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# Thermodynamic and Spectroscopic Parameters in Metal Complexes: Extension of a Linear Relationship to Nickel(II) Derivatives

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A previous correlation between the thermodynamic heat of formation in aqueous solution of some 30 copper(II) complexes and their electronic band maxima has been extended to nickel(II) and iron(II). Three alternative correlations are reported from some 40 nickel(II) complexes containing one to six amine ligands. These involve correlations with directly observable transition energies and also with a calculated function based on the orbital angular overlap model. The difference ( $\sigma_N$  $-\sigma_0$  is shown to correlate well with  $-\Delta H_1$  in substituted complexes. Although only very limited data are available, iron(II) amine derivatives exhibit similar behavior. It is shown that outer-sphere solvation energies cancel, fortuitously, from this correlation. These studies now permit the derivation of heats of formation of amine complexes of copper(II), nickel(II), and possibly iron(II) with reasonable accuracy.

We have recently discussed a relationship<sup>3</sup> observed between the heat of formation, in aqueous solution, of a series of copper(II) amine derivatives (eq 1) and the band energy of the maximum intensity absorption in their crystal field spectrum (eq 3, 4), i.e., for the process

$$Cu(H_2O)_6^{2+}(aq) + nL(aq) \rightarrow CuL_n(H_2O)_{6-n}(aq) + nH_2O(1)$$
  

$$n = 1, 2, 3, 4 \qquad \Delta H_{aq} \qquad (1)$$

we find, for ammonia

$$-\Delta H^{\circ}_{ac} = 4.90\nu(d-d) - 61.01$$
(2)

and for polyamines in general

$$-\Delta H^{\circ}_{aq} = 4.33\nu(d-d) - 54.43$$
  

$$\Delta H^{\circ} \text{ in kcal mol}^{-1} \text{ and } \nu(d-d) \text{ in cm}^{-1} \times 10^{3} \qquad (3)$$

Some 30 amine complexes including simple ammonia derivatives,  $Cu(NH_3)_x(\dot{H}_2O)_{6-x}$ , linear tetradentate amines, and also macrocyclic derivatives<sup>5</sup> were shown to obey these closely similar relationships. It was demonstrated that complexes were well behaved if there was free access for water molecules to occupy both axial sites of the molecule. In addition to providing a pragmatic procedure for evaluating heats of formation in aqueous solution, such studies should lead to a better understanding of such factors as outer-sphere solvation (hydration) energy and strain energy.

Of longer term importance is the eventual derivation of fundamental gas-phase thermodynamic data by spectroscopic methods.

### **Experimental Section**

Much of the calorimetric and spectroscopic data were obtained from the literature as referenced in Table I.

Data for the 1:1, 2:1, and 3:1 ligand-to-metal ratio complexes of ethylenediamine (en), 1,3-propylenediamine (tn), 2,2'-bipyridyl (bpy), 2-aminomethylpyridine (2-AMP), and 2-aminoethylpyridine (2-AEP) were obtained by the following general procedure. The  $NiL_3^{2+}$  species were prepared in the solid state from nickel nitrate or perchlorate with the corresponding diamine in ethanol solution. In the case of 2-AEP only the bis ligand complex could be prepared. Satisfactory nickel analyses were obtained to ensure purity.

Approximately  $2 \times 10^{-2}$  M solutions of these complexes were made up in aqueous solution, and their spectra recorded (Perkin-Elmer/ Hitachi PE 340 or Beckman DK2A spectrometer). Calculated amounts of solid hydrated nickel nitrate or perchlorate were then added to these solutions to generate solutions in which the ligand to metal ratio was 2:1 and 1:1. These solutions were left overnight to achieve equilibrium, and their spectra then recorded. Such a procedure will not provide a solution containing solely the  $NiL_2^{2+}$  or  $NiL^{2+}$  aquated species but rather a mixture depending upon the relative stability constants. However, calculation (using data from ref 6) shows that each of these solutions contains primarily the desired species (Table II).

#### **Results and Discussion**

A considerable body of calorimetric data exists for nickel(II). However, it is not obvious how this may be correlated with the corresponding spectroscopic data. We must therefore seek a general model for correlating thermodynamic and spectroscopic data, which could be used for any metal. The orbital angular overlap model<sup>7,8</sup> would appear to provide such a procedure, and we return therefore to the copper(II) relationship to develop this aspect.

Consider a general copper amine complex  $CuN_x^{E}$ - $(H_2O)_{4-x}^{E}(H_2O)_2^{A}$  where N represents the ligating nitrogen atoms in the molecular plane and E and A represent equatorial and axial sites, respectively. We make the reasonable assumption that  $\pi$  bonding is not important in these complexes, though this may not be true for strongly  $\pi$  accepting ligands such as biguanide. There is also the pragmatic reason that there generally exist insufficient data to calculate the extent of any  $\pi$  bonding in these systems.

