Nuclear Magnetic Resonance Study of Intramolecular Hydrogen Bonding in Halogeno(diethylthiourea)zinc(II) Complexes

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Variable-temperature n.m.r. spectra of mixed complexes of Zn^{II} with sulphur-bonded diethylthiourea and halogens (Cl, Br, and I) have been recorded in the range +30 to −90 °C. The measurements clearly show the presence in acetone solution of intramolecular $-NH \cdots X$ interactions. Hydrogen bonding to the solvent is evident at low temperature.

STRUCTURES of several tetrahedral and octahedral thiourea–halogen–metal complexes have been solved.[1-7] Some short nitrogen–halogen distances, suggesting the presence in the solid state of intra- and inter-molecular hydrogen bonding, have been found.

In a recent paper,[8] the existence of intramolecular hydrogen bonds of the type $-NH \cdots X$ has been reported for complexes of Co^{II} with thioureas and halogens, in solution. The intramolecular $-NH \cdots X$ interaction is stronger in complexes with *NN'*-substituted thioureas than in simple thiourea complexes. Similar results were reported for the analogous Zn^{II} complexes.[8]

The complexes, $Zn(L)_2X_2$ (L = diethylthiourea and X = Cl, Br, I) have been studied by n.m.r. spectroscopy in acetone solution, zinc being chosen as cation because its complexes are diamagnetic and much data has already been recorded for $Zn(L)_2Cl_2$.[8-10]

EXPERIMENTAL

The complexes [8] were provided by Dr. Piovesana of the University of Perugia.

N.m.r. spectra were recorded with a Bruker HX-90 spectrometer. Some spin-decoupling experiments have been run on a JEOL PS-100 instrument and some on a Bruker HX-90, with field stabilization on ^{19}F ($CFCl_3$). Standard 5 mm o.d. tubes were employed. Tetramethylsilane was always present as internal reference. Deuteriated acetone (Merck UVASOL) was used as solvent.

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[3] M. Nardelli, L. Cavalca, and A. Braibanti, *Gazzetta*, 1957, **87**, 137.

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[10] A. M. Giuliani, preceding paper.

RESULTS

Variable-temperature n.m.r. spectra of $Zn(L)_2Cl_2$, in $[^2H_6]$acetone, have been registered from room temperature to −90 °C. The data are collected in Table 1. The NH proton signals are shown in Figure 1. The methyl, methylene, and NH resonances (ratio of areas 3 : 2 : 1) are all split into two as the temperature is lowered. The coalescence temperature is 22 ± 2 °C. Integral curves show that the relative areas (determined both for the NH and the CH_2 signals) of the two signals are equal. The two methyl triplets are always partly overlapping and the relative areas cannot be determined. Spin-decoupling experiments indicate that the low-field NH triplet is coupled to the high-field methylene signal. This, in turn, is coupled to the low-field methyl signal.

TABLE 1

Chemical shifts of $Zn(ettu)_2Cl_2$ in $[^2H_6]$acetone

t (°C)	CH_3–		–CH_2–		–NH	
	δ (p.p.m. from tetramethylsilane)					
35	1·32t		3·57m		7·82b	
30					7·85b	
25					7·85b	
22 (coalescence)					7·70—8·09b	
20					7·70b	8·09b
10			3·52b		7·67b	8·18b
0			3·39b	3·63b	7·69b	8·22b
−10	1·27t	1·31t	3·39m	3·67m	7·73b	8·23b
−30	1·27t	1·32t	3·37dq	3·66m	7·84t	8·26t
−50	1·26t	1·32t	3·37dq	3·66dq	7·96t	8·30t
−70	1·26t	1·32t	3·37m	3·66m	8·07t	8·30b
−90	1·25b,t	1·32b,t	3·37b	3·67b	8·17b	8·32b

At 90 MHz, concentration 160 g l^{-1}, with tetramethyl silane as internal standard; t = triplet, m = multiplet, b = broad, dq = doublet of quartets.

