Inorganica Chimica Acta, 14 (1975) 151–156

Thermodynamics of Equilibrium between Pentacoordinated Ni(Bidentate)(Tridentate) and Its Octahedral Monohydrate

S. GUPTA and A. CHAKRAVORTY
Department of Chemistry, Indian Institute of Technology, Kanpur-208016, U.P., India
Received October 26, 1974

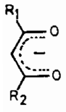
The syntheses, electronic spectra and magnetic susceptibility of several pseudooctahedral species of the type NiAB·H_2O are reported (A = bidentate ligand, B = tridentate ligand). The anhydrous species NiAB can also be isolated and on the basis of electronic spectra they have square pyramidal geometry. The equilibrium NiAB + $H_2O \rightleftharpoons$ NiAB·H_2O occurs in solution. The thermodynamics of this equilibrium has been studied using variable temperature spectral data. The $\Delta H°$ and $\Delta S°$ values lie close to –13 kcal mol^{-1} and –35 eu respectively for all the systems studied.

Introduction

Thermodynamic data for several equilibria of the type

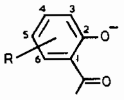
$$C + nD \rightleftharpoons E \qquad (1)$$

where C and E are electrically neutral chelates and D is a monodentate neutral donor are known. The most common reactions are those in which D is an amine. Good examples are those in which C is a β-diketone complex,[1] a Schiff base complex,[2–5] a dialkyldithiophosphato complex,[6,7] a halide complex[8] or a triazine-1-oxide complex.[9] Some of these works have been reviewed.[10] In practically all these cases C is tetracoordinated and E is either pentacoordinated (n = 1) or hexacoordinated (n = 2). In two cases[6,11] C and E are respectively pentacoordinated and hexacoordinated (both high-spin) and D = pyridine (n = 1). There are no cases reported where D = H_2O except in one instance[12] (work from this laboratory). In this paper we report the syntheses of new chelates which show stereochemical equilibria involving reversible dissociation of water. Thermodynamic characterization of such equilibria is achieved using variable temperature spectral data. In this study C is Ni(acac)(napNR_2), Ni(bzac)(napNR_2) or Ni(nap)(napNR_2); D = H_2O and n = 1.



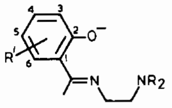
1

$R_1 = R_2 = CH_3$; acac
$R_1 = CH_3, R_2 = C_6H_5$; bzac



2

R = H ; sal
R = 5,6-benzo; nap



3

R' = H ; sal NR_2
R' = 5,6-benzo; napNR_2

Results and Discussion

Syntheses and Characterization

The complexes containing β-diketones are obtained as green crystalline substances by procedures analogous[12] to those used for the synthesis of Ni(acac)(salNR_2)·H_2O. The monohydrates can be dehydrated to brown anhydrous glasses by heating to 80–100° C at 5 mm.

Reaction of hydrated or anhydrous $Ni(nap)_2$ and $Ni(napNR_2)_2$ in boiling toluene in the molar ratio 1:1 leads to a brown solution. By allowing such solutions to crystallize in open air, green crystals of Ni(nap)(napNEt_2)·2H_2O or Ni(nap)(napNMe_2)·H_2O are obtained. The former looses one molecule of water at 5 mm (25° C) giving Ni(nap)(napNEt_2)·H_2O. The same species can also be made by reacting $Ni(nap)_2$ with N,N-dialkylethylenediamine in 1:1 molar ratio in boiling toluene. The monohydrates can be dehydrated to amorphous brown compounds by heating in vacuum.

