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Rotational Barriers in Metal Chelates. Hindered Rotation about the Terminal NC(X)-Bond in Ni-Coordinated Isomeric Unsaturated 1,3-(S,O)-Ligands

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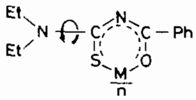
The barrier of hindered rotation about the terminal NC(X)-bond has been measured in the ligands as well as in the nickel(II) chelates using ^1H *NMR.*

The free energy of activation for hindered rotation is lower in the cases where charge delocalization occurs in the chelate ring (chelates with methine groups) and higher in the cases where it takes place in a smaller degree (aza-analogous chelates).

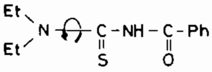
Thus the bonding situation investigated by ^1H *NMR corresponds fairly well with that determined by other methods.*

Introduction

Recently [1] we showed by ^1H NMR that in 1,1-diethyl-3-benzoylthiourea the barrier of hindered rotation about the terminal NC-bond increases when the ligand is coordinated at a metal centre:



$\Delta G_c^{\ne} = 68{,}0-76{,}1\ kJmol^{-1}$

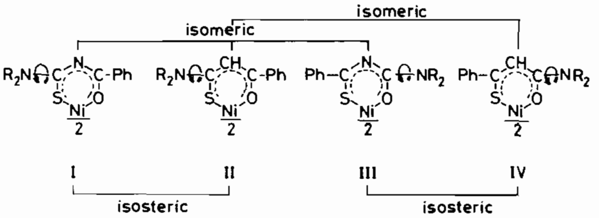


$\Delta G_c^{\ne} = 64{,}8\ kJmol^{-1}$

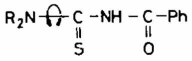
M = Tl (n = 1); Co (n = 3);
Pd, Pb, Zn, Ni (n = 2)

Substitution of sulfur by selenium (*i.e.* in acylselenoureas) further increases this barrier in the chelate, depending specifically on the metal ion.

Thus keeping Ni as central metal and sulfur and oxygen as ligand atoms we changed the relative position of the latter in the chelate ring to study its influence on the barrier of hindered rotation about the terminal NC-bond. With this aim we studied the hindered rotation of the terminal bond (N–C) in the following Ni(II) chelates (I–IV) by means of ^1H NMR:

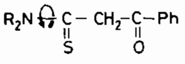


I and III are isomers as well as II and IV provided the substituents R are identic. On the other hand I and II are then isosteric pairs (with respect to N *versus* CH) as well as are III and IV. We compared ligands 1–4 (depicted without respect to tautomeric equilibria):


$R_2N-\underset{\underset{S}{\|}}{C}-NH-\underset{\underset{O}{\|}}{C}-Ph$

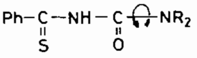
1

N-benzoylthioureas


$R_2N-\underset{\underset{S}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-Ph$

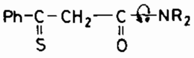
2

Benzoylthioacetamides


$Ph-\underset{\underset{S}{\|}}{C}-NH-\underset{\underset{O}{\|}}{C}-NR_2$

3

N-thiobenzoylureas


$Ph-\underset{\underset{S}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-NR_2$

4

Thiobenzoylacetamides

Results

Table I contains the free energy of activation $\Delta G_c^{\ddagger}$ [kJ mol^{-1}] (for hindered rotation about the terminal NC-bond), the coalescence temperature T_c [K] and the low temperature splitting $\Delta\nu$ [Hz] for the $N-CH_2-$ or $N-CH_2-CH_3-$ protons respectively.

The following equation [2] is used for $\Delta G_c^{\ddagger}$:

$$\Delta G_c^{\ddagger} = 19.14\ T_c\left(10.37 + \log\frac{T_c\sqrt{2}}{\pi\cdot\Delta\nu}\right)$$

With exception of 4a ($\Delta G_c^{\ddagger}$ not detectable due to tautomeric equilibria: 22% thioketonic form, 49% thioenolic form and 29% enolic form) all species

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TABLE I. Substituents and Values of Free Energy of Activation of Compounds.

