Substituted Thioureas. Part II.[1] Trimethylthiourea and its Complexes with Cobalt(II) and Halogens

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The n.m.r. behaviour of Co(tmtu)$_2$X$_2$ (X = Br or I) complexes has been examined in acetone solutions. The effects of temperature and of excess of ligand on the isotropic shifts of the compounds have been studied. The complexes are partly dissociated and a fast ligand exchange takes place at room temperature. The position of the lines allows determination of the steric arrangement of the ligand in the complexes: only the conformer with the NH proton *trans* to sulphur is detectable in solution and therefore the formation of intramolecular hydrogen bonds is not possible.

THE magnetic anisotropy of the thioamide group has been discussed in detail by Walter and co-workers.[2] The *N*-substituents of thioureas are subject to different magnetic influences according to their position (*cis* or *trans*) relative to the sulphur atom, because of the hindered rotation about the SC–N bond.

Different chemical shifts are therefore expected, and found, in the n.m.r. spectra of thioureas for *cis* and *trans* groups.

Eaton and Zaw in a recent paper[3] on cobalt(II) complexes of thiourea and related ligands have shown that this effect is extremely marked in such paramagnetic complexes: the *trans* (inside) NH protons resonate at low field from tetramethylsilane (TMS), whereas the *cis* (outside) NH protons resonate at much higher field than TMS.

The proton magnetic resonance spectra of such complexes provide therefore a very sensitive test for the steric arrangement of the ligand. We have used this method to establish the conformation of trimethylthiourea (tmtu) in its complexes with cobalt(II).

EXPERIMENTAL

Preparations.—The complexes of general formula Co(tmtu)$_2$X$_2$ (X = Cl, Br, or I) have been prepared by literature methods[4,5] and recrystallized from ethanol–light petroleum mixtures.

The ligand was deuteriated at the nitrogen by dissolving it in D$_2$O and drying it under vacuum several times. The degree of deuteriation was checked by n.m.r.: the NH signal had completely disappeared and the methyl attached to it appeared as a sharp singlet.

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[1] Part I, D. Gattegno, A. M. Giuliani, M. Bossa, and G. Ramunni, *J.C.S. Dalton*, 1973, 1399.

[2] W. Walter, E. Schaumann, and H. Paulsen, *Annalen*, 1969, **727**, 61.

[3] D. R. Eaton and K. Zaw, *Canad. J. Chem.*, 1971, **49**, 3315.

[4] F. A. Cotton, O. D. Faut, and J. T. Mague, *Inorg. Chem.*, 1964, **3**, 17.

[5] O. Piovesana and C. Furlani, *J. Inorg. Nuclear Chem.*, 1970, **32**, 879.

The ligand, so treated, was refluxed in monodeuterioethanol for *ca.* 30 min with the stoicheiometric amount of anhydrous $CoBr_2$ to yield, with the usual procedure, $Co(tmtu)_2Br_2$ deuteriated at the nitrogen atom. The iodide complex was obtained, in the same way, using cobaltous iodide recrystallized four times from D_2O.

The virtually complete disappearance of the NH bands in the i.r. spectra of the complexes so prepared indicate a satisfactory degree of deuteriation.

Even after several recrystallizations, the complexes, and particularly the bromide, always contained small amounts of impurities, mainly tmtu.

According to previous data [5] the complexes are tetrahedral, non-electrolytic and essentially monomeric in solution.

Spectral Measurements.—The n.m.r. spectra have been recorded with a Bruker HX-90 spectrometer operating at 90 MHz and with a 25 kHz modulating frequency, equipped with a variable temperature unit. The uncertainty in the temperature values is considered to be ±2°.

The reading error for the isotropic shift values is always taken as ±20 Hz, unless otherwise indicated.

Standard 5 mm o.d. tubes have been used; TMS has been used as internal reference and for field stabilization. Deuteriated Merck UVASOL acetone has been used as solvent.

