm.$^{-1}$. This may indicate a residual entropy contribution to δH_{Ni}, but the other peaks of the complex are consistent with the value given. At any rate, the spectra indicate that any entropy effects probably are small and to a good approximation the δH_{Ni} and E_r values used in their calculation are a measure of the bonding heats.[26]

Discussion

The E_r Values.—The E_r values[27] are plotted in Fig. 1 *vs.* the number of bonded ligand atoms replacing water molecules in the coördination spheres of the metal ions. The upper solid line in the figure represents

(26) An interesting feature of the spectra is the sensitivity of ν_1 to the substitution of one molecule of diamine for two coördinated water molecules. The difference in δH_{Ni} between the aquo ion and the N,N′-TetraMeen complex is two units and the ν_1 positions differ by 1100 cm.$^{-1}$, whereas, between the TetraMeen and en complexes, the ν_1 differ by only 700 cm.$^{-1}$ for the same increment in δH_{Ni}. McClure (ref. 34b) has shown that for substitution reactions the ligand-field parameter, Δ (which is given by ν_1 in paramagnetic nickel(II) complexes), is changed by $^2/_3(\delta\sigma - \delta\pi)$ when one ligand replaces another. In substituting amine groups for water molecules, the σ antibonding level is raised in energy, but the π antibonding level is decreased, so both effects act to increase Δ. On the other hand, within the amines only $\delta\sigma$ changes, so a smaller effect results.

(27) The Benjamin and Gold hydration energies (*Trans. Faraday Soc.*, **50**, 797 (1954)) were used in the calculations.

<div align="center">

Table II

The δH Values and Spectral Band Positions of the Nickel(II) Complexes with Substituted Ethylenediamines

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Substituent or ligand	δH_{NiL}	δH_{NiL_2}	Spectra of NiL^{++}, ν (cm.$^{-1}$)			
			ν_1	ν_2	ν_3	ν_4
Ethylenediamine	38^a	42^a	10,300	(13,600)	16,020	26,900
trans-1,2-Diaminocyclohexane	38	42	10,300	(13,700)	16,100	27,000
N,N'-Dimethyl-	37.6	..	10,250	(13,500)	16,000	26,800
m-bn^b	36.9	39.7	10,350	(13,500)	16,000	26,800
N,N'-Diethyl-	35.7	..	10,000	(13,450)	15,750	26,300
N,N'-Tetramethyl-	35.9	..	9,600	(13,400)	15,400	26,000
C,C'-Tetramethyl-	<36	41.8	...	...	...	...
Ni(H$_2$O)$_6$$^{++}$	34	..	8,500	13,800	(15,200)	25,400

^{a} From ref. 13. ^{b} Band positions of the paramagnetic species. A band with a maximum at 22,600 cm.$^{-1}$ due to the diamagnetic form also is observed.

the results for mercaptide coördination[15] and the thick banded line represents those for en. The upper boundary of the en line has been calculated from the results of Bjerrum as reported in ref. 25, part I, while the lower boundary represents the values reported in ref. 13 after correcting for a slight difference between the hydration energies used by George and McClure and those reported by Benjamin and Gold.

Within the uncertainties N-substitution does not appear to have an appreciable effect on E_r. The value for N,N'-TetraMeen seems to be low, possibly indicating the effect of water–diamine hindrance in this last case. With C-substitution, on the other hand, larger effects are observed. A substantial change in E_r in the direction expected for an increase in ligand nucleophilicity is observed with the introduction of the four methyl groups of C,C'-TetraMeen. The effect is smaller with *t*-chx and *m*-bn but, nevertheless, is in the same direction. The linear relationship shown in Fig. 1 for C,C'-TetraMeen and *m*-bn is a good indication that ligand–ligand hindrance is negligible in these complexes although the reluctance of zinc(II) to form tris complexes with these compounds must surely result from crowding in the higher species.

With the N-substituted ligands there is some evidence for diamine–diamine interference in the bis complexes. Comparing the ratios of the stepwise constants, q_1/q_2, for the addition of the first two ligands to Zn^{++}, the results are 5.2, 5.9, 9.2, 15, 19.5, 55, and 87 for C,C'-TetraMeen, en, *m*-bn, *t*-chx, N,N'-DiMeen, N,N'-TetraMeen, and N,N'-DiEten, respectively. With the last two ligands, it is evident that the relative constants for the formation of the bis complexes are appreciably low. These observations are in agreement with the results of the earlier studies using nickel(II) and copper(II),[2] where it was concluded that with the N-substituted ligands hindrance is more serious between two coördinated amine molecules than between one amine and coördinated water molecules.

