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Evidence for an Unexpected Chiral Axis in Tetraethyldithiooxamide and in its Platinum(II) Coordination and Organometallic Complexes.

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Abstract: Tetraethyldithioxamide (Et_4-DTO) shows in solution high energy barriers either for chiral torsion around C-C axis or for achiral torsion around C-N axis. A chiral C-C axis was also evidenced by a crystal structure determination on a single crystal, which showed clearly the right absolute configuration in the $P4_3$ space group. ^{1}H-NMR signals of the prochiral probe -C_2H_5 in Et_4-DTO provided unequivocal evidence for the persistence of the chiral C-C axis also in co-ordination and organometallic complexes of platinum(II) of the chelate ligand Et_4-DTO.

We have exploited tetraethyldithoxamide (Et_4-DTO) in an attempt to substitute only neutral groups in cis-PtL_2Cl_2 type complexes since N,N'-dialkyl substituted dithioxamides cause the undesired loss of chloride from the co-ordination sphere of platinum(II), leading to tight ion pairs $\{Pt(H_2\text{-}R_2\text{-DTO})_2^{++},(Cl^-)_2\}$ in low polarity solvents or to rubeanate compounds $[Pt(H\text{-}R_2\text{-DTO})_2]$ in basic solvents[1].

The ^{1}H-nmr spectrum of Et_4-DTO in C_6D_6 (fig. 1) exhibits two equally intense triplets ($\delta = 0.99$, $^3J_{HH} = 7.1$ Hz; $\delta = 0.86$, $^3J_{HH} = 7.1$ Hz; 12H, methyl protons) and four equally intense multiplets ($\delta = 3.77$, $^3J_{HH} = 7.1$ Hz; $^2J_{gem} = 13.2$ Hz; $\delta = 3.42$, $^3J_{HH} = 7.1$ Hz, $^2J_{gem} = 13.2$ Hz; $\delta = 3.20$, $^3J_{HH} = 7.1$ Hz, $^2J_{gem} = 13.9$ Hz; $\delta = 3.03$, $^3J_{HH} = 7.1$ Hz, $^2J_{gem} = 13.9$ Hz; 8H, methylene protons).

This spectral pattern features two non equivalent ethyl groups, which result in a pair of equally intense ABX_3 schemes. This means that the ethyl groups in each amide fragment are diastereotopic, owing to the hindered rotation about the C-N axis; at the same time, the methylene protons in each ethyl fragment are also diastereotopic, so providing unequivocally evidence for the presence of a chiral C-C axis in the N-C(=S)-C(=S)-N fragment. Thus, the N-C=S planes must be tilted relative to each other in solution, where torsional barriers (chiral torsion around the C-C axis and achiral torsion around the C-N axis) are both high, at least on the NMR time scale.

This was confirmed by variable temperature NMR experiments, performed both in benzene and in other solvents: temperature (up to 345 °K) left unchanged the double ABX_3 spectral pattern of Et_4-DTO.

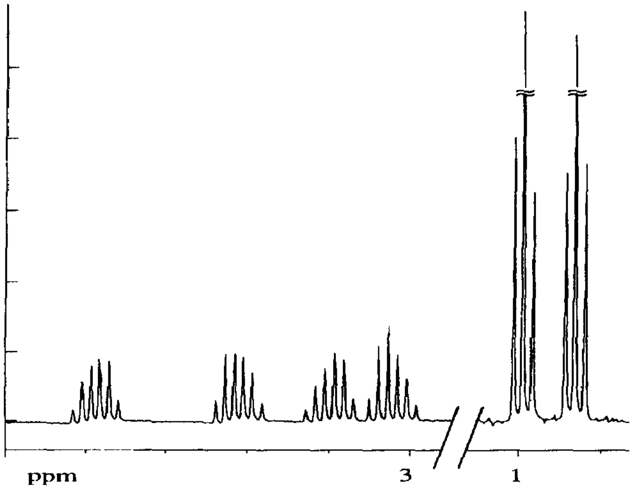

Fig 1 ^{1}H NMR spectrum of tetraethyldithiioxamide in C_6D_6.