Characterization data for all chelates are shown in Table I. The infrared spectra of the complexes (monohydrates) show the O–H stretching frequency in the region 3450–3510 cm^{-1}. The complexes also show other expected features.[12,13] Molecular weights of a few complexes were determined cryoscopically in pure benzene in the presence of sodium sulphate which keeps the concentration of water in benzene more or less invariant.[14] Consequently the observed molecular weight did not depend on whether the hydrated or the anhydrous compound was used for measurements. Results are shown in Table II. These results together with spectroscopic observations described later unequivocally establish that all chelates under discussion are monomeric in nature. The behaviour of Ni(nap)(napNR_2) is in striking contrast to that of Ni(sal)(salNR_2) which is anhydrous and dimeric.[13] While both

TABLE I. Characterization Data.

Compound	Mp, °C[a]	%C		%H		%N		%Ni		%H_2O[b]	
		Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
Ni(acac)(napNEt$_2$)·H_2O	96	61.87	61.66	6.09	6.17	6.56	6.57	13.16	13.15	4.03	4.05
Ni(bzac)(napNEt$_2$)·H_2O	120–121	63.94	64.29	6.32	6.11	5.52	5.49	11.58	11.51	3.55	3.56
Ni(bzac)(salNEt$_2$)·H_2O	114	60.43	59.99	6.56	6.15	6.13	6.18	12.85	12.78	3.94	3.97
Ni(bzac)(napNMe$_2$)·H_2O	190–192	62.66	63.06	5.85	6.08	5.85	5.94	12.26	12.23	3.76	3.75
Ni(bzac)(salNMe$_2$)·H_2O	187–189	58.74	58.38	6.06	6.12	6.52	6.44	13.69	13.46	4.19	4.15
Ni(nap)(napNEt$_2$)·H_2O	145–146	64.99	64.81	5.80	5.50	5.41	5.10	11.35	11.32	3.48	3.52
Ni(nap)(napNMe$_2$)·H_2O	189–191	63.80	63.52	5.72	5.61	5.72	6.03	12.01	12.13	3.68	3.71

[a] All melting points are uncorrected. [b] Estimated from the loss of water when chelates are heated in vacuum (80–110° C, 5 mm).

TABLE II. Molecular Weights in Benzene.

Compound	Molecular Weight	
	Found	Calculated
Ni(acac)(napNEt$_2$)	420 ± 10	427
Ni(bzac)(napNEt$_2$)	485 ± 10	489
Ni(nap)(napNEt$_2$)	495 ± 10	499

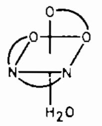
TABLE III. Magnetic Moments of Monohydrates.

Compound	Phase	Temperature °C	μ_{eff}(BM)
Ni(acac)(napNEt$_2$)·H_2O	Solid	27	3.17
	Benzene	18	3.13
	Benzene	48	3.09
	Benzene	69	3.06
Ni(bzac)(napNEt$_2$)·H_2O	Solid	27	3.16
	Benzene	19	3.12
	Benzene	56	3.07
Ni(bzac)(salNEt$_2$)·H_2O	Solid	28	3.10
Ni(bzac)(napNMe$_2$)·H_2O	Solid	27	3.12
Ni(bzac)(salNMe$_2$)·H_2O	Solid	26	3.04
Ni(nap)(napNMe$_2$)·H_2O	Solid	23	3.16
Ni(nap)(napNEt$_2$)·H_2O	Solid	22	3.11
	Benzene	18	2.96
	Benzene	47	2.95

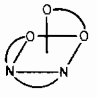
steric and electronic factors may be responsible, it is not clear to us how exactly this difference arises.

Structure in the Solid State

The monohydrates are uniformly high-spin in the solid state (Table III) and are pseudoctahedral (*4*) on the basis of electronic spectra (Table IV). As in the case[12] of Ni(acac)(salNR$_2$) the anhydrous β-diketone complexes are pentacoordinated (*5*) (film spectra in Table V). Good films of Ni(nap)(napNR$_2$) could not be obtained.