TABLE 1

Isotropic shifts [a] of $Co(tmtu)_2Br_2$ at different temperatures in $[^2H_6]$acetone

t/°C	*cis* N–CH_3	*cis* N–CH_3	*trans* –NH	*trans* N–CH_3	tmtu
+25	−730	−770sh		−1840 ±200	
+10	−740	−880		−3300 ±200	
0	−720	−1000		−3770 ±200	
−10	−730	−1040 ±50		−4100 ±100	
−20	−720	−1060 ±40		−4300 ±100	
−30	−710	−1080		−4650 ±50	
−50	−710	−1160		−5230	
−60	−700	−1180		−5500	−230
−70	−680	−1180		−5780	−270
−80	−640	−1180	−1280	−6110	−280
−90	−630	−1160	−1340	−6560	−300/−260

[a] Shifts in Hz from TMS at 90 MHz.

TABLE 2

Isotropic shifts [a] of $Co(tmtu)_2I_2$ at different temperatutes in $[^2H_6]$acetone

t/°C	*cis* N–CH_3	*cis* N–CH_3	*trans* –NH	*trans* N–CH_3	tmtu
+25	−770	−770	−850	−4100 ±100	
+9	−790	−940 ±50	−940 ±50	−4400 ±100	
0	−805	−1020 ±50	−1020 ±50	−4600 ±50	
−20	−830	−1130 ±30	−1130 ±30	−5140 ±50	
−40	−850	−1120	−1300	−5630	
−60	−850	−1110	−1460	−6210	
−70	−840	−1080	−1560	−6390	
−80	−820	−1010	−1740	−7060	−400/—260
−89	−790	−960	−1840	−7380	−430/−240

[a] See Table 1.

Data on the chloride complex have not been obtained because of its too low solubility in acetone.

RESULTS AND DISCUSSION

Variable temperature ^1H n.m.r. spectra have been recorded for the bromide and iodide complexes, both alone and in presence of an excess of ligand in acetone solutions. The chemical shift data for the two complexes are reported in Tables 1 and 2. Some of the spectra are shown in Figures 1 and 2.

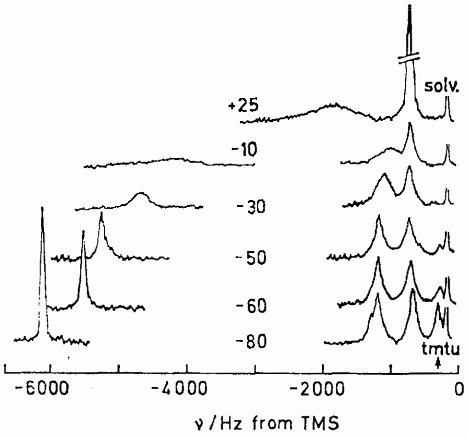

FIGURE 1 ^1H N.m.r. spectra of $Co(tmtu)_2Br_2$ in $[^2H_6]$acetone at different temperatures ($\nu_0 = 90$ MHz, numbers on curves indicate the temperature in °C)

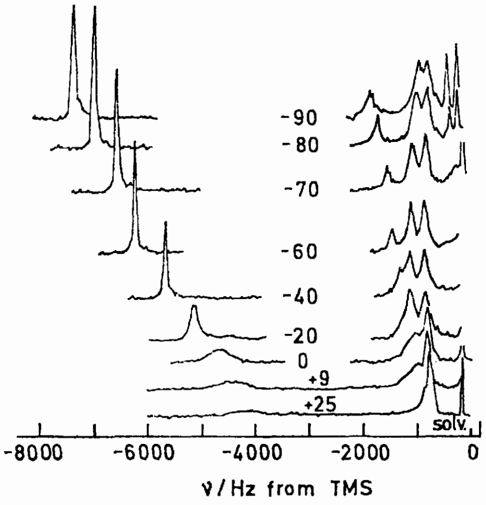

FIGURE 2 ^1H N.m.r. spectra of $Co(tmtu)_2I_2$ in $[^2H_6]$acetone at different temperatures ($\nu_0 = 90$ MHz, numbers on curves indicate the temperature in °C)

No signal has been found on the high-field side of TMS up to 12 kHz.

The resonances, which at room temperature are not resolved, and in some cases very broad, become separated and sharper in the low-temperature range.

The signal, or group of signals, which at low temperatures appears in the region −250 to −450 Hz from TMS, has been assigned to free tmtu by comparison with spectra recorded in presence of an excess of ligand (Table 3).