In seeking a general treatment we also neglect any offdiagonal contribution to the energy of the d states. Such contributions will arise in some of the less symmetric complexes but are not expected to be very important.

The crystal field maximum used earlier<sup>3</sup> generally corresponds to the  $xz, yz \rightarrow x^2 - y^2$  transition. By use of an orbital angular overlap approach with the assumptions outlined above, the (xz, yz) pair of orbitals may be assumed to remain degenerate and to possess an energy of zero with respect to the

# Thermodynamic Parameters in Metal Complexes

spherically perturbed level. The acceptor  $x^2 - y^2$  orbital in the general complex described above can be shown to possess the energy

$$E(x^{2} - y^{2}) = 3\sigma_{0} + N[(3/4)\sigma_{N} - (3/4)\sigma_{0}]$$
  

$$N = 1 - 4$$
(4)

where  $\sigma_0$  and  $\sigma_N$  are the antibonding contributions to the energy of this level due to binding to water and an amine nitrogen atom, respectively, and N is the number of amine nitrogen atoms bound in the "molecular plane".

Since in these copper(II) complexes  $\sigma_N > \sigma_{O(H_2O)}$ , there is clearly a general shift to higher energy with increasing substitution of water by the amine. The existence of this relationship in aqueous solution implies that all these complexes may be considered to be derivatives of a distorted octahedron. Complexes which have a distorted nonoctahedral structure are not expected to obey this relationship.

The origin for the previous relationships (eq 2, 3) is occupied by the  $[Cu(H_2O)_6]^{2+}$  ion with  $\Delta H^o_{aq} = 0$ . In this case the energy of this transition is given by  $3\sigma_0$  (eq 4, N = 0), after it is recognized that eq 4 also represents the desired transition energy  $[xz,yz \rightarrow x^2 - y^2]$ . We may then rewrite the previous relationship (ref 3, eq 3) relative to the hexaaquo ion as origin, by subtracting  $3\sigma_0$ , namely

$$-\Delta H^{\circ}_{aq} = fN[(3/4)\sigma_{\rm N} - (3/4)\sigma_{\rm O}] + [\Delta \text{solv} + \Delta E] \qquad (5)$$

" $\Delta$ solv" is the difference in *outer-sphere* hydration energy of the complex vs. its constituents (M(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup>, L) and  $\Delta E$  is the difference in the spherical electrostatic terms between M(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> and the complex. These definitions differ from those used previously<sup>3</sup> (see below). It would seem appropriate therefore to calculate the function F

$$F = (3/4)N(\sigma_N - \sigma_0) \tag{6}$$

and plot this for a series of nickel(II) complexes. Certainly this function, being a difference between the two  $\sigma$  parameters, would seem to be pleasingly appropriate to show a correlation with the heat of formation.

Calculation of F can be achieved fairly readily with the *trans*-NiN<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub> systems when the transition  ${}^{3}B_{2g} \leftarrow {}^{3}B_{1g}$  is observed. The energy of this transition is related to the desired parameters through

$$E[{}^{3}B_{2g} \leftarrow {}^{3}B_{1g}] = 10Dq_{xy} = 3\sigma_{N} - 4\pi_{N}$$
$$= 3\sigma_{N}$$
(7)

where the  $\pi$  parameter for an amine is assumed to be zero. Figure 1 shows such a plot where, for the purposes of the calculation,  $\sigma_0$  is assumed to be 2.833 × 10<sup>3</sup> cm<sup>-1</sup> (10Dq-(Ni(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup>) = 8.500;<sup>10</sup>  $\sigma_0$  = 8.500/3;  $\pi_0$  assumed zero). An exceptionally good straight line is observed, passing close to the origin (intercept +1.207 kcal) (eq 8). This is exactly the

$$-\Delta H^{\circ}_{aq} = 3.589F + 1.207$$
  
$$-\Delta H^{\circ}_{aq} = 3.589(3\sigma_{N} - 3\sigma_{O}) + 1.207 \qquad (8)$$
  
$$N = 4$$

equivalent to the copper relationship which also passes close to the origin (intercept +0.73 kcal) if the energy of the copper hexaaquo transition energy ( $12.6 \times 10^3 \text{ cm}^{-1}$ ) is subtracted out. The slope of this nickel(II) line, 3.59, is rather less than that observed, 4.9, with copper. Statistical analysis reveals an excellent correlation between these two plotted functions with a correlation coefficient of 0.99. It is possible that complexes containing fewer than four nitrogen atoms might also lie on this line. However, it is much more difficult to obtain accurate values for  $\sigma_N$  in aqueous solution for such species. Such species generally display a spectrum not unlike that of a regular octahedral nickel(II) complex, perhaps with some sign of structure, usually ill-defined, on the first band



**Figure 1.** Plots of the function F(eq 6) vs.  $-\Delta H^{\circ}_{aq}$ , for  $(\Box) N = 4$  and (O) N = 6 systems. The solid line is a least-squares plot which, in the case of NiN<sub>6</sub>, omits certain complexes as designated in Table I.