4



5

Thermodynamics of Solution Equilibrium

In solution the spectral behaviour of all the complexes containing β-diketonate anion is very similar to that described[12] for Ni(acac)(salNR$_2$)·H_2O. One typical case is illustrated in Figure 1. Ni(nap)(nap NR$_2$)·H_2O behaves similarly (Figure 2). Clearly the equilibrium,

$$5 + H_2O \rightleftharpoons 4 \qquad (2)$$

is present in solution. The solution magnetic moments remain close to 3 BM over the entire range of measurement (Table III) showing that only high-spin species are present in solution.

The thermodynamics of equilibrium (2) was determined from variable temperature spectral data. The concentration of *5* was calculated from the intensity of the band at ~7000 cm^{-1}. The enthalpy and the entropy parameters $\Delta H°$ and $\Delta S°$ were obtained from linear plots of logK *versus* 1/T where K is the equilibrium constant and T is the absolute temperature. The experimental $\Delta H°$ and $\Delta S°$ values are set out in Table VI. Both $\Delta H°$ and $\Delta S°$ are negative since in going from *5* to *4* a new Ni–OH_2 bond is formed and several degrees of freedom of the H_2O molecule is lost. In Table VI are also shown the thermodynamic parameters for the Ni(acac)(salNEt$_2$)–H_2O system[12] and two other systems in which pentacoordinated-hexacoordinated equilibria arise from reversible association of pyridine (py).

Experimental Section

Preparation of Compounds

Bis(acetylacetonato)nickel(II) dihydrate and its anhydrous analogue were prepared by published proce-

TABLE IV. Electronic Spectra of Monohydrates in Nujol Mull.

Compound	Assignments[a] of Band Positions (cm^{-1})		
	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	$\rightarrow {}^1E(D)$	$\rightarrow {}^3T_{1g}(F)$
Ni(acac)(napNEt$_2$)·H$_2$O	10,870[b]	13,500	17,200
Ni(bzac)(napNEt$_2$)·H$_2$O	10,400[b]	13,510	16,950
Ni(bzac)(salNEt$_2$)·H$_2$O	11,350[b]	13,150	16,950
Ni(bzac)(napNMe$_2$)·H$_2$O	11,100[b]	13,000	17,400
Ni(bzac)(salNMe$_2$)·H$_2$O	11,100[b]	13,160	16,950
Ni(nap)(napNEt$_2$)·H$_2$O	10,750[b]	13,160	16,900
Ni(nap)(napNMe$_2$)·H$_2$O	11,000[b]	13,160	17,250

[a] The assignments are based on pseudooctahedral geometry. [b] A shoulder often appears on the higher energy side of this band.

TABLE V. Electronic Spectra of Anhydrous Compounds in Thin Films.

Compound	Assignments[a] of Band Positions (cm^{-1})				
	$^3B_1(F) \rightarrow {}^3E(F)$	$\rightarrow {}^3A_2(F)$	sft[b]	$\rightarrow {}^3B_2(F)$	$\rightarrow {}^3E(F)$
Ni(acac)(napNEt$_2$)	7,200	10,400	11,400	13,050	16,550
Ni(bzac)(napNEt$_2$)	7,300	10,400	11,500	13,100	16,550
Ni(bzac)(salNEt$_2$)	7,300	10,400	11,450	13,100	16,550

[a] Assignments are based on idealised square pyramidal geometry (ref. 12). [b] Spin forbidden transition which appears as a shoulder.