No.	NR_2[a]	$\Delta\nu$ [Hz]	T_c [K]	$\Delta G_c^\ddagger$ (kJ mol^{-1})	ref.
1a	N(Me)$_2$	19.5	322.7	69.1 ± 0.8	13
Ia		5.8	333.2	74.8 ± 0.8	13
1b	N(Et)$_2$	43.3	313	64.9 ± 0.8	13
Ib		3.0	327.5	76.4 ± 0.8	13
1c	N(Bu^n)$_2$	35.6	319.5	66.8 ± 0.8	14
Ic		6.0	336.5	75.9 ± 0.8	14
1d	N(Bu^i)$_2$	37.0	322.0	67.2 ± 0.8	13
Id		5.2	337.5	76.7 ± 0.8	13
1e	Pyr	27.0	310.0	65.5 ± 1.0	13
Ie		13.0	389.0	85.2*	13
1f	Pip	34.4	195.5	40.1 ± 1.0	13
If		9.6	309.1	67.9	13
1g	N(Bz)$_2$	42.4	314.8	65.3 ± 0.8	14
Ig		8.5	349.5	77.5 ± 0.8	14
		10.8	353.5	77.7 ± 0.8*	
IIa	N(Et)$_2$	6.4	253.0	56.3 ± 0.6	15
2b	N(Bu^n)$_2$	23.5	301.0	63.9 ± 1.0	15
IIb		19.5	243.0	51.7 ± 0.8	15
2c	N(Bu^i)$_2$	25.0	320.5	69.0 ± 1.2	15
IIc		20.0	235.5	49.8 ± 0.8	15
2d	Pyr	12.3	330.6	72.1 ± 1.2	17
		28.5	345.0	73.0 ± 0.8*	
2e	Pip	27.0	341.6	50.5 ± 1.2	16
3a	N(Et)$_2$	6.8	263.0	58.2 ± 1.2	9
IIIa		19.0	401.0	86.7 ± 1.2*	9
3b	N(Bu^n)$_2$	12.0	288.0	62.6 ± 1.2	9
IIIb		7.2	395.0	88.5 ± 1.2	9
4a IVa	N(Bu^n)$_2$	6.8	314.5	70.1 ± 1.2	This paper

*Solvent 1,2-dichlorobenzene. [a]Me = methyl, Et = ethyl, Bu^n = n-butyl, Bu^i = i-butyl, Pyr = pyrrolidino, Pip = piperidino, Bz = benzyl.

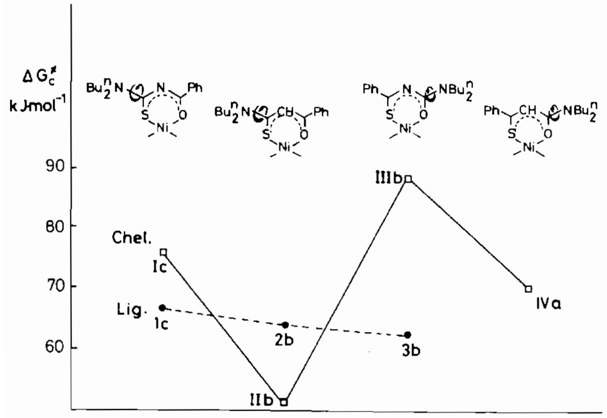


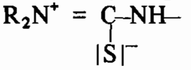
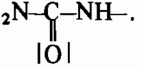
Fig. 1. Rotational barriers in isomeric 1,4-thioxoligands and its Ni(II) chelates.

with R = n-butyl could be studied. Table I shows that variations of noncyclic N-alkyl groups have only small influence on $\Delta G_c^\ddagger$ values. If the amide nitrogen is involved in a cyclic alkyl chain, deviations from the averaged $\Delta G_c^\ddagger$ value of noncyclic N-alkyl groups are observed according to PITZER-strains within the cycle [11] and steric hindrance between R_2N and the core of the molecule [12]. The $\Delta G_c^\ddagger$ values for 1c, 2b, 3b and Ic, IIb, IIIb, IVa are depicted in Fig. 1.