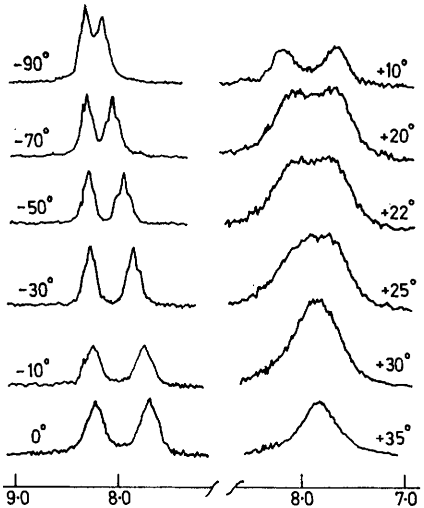

FIGURE 1 $Zn(ettu)_2Cl_2$ in acetone solution: NH resonance at different temperatures; at 90 MHz, tetramethylsilane as internal reference

At sufficiently low temperature ($t \leqslant -30$ °C) the NH protons appear as triplets and the coupling constant J_{CH_2-NH} is different for the low-field (J = 4·2 ± 0·2 Hz) and the high-field (J = 5·2 ± 0·2 Hz) resonances.

Dilution with benzene of the acetone solutions causes a larger upfield shift for the high-field than for the low-field methylene multiplet. This is an indication [11,12] that the former is in the *trans*-position relative to the C=S sulphur atom.

The n.m.r. data relative to a solution of $Zn(L)_2Br_2$ in $[^2H_6]$acetone, at variable temperature (from room temperature to −90 °C) are reported in Table 2. In Figure 2 the signals of the NH groups are shown at different temperatures. In this case, too, there is a splitting of the resonances as the temperature is lowered; the coalescence temperature is 15° ± 2 °C. It is impossible to determine the relative areas of the two NH signals, because they are always partially overlapping (Figure 2).

TABLE 2

Chemical shifts of $Zn(ettu)_2Br_2$ in $[^2H_6]$acetone

t (°C)	CH_3–		–CH_2–		–NH	
	δ (p.p.m. from tetramethylsilane)					
32	1·30t		3·54b		7·70	
22			3·53b		7·70	
15 (coalescence)					7·73	
13					7·69	7·83
10			3·49b	3·60b	7·70	7·86
8					7·68	7·86
5					7·69	7·88
−10	1·24t	1·29t	3·40dq	3·67m	7·74	7·93
−34			3·38dq	3·67m	7·87	7·93
−50			3·37dq	3·65m	7·94	7·96
−70	1·23t	1·31t	3·36m,b	3·63m,b	8·04	7·96t
−90	1·25t,b	1·31t,b	3·36b	3·63b	8·14t	7·97b

As for Table 1 but here concentration 158 g l^{-1}.

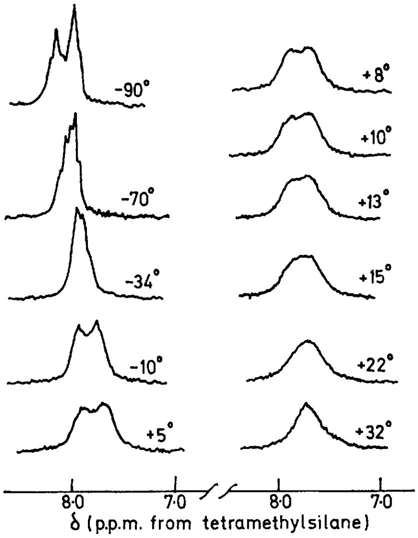

FIGURE 2 $Zn(ettu)_2Br_2$ in acetone solution: NH resonance at different temperatures; at 90 MHz, tetramethylsilane as internal reference

Only at −90 °C, the lowest temperature that can be reached with acetone as solvent, the NH signals show a triplet structure.