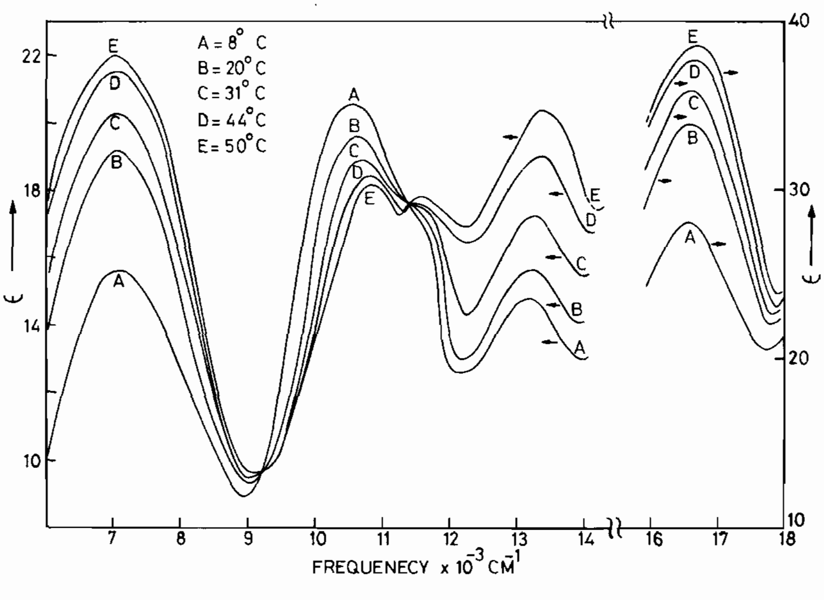


Figure 1. Variable temperature electronic spectra of Ni(acac)(napNEt$_2$)·H$_2$O in dry benzene.

dures.[15] A similar procedure was adopted for the preparation of bis(benzoylacetonato)nickel(II). Ni(nap)$_2$ and Ni(napNR$_2$)$_2$ were prepared as described in literature.[16] Ni(β-diketonato)(salNR$_2$)·H$_2$O and Ni(β-diketonato)(napNR$_2$)·H$_2$O were prepared by the procedure similar to those described[12] for Ni(acac)(salNR$_2$)·H$_2$O.

Ni(nap)(napNR$_2$)·H$_2$O can be obtained by two routes: (i) To a green solution of Ni(napNR$_2$)$_2$ (0.01 mol) in 60 ml toluene, 0.01 mol of hydrated or an-

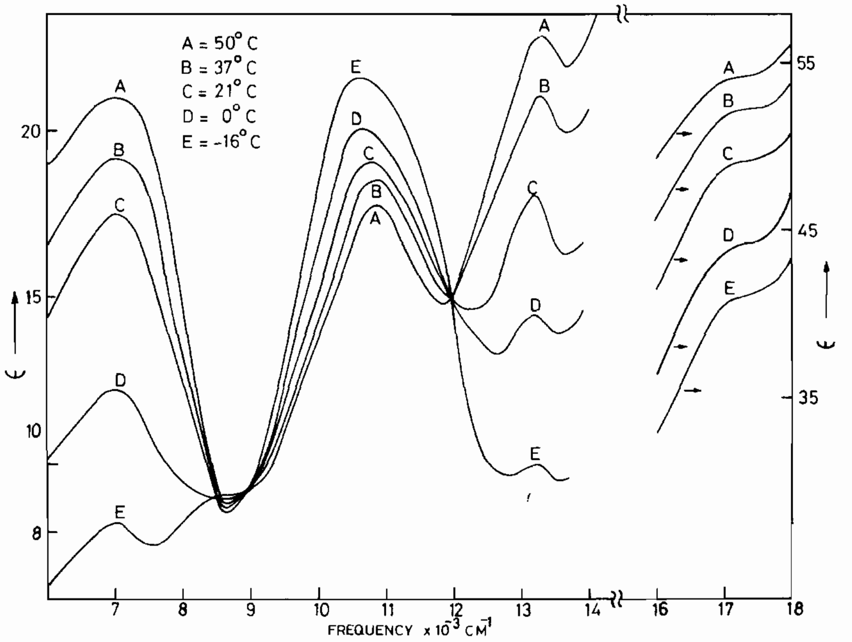


Figure 2. Variable temperature electronic spectra of Ni(nap)(napNEt$_2$)·H$_2$O in dry toluene.

TABLE VI. Enthalpy ($\Delta H°$) and Entropy ($\Delta S°$) Parameters for Equilibrium (2).

