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IR AND NMR STUDIES OF SYMMETRICALLY AND UNSYMmetrically BONDED N,N-DIALKYLDITHIOCARBAMATES

BY

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In order to find characteristic differences between symmetrically and unsymmetrically bonded N,N-dialkyldithiocarbamates, their IR and \(^1\)H NMR spectra have been examined. The IR data firmly underline a previously reported infrared criterion which makes it possible to distinguish the two types of bonding. In the spectra of the unsymmetrical N,N-diethyldithiocarbamates a band at 1000 cm\(^{-1}\) is assigned to the C=S stretching mode.

Although the rotation around the S\(_2\)C—NR\(_2\) bond in several dithiocarbamato complexes will be strongly hindered at low temperatures, no splitting of the NMR signals of the N-alkyl groups could be observed. This may be attributed to an extremely small difference in magnetic environment of the N-alkyl moieties in the rotamers.

**IR-spectra**

On the basis of limited data Bonati and Ugo\(^1\) reported an infrared criterion by which unsymmetrically coordinated N,N-diethyldithiocarbamates (Et\(_2\)DTC) could be distinguished from the symmetrical ones (Fig. 1). They found

![Diagram of unsymmetrical and symmetrical N,N-diethyldithiocarbamates](image)

that the presence of two absorption bands in the region of 1050–950 cm\(^{-1}\) is characteristic of the unsymmetrically bonded Et\(_2\)DTC groups. For the spectra of the symmetrical Et\(_2\)DTC derivatives only one band is observed in this region.

We have examined the IR-spectra of a series of Et\(_2\)DTC compounds.

It appeared that the spectra of the compounds, the Et₂DTC groups of which are known to be unsymmetrically coordinated, contain the two bands without exception, whereas in the spectra of the bidentate (symmetrical) Et₂DTC complexes only one band is observed (Table I). In Fig. 2 this is illustrated for N,N,N',N'-tetraethylthiuram disulfide [(Et₂NCSS)₂ = Et₄TDS] and the bisdiethyldithiocarbamato complex of Zn(II).

These results give a broader basis for the criterion of Bonati and Ugo; it is probably of general applicability for DTC complexes. It should be noted that we have considered the data measured in solution rather than those in the solid state. The presence of two bands in the spectra of unsymmetrical Et₂DTC derivatives might be due to splitting of degenerate vibrational states. However, the spectra of symmetrical dithiocarbamates as e.g., Ni(Et₂DTC)₂ (D₂h) and Cu(Et₂DTC)₂ (in the solid state the symmetry is lower than D₂h³), the symmetries of which do not allow degenerate states for the ligand vibrations, show notwithstandingly only one band. So no theoretical foundation for this criterion has been found.

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Upon complexation of Et₄TDS to Zn, Cd and Hg₃ band I shifts to a lower frequency just like the band at 918 cm⁻¹ (band III) which is present in the spectra of all Et₂DTC derivatives investigated. Band III was recently assigned to a CSS vibration on the basis of a comparative IR study of Et₂DTC and N,N-diethyldiselenocarbamato (Et₂DSC) complexes⁴. For band II no significant change could be observed. From the structure of the thiuram disulfide complexes which was indicated previously⁵ and confirmed recently by crystallographic work⁶, it follows

