Interaction of N-acylthiourea Nickel(II) Chelates with Nitrogen Bases in Solution and in the Solid State

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Received March 13, 1984

In this work we report the study of adduct formation in solution and in the solid state between bis-N,N-diethyl-N'-benzoylthiourea)Ni(II) and bis(piperidil-N'-benzyolthiourea)Ni(II) and some nitrogen bases. Thermodynamic data and equilibrium constants were determined by calorimetric and spectrophotometric methods. The log β_1 *and* log β_2 *values are between 0.24 and 1.78 while the* $-\Delta H_1$ *and* $-\Delta H_2$ *values are between 14.4 and 77.8 kJ mol*$^{-1}$*. These results suggest that the adducts have low stability, i.e. the nickel chelates interact with the ligands only with difficulty. In the solid state the adducts show a small thermal stability, with the ligands being lost below 100 °C. The infrared spectra were recorded between 4000 and 180 cm*$^{-1}$*. The stretching frequencies were assigned for the adducts between 430 and 490 cm*$^{-1}$ *for* ν_{NiO}*, 320 and 410 cm*$^{-1}$ *for* ν_{NiS} *and 215–230 cm*$^{-1}$ *for* ν_{NiN} *bands.*

Introduction

Acylthiourea, $R_1R_2N{-}CS{-}NH{-}CO{-}R$, has given rise to many investigations because of the ability of this molecule to coordinate with several metals primarily related with the preparation and characterization of the metallic complexes [1–3] and more recently, with the structure and property of these complexes [4–6].

Complexes of nickel(II) with these ligands are normally planar and diamagnetic [1, 2]. The behavior is similar to that observed for complexes of Ni(II) with thio-β-diketones, where the substitution of one or two ogygens by sulphur in the β-diketonate complex stabilizes the planar form [7, 8].

The nickel(II) acylthiourea chelates can act as Lewis acids [1]. The adducts formed are apparently not stable, resembling once more those of the nickel(II) thio-β-diketonates [9].

In this work we report the study of adduct formation in solution and in the solid state between bis(N,N-diethyl-N'-benzoylthiourea)Ni(II) and bis(piperidil-N'-benzoylthiourea)Ni(II) with some bases, *i.e.* pyridine, β- and γ-picoline, piperidine and pyrazole. Stability constants and heats of reaction were determined in solution and compared with data existing for adducts of Ni(II) monothio-β-diketonates [9]. We also report the infrared spectra study between 4000–180 cm^{-1} in the solid state.

Experimental

N,N-diethyl-N'-benzoylthiourea (Hdebt) and piperidyl-N'-benzoylthiourea (Hppbt) were prepared by adding dropwise amine (diethylamine or piperidine in dry ether) on benzoylisothiocyanate. The addition was performed with stirring of the reaction mixture while cooling in an ice bath [10]. The solids obtained were recrystallized in ethanol. The purity was checked by infrared spectra and by C, H and N analysis. $Ni(debt)_2$ and $Ni(ppbt)_2$ were prepared according to published methods [1].

The adducts were prepared by dissolving the chelate in chloroform and adding to the resulting solution a large excess of the ligand. The solution was cooled in an ice bath and the adducts were precipitated by adding methanol. The green crystals were collected by filtration at low temperature, washed with cold methanol and dried in a vacuum desiccator for a few hours. The adduct $Ni(debt)_2(\gamma\text{-pic})_2$ was prepared by the use of n-hexane in the place of chloroform. Adducts with pyrazole could not be isolated for both chelates and a piperidine adduct was isolated only with $Ni(ppbt)_2$. The results of C, H and N analyses indicated the composition: $Ni(debt)_2L_2$, $Ni(ppbt)_2L_2$ (L = py, β- and γ-pic) and $Ni(ppbt)_2 \cdot L$ (L = piperidine).

The method used to determine the stability constants was spectrophotometric and the solvent used was 1,2-dichloroethane. The concentration of the chelate was in every case 3.00×10^{-3} *M* and the region between 510–550 nm was selected for the photometric measurements. The concentration of the free chelate is directly determined in this region and the free concentration of the ligand, [B], is deter-

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0020-1693/84/$3.00

mined by successive approximations starting with the initial assumption that CL$\simeq$[B] (CL = total concentration of the ligand). The stability constants are then determined by the Leden–Fronaeus method [11] by plotting a set of data (X – 1) *vs.* [B] where $X = 1 + \Sigma_{j=1}^{N}\beta_j[B]^j$, where β_j is the stability constant of the MA_2B_j species, and N is the number of bases which can coordinate to the chelate.