System	$-\Delta H°$ (kcal mol^{-1})	$-\Delta S°$ (eu)	Reference
Ni(acac)(salNEt$_2$)–H$_2$O	13 ± 1	36 ± 5	12
Ni(acac)(napNEt$_2$)–H$_2$O	13 ± 1	40 ± 5	This work
Ni(bzac)(napNEt$_2$)–H$_2$O	14 ± 1	38 ± 5	This work
Ni(nap)(napNEt$_2$)–H$_2$O	12 ± 1	33 ± 5	This work
Ni(L$_2$)(py)–py[a]	12	30	6
NiL′–py[b]	6–9	12–18	11

[a] L = Dialkyldithiophosphate anion. [b] L′ = Pentadentate ligand derived from condensation of sal and H$_2$N(CH$_2$)$_3$N(R)(CH$_2$)$_3$NH$_2$ (R = H or CH$_3$).

hydrous Ni(nap)$_2$ was added. The mixture was heated to reflux for 2 hr. The brown solution thus obtained was filtered, concentrated to 20 ml and then cooled in open air. Brownish green crystals of Ni(nap)(napNMe$_2$)·H$_2$O appeared after 3–4 hr, whereas green crystals of Ni(nap)(napNEt$_2$)·2H$_2$O appeared after 30–36 hr. The crystals were collected by filtration and were recrystallized from toluene. The yield was 60–70%. The crystals of Ni(nap)(napNEt$_2$)·2H$_2$O and Ni(nap)(napNMe$_2$)·H$_2$O were dried in vacuum (25° C, 5 mm). Under this condition the former looses a molecule of water to give Ni(nap)(napNEt$_2$)·H$_2$O.

(ii) To a suspension of hydrated or anhydrous Ni(nap)$_2$ (0.01 mol) in 100 ml toluene, N,N-dialkylethylenediamine (0.01 mol) was added. The mixture was heated to reflux for 2 hr. The solution was treated further as described above to obtain the monohydrates.

Physical Measurements

Magnetic moments were studied using a sensitive Gouy balance described elsewhere.[4] Infrared spectra were recorded on a Perkin–Elmer 521 recording spectrophotometer. Molecular weights were determined cryoscopically in purified dry benzene containing suspended sodium sulphate.[14] Electronic spectra were studied on a Cary Model 14 recording spectrophotometer. The solid monohydrated compounds were examined in nujol mulls. The films of anhydrous compounds were prepared by squeezing approximately 0.1 g of monohydrate complex between hot quartz plates. Variable temperature solution measurements were made by circulating thermostated (±0.1° C) water or 95% ethanol through an appropriate cell holder.

Calculation of Thermodynamic Parameters

The values of $\Delta H°$ and $\Delta S°$ were computed from the least squares plots (these plots have excellent linearity) of logK *vs.* 1/T using the relation (T is absolute temperature),

$$\Delta H°/T - \Delta S° = -R\ln K \qquad (3)$$

where

$$K = \frac{1-\varepsilon/\varepsilon_o}{(a\varepsilon/\varepsilon_o)(\varepsilon/\varepsilon_o + w/a)} \qquad (4)$$

TABLE VII. Thermodynamic Data[a] on the Equilibrium (2).

	Temperature (°C)	a × 10^2	w × 10^2	ε	K	logK
Ni(acac)(napNEt$_2$)–H_2O system in benzene						
	8	1.525	–	15.6	38.2	1.58
	21	1.512	–	18.5	13.4	1.13
	31	1.503	–	19.6	3.3	0.52
	40	1.446	3.98	20.4	1.9	0.27
	59	1.428	3.89	21.2	1.1	0.03
Ni(bzac)(napNEt$_2$)–H_2O system in benzene						
	8	1.552	–	13.1	69.8	1.84
	20	1.540	–	18.5	25.6	1.41
	33	1.518	–	22.5	8.0	0.90
	31	1.212	3.98	16.2	10.5	1.02
	40	1.190	3.94	20.0	4.2	0.62
	59	1.161	3.86	21.8	2.1	0.32
Ni(nap)(napNEt$_2$)–H_2O system in toluene						
	−15.5	2.114	–	8.0	200.5	2.30
	−1.0	2.102	–	12.1	62.5	1.80
	21.0	1.989	–	17.5	12.1	1.08
	37.0	1.978	–	19.2	5.1	0.71