 $(v_1^{3}T_{2g} \leftarrow {}^{3}A_{2g} \text{ in } O_h \text{ symmetry}).$ 

By using the energy of the first spin-allowed band,  $\nu_1$ , and by assuming the average environment rule,<sup>9</sup> we may derive a value for  $\sigma_N$ . Unfortunately this does not prove to be a very accurate procedure and points so calculated generally lie fairly close to, but not on, the line generated by the NiN<sub>4</sub> species. Future low-temperature studies of the electronic spectra of such lower substituted species in frozen glasses might provide more definitive data to test this relationship. However, in the absence of single-crystal spectra of aquated species, there will still remain problems of correct identification of levels.

Accurate values of  $\sigma_N$  can be calculated from the spectra of NiN<sub>6</sub> complexes; values of the function F (eq 6) are included in Figure 1. Clearly they are rather badly scattered. However, if one reasonably excludes the unsaturated ligands and the tripod ligand dpt, a good line is obtained, which passes close to the origin (eq 9). It is evident that further data are required

$$\Delta H^{\circ}_{aq} = 6.74F - 4.48$$
  
= 10.11(3 $\sigma_{N}$  - 3 $\sigma_{O}$ ) - 4.48 (9)

to convincingly establish the utility of this relationship for N = 6.

The copper relationship is good for N = 1-4 but not for N=5, 6. For copper one can readily understand this observation in that the transition being monitored,  $xz,yz \rightarrow x^2 - y^2$ , will not be very sensitive to the replacement of the fifth and sixth axial water molecules, lying on the z axis, by amine nitrogen atoms. Moreover it is known<sup>3</sup> that the copper relationship only works well when there is free access for water along a molecular axis.

A first-order analysis<sup>10</sup> of the electronic spectrum of a trans-NiN<sub>4</sub>Z<sub>2</sub> species shows that the second  ${}^{3}E_{g}{}^{b}$  transition (from  ${}^{3}T_{1g}(F)$ ) corresponds to the excitation  $xz_{.}yz \rightarrow x^{2} - y^{2}$ , i.e., the relevant transition discussed above. The second observed "octahedral" band,  $v_{2}$ , corresponds approximately to this transition, <sup>9,10</sup> though there cannot be a direct correlation because of mixing with the other  ${}^{3}E_{g}$  states. Nevertheless it has the advantage that it is directly observable without recourse to any calculations or approximations. Data for some presumed trans-Ni(amine)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub> complexes are shown in Figure 2 which depicts a plot of the energy of the second  ${}^{3}E_{g}{}^{b}$  transition ( $v_{2}$ ) against  $-\Delta H^{o}{}_{aq}$ . A very good straight-line relationship is observed with only a few systems being poorly behaved. Utilizing 14 complexes and omitting those which are badly behaved (see table), linear regression provides the relationship (eq 10) which is extraordinarily similar to the

$$-\Delta H^{\circ}_{ag} = 4.056({}^{3}\text{E}_{g}^{b}) - 55.45 \quad (N = 4) \tag{10}$$