In contrast to the behavior of E_r, the δH_{Ni} values given in Table II are for the most part smaller with the substituted ligands than with en. In fact, as E_r increases the δH_{Ni} tend to decrease. Although the depressions are not large, they indicate the existence of greater effects, since usually the δH_{Ni} values increase proportionately to increases in E_r.[12,13] The primary

cause for this effect appears to be steric in nature since the magnitude of δH becomes smaller as the size or number of substituents increases. The result for the *t*-chx complex gives confirmatory evidence for this view because the ring structure tends to tie back the methylene groups bonded to the α-carbons of the ethylenediamine skeleton. For this ligand δH_{Ni} is equal to that for en. *t*-chx also forms a fairly stable tris complex with nickel, a further indication of lower hindrance between the rings and other coördinated groups.

In qualitative agreement with the predictions made above, the stabilities of the nickel(II) complexes appear to be more sensitive to steric factors than are those of manganese(II) or zinc(II). The fact that with Ni(II) ions the coördinated water molecules tend to be confined to well defined sites must be a contributing factor. In the complexes with the paramagnetic Ni(II) ions the effects of substitution on either carbon or nitrogen appear to be comparable in magnitude.

The failure to detect the mono-C,C'-TetraMeen Ni(II) complex therefore results from the combination of an abnormally low stability for this complex arising from water–diamine hindrance together with a more nearly normal stability for the diamagnetic bis species.[28] The mono-(N,N'-TetraMeen) nickel(II) complex is observed in spite of its low stability because higher complexes (either paramagnetic or diamagnetic) have even lower relative stabilities, through diamine–diamine hindrance.

The relatively high stability of diamagnetic Ni(C,C'-TetraMeen)$_2$$^{++}$ seems most reasonably to result from relief of strain by lengthening the bonds to the axial water molecules together with the opportunity furnished by the more polarizable in-plane ligands to form stronger bonds. Another factor which can be taken advantage of by the C-substituted ligands is the shorter metal ion–nitrogen bond distance which probably exists in the diamagnetic modification. The data of Hush and Pryce[17] for the transition metal ion hydrates show that the presence of electrons in the orbitals directed toward the ligands tends to increase the bond lengths. Promotion of an electron in Ni(II) from the $d_{x^2-y^2}$ orbital to the d_{z^2} should permit shortened bond distances to the

(28) From the magnitude of E_r a value in the range of 15–16 is estimated for the log Q_2 of the hypothetical (unhindered) paramagnetic species. The actual log Q_2 for this paramagnetic species must be less than 12.6.

in-plane ligands. The shorter bonds would increase the bond strength the more so the greater the polarizability of the ligands.

The substituent effect which results in increased ligand polarizability must in part arise from a direct contribution by the substituent electrons. It is difficult to understand, however, how this effect acting through carbon and nitrogen atoms in the case of the C-substituted diamines can account for more than a small part of the observed results. The greater part of the effect seems most reasonably to have its origin in shielding. Molecular models show that methyl groups substituted on the carbon backbone of complexed ethylenediamine are so oriented that they protect the region of the metal ion nitrogen bond from the solvent. Replacing high dielectric constant solvent by low dielectric constant hydrocarbon must certainly result in an increased electrostatic interaction between the metal ions and nitrogen dipoles. A similar effect of shielding by alkyl substituents is considered[29] to bring about the marked increases observed in the K_{1a}/K_{2a} ratios of the dicarboxylic acids as alkyl groups are introduced. Along these lines it is pertinent to observe that the difference $pK_{2a} - pK_{1a}$ for the ligands increases in the order en < N,N'-DiEten ∼ N,N'-DiMeen < m-bn ∼ N,N'-TetraMeen < t-chx < C,C'-TetraMeen. This comparison should not be carried too far, however, since the coördination of one and two protons to a diamine molecule is not quite analogous to the coördination of one and two diamine molecules to a metal ion.

Shielding also would explain why t-chx and 1,10-phenanthroline, both of which furnish relatively large E_r values, do not bring about spin pairing in the bis complexes with nickel(II) ions. With both of these ligands the hydrocarbon groups are directed away from the region of the metal ion–nitrogen bonds.

Dissociation Rates.—There is a body of evidence that in the dissociation of complexes bond breaking is involved in the rate-determining step.[30] It is expected then that some correlation should exist between the δH_{Ni} values and the activation energies for the dissociation of the complexes. As yet, relatively little is known regarding the dissociation of the nickel(II)-amines, but the few data which appear to be available are given in Table III.