[a] Symbols in this table have the same meaning as in equation (4) of text.

In equation (4) a is the concentration of hydrated species, w is the concentration of water added externally, and ε and ε_0 are observed and limiting intensities of the ~7000 cm^{-1} band. The derivation of equation (4) is described elsewhere.[12]* The limiting values of ε_0 for Ni(acac)(napNEt$_2$)–H_2O, Ni(bzac)(napNEt$_2$)–H_2O and Ni(nap)(napNEt$_2$)–H_2O systems were taken as 22.4, 24.1 and 21.0 l mol^{-1} cm^{-1} respectively. The extinction coefficients in the respective cases did not increase beyond these values as temperature was raised. Equilibrium data are collected in Table VII.

---

* Equation (4) is the same as equation (5) of reference 12. In the latter an extra *a* has appeared in the denominater. This is a misprint.

References

1 W.R. May and M.M. Jones, *J. Inorg. Nucl. Chem.*, *25*, 507 (1963).
2 H.C. Clark and A.L. Odell, *J. Chem. Soc.*, 3431 (1955).
3 L. Sacconi, G. Lombardo and P. Paoletti, *J. Chem. Soc.*, 848 (1958); L. Sacconi, G. Lambardo and R. Ciofalo, *J. Am. Chem. Soc.*, *82*, 4182 (1960); L. Sacconi, G. Lombardo and P. Paoletti, *J. Am. Chem. Soc.*, *82*, 4185 (1960).
4 T.S. Kannan and A. Chakravorty, *Inorg. Chem.*, *9*, 1153 (1970).
5 B.O. West, "New pathways in Inorganic Chemistry", Ed. E.A.V. Ebsworth, A.G. Maddock and A.G. Sharpe, Cambridge University Press, Cambridge, 1968, p. 308.
6 R.L. Carlin, J.S. Dubnoff and W.T. Huntress, *Proc. Chem. Soc.*, 228 (1964); R.L. Carlin and D.B. Losee, *Inorg. Chem.*, *9*, 2087 (1970).
7 A. Sgamellotti, C. Furlani and F. Margini, *J. Inorg. Nucl. Chem.*, *30*, 2655 (1968).
8 S.M. Nelson and T.M. Shepherd, *J. Chem. Soc.*, 3284 (1965); H.C.A. King, E. Körös and S.M. Nelson, *J. Chem. Soc.*, 5449 (1963); 4832 (1964).
9 P.S. Zacharias and A. Chakravorty, *Inorg. Chim. Acta*, *6*, 623 (1972).
10 G. Beech, *Quart. Rev.*, *23*, 410 (1969).
11 L. Sacconi and I. Bertini, *J. Am. Chem. Soc.*, *88*, 5180 (1966).
12 R.H. Balundgi and A. Chakravorty, *Inorg. Chim. Acta*, *8*, 261 (1974).
13 R.H. Balundgi, T.S. Kannan and A. Chakravorty, *Inorg. Chim. Acta*, *7*, 251 (1973).
14 H.N. Roberts and C.R. Bury, *J. Chem. Soc.*, *123*, 2037 (1923).
15 R.G. Charles and M.A. Powlikowski, *J. Phys. Chem.*, *62*, 440 (1958).
16 L. Sacconi, P. Nanneli, N. Nardi and U. Campigli, *Inorg. Chem.*, *4*, 943 (1965).