				2 III X I-1-				÷				
							$-\Delta H$	$-\Delta H$	$-\Delta H$	$-\Delta H$		1
complex	N	P.I	V2	۴ <i>a</i>	$N\nu_1$	٩N	(psqo)	(calcd $N\nu_1$ )	(calcd $\nu_2$ )	(calcd F)	spectra	therm
Ni(H O) 2+	0	8.50	13.80	25.30	0						a	
Ni(olvcine)(H O) +		9.73	15.54	26.18	9.73		4.14	4.0			q	2
Ni(en)(H O) 2+	"	9.80	$15.80^{aa}$	26.80	19.6		9.05	7.5	6.5		c	-
Ni(tn)(H O) 2+		10.15	16.19		20.3		7.2	<i>T.T</i>	7.1		q	¥ .
Nithny/H O) 2+	10	10.905	17.36		21.81		9.6	8.25	9:0		q	1
Ni(CC Maan)(H O) 2+	<i>،</i> د		16.16	26.845			7.05		7.1		q	ш
NI(CC-MCII)(II <sub>2</sub> O) <sub>4</sub> Ni(FDTA)	، د	10.00	17.00	26.30	20.0		7.55	7.6	8.4		q	u
NI(EULA) NEO AMB/(ILO) 2+	۰ <i>د</i>	10.73	17 24		21.44		8.82	8.1	8.8		q	k
$NI(2-AMF)(H_2O)_4^{-1}$	4 (	10.05	15 07	76.34	201		6 92	7.6	9.6		q	k
NI(2-AEP)(H <sub>2</sub> O) <sub>4</sub> <sup>-</sup>	7	10.02	10.01	10.02	11 066		11.2	2	8		q	1
$Ni(o-phen)(H_2U)_4$	7 0	10.50	10.01		0.12		2:11	76	67		4	q
$Ni(a-dimen)(H_2O)_4^{2+}$	7	56.6 200	06.01	00,00	10.77		0.0	2.5	1.0		<i>h o</i>	2
Ni(glycine) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	7	9.80	10.13	20.02	19.12		11.05	5 T	2		с, с Ч	
$Ni(den)(H_2O)_{3}^{2+}$	ŝ	10.53	17.02	27.78	96.15		C0-11	11./			<i>د</i> م	5
Ni(dpt)(H, O), <sup>2+</sup>	ę	10.53	16.67		32.8		90.01	1.21			o -	4
Ni(2.3)(H, O), <sup>2+</sup>	ŝ	11.56	17.28	27.80	34.7		13.54	12.8			<i>a</i> .	
Ni(en) $(H O)^{2+}$	4	10.50	17.90	28.10	42		17.9	15.4	17.2		q	<b>~</b> '
$\operatorname{Ni}(\operatorname{fm}) / \operatorname{II} O $	•	10.58	17,28	28.57	42.32		14.6	15.5	14.6		b, c	¥
	• •	10.50	17 80	27 RU	42		15.15	15.4	16.75		q	S
Ni(ITER) $(H_2O)_2^-$	<del>,</del> t	00.01	16 2066	00.17	40 80ee		919		13.1		t	t
Ni(tpt)( $H_2$ (0) <sub>2</sub> <sup>-1</sup>	t •	10.20	10.01		0000	A 03	741			23.8	f	п
Ni(14-ane)( $H_2$ U) <sub>2</sub> <sup></sup>	4 •		0.01	τ οι		4.60	10.7		17.6	20.2	, <b>-</b> -	<i>u</i> .1
$Ni(2-3-2)(H_2O)_2^{4}$	4.		18.0	7.07	0.01	00.4		16.0	16.35	14.7		3
$Ni(2-2-2)(H_2O)_{2}^{2+}$	4	10.96	1/./1	CQ-17	40.0	+.0.+	1 - 1	0.01	12.2	13.05	, <b>4</b>	: >
$Ni(3-3-3)(H_2O)_{1}^{2+}$	4		16.95	27.05		5.5 5 1	10.1		18.4	12.8	- <b>,</b> 4-	< >
$Ni(3-2-3)(H_2O)_2^{2+}$	4		18.20			4.4/	19.2		10.1	10.0	-, -4	~ ~
$Ni(a-dimen)_{2}(H_{2}O)_{2}$	4	9.95	16.7		39.8		13.08	14.0	12.3		0 4	
Ni(o-phen), $(H, O)$ , $2^{4}$	4	11.1	18.44				20.05		CC-61		a •	
Ni(hpv), $(H,O)$ , $^{2+}$	4	11.10	18.52		44.4 <sup>ee</sup>		19.0		19.7		a	1
Ni(CC-Meen) (H O). <sup>2+</sup>	4	10.53	17.43	27.73	42.12		15.4	15.45	15.25		q	u ,
Ni(2-AMP) (H O) 2+	4	$10.96_{\circ}$	17.86		43.86		17.36	16.1	17.00		a ·	2
Ni(7-AFP)_(H_0)_2+	4	$10.52^{\circ}$	$17.06_{\circ}$	27.47	42.1		13.92	15.4	13.8		q	¥
Ni(histidine)	4	$10.70^{\circ}$	18.00	28.00	42.8		16.6	15.7	17.6		q	Ь
$Ni(tetren)(H_0)^2$	5	11.17	18.28		55.85		18.9	20.3			9	N ·
Ni(en) <sup>2+</sup>	9	11.6	18.35	29.00	69.6	3.87 <sup>dd</sup>	27.4	25.2		27.0	°0,	~'
$Ni(tn)^{2+}$	9	10.9	17.80	28.20	65.4	3.63	21.72	23.7		19.7	q	×
Ni(den) <sup>2+</sup>	9	11.5	18.7	29.1	69.0	3.83	25.3	25.0		25.7	q	0
Ni(dnt) <sup>2+</sup>		10.97	17.57	28.07	65.8 <sup>ee</sup>	3.66	17.64				$\overline{q}$	9
Ni(7 3) 2+	, v	11.46	18.52	29.03	68.8	3.8	27.27	24.9		24.8	q	~ •
Ni(hnv) 2+	9	12.76	19.53		76.56	4.25	28.2	27.7			ЪC	
Ni(o-nhen) <sup>2+</sup>	9	12.7	19.3		76.2	4.23	30.0	27.5			ьс,	1
Ni(CC-Meen) <sup>2+</sup>	e ve		17.9	28.37			18.4				q	ш
Nifimid) <sup>2+</sup>	, <b>'</b>	11.10	18.15	28.70	66.6 <sup>ee</sup>	3.70	18.4			21.8	ч	aa
Ni(7-AMP) 2+	o vo	11.56	18.37		69.4	3.85	25.89	25.1		26.3	q	ĸ