The presence of the free ligand signals, even when no excess had been added, is ascribed to partial dissociation of the compounds (as found by spectroscopic studies for similar compounds in solvents like acetone) and to the small amounts of tmtu present as an impurity even after repeated recrystallizations.

The four signals found at low temperatures, both for the bromide and the iodide species, have been assigned by comparison with the spectra and following the arguments of Eaton and Zaw.[3]

It appears, from the data of Table 2 and the spectra in Figure 2, that the signal assigned to the thioamide NH proton moves rapidly downfield with decreasing temperature but, from room temperature down to −40 °C, it is covered by the *cis*-methyl resonances. In the case of bromide, this behaviour is even more pronounced, since the NH resonance can be observed separately only below −80 °C.

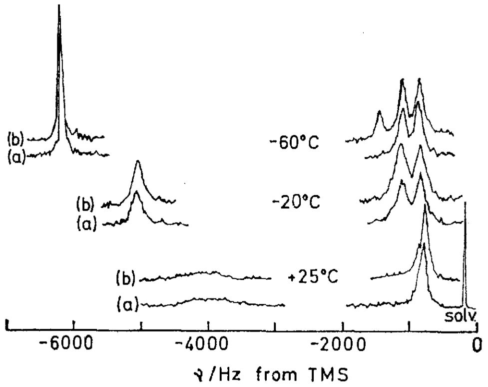

FIGURE 3 ^{1}H N.m.r. spectra of Co(tmtu)$_2$I$_2$ (a) in [^{2}H$_6$]acetone compared with the corresponding spectra of the deuteriated complex (b) at different temperatures (ν_0 = 90 MHz)

To confirm the assignment, we have recorded also the spectra of the deuteriated complexes. In Figure 3 the spectrum of deuteriated Co(tmtu)$_2$I$_2$ is compared with that of the protonated species at three different temperatures, leaving no doubt about the assignment. This NH signal is attributed to a proton *trans* to the sulphur atom.

Of the three methyl signals, the lower field one is assigned to a CH$_3$ group *trans* to sulphur; finally the other two resonances are assigned to two methyl groups *cis* to sulphur.

The two conformers (A) and (B) of the ligand[1] are both possible, at least in principle.

It may however be recalled that conformer (A) is strongly favoured over (B) on energetic grounds. In the present case conformer (B) can safely be excluded because no signal is found at higher field than TMS, where a *cis* NH proton should resonate and two signals of about equal relative areas appear in the region where *cis*-methyls should be found.[3]

The assignment of the resonances of the *cis*-methyl groups of conformer (A), cannot be done unambiguously. We can tentatively assign the lower field signal to the NH-*CH$_3$* group by comparison of its position with the resonance frequency of the NH-*CH$_3$* *cis*-methyl in similar complexes.[3]

In Table 3 are reported the data obtained in presence of an excess of ligand, at different temperatures. The assignment of the resonances is indicated. In the case of Co(tmtu)$_2$Br$_2$ at low temperature, the signal of the *cis*-N-CH$_3$ at *ca.* −640 Hz overlaps the NH peak of free tmtu.

TABLE 3

Isotropic shifts for cobalt(II)–tmtu complexes in the presence of an excess of ligand [a]

Co(tmtu)$_2$Br$_2$ 9·0 g l^{-1} + tmtu 4·0 g l^{-1}

t/°C	*trans* NCH$_3$	*trans* NH	*cis* NCH$_3$	*cis* NCH$_3$ [b]	tmtu
+25	−880 ±60			−490	−337(m)
0	−3700 ±200			−490 [c]	−350(m)
−10	−4080 ±100			−440 ±30 [c]	−340(m)
−30	−4560 ±40		−1030 ±50	−500	−360(m)
−40	−4940 ±30		−1120 ±40	−650 ±50	−300(m)
−50	−5220		−1160	−680 ±50	−270(m)
−70	−5830		−1180	−640	−270(m)
−80	−6100	−1270	−1160	−640	−260(m)
−90	−6560	−1340	−1140 ±30	−640	−270(m)
Co(tmtu)$_2$I$_2$ 11·6 g l^{-1} + tmtu 3·3 g l^{-1}					
+20	−4500 ±50		−1080 ±60	−690 ±100	−340(m)
0	−4540 ±50		*ca.* −1080sh	−700 ±60	−310(m)
−10	−4840 ±40		−1100 ±40	−780 ±30	−330(m)
−20	−5080		−1140	−840 ±40	−300(m)
−40	−5570	−1290	−1140	−840	−640 ± 30/ −280(m)
−60	−6250	−1450	−1100	−840	−620/ −260(m)
−80	−7030	−1700	−1020	−810	−640/ −270(m)