<table>
<thead>
<tr>
<th>Unsymmetrical</th>
<th>Band I $\nu$(C=S(I))</th>
<th>Band II $\nu$(CSS)(cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Et(ET₂DTC)</td>
<td>1007 m</td>
<td>990 m 920 m</td>
</tr>
<tr>
<td>Me(ET₂DTC)</td>
<td>1012 m</td>
<td>990 m 919 m</td>
</tr>
<tr>
<td>Hg₂Me(ET₂DTC)</td>
<td>1002 m-w</td>
<td>989 m 909 m</td>
</tr>
<tr>
<td>Et₄TDS</td>
<td>1008 m</td>
<td>972 m 918 m</td>
</tr>
<tr>
<td>Hg₄(ET₄TDS)</td>
<td>1000 m-w</td>
<td>972 m 910 m</td>
</tr>
<tr>
<td>Cd₄(ET₄TDS)</td>
<td>992 m-w</td>
<td>971 m 907 m</td>
</tr>
<tr>
<td>Zn₄(ET₄TDS)</td>
<td>991 m-w</td>
<td>971 m 907 m</td>
</tr>
<tr>
<td>As(ET₂DTC)₃</td>
<td>1004 m-w</td>
<td>988 m 915 m</td>
</tr>
<tr>
<td>Sb(ET₂DTC)₂</td>
<td>1000 sh</td>
<td>988 m 915 m</td>
</tr>
<tr>
<td>Bi(ET₂DTC)₂</td>
<td>1000 sh</td>
<td>985 m 913 m</td>
</tr>
<tr>
<td>Se(ET₂DTC)₂</td>
<td>1005 m</td>
<td>983 m 915 m</td>
</tr>
<tr>
<td>Te(ET₂DTC)₂</td>
<td>1002 m</td>
<td>986 m 916 m</td>
</tr>
<tr>
<td>Sn(ET₂DTC)₄</td>
<td>1000 sh</td>
<td>991 m 917 m</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>symmetrical</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(ET₂DTC)₃</td>
<td>1005 m-w</td>
<td>918 m-w</td>
</tr>
<tr>
<td>Zn(ET₂DTC)₂</td>
<td>991 m</td>
<td>914 m</td>
</tr>
<tr>
<td>Hg(ET₂DTC)₂</td>
<td>989 m</td>
<td>913 m</td>
</tr>
<tr>
<td>Ni(ET₂DTC)²</td>
<td>993 m</td>
<td>914 m</td>
</tr>
<tr>
<td>Ni(ET₂DTC)³⁺</td>
<td>998 m-w</td>
<td>913 m</td>
</tr>
<tr>
<td>Cu(ET₂DTC)²</td>
<td>998 m</td>
<td>915 m</td>
</tr>
</tbody>
</table>

* The spectra were recorded in KBr. The accuracy of the data given is ±2 cm⁻¹; as reference the band at 1028 cm⁻¹ of polystyrene was used. m = moderate intensity, w = weak intensity, sh = shoulder

that the $\text{C=S}[(\text{C=S}(\text{I}))$ bond lengths become longer upon complex formation. This weakening of the $\text{C=S}$ bond correlated with the shift of band I to lower frequency leads to the assignment of this band to a vibrational mode wherein the contribution of the $\text{C=S}$ stretching vibration is important. To verify this assignment a new complex $\text{HgI}_2\text{Me(ET}_2\text{-DTC)}$ was prepared simply by adding equimolar amounts of $\text{HgI}_2$ and $\text{MeS(S)CNEt}_2$ in acetone solution.

The $\text{ET}_2\text{DTC}$ ester will complex mainly by means of the terminal sulfur atom $[\text{S(I)}]$ like the $\text{R}_4\text{TDS}$ ligands. The shift of the bands I and IIII to lower frequencies upon complexation gives support to our assignment of band I.