The heats of reaction were determined by breaking a small ampoule containing the chelate in the calorimetric vessel filled with the ligand dissolved in 1,2-dichloroethane. As the concentration of the chelates and of the ligands were those used to determine the stability constants, the enthalpy of the reactions was calculated by solving a set of equations $Qobs_{(i)} = \Sigma_{j=1}^{N} n_{ij}\Delta H_j$ where $Qobs_{(i)}$ is the observed heat corrected for the dilution of the chelate; $n_{ij} = V\alpha_j CM$ where V = volume of the solution, α_j is the degree of formation of the MA_2B_j species and CM is the total concentration of the chelate. The photometric measurements were made at 25 ± 1 °C, with Zeiss PMQ II and DMR-21 spectrophotometers.

The calorimetric measurements were made in a precision calorimeter LKB-8700-2 and the reaction vessel was thermostatted at 25.00 ± 0.05 °C.

The infrared spectra were obtained between 4000–180 cm^{-1}, from fluorocarbon and paraffin oil mulls of the compounds between CsI and polyethylene windows (see results in Tables II and III). The equipment used was a Perkin-Elmer 180 spectrophotometer.

Thermogravimetric analyses were made in a thermobalance Perkin-Elmer TGS-1 equipped with a microbalance Cahn-RG.

Results and Discussion

Complexes in Solution

In a solution of 1,2-dichloroethane, the chelates $Ni(debt)_2$ and $Ni(ppbt)_2$, show respectively a transition at 508 nm (ϵ = 187 l mol^{-1} cm^{-1}) and at 510 nm (ϵ = 198 l mol^{-1} cm^{-1}). These absorption bands are identified as the d–d transition involving the $d_{x^2-y^2}$ and d_{xy} orbitals of the metal in a planar field [12, 13].

In the presence of base the solution, originally reddish-brown in both cases, became green and the absorption bands shifted to a region between 610–660 nm (ϵ = 13–23 l mol^{-1} cm^{-1}). In Fig. 1 we show how the electronic spectrum of $Ni(debt)_2$ changes in the presence of pyridine. Only a higher concentrations of the base, *i.e.* the ratio [py] : [chelate] as high as 2093, is the chelate all in the adduct form.

In Table I we present the stability constants and calorimetric data for the reactions:

$$MA_2\ solv. + B\ solv. \rightleftharpoons MA_2B\ solv. \qquad K_1, \Delta H_1$$

$$MA_2B\ solv. + B\ solv. \rightleftharpoons MA_2B_2\ solv. \qquad K_2, \Delta H_2$$

where

$$\beta_1 = K_1 = \frac{[MA_2B]}{[MA_2][B]} \quad \text{and}\ \beta_2 = K_1K_2 = \frac{[MA_2B_2]}{[MA_2][B]^2}$$

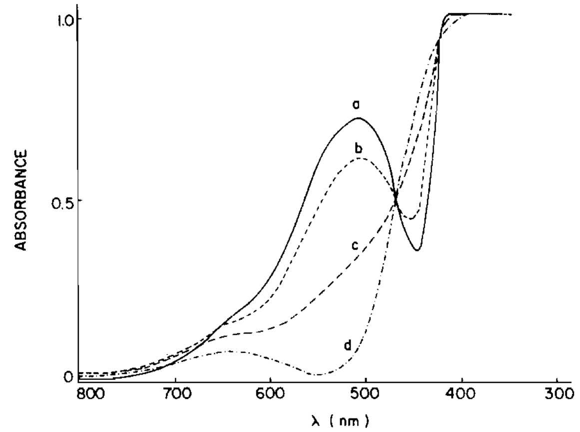

Fig. 1. Influence of pyridine concentration on absorption spectra of $Ni(debt)_2$ in 1,2-dichloroethane. Nickel(II) chelate 3.00 × 10^{-3} *M*; pyridine (a) 0, (b) 0.08 *M*, (c) 0.28 *M*, (d) 6.28 *M*.

TABLE I. Equilibrium Constants and Thermodynamic Data[a] for Adducts of Nickel(II) Chelates at 25 °C in 1,2-Dichloroethane.