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bletti, P.; Vacca, A. J. Chem. Soc., Dalton Trans., 1973, iations: en = ethylenediamine; tn = 1,3-propylenediamine; pyridine; 2-AEP = 2-aminoethylpyridine; o-phen = 1,10- ylenediamine; tren = 2,2',2"-triaminotriethylamine; tpt = $f(CH_2)_pNH_2$ ; tetren = tetraethylenepentamine; penten = regetically, very similar to the aquo complex for which such	
5-20. <b>*</b> Barbucci, R.; Fabbrizzi, L.; Paoletti, P. J. <i>Chem. Soc., Dalton Trans.</i> , 1972, 745-9. <b>*</b> Barbucci, R.; Fabbrizzi, L.; Pacti, P.; Vacca, A. J. <i>Chem. Soc.</i> , 1964, 5051-7. <sup><i>ad</i></sup> Bauman, J. E., Jr.; Wang, J. C. <i>Inorg. Chem.</i> 1964, 3, 368-73. <sup><i>bb</i></sup> Abbrev idyl; <i>CC-Meen = C, C'</i> dimethylethylenediamine; EDTA = <i>N,N,N',N'</i> ethylenediaminetetraacetic acid; 2-AMP = 2-aminomethyl a-dimenter $= N_N$ dimethylethylenediamine; EDTA = <i>N,N,N',N'</i> ethylenediaminetetraacetic acid; 2-AMP = 2-aminomethyl a-dimenter $= N_N$ dimethylethylenediamine; data = <i>dipropylenetiametetraacetic acid</i> ; 2-MP = 2-aminomethyl a-dimenter $= N_N$ dimethylethylenediamine; data = <i>dipropylenetiamine</i> ; 2, 3 = <i>N</i> (aminoethyl)-1,3-proparine = <i>escondet (macrocycle); (p-q-p)</i> (where <i>p</i> and <i>q</i> are 2 or 3) are the linear tetradentets $N_1$ , $C(H_2)_pNH(CH_2)_qNP$ (and $M_2$ concurvations). <i>esc</i> Calculated as one-third of $10Dq_{xx}$ for the dimenter complex which is likely to be; and <i>d</i> of <i>Coloritot 4</i> or <i>conservice</i> . <i>esc</i> Calculated as one-third of $10Dq_{xy}$ for the dimenter complex which is likely to be; and <i>d</i> of <i>Coloritot 4</i> or <i>conservice</i> . <i>esc Coloritot 4</i> or <i>conservice</i> .	

atio	% NiL	% NiL <sub>2</sub>	% NiL <sub>3</sub>	% Ni
		Ethylenedian	nine	
1:1	62.3	18.8	0	18.9
1:2	6.1	88.1	5.8	0
1:3	0	10.0	90.0	0
		Bipyridyl,		
1:1	37.2	25.6	3.9	33.3
1:2	18.8	48.9	27.8	4.5
1:3	0	$0.2_{s}$	99.7 <sub>s</sub>	0

species

Table III. Iron(II) C	omplexes w	ith Polyamir	nes	
	–∆H° <sub>aq</sub> , kcal/mol	$\nu(d-d),^a$ cm <sup>-1</sup> × 10 <sup>3</sup>	$\frac{N\nu_{\mathbf{a}}, \mathbf{b}}{\mathrm{cm}^{-1} \times 10^3}$	fef
Fe(en),2+	15.85	11.42	68.52	J
$Fe(den)^{2+}$	12.95	9.43	62.79	q
		11.50		
Fe(tetren)-	8.7	8.77	45.85	e
(H, O) <sup>2+</sup>		9.57		
Fe(penten) <sup>2+</sup>	9.65	8.45	54.15	<b>ب</b> ر
, ,		9.60		

within the <i>D</i> term. number of nitrogen L. J. Chem. Soc.	, Sacconi, L. J. a, A. J. Chem. Soc.	ıpolini, M. J. Chem.
in-allowed transition g weighted by N, the Paoletti, P.; Sacconi,	olini, M.; Paoletti, P. e Paoletti, P.; Vacc	, L.; Paoletti, P.; Cian
<sup>a</sup> Components of the spi <sup>a</sup> Average D term splitting ttoms. <sup>c</sup> Ciampolini, M.;	1960, 4553–61. <sup>d</sup> Ciamp <i>Them.</i> Soc. 1961, 2994–9	1964, 5051-7. f Sacconi Soc. 1964, 5046-51.