$\text{H NMR-spectra}$

It was reported that hindered rotation around the $\text{C=N}$ bond can be observed by $\text{H NMR}$ for unsymmetrical $\text{R}_2\text{DTC}$ derivatives like $\text{R}_2\text{DTC}$ esters$^8,9$, $\text{R}_4\text{TDS}$ and its complexes$^9$. Hindered rotation for symmetrical $\text{R}_2\text{DTC}$ derivatives in general cannot be observed by NMR. The compounds $\text{Mo(NO)(R}_2\text{DTC)}_3$ and $\text{Ru(NO)(R}_2\text{DTC)}_3$, which were studied by Johnson, Al-Obaidi and McCleverty$^{10,11}$, form an exception. This is caused by the non-equivalence of the $\text{N}$-alkyl groups with respect to the other ligands coordinated to the central atom. We have studied some unsymmetrical $\text{R}_2\text{DTC}$ compounds in order to check if they could be distinguished from the symmetrical ones by NMR. For the compounds investigated only hindered rotation around the $\text{C=N}$ bond is observed in $\text{N,N,N',N'-tetramethylthiuram monosulfide (Me}_4\text{TMS)}$ which shows two singlets of equal intensity in its NMR-spectrum recorded at 30° in $\text{CDCl}_3$ solution with a spectrometer operating at 100 MHz. The splitting between the signals is 7 Hz. For $\text{As(ET}_2\text{DTC)}_3$, its Sb and Bi analogues, $\text{As(Me}_2\text{DTC)}_3$, $\text{Se(ET}_2\text{DTC)}_2$ and $\text{Te(ET}_2\text{DTC)}_2$, however, no splitting of the $\text{N}$-alkyl proton resonances in $\text{CDCl}_3$ and $\text{CS}_2$ solutions could be observed at temperatures as low as $-60°$. Even a spectrum of $\text{As(ET}_2\text{DTC)}_3$, recorded with a 220 MHz NMR spectrometer at $-50°$ in a $\text{CS}_2$-toluene solution, shows no line broadening of the ethyl proton resonance peaks with respect to the $\text{CH}_3$-signal of toluene. This might be due either to a small, undetectable difference in the magnetic environments of the $\text{N}$-alkyl groups in the rotamers or to a small barrier to internal rotation. The former is sometimes found.

References:
8 a. C. E. Holloway and M. H. Gitlitz, Can. J. Chem., 45, 2659 (1967);
pending upon solvent, for the $N$-CH$_3$ protons of some alkyl-$N$-(arenesulfonfylmethyl-$N$-methylcarbamates $(XC_6H_4SO_2CH_2N(CH_3)CO_2R)$\textsuperscript{12,13}.

From the small differences in the C–N bond length found for Et$_4$TDS\textsuperscript{14} and As(Et$_2$DTC)$_3$\textsuperscript{15} and the slight variations in the C–N stretching frequencies of the complexes investigated, R$_4$TDS and R’(R$_2$DTC) (Table II), it is concluded that the first explanation (valid at the temperatures mentioned) is most probably correct.

**Experimental Part**

$^1$H NMR spectra were recorded using a Varian HA-100 NMR spectrometer operating at 100 MHz. For recording the 220 MHz $^1$H NMR spectrum the Varian AR 220 MHz NMR spectrometer was used. The infrared data were obtained, unless reported otherwise.

<table>
<thead>
<tr>
<th>Table II</th>
<th>The C–N stretching frequencies of a number of Me$_2$DTC and Et$_2$DTC derivatives; crystallographic data of the C–N bond lengths.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\nu$(C–N) (cm$^{-1}$)</td>
</tr>
<tr>
<td>Me$_4$TDS</td>
<td>1505</td>
</tr>
<tr>
<td>Me$_4$TMS</td>
<td>1508</td>
</tr>
<tr>
<td>Me(Me$_2$DTC)</td>
<td>1498*</td>
</tr>
<tr>
<td>Et(Me$_2$DTC)</td>
<td>1498*</td>
</tr>
<tr>
<td>As(Me$_2$DTC)$_3$</td>
<td>1507</td>
</tr>
<tr>
<td>Me(Et$_2$DTC)</td>
<td>1493</td>
</tr>
<tr>
<td>Me(Et$_2$DTC)</td>
<td>1489*</td>
</tr>
<tr>
<td>Et(Et$_2$DTC)</td>
<td>1493</td>
</tr>
<tr>
<td>Et(Et$_2$DTC)</td>
<td>1489*</td>
</tr>
<tr>
<td>Et$_4$TDS</td>
<td>1496</td>
</tr>
<tr>
<td>As(Et$_2$DTC)$_3$</td>
<td>1494</td>
</tr>
<tr>
<td>Se(Et$_2$DTC)$_3$</td>
<td>1497</td>
</tr>
<tr>
<td>Te(Et$_2$DTC)$_3$</td>
<td>1493</td>
</tr>
</tbody>
</table>

The spectra were recorded in CHCl$_3$ solution, using a Beckmann IR 4 spectrophotometer.