It is seen in the figures of Table III that, in general, changes in the activation energies follow changes in the δH_{Ni} values. Small variations due to the specific ligands are to be expected, e.g., noticeable differences should exist between the dissociation of a monodentate ligand and one end of a bidentate ligand. Even so, the activation energy for the N,N'-TetraMeen complex is exceptionally high either for its δH_{Ni} value or for its formation constant.[31] As noted earlier, the equilibria involving this ligand are rather complicated and the dissociation may not be a simple process. Judging

(29) E. S. Gould, "Mechanism and Structure in Organic Chemistry," H. Holt and Co., New York, N. Y., 1959, p. 203.

(30) Reference 14, p. 163.

TABLE III

THE ACTIVATION ENERGIES FOR THE DISSOCIATION OF SOME MONO NICKEL(II) COMPLEXES

Ligand	δH_{Ni}	E_{act}, kcal./mole	log A, sec.$^{-1}$	Ref.
Ethylenediamine	38	20.5	14.2	6, 7
t-chx	38	19.5	12.9	6, 7
N,N'-DiEten	35.7	17.1	11.8	6, 7
N,N'-TetraMeen	36	20.9	14.5	6, 7
NH₃	36 est.[a]	14.3	11.2	31
Pyridine	35 est.[b]	16.3	13.6	31
H₂O[c]	34	12.2	13.5	32

[a] Taken to be equal to the δH_{Ni} values for the aminocarboxylic acids given in ref. 13. This value may be higher than that for NH₃ because of shielding effects in these complexes. [b] From the data of J. Bjerrum, *Chem. Rev.*, **46**, 381 (1950). [c] Water exchange by n.m.r. methods.

from these relatively few examples, it appears that δH_{Ni} values may possibly be used to give rough estimates of dissociation activation energies or to establish unusual behavior in this process.

The Nickel(II)–Mercaptide Complexes.—Nickel(II) ions react with mercaptides to form bis complexes which are diamagnetic and are characterized by somewhat lower stabilities than expected considering the stabilities of the corresponding zinc(II) complexes.[15,33] Earlier it had been proposed[15] that energy losses in electron pairing accounted for the relatively low stabilities, but the nearly normal stability of Ni(C,C'-TetraMeen)$_2^{++}$ implies that on this basis alone mercaptide ions with their higher polarizabilities also should form Ni(II) complexes having normal stabilities. Molecular models rule out the operation of steric forces but it is possible to attribute the destabilization to $d\pi - p\pi$ antibonding effects. It already has been shown[34] that the $d\pi - p\pi$ bonding is manifested in the spectra of the complexes of the transition metal ions with oxygen donor atoms. With mercaptide donors the effect appears to be larger and apparently is enhanced because of greater overlap between the metal ion d_{xz}, d_{yz} orbitals and the sulfur $p\pi$ orbitals.

Supporting evidence for this view is obtained from a comparison of the spectra. The spectrum of Ni(C,C'-TetraMeen)$_2^{++}$, where ligand $p\pi$ electrons are not present, shows one d–d transition with a maximum lying at 23,050 cm.$^{-1,3,e}$ while the spectra of the nickel(II)–mercaptide complexes are characterized by two such transitions. For example, the dimercaptopropanol complex, Ni(DMP)$_2^{-2}$, has maxima at 21,050 and 16,390 cm.$^{-1.35}$ The splitting in the latter case results from π-bonding.[36] Comparing different mercaptides[35] the

(31) R. G. Wilkins, private communication.

(32) R. E. Connick, private communication; see also R. E. Connick and E. D. Stover, *J. Phys. Chem.*, **65**, 2075 (1961).

(33) R. J. P. Williams, Plenary Lecture, VIth International Conference on Coördination Chemistry, Detroit, Mich., 1961.

(34) (a) R. J. P. Williams, *Discussions Faraday Soc.*, **26**, 123 (1958); (b) D. S. McClure, VIth International Conference on Coördination Chemistry, Detroit, Mich., 1961; C. H. Yamatera, *Bull. Chem. Soc. Japan*, **31**, 95 (1958).

(35) D. L. Leussing, *J. Am. Chem. Soc.*, **81**, 4208 (1959).