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Figure 2. Plots of  $\nu_2$  against  $-\Delta H^{\circ}_{ag}$  for N = 2, N = 4 atoms. The solid lines are least-squares plots which omit the most badly behaved systems (see Table I). The triangle on the abscissa locates  $Ni(H_2O)_6^{2+}$ .

corresponding copper(II) relationship (eq 2). An excellent correlation coefficient of 0.898 is obtained. This plot intercepts the  $\Delta H = 0$  axis at 13.55  $\times 10^3$  cm<sup>-1</sup> satisfactorily close to the  ${}^{3}E_{g}^{b}$  level for Ni(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> at 13.80 × 10<sup>3</sup> cm<sup>-1</sup>. Evidently configuration interaction does not seriously vitiate this correlation. Extension to other values of N shows that, for N =2, the only other set for which there is a significant quantity of data (seven complexes), a similarly convincing relationship is seen (eq 11) for which there is a good correlation (0.914),

$$-\Delta H^{\circ}_{aq} = 1.581\nu_2 - 18.47 \quad (N = 2) \tag{11}$$

Figure 2. The intercept  $(11.68 \times 10^3 \text{ cm}^{-1})$  is close to Ni- $(H_2O)_6^{2+}$  but not as good for N = 4. Further data points may improve this agreement. The NiN<sub>6</sub> complexes are included, although the energy of the  $x^2 - y^2$  level is, to first order, unaffected by addition of a fifth and sixth ligand to the z axis. Probably for this reason a much more scattered correlation is observed, with little utility at this stage of development.

We are plotting an approximation to function (4), which contains N, the number of nitrogen atoms, and expect the slope of the N = 4 line to be double the slope of the N = 2 line; the actual ratio is 2.15, not unreasonable agreement. Clearly the increase in slope arises through the second-order mixing in of the higher excited  ${}^{3}T_{1g}(P)$  term which corresponds to a doubly excited transition whose first-order energy, therefore, is proportional to 2N.

The use of function (6) while apparently accurate when accurate data are available suffers from the disadvantage that for many complexes such accurate data are unlikely to become available. It is also unfortunate that in this case six nitrogen systems fall on a different line. The utilization of the  ${}^{3}E_{a}{}^{b}(\nu_{2})$ level while facile has the disadvantage that different equations are necessary depending upon N, and the correlation is also poor for N = 6. A third plot was therefore sought; such a plot should be readily constructed and should suffice for all nickel amine complexes.

It transpires that although a simple plot of 10Dq vs.  $-\Delta H^{\circ}_{aq}$ is of little value in this context, if the former values are weighted by the number of nitrogen atoms, then a useful plot is indeed obtained. Figure 3 shows a plot of  $-\Delta H^{\circ}_{aq}$  vs.  $N\nu_1$ .

The linear regression line is, neglecting very poorly behaved complexes

$$-\Delta H^{\circ}_{aq} = 0.367(N\nu_1) + 0.177$$
(12)



**Figure 3.** A plot of  $N\nu_1$  vs.  $-\Delta H^{o}_{aq}$ . The solid line is a least-squares plot of all the complexes except the most badly behaved systems (see Table I).

and the correlation coefficient is good (0.97) (29 complexes).

Most of the nickel amine complexes considered in this study including the six nitrogen systems fall on or close to this line, which also passes close to the origin which significantly would be the point for Ni(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> with N = 0.

From a pragmatic viewpoint therefore this relationship provides a quick, useful, and fairly accurate procedure for estimating  $-\Delta H^{o}_{ac}$  when the energy of  $\nu_{1}$  is known.

This procedure may be theoretically defended on the following basis. In using the first allowed d-d transition energy, we may assume we are plotting the average, unresolved, energy of the several transitions to the  $x^2 - y^2$  and  $z^2$  levels from the xz, yz, and xy orbitals. Again taking a very simple view, neglecting  $\pi$  bonding, it may be shown that the average transition energy to these levels, from the  $\pi$  bonding set written as zero, is

$$E_{\rm av} = 3\sigma_{\rm O} + (N/2)(\sigma_{\rm N} - \sigma_{\rm O}) \tag{13}$$

The electronic spectrum reflects the average increase in field strength when an amine replaces a water molecule, and it is evident from eq 13 that this energy is proportional to the difference in the binding of the amine and of water. Multiplication by an additional factor N is tacit recognition that the heat of formation of a hexaamine, for example, is approximately 6 times the heat of formation of a monoamine with small differences in this average heat per nitrogen bound being reflected in variations in average crystal field strength.