Discussion

Ligands

The slight decrease of $\Delta G_c^\ddagger$ in 2b with respect to 1c can be explained by omission of the electron withdrawing effect of the *meso*-imino nitrogen (which increases the partial double bond of the terminal NC-bond in 1c). In the ligands the chalcogen atom X predominantly determines the rotational barrier in the terminal fragment NC(X) (X = O, S): Sulfur increases the value (*cf.* 1c: $\Delta G_c^\ddagger$ = 66.8 kJ mol^{-1})

because of its polarizability represented by the canonical formula  $R_2N^+ = \underset{|\overline{S}|^-}{\underset{|}{C}}\text{–NH–}$ [3] in contrast with oxygen which is less polarizable (*cf.* 3b: $\Delta G_c^\ddagger$ = 62.6 kJ mol^{-1}) corresponding to  $R_2\bar{N}\text{–}\underset{|O|}{\underset{\|}{C}}\text{–}\bar{N}H\text{–}$.

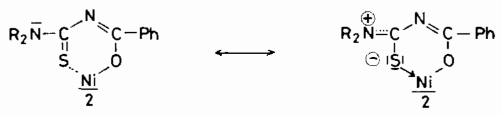
This is in accordance with the greater rotational barrier in N,N-dialkylsubstituted thioformamides with respect to formamides [4]. The difference between the S- and O-species of the present paper is in fact much smaller than the unvaried NC(X)-bonding in the amides. For the type 2 the $\Delta G_c^\ddagger$ values are approximately 70 kJ mol^{-1} smaller than for N,N-dialkylthioformamides [5]. Thus for ligands 1–3 the difference in $\Delta G_c^\ddagger$ is small.

Ni(II) Chelates

In the chelates the $\Delta G_c^\ddagger$ values are dramatically changed compared with the non-coordinated ligands (see Table I and Fig. 1).

Type I: Bis(1,1-dialkyl-3-benzoylthioureato)-nickel(II)

Complex formation principally increases the rotational barrier [1] compared with the nonchelated ligand and depending specifically on the metal. The main reason is a dative bond formed between the sulfur ligand and the metal which independently has been proved by ESCA [6]. Thereby the electrophilic central atom draws electrons from the adjacent terminal CN-bond *via* the sulfur:

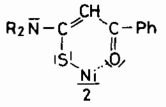


There is obviously only a small effect of the chelate ring formation upon the rotational barrier in type I. In Cu(I)(Et$_2$NCSNHCOPh)$_3$Cl [1], where the ligands are exclusively monodentate S-bonded, $\Delta G_c^\ddagger$ is of the same order (69.3 kJ mol^{-1}) as for the inner-complex chelates.

Type II: Bis(benzoylthioacet-N,N-dialkylamidato)-nickel(II)

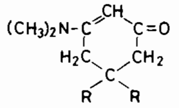
The effect of formation of Ni(II) chelate rings in the CH-isosteric species II and IV on $\Delta G_c^\ddagger$ is significant. Despite of the action of the electrophilic central metal and the presence of the same fragment NiSC–N (like in I) the rotational barrier in II is dramatically lowered to a value which is even beneath that of the non-coordinated ligand 2 (*cf.* Table I).

β-Thioxoketonate chelate rings show more effective charge delocalization than type I, due to the inclusion of the methine group. Therefore no direct electron attraction upon the terminal NC-bond can be detected. The NiS-bond gains in covalency, *i.e.* the canonical form



is getting more significance.

This interpretation is supported by the $\Delta G_c^\ddagger$ values found for enaminoketones: 54.5 kJ mol^{-1} (R = H), 56.5 kJ mol^{-1} (R = CH$_3$) [7],

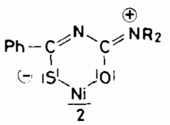


(*cf.* IIa: 56.3 kJ mol^{-1}).

In addition bond dissociation energies of a Ni(II) chelate of a similar monothio-β-diketone (bis(5-mercapto-2,2,6,6-tetramethylhept-4-en-3onato)nickel(II)) [8] determined calorimetrically yield: *D*(Ni–S) 232 ± 15 kJ mol^{-1} > *D*(Ni–O) 209 ± 17 kJ mol^{-1}, whereas the values for the ligand are *D*(O–H) 418 ± 20 kJ mol^{-1} > *D*(S–H) 377 ± 20 kJ mol^{-1}. Thus in the latter the stronger bond is between O and H, and in the Ni(II) chelate between Ni and S. This is also confirmed by β_2 of IIb (log β_2 = 18.2), which is hundred times more stable than Ic (log β_2 = 16.0).