[a] Shifts in Hz from TMS at 90 MHz; solvent: [^{2}H$_6$]acetone. [b] See text. [c] Broad tail to low field.

The shift of the resonances towards their diamagnetic positions (Table 3 and Figure 4) with increasing temperature, indicates a relatively fast ligand exchange at room temperature, in analogy with related complexes.

On the other hand the exchange becomes very slow on the n.m.r. time scale, and virtually stops in the low temperature region. This fact is made evident by the increasing separation and marked sharpening of the signals at decreasing temperatures and by the presence of sharp signals at the free ligand resonance frequencies.

The fast equilibrium between complexed ligand and an outer sphere site or a fifth co-ordination position, found for similar compounds[3] has not been detected in our case. Indeed the complexed ligand lines are not shifted by addition of increasing amounts of tmtu in the slow exchange region (up to *ca.* —30 °C).

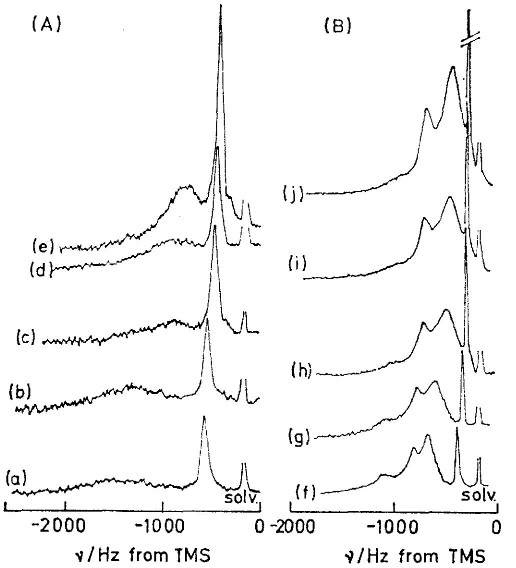

FIGURE 4 ^{1}H N.m.r. spectra of Co(tmtu)$_2$X$_2$ in [^{2}H$_6$]acetone in presence of excess of ligand ($t = +30$ °C, $\nu_0 = 90$ MHz); (A) Co(tmtu)$_2$Br$_2$ 9·2 g l^{-1}; (a) 1·7; (b) 2·3; (c) 4·0; (d) 5·0; (e) 8·3 g l^{-1} tmtu. (B) Co(tmtu)$_2$I$_2$ 11·3 g l^{-1}; (f) 1·4; (g) 2·5; (h) 5·0; (i) 6·4; (l) 7·6 g l^{-1} tmtu

We have disregarded water as a competitive ligand, because of its low concentration in the [^{2}H$_6$]acetone; indeed water is a very poor ligand in low concentrations, as shown by Eaton and Zaw.[3]

From the previous discussion it clearly appears that only species which contain the ligand in conformation (A) are detectable in solution. This conclusion is in complete agreement with previous findings for zinc complexes and with theoretical calculations on the free ligand.[1] The existence of intramolecular hydrogen bonding of the type NH · · · X can therefore be safely excluded in trisubstituted thiourea complexes, since the assignment of an NH resonance to *cis* or *trans* environments (which respectively allow and do not allow intramolecular hydrogen bonding) is quite unambiguous in these paramagnetic complexes.

Moreover, the strong preference of trisubstituted thioureas for conformation (A) has been demonstrated also by Isaksson and Sandström[6] in the case of *N*-aryl-substituted trimethylthioureas.

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[6] G. Isaksson and J. Sandström, *Acta Chem. Scand.*, 1970, **24**, 2565.