(36) C. K. Jørgensen, private communication; see also, J. Chatt, G. A. Gamlen, and L. E. Orgel, *J. Chem. Soc.*, 486 (1958), who discuss the similar situation in the Pt(II) ammine-chloride complexes. Differing from the present view these latter authors consider $d\pi - d\pi$ bonding to be more important in the Pt(II)–Cl$^-$ complexes.

splitting is the largest for DMP, 4600 cm.$^{-1}$, intermediate for mercaptoacetate, 4000 cm.$^{-1}$, and the smallest for cysteine, 3000 cm.$^{-1}$. The stabilities of both the mercaptoacetate and DMP complexes[15,35,37,38] are found to be lower with nickel(II) than with zinc(II), but the stability of the nickel(II)–cysteine complex is 1.1 log Q_2 units greater than that of the zinc complex.[39] This last difference is still less than expected, although the order conforms to the usual Irving–Williams sequence. Thus, both the spectral and stability data

are consistent with what is expected from the operation of $d\pi$–$p\pi$ antibonding effects and not with what is expected from either σ or $d\pi$–$d\pi$ effects.

In further support of these views, in the polynuclear nickel(II)–mercaptides, where $d\pi$–$d\pi$ bonding results in the donation of metal ion electrons to *empty* sulfur d orbitals,[15,40] the normal order of stabilities results.

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(38) D. L. Leussing, *ibid.*, **80**, 4180 (1958).

(39) A. Albert, *Biochem. J.*, **50**, 690 (1952).

(40) J. Chatt and F. A. Hart, *J. Chem. Soc.*, 263 (1953); 2807 (1960).

Stabilities of Chelates of Certain Substituted 8-Quinolinols

By JAMES FRESCO and HENRY FREISER

The acid dissociation constants of 8-quinolinol-5-sulfonic acid, 2-methyl-8-quinolinol-5-sulfonic acid, 2-methyl-7-bromo-8-quinolinol-5-sulfonic acid, 2-methyl-7-nitro-8-quinolinol-5-sulfonic acid, and 7-nitro-8-quinolinol-5-sulfonic acid have been determined. The stability constants of the corresponding chelates with copper(II), nickel(II), cobalt(II), and zinc(II) were determined potentiometrically at 25° by the Bjerrum method. The complexes of the methyl-substituted ligands are less stable then the corresponding complexes of the unsubstituted ligands. The stability decrease arises from steric repulsions of the 2-methyl groups.

Studies of the thermodynamics of formation of divalent metal chelates of substituted 8-quinolinols have indicated how variations in the structure of 8-quinolinol influence the stability of the corresponding chelates. For example, comparisons of the free energies and enthalpies of formation of the chelates of 8-quinolinol, 2-methyl-8-quinolinol, and 4-methyl-8-quinolinol have provided evidence for reduced chelate stability from a sterically hindering substituent.[1,2] It is of interest to note that the differences in the stabilities of corresponding metal complexes of 8-quinolinol[3-5] and 8-quinolinol-5-sulfonic acid[3,6] are not great, whereas the corresponding pK values differ by one log unit. This may reflect, first, enhanced resonance stabilization of the chelate by conjugation with the sulfonate group and, second, a greater degree of charge neutralization between the metal ion and the doubly-charged anion of 8-quinolinol-5-sulfonic acid in the first formation step, at least. In the present investigation, the formation constants of the metal chelates of these polysubstituted 8-quinolinols are compared: 2-methyl-8-quinolinol-5-sulfonic acid, 2-methyl-7-bromo-8-quinolinol-5-sulfonic acid, 2-methyl-7-nitro-8-quinolinol-5-

sulfonic acid, 7-nitro-8-quinolinol-5-sulfonic acid, and 8-quinolinol-5-sulfonic acid.
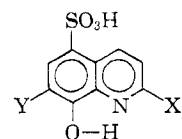
X = H or CH$_3$
Y = H, NO$_2$, or Br

Substituted 8-quinolinol-5-sulfonic acids

Experimental

Preparation of Compounds.—8-Quinolinol-5-sulfonic acid was prepared by the sulfonation of 8-quinolinol according to the procedure of Matsumura.[7] After three recrystallizations from boiling water, the compound was dried at 105°. The equivalent weight determined by titration with standard sodium hydroxide was found to be 238 (theoretical for the monohydrate: 243). 2-Methyl-8-quinolinol-5-sulfonic acid was prepared by the sulfonation of 2-methyl-8-quinolinol according to the procedure of Matsumura recommended by Phillips.[8] After three recrystallizations from boiling water the compound was dried at 105°. The equivalent weight determined by titration with standard sodium hydroxide was found to be 257 (theoretical for the monohydrate: 257). 2-Methyl-7-nitro-8-quinolinol-5-sulfonic acid was prepared by dissolving 5 g. of 2-methyl-8-quinolinol in 50 ml. of 15% fuming sulfuric acid with gentle heating. After cooling

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