The high torsional barrier around the C-C axis is not easily understandable. In fact, steric factors could not dramatically differ from those exhisting in the corresponding diamide $(Et)_2$-C(=O)-(C=O)-$(Et)_2$, in which the -CH_2- protons of the prochiral probe are enantiotopic. On the other hand electronic repulsion between non-bonding orbitals, which has been recognized as a probable origin for axial chirality in quinolinone, hidroxylamine and sulfenamide derivatives[2], can't play a similar role in Et_4-DTO since the sulphur atoms are not adjacent. The filled p orbilals of sulfur atoms, which are more expanded with respect to those of the oxygen atoms in the corresponding amides, could well enhance the energy level of the Z form of Et_4-DTO, but should leave quite unaffected the energy barrier between the two chiral enantiomers and the E isomer of tetraethyldithioxamide. If other factors are not taken into consideration, it is possible to think that an energy barrier, high enough to be responsible for the hindered rotation, could be a consequence of a more favourable electronic delocalization over each SCN fragment on cyanine distortion; Et_4-DTO being constituted of two coupled merocyanine-type moieties[3].

Following the above observations, the MoKα x-ray analysis was performed on a single crystal, revealing it to belong to the tetragonal system, characterized by a=b=7.878(2) Å and c=22.072(3) Å, with the two possible polar space groups $P4_3$ or $P4_1$, according to the systematic absences. The refined value 0.9(2) of the enantiomer Flack parameter[4] suggested clearly the right absolute configuration of the structure into the $P4_3$ space group for which the model refinement reached up to R=2.93 % and *w*R=3.76 %, with a data-to-parameter ratio 12:1.

The solid state structure determination (fig. 2) confirms all the spectroscopic expectations, showing two equivalent diethylthioamide fragments —CS-N(C-$)_2$ almost perfectly planar and placed orthogonal to each other, as evidenced by the value 89.8(3)º observed for the torsion angle S-C-C-S. The quite perfect sp^2 geometry of each nitrogen evidences the strong electron delocalization of the rigid S-C-N groups, characterized by longer C-S and shorter C-N distances with respect to the usual values for the corresponding un-conjugated bonds, while it clearly does not involve the dithionic SC—CS bond (1.493(4)Å).

A survey of the crystal structure data for either uncoordinated dithioxamides or diamides shows that in most of the compounds the NCS and NCO moieties are nearly coplanar. Notwithstanding, all the measured C-C bond lenghts are over 1.5 Å, thus proving the absence of S=C-C=S conjugation either in diamides or in dithioxamides, independently of the torsional angle about the C-C axis.

Et_4-DTO reacts either with the coordination compound cis-$(Me_2SO)_2PtCl_2$ or with the organometallic complexes cis-$(Me_2SO)PtR_2$ (R = Me, Ph), leading to (Et_4-DTO S,S' Pt)PtX_2 and (Et_4-DTO S,S' Pt)PtR_2 respectively.

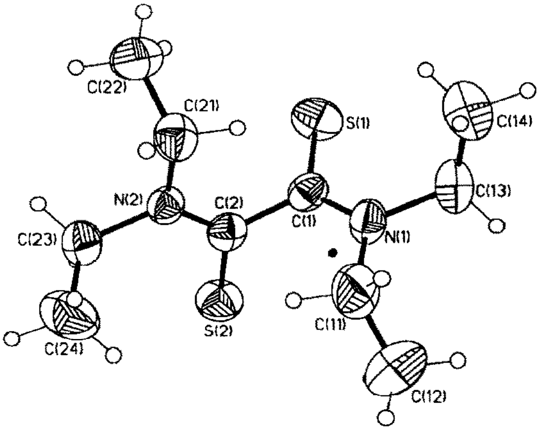

Fig 2. Perspective view of tetraethyldithioxamide with crystallographic numbering.