Compounds	$\log\beta_1$	$\log\beta_2$	$-\Delta H_1$	$-\Delta H_2$	$-\Delta S_t$[b]	$-\Delta G_t$[b]
$Ni(debt)_2(py)_2$	0.36	1.03	50.0 ± 5.0	70.9 ± 7.0	386 ± 39	5.89 ± 0.6
$Ni(debt)_2(\beta\text{-pic})_2$	0.24	0.93	54.5 ± 5.0	68.6 ± 7.0	395 ± 39	5.31 ± 0.5
$Ni(debt)_2(\gamma\text{-pic})_2$	0.62	1.34	22.1 ± 2.0	77.8 ± 8.0	309 ± 30	7.62 ± 0.7
$Ni(debt)_2(pip)$	1.13	–	24.3 ± 2.0	–	60 ± 6	6.45 ± 0.6
$Ni(debt)_2(pyrazole)_2$	0.82	0.98	14.4 ± 1.0	72.9 ± 7.0	274 ± 27	5.58 ± 0.6
$Ni(ppbt)_2(py)_2$	0.34	1.37	22.9 ± 2.0	64.0 ± 6.0	265 ± 26	7.82 ± 0.8
$Ni(ppbt)_2(\beta\text{-pic})_2$	0.36	1.39	47.3 ± 5.0	41.7 ± 4.0	272 ± 27	7.92 ± 0.8
$Ni(ppbt)_2(\gamma\text{-pic})_2$	0.80	1.32	44.0 ± 4.0	51.4 ± 5.0	295 ± 30	7.56 ± 0.8
$Ni(ppbt)_2(pip)$	1.17	–	22.9 ± 2.0	–	82 ± 8	6.69 ± 0.7
$Ni(ppbt)_2(pyrazole)_2$	1.09	1.78	60.5 ± 6.0	34.1 ± 3.0	280 ± 28	10.6 ± 1.1

[a] Units: β_1, l mol^{-1}; β_2, l^2 mol^{-2}; ΔH and ΔG, kJ mol^{-1}; ΔS, K^{-1} J mol^{-1}.
[b] ΔS_t and ΔG_t are the total entropy and free energy.

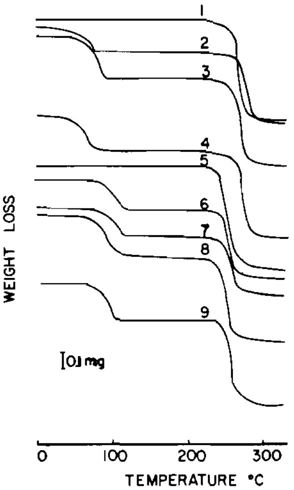

Fig. 2. TGA curves of: 1) $Ni(debt)_2$, 2) $Ni(debt)_2(py)_2$, 3) $Ni(debt)_2(\beta\text{-pic})_2$, 4) $Ni(debt)_2(\gamma\text{-pic})_2$, 5) $Ni(ppbt)_2$, 6) $Ni(ppbt)_2(py)_2$, 7) $Ni(ppbt)_2(\beta\text{-pic})_2$, 8) $Ni(ppbt)_2(\gamma\text{-pic})_2$, 9) $Ni(ppbt)_2pip$.

The reluctance of the $Ni(debt)_2$ and $Ni(ppbt)_2$ to undergo axial interaction is comparable with that presented by nickel(II) chelates of thio-β-diketones [9].

The stability of the complexes was due to the ΔH which counteracts the negative value of ΔS. The value of ΔG remains relatively constant in all cases.

Only one equilibrium constant was detected for the piperidine adduct. Steric requirement for axial approximation of the ligand to the metal appears to be the main factor when considering the N-sp^3 donor atom compared with N-sp^2 donor atom of the pyridinic ligands.

Adducts in the Solid State

As was described in the Experimental section, some adducts observed in solution could not be isolated in the solid state. Those which are isolatable in the solid state show a small thermal stability (see Fig. 2). In every case, the ligands are lost below 100 °C.

The uncomplexed chelate shows a planar structure, with the C_{2v} symmetry of the NiO_2S_2 skeleton [3]. The introduction of two more ligands in axial positions may not change the symmetry of the skeleton ($NiO_2S_2N_2$) of the adduct. Exception is made for $Ni(ppbt)_2 \cdot pip$ whose NiO_2S_2N skeleton may present a C_s symmetry.

For the free ligands, the carbonyl stretching bands ν_{CO} are assigned at 1681 cm^{-1} for Hdebt and at 1648 cm^{-1} for Hppbt (Tables II, III). For the corresponding chelates, the assignment of ν_{CO} bands becomes more complex because the vibrational modes are presumably coupled to a considerable extent [14] due to the extensive π bond delocalization. Despite the inherent complexity of the system the bands observed at *ca.* 1490 cm^{-1} for $Ni(debt)_2$ and adducts, and at *ca.* 1475 cm^{-1} for $Ni(ppbt)_2$ and adducts, were tentatively assigned as being due to ν_{CO} bands. These assignments are supported by comparison with those made for a series of chelates of monothio-β-diketones [15].