It is impossible to determine precisely the coupling constants, but the low-field NH triplet is definitely broader,

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[11] J. V. Hatton and R. E. Richards, *Mol. Phys.*, 1960, **3**, 253.
[12] J. V. Hatton and R. E. Richards, *Mol. Phys.*, 1962, **5**, 139.

and therefore has a larger *J* value, than the high-field signal. Looking at the methylene multiplets, one obtains a larger coupling constant for the low-field double quartet. Spin-decoupling experiments, at −90 °C, demonstrate that indeed the low-field NH triplet is coupled to the low-field CH_2 multiplet. Upon addition of benzene to the acetone solution, the high-field methylene double quartet is shifted farther to high field than the other, and therefore is presumably *trans* to the thioamide sulphur atom.[11,12]

TABLE 3

Chemical shifts of $Zn(ettu)_2I_2$ in $[^2H_6]$acetone

δ (p.p.m. from tetramethylsilane)

t (°C)	CH_3–		–CH_2–		NH–	
35					7·57b	
20					7·61b	
12 (coalescence)					7·62b	
10					7·59b	7·72s
8					7·58b	7·73s
5					7·58b	7·76b
0	1·29t	1·38t	3·42dq	3·68m	7·58b	7·79b
−10	1·28t	1·37t	3·41dq	3·68m	7·60b	7·89b
−30	1·26t	1·36t	3·39dq	3·66m	7·60t,b	8·01t,b
−50	1·27t	1·37t	3·39dq	3·66m	7·63t	8·14t
−70	1·26t	1·36t	3·39m,b	3·66m,b	7·63b	8·28t
−90	1·22t,b	1·33t,b	3·37b	3·63b	7·62b	8·36b

As for Table 1, but here concentration 230 g l^{-1}, s = shoulder.

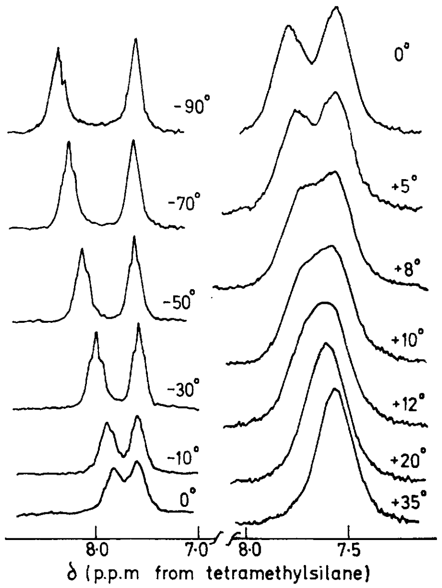

FIGURE 3 $Zn(ettu)_2I_2$ in acetone solution: NH resonance at different temperatures; at 90 MHz, tetramethylsilane as internal reference

A similar series of measurements has been made for $Zn(L)_2I_2$ in acetone solution. Data are reported in Table 3. Figure 3 shows the NH signals at different temperatures. At low temperature the resonance is split in two, the coalescence temperature is 10° ± 2 °C.

For $t < -30$ °C, the NH protons appear as two triplets; the coupling constants to the methylene protons are $J = 5{\cdot}0 \pm 0{\cdot}2$ Hz for the low-field triplet and $J = 4{\cdot}2 \pm 0{\cdot}2$ Hz for the high-field one. The low-field methylene multiplet shows a larger coupling constant than the high-field double quartet; it should, therefore, be coupled to the low-field NH triplet. Spin-decoupling experiments confirm this conclusion.

Dilution shifts indicate that the high-field methylene group should be *trans* to the thiocarbonyl group.

The position and separation of the resonances are unaffected by concentration for all three complexes.

DISCUSSION

It has been shown that in acetone solution only two of the three possible rotational isomers of *NN'*-diethylthiourea are present,[10] namely the *cis–cis*- and the *cis–trans*-isomers. The *trans–trans*-isomer is not present in detectable amounts, probably because of the steric interaction [11,13] between the two *trans*-ethyl groups.

It may reasonably be assumed that also in the case of complexes containing *NN'*-diethylthiourea as ligand only the *cis–cis*- and the *cis–trans*-configurations are present.

The n.m.r. spectra of the $Zn(L)_2X_2$ complexes, examined at low temperature, always exhibit only two NH resonances of equal relative areas.

This suggests that the ligand probably occurs only in the *cis–trans*-conformation. Examination of Figure 1 shows that the low-field NH signal (triplet, $J = 4{\cdot}2 \pm 0{\cdot}2$ Hz) is almost independent of temperature ($\Delta\nu = 9$ Hz over a range of 90°) and is therefore probably involved in an intramolecular hydrogen bond.