Some complexes may be identified as poorly behaved in all three correlations (Table I). These include dpt and tpt where steric constraints undoubtedly generate severe distortion and imidazole where  $\pi$  bonding may not be negligible. Other systems are poorly behaved in one correlation but well-behaved in another. Until a larger data base is available, it is not feasible to clearly identify the conditions which lead to a good behavior for a given correlation. Some amino acids are included because the heat of substitution of a water molecule by carboxyl is close to zero.<sup>6</sup> However, these systems are not generally well-behaved. Although care has been taken to include only those thermodynamic data which seem quite reliable, it is possible that some of the observed  $\Delta H$  values are erroneous. Most significantly, the well-behaved complexes include bipyridyl, o-phenanthroline, and the macrocycle (14-ane).

Assuming that prediction to within 10% of the observed



Figure 4. A plot of the average D term splitting, weighted for the number, N, of nitrogen ligands, against  $-\Delta H^{o}_{aq}$  for some iron(II) complexes (Table III).

value is considered acceptable and neglecting distorted molecules, we find that all predictions using function F (eq 6) fall within this limit for N = 4 and seven of nine complexes for N = 6 are acceptable. Using  $\nu_2$  as a guide, we find some 18 of 24 complexes fall within these limits, while for  $N\nu_1$  21 out of 33 complexes are well-behaved.

In that these various correlations pass through or close to the coordinate occupied by the nickel hexaaquo ion, we are led, through the relationship (5), to conclude that the intercept term ( $\Delta$ solv +  $\Delta E$ ) is close to zero or is itself a function of  $\nu$ (d-d). The latter seems most improbable.

If we consider that the electrostatic, spherical, term arising from an oxygen ligand is similar to that due to the dipole of a nitrogen ligand, we may conclude that the *difference* between the value of E for various  $MN_nO_{6-n}$  species and for  $M(H_2O)_6^{2+}$ is indeed small. The solvation term may be written

"
$$\Delta \text{solv"} = \Delta H_{\text{hydr}}(M(H_2O)_{6-n}L_n) + n\Delta H'(H_2O) - n\Delta H_{\text{hydr}}(L) - \Delta H_{\text{hydr}}(M(H_2O)_6^{2+})$$
(14)

Since these terms are all outer-sphere solvation terms, the value of " $\Delta$ solv" might also reasonably be small. In view of the variety of complexes which experimentally lie on a line whose intercept is close to zero, we conclude that the two terms  $\Delta E$  and " $\Delta$ solv" are indeed small and possibly are of opposite sign.

Although there must be marked variations in the strain energies in systems as diverse as en, tetradentates such as (2-2-2), and the macrocycle (14-ane), this does not seem to be reflected in bad behavior, at least not to any marked extent. Such strain must be, partially or wholly, compensated in that any reduction in  $-\Delta H_{aq}$  as a consequence of strain energy, must also result in a parallel reduction in the spectroscopic parameter. However, when further data are available it may be feasible to rationalize deviations from good behavior, especially by using function F, in terms of more subtle changes in outer-sphere solvation energy, strain energy, or other steric phenomena.

### **Extension to Other Metal Ions**

We are now convinced that this study may be extended to other metal ions. Initially we expect good behavior from first-row transition-metal ions, where  $\pi$  bonding is not an important consideration. Unfortunately outside nickel(II) and copper(II) there is not a great wealth of data to test these correlations. Table III contains some preliminary data for iron, where we note a possible correlation between  $-\Delta H^{o}_{aq}$  and the energy of the average splitting of the *D* term weighted by the number of nitrogen atoms. The reasonably good correlation, albeit with very few data points, is shown in Figure 4 and is described by

$$-\Delta H^{\circ}_{ag} = 0.318 N \nu_{a} - 6.59 \tag{15}$$

The correlation coefficient is 0.97. The slope is essentially the same as for the corresponding nickel(II) relationship (eq 12).

We hope that this study will stimulate others to add to the thermodynamic and spectroscopic data base to test these relationships. A more detailed study of these systems which do not fall on the lines should provide a direct thermodynamic measure of such quantities as strain energy and solvation energy. Once clearly defined, these spectroscopic/thermodynamic correlations can be used to obtain thermodynamic data in systems such as metalloproteins where the classical thermodynamic approaches are not appropriate.

Finally we note a similarity of this approach to the E and C parameter technique pioneered by Drago and co-workers.<sup>11,12</sup> The first term involving the spectroscopic parameter correlates with the  $C_A C_B$  covalent parameter product, while  $E_A E_C$ , which appears small in our case, contains both the electrostatic term and a solvation term, apparently of opposite sign. This approach has the advantage that data can be collected for metal ions both in aqueous media and, in future studies, in nonaqueous media.