The ν_{CS} band may occur below 800 cm^{-1} [6, 16] but the presence of phenyl ring bands in the region makes the assignment very difficult.

Metal–ligand stretching vibration bands should

TABLE II. Infrared Frequencies (cm^{-1}) of the Hdebt, $Ni(debt)_2$ and the Corresponding Adducts.[a]

Hdebt[b]	$Ni(debt)_2$	$Ni(debt)_2(py)_2$	$Ni(debt)_2(\beta\text{-pic})_2$	$Ni(debt)_2(\gamma\text{-pic})_2$	Assignments
3208m,b					ν_{NH}
1681vs	1492vs	1490vs	1491vs	1482vs	ν_{CO}
1282s	1248m	1249m	1250s	1243m	ν_{CS}
	476m	483m	485s	488m	ν_{MO}
465s	461m	463m		465m	
		448m	453m	446m	ν_{MO}
438m	428m	428m	419m	420m	
400s,b		416m			
	406m	386m	391m	390m	ν_{MS}
348m		348m	343m	348w	
318m	308m	320w	321w		
	301vw	296vw			
288s	278m				
	250m	252w	250w	260w	
	228w		224sh		
		222vs	216s,b	224m	ν_{MN}
	214w				
202w	205w	200w		209w	

[a] Between 4000 and 500 cm^{-1} only the frequencies of interest were listed.

[b] v = very, s = strong, m = medium, b = broad, sh = shoulder.

TABLE III. Infrared Frequencies (cm^{-1}) of the Hppbt, $Ni(ppbt)_2$ and the Corresponding Adducts[a].

Hppbt	$Ni(ppbt)_2$	$Ni(ppbt)_2(py)_2$	$Ni(ppbt)_2(\beta\text{-pic})_2$	$Ni(ppbt)_2(\gamma\text{-pic})_2$	$Ni(ppbt)_2\cdot pip$	Assignments
3198sh						
3161m						ν_{NH}
1648s	1484s	1475vs	1477s	1472s	1475s	ν_{CO}
1278s	1211s	1210s	1206s	1203m	1201m	ν_{CS}
				489s		
484s	478s	470s	475s	475m	476s	
	460m	464s	463m	460m	459s	ν_{MO}
		432s	439m	439m	439w	ν_{MO}
442m	448sh	442vw				
423m	419m	422w	410s	417m	419s	
408sh						
399s						
	378m	373m	365m	363m	373m	ν_{MS}
		322m	327m	327m	326m	
	300m	299w	297vw	316m		
276s	274m	276w	277m	282m	284m	
	264sh		263vw	264m	263w	
251vw	252w	250w	250vw		251vw	
225vw	233w				236vw	
		226s	225vs	225s,b	219s,b	ν_{MN}
				216s,b		
197m	210w	206sh		202sh	204w	

[a]See footnote in Table II.

appear below 500 cm^{-1}. These bands belong to $2A_1 + 2B_2$ for $NiO_2S_2 - C_{2v}$ skeleton, $3A_1 + 2B_2 + B_1$ for $NiO_2S_2N_2 - C_{2v}$ skeleton and $3A' + 2A''$ for $NiO_2S_2N - C_S$ skeleton.

For $Ni(debt)_2$ and the adducts we observed bands at *ca.* 480 and *ca.* 450 cm^{-1} which are assigned to ν_{NiO}, while for $Ni(ppbt)_2$ and in the adducts these bands are observed at *ca.* 460 and *ca.* 439 cm^{-1}.

The ν_{MS} stretching frequency has been assigned between 399–360 cm^{-1} in various complexes of thio-β-diketones [14, 15, 17]. In our case, the ν_{MS} band was assigned at *ca.* 390 cm^{-1} for $Ni(debt)_2$ and the corresponding adducts and at *ca.* 370 cm^{-1} for $Ni(ppbt)_2$ and the corresponding adducts.

A relatively intense band is observed at *ca.* 220 cm^{-1} in adducts of $Ni(debt)_2$ and $Ni(ppbt)_2$. According to the assignment made for the adduct $Ni(acac)_2(py)_2$ [18], the observed band can be assigned as being due to ν_{NiN}.

Acknowledgements

The authors are indebted to FINEP for financial support and Rhodia S/A for the chemical analysis. C.M.M.C. is also indebted to Universidade Estadual de Maringá - CAPES/PICD for a fellowship.

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