If this is the case, the proton is *cis* to the sulphur atom. The high-field methylene signal, coupled to this NH triplet, would then be attributed to a –CH_2– group *trans* to the sulphur atom. If only the *cis–trans*-configuration of the ligand is present, the second methylene resonance arises from a group *cis* to the thiocarbonyl group; hence the *trans*-methylene resonates at higher field than does the *cis*. Dilution shifts, obtained by adding benzene to the acetone solution of the complex, support this assignment.

The same relative position of the *cis*- and *trans*-resonances of the methylene protons has already been observed for the ligand alone, both in acetone and in chloroform solutions.[10]

The internal chemical shift of the NH protons, $\Delta\nu_{NH}$, increases (Figure 1) with decreasing temperature, but does not reach a limiting 'non-exchange' value. In fact, at temperatures below −10 °C, $\Delta\nu_{NH}$ decreases again because the temperature-dependent NH resonance moves rapidly downfield. This behaviour may be ascribed to the formation of hydrogen bonds with acetone. Indeed extensive hydrogen bonding has been observed for the free ligand in acetone solutions.[10]

In the case of X = Br (Figure 2), one of the two NH signals remains in almost the same position as the temperature changes (δ varies between 7·92 p.p.m. at 0 °C and 7·96 p.p.m. at −90 °C).

The other NH signal is at higher field for $t > -30$ °C, then the two NH resonances overlap and finally the temperature-dependent signal is found at lower field

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[13] A. S. Tompa, R. D. Barefoot, and E. Price, *J. Phys. Chem.*, **1969**, **73**, 435.

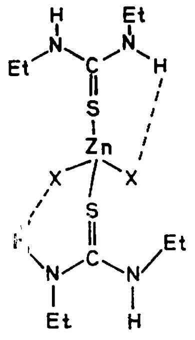
than the other. The fact that the resonance at $\delta = 7{\cdot}96$ p.p.m. does not move with temperature suggests the presence of intramolecular hydrogen bonding. The temperature dependence of the other NH signal is attributable to hydrogen bonding to the solvent as in the case of the chloride complex.

The iodide complex exhibits completely similar behaviour (Figure 3). In this case too, one NH signal (the high-field one) is almost temperature independent and suggests the existence of H bonding to the halogen in the same molecule. The second NH proton signal is found at lower fields and the internal chemical shift increases with decreasing temperature, without reaching a limiting ' non-exchange ' value. Hydrogen bonding to the solvent, which increases with decreasing temperature, is probably the origin.

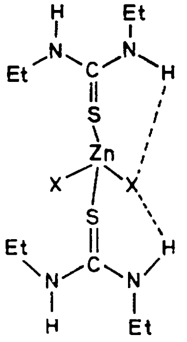
The n.m.r. data presented here strongly suggest that intramolecular hydrogen bonding occurs in $Zn(L)_2X_2$ complexes in acetone solutions. *X*-Ray structural studies have often revealed the presence of such bonds in mixed thiourea complexes. In most cases more than one hydrogen bond to the same halogen atom has been found. In addition, in the case of $Zn(L)_2Cl_2$, the crystal structure[9] has revealed molecules of two types, (A) and (B).

The structure in solution could obviously be different, but the presence of internal hydrogen bonds, in a variety of solvents ranging from the apolar CCl_4 to the highly polar CH_3CN, has already been suggested by comparison of the i.r. spectra of the ligand and of the $Zn(L)_2X_2$ complexes.[8] In complexes the NH stretching bands shift to lower frequencies, and this shift increases in the order I < Br < Cl.

Bearing in mind the i.r. and structural data, it may be inferred with confidence from the n.m.r. spectra that the complexes $Zn(L)_2X_2$ have a structure of type (A) or (B) in solution.



(A)



(B)

In addition, even the coalescence temperatures, much higher than for the ligand alone in the same solvent ($t_c = -30$ °C), suggest some kind of internal interaction which stabilizes one of the possible configurations.

Moreover, the values of these coalescence temperatures, decreasing in the order Cl > Br > I, indicate that the energy necessary to break this interaction is larger for the chloride complex. This is consistent with the presence of internal $-NH \cdots X$ bonds, whose strength increases in the order I < Br < Cl, *i.e.* according to the electronegativity of the halogen.

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