$^*$ The spectra were recorded in CH$_2$Cl$_2$ solution.

\textsuperscript{12} S. van der Werf, Thesis, Groningen 1969, pg 50 and 51.


using a Perkin Elmer 157. The known compounds were prepared as described in the literature: Me₄TMS₃⁷, As(ET₂DTC)₃, Sb(ET₂DTC)₃, Bi(ET₂DTC)₃, Se(ET₂DTC)₂, Te(ET₂DTC)₂, Me(ET₂DTC), Co(ET₂DTC)₂, Zn(ET₂DTC)₂, Hg(ET₂DTC)₂, Cu(ET₂DTC)₂, Ni(ET₂DTC)₂, Me₄TDS, Et₄TDS, HgMe₂TDS, and Sn(ET₂DTC)₄. The preparation of the thiuram disulfide complexes and Ni(ET₂DTC)₃⁺I₂⁻ was as described in ref. 3. The synthesis of HgI₂(ET₂DTC) was reported earlier⁸.

CdI₂(ET₄TDS). A concentrated solution of I₂ (1 mole) in CS₂ was added to a concentrated solution of Cd(ET₂DTC)₂ in the same solvent. The white precipitate obtained was dissolved in acetone and reprecipitated by addition of petroleum ether (60–80°). The colourless needles melted at 139–142°.

\[
\text{Found: } \text{Cd 16.9; C 18.3; H 3.0} \\
\text{Calc. for CdI₂·C₁₀H₂₀N₂S₄ (662.7): Cd 17.0; C 18.1; H 3.0}
\]

ZnI₂(ET₄TDS) was obtained like CdI₂(ET₄TDS). Instead of acetone, chloroform was used for recrystallisation. Colourless needles were formed; m.p. 153–156°.

\[
\text{Found: } \text{Zn 10.6; C 19.7; H 3.3} \\
\text{Calc. for ZnI₂·C₁₀H₂₀N₂S₄ (615.7): Zn 10.6; C 19.5; H 3.3}
\]

Ni(ET₂DTC)₃I₂. An excess of iodine was added to a solution of Ni(ET₂DTC)₂ in chloroform. The separated oil solidified on addition of petroleum ether (60–80°). Recrystallisation in acetone solution yielded needles which melted at 121–123°.

\[
\text{Found: } \text{Ni 6.5; C 20.7; H 3.5} \\
\text{Calc. for NiI₃·C₁₅H₃₀N₂S₄ (884.2): Ni 6.6; C 20.4; H 3.4}
\]

HgI₂Me(ET₂DTC). HgI₂ (1 mole) was added to a concentrated solution of Me(ET₂DTC) (1 mole) in acetone. After the HgI₂ had dissolved by complexation with the ester, light yellow plates were obtained on addition of petroleum ether (60–80°); m.p. 101–103°.

\[
\text{Found: } \text{C 12.0; H 2.2} \\
\text{Calc. for HgI₂·C₆H₁₃NS₂ (617.7): C 11.7; H 2.1}
\]

Acknowledgements

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We wish to thank Prof. J. J. Steggerda for helpful discussions and are grateful to Ir. P. E. J. Verwiel (TNO) for recording the 220 MHz ¹H NMR spectrum. The authors wish also to thank Mr. H. Smeets for recording the other NMR spectra and Mr. H. Langhout for performing the analyses.

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