Type III. Bis(1,1-dialkyl-3-thiobenzoylureato)-nickel(II)

Type III has the lowest complex stability (IIIa: log β_2 = 11.7) and the highest $\Delta G_c^\ddagger$ for the hindered rotation about the terminal NC-bond (IIIa: $\Delta G_c^\ddagger$ 86.7 kJ mol^{-1}). Also the difference between the values of the coordinated and non-coordinated ligand is greatest ($\Delta G_c^\ddagger$ (IIIa) – $\Delta G_c^\ddagger$ (3a) = 28.5 kJ mol^{-1}), *i.e.* the rotational barrier is significantly increased by complex formation despite the fact that the metal withdraws electrons not directly *via* the fragment SC–N. However this dramatic increase of $\Delta G_c^\ddagger$ can be understood if the system is taken as an azavinylogous thioamide considering that the chelate stability is low, *i.e.* the NiO-bond is weak. This is depicted in the following canonical form



This situation is further indicated by the mercaptide-like behaviour of the brown Pb(II) complex of 3a (m.p. 360 °C) compared with its uncolored isomer of 1b (m.p. 135.5–136.5 °C) [9].

Type IV: Bis(thiobenzoylacet-N,N-dialkylamidato)nickel(II)

Substitution of the imino-nitrogen in III by the methine group lowers the rotational barrier in IV (see above for type II). According with that the stability of IV a is great (log $\beta_2 = 21.3$).

It turns out therefore that the free energy of activation of the hindered rotation (determined by ^{1}H NMR) is a good probe for even small bond differences in diamagnetic metal chelates. It can be proved that substitution of N by CH within the chelate ring changes the bond situation. In the aza-analogous chelates the thioamide system predominates, whereas in the 'methin' chelates (CH) there is a nearly complete charge delocalization, no matter if there is an amide group ($R_2N–C(O)–$) in the ligand or a thioamide group ($R_2N–C(S)–$). This statement is strongly underlined by the relative heights of the S2p binding energies of some nickel chelates (types I–IV) in the ESCA-spectra (Ib: 162.8 eV; IIIb: 162.7 eV; IIb: 162.5 eV; IVa: 162.4 eV).

Experimental

The ligands 1–3 and their Ni(II) chelates I–III were prepared according to references in Table I.

Thiobenzoylacet-N,N-di-n-butylamide (4a) and *bis(thiobenzoylacet-N,N-di-n-butylamidato)nickel(II)* (IVa): Ethylbenzoylacetate and di-n-butylamine (molar ratio 1:1.2) yield after 6 h stirring at 130 °C benzoylacet-N,N-di-n-butylamide (85%) as a pale viscous liquid, b.p. 173–5 °C/0.1 mm Hg, n_D^{20} 1.5430, MS 275 confirmed, elemental analysis with satisfying values. Benzoylacet-N,N-di-n-butylamide is treated (according with [10]) with H_2S in 5% (w/w) methanolic solution (saturated with HCl) for 40 h at 0 °C. The red solution is poured into ice-water, the mixture is extracted with ethylacetate and the extract is washed until neutral, and dried over Na_2SO_4. After evaporation of the solvent *in vacuo*, the residue is dissolved in methanol and mixed with a methanolic solution of Ni(II) acetate. After stirring for 1 h precipitation is complete. The crystals are collected on a crucible, washed with methanol and recrystallized from ethanol (Yield 60% referred to benzoylacet-N,N-di-n-butylamide). Blackbrown needles of the product bis(thiobenzoylacet-N,N-di-n-butylamidato)-nickel(II), $C_{34}H_{48}N_2NiO_2S_2$ (MS 638 confirmed, m.p. 117–8 °C (ethanol)) give satisfactory elemental analysis values. The free ligand, which is very sensitive towards heat and air, is released from the stable nickel chelate in inert atmosphere by extractive decomposition with 4 *M* HCl and toluene. The toluene layer is washed until free of acid, dried over Na_2SO_4 and carefully evaporated *in vacuo*, giving a yellow viscous oil.

The ^{1}H NMR spectra were recorded with the 80 MHz spectrometer BS 480 C (Tesla, ČSSR), equipped with a temperature control unit (Tesla). $CDCl_3$ was used as solvent in most cases (*cf.* Table I). For $\Delta\nu$ determination the spectra were recorded with 0.2 Hz/mm. Determination of the coalescence temperature T_c of secondary amino group resonances was done in the recording range of 0.5 Hz/mm (multiplets) or 0.2 Hz/mm (singlets).

Acknowledgement

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