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**Registry No.** Ni(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup>, 15365-79-4; Ni(glycine)(H<sub>2</sub>O)<sub>4</sub><sup>+</sup>, 14362-86-8; Ni(en)(H<sub>2</sub>O)<sub>4</sub><sup>2+</sup>, 15615-30-2; Ni(tn)(H<sub>2</sub>O)<sub>4</sub><sup>2+</sup>, 31082-54-9; Ni(bpy)(H<sub>2</sub>O)<sub>4</sub><sup>2+</sup>, 28660-84-6; Ni(CC-Meen)(H<sub>2</sub>O)<sub>4</sub><sup>2+</sup>, 69622-22-6; Ni(EDTA), 13077-29-7; Ni(2-AMP)(H<sub>2</sub>O)<sub>4</sub><sup>2+</sup> 69622-23-7; Ni(2-AEP)(H<sub>2</sub>O)<sub>4</sub><sup>2+</sup>, 69622-24-8; Ni(*o*-phen)(H<sub>2</sub>O)<sub>4</sub><sup>2+</sup>, 15662-60-9; Ni(*α*-dimen)(H<sub>2</sub>O)<sub>4</sub><sup>2+</sup>, 31355-69-8; Ni(glycine)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>, 14215-54-4; Ni(den)( $H_2O$ )<sub>3</sub><sup>2+</sup>, 15662-52-9; Ni(dpt)( $H_2O$ )<sub>3</sub><sup>+</sup>, 69622-25-9; Ni(2,3)( $H_2O$ )<sub>3</sub><sup>2+</sup>, 69631-51-2; Ni(en)<sub>2</sub>( $H_2O$ )<sub>2</sub><sup>2+</sup>, 15554-67-3; Ni(tn)<sub>2</sub>( $H_2O$ )<sub>2</sub><sup>2+</sup>, 46140-10-7; Ni(tren)( $H_2O$ )<sub>2</sub><sup>2+</sup>, 36470-72-1; Ni(tpt)( $H_2O$ )<sub>2</sub><sup>2+</sup>, 69622-26-0; Ni(14-ane)( $H_2O$ )<sub>2</sub><sup>2+</sup>, 64616-26-8; Ni(2-3-2)( $H_2O$ )<sub>2</sub><sup>2+</sup>, 23236-28-4; Ni(2-2-2)( $H_2O$ )<sub>2</sub><sup>2+</sup>, 15662-53-0; Ni(3-3-3)( $H_2O$ )<sub>2</sub><sup>2+</sup>, 69622-27-1; Ni(3-2-3)( $H_2O$ )<sub>2</sub><sup>2+</sup>, 54468-57-4; Ni(a-dimen)<sub>2</sub>( $H_2O$ )<sub>2</sub><sup>2+</sup>, 69631-50-1; Ni(a-nhen)<sub>2</sub>= 54468-57-4; Ni( $\alpha$ -dimen)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub><sup>2+</sup>, 69631-50-1; Ni( $\alpha$ -phen)<sub>2</sub>-(H<sub>2</sub>O)<sub>2</sub><sup>2+</sup>, 56235-16-6; Ni(bpy)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub><sup>2+</sup>, 28660-85-7; Ni(*CC*-Meen)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub><sup>2+</sup>, 6964-54-4; Ni(2-AMP)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub><sup>2+</sup>, 69622-28-2; Ni(2-AEP)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub><sup>2+</sup>, 69668-01-5; Ni(histidine)<sub>2</sub>, 15130-07-1; Ni- $(tetren)(H_2O)^{2^+}$ , 15662-54-1; Ni(en)<sub>3</sub><sup>2+</sup>, 15390-99-5; Ni(tn)<sub>3</sub><sup>2+</sup>, 18347-71-2; Ni(den)<sub>2</sub><sup>2+</sup>, 19358-75-9; Ni(dpt)<sub>2</sub><sup>2+</sup>, 46933-28-2; Ni-(2,3)<sub>2</sub><sup>2+</sup>, 69622-29-3; Ni(bpy)<sub>3</sub><sup>2+</sup>, 21595-29-9; Ni(*o*-phen)<sub>3</sub><sup>2+</sup>, 17085-38-0; Ni(CC-Meen)<sub>3</sub><sup>2+</sup>, 53494-39-6; Ni(imid)<sub>6</sub><sup>2+</sup>, 47664-46-0;  $Ni(2-AMP)_{3}^{2+}$ , 18347-74-5;  $Fe(en)_{3}^{2+}$ , 14972-42-0;  $Fe(den)_{2}^{2+}$ 69622-30-6; Fe(tetren)(H<sub>2</sub>O)<sup>2+</sup>, 69622-31-7; Fe(penten)<sup>2+</sup>, 69622-32-8.

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