These compounds, dissolved in different solvents for either the solubility or stability reasons, gave ^{1}H-nmr spectra in which the double ABX_3 pattern for two non-equivalent prochiral ethyl groups was generally well evidenced[5] (fig. 3); hence Et_4-DTO, even when coordinated, retains its molecular distortion and has an high rotational barrier which does not allow a fast racemization (at least on nmr time scale).

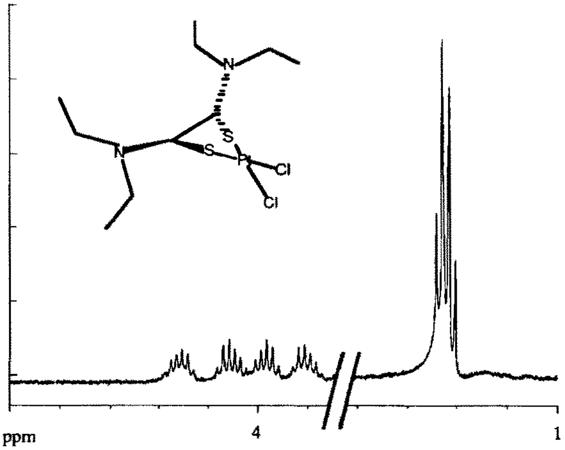

Fig. 3 ^{1}H NMR spectrum of (Et_4-DTO)$PtCl_2$ in d_7-DMF

Few reports concerning R_4-DTO metal complexes have appeared up to date[6,7]; in one of them[7] a dihedral angle of about 80° between the two NCS planes has been measured for $(Et_4\text{-DTO})Re(CO)_3Br$ which is the only R_4-DTO metal complex whose crystal structure has been determined. However, chirality was not evidenced either in the above complex or in other tetrasubstituted dithioxamides derivatives, at least to our knowledge. For this reason, we think that this particular aspect in the chemistry of tetrasubstituted dithiooxamide derivatives should be focused, on account of the importance of metal complexes of chiral chelate ligands in the asymmetric catalysis[8].

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5) (**a**) $[PtCl_2(Et_4DTO)]$ in dmf-d_7: $\delta = 1.43$ (t), $^3J_{HH} = 7.2$ Hz; $\delta = 1.46$(t), $^3J_{HH} = 7.2$ Hz (12H, methyl groups); $\delta = 3.80$ (dq), $^3J_{HH} = 7.2$ Hz; $^2J_{gem} = 13.8$ Hz; $\delta = 3.97$ (dq), $^3J_{HH} = 7.2$ Hz; $^2J_{gem} = 13.8$ Hz; $\delta = 4.10$ (dq), $^3J_{HH} = 7.2$ Hz; $^2J_{gem} = 13.3$ Hz; $\delta = 4.31$ (dq), $^3J_{HH} = 7.2$ Hz; $^2J_{gem} = 13.4$ Hz (8H, methylene groups); (**b**) $[Pt(CH_3)_2(Et_4DTO)]$ in C_6D_6: $\delta = 0.72$ (t), $^3J_{HH} = 7.2$ Hz; d = 0.84 (t), $^3J_{HH} = 7.2$ Hz (12H, methyl groups); $\delta = 2.12$(s), $^2J_{PtH} = 93.4$ Hz (6H, Pt-CH_3 groups); $\delta = 2.42$ (m), $^3J_{HH} = 7.2$ Hz (4H, methylene groups); $\delta = 2.55$(dq), $^3J_{HH} = 7.2$ Hz; $^2J_{gem} = 14.1$ Hz (2H, methylene group); $\delta = 2.81$ (dq), $^3J_{HH} = 7.2$ Hz; $^2J_{gem} = 14.1$ Hz (2H, methylene group); (**c**) $[Pt(C_6H_5)_2(Et_4DTO)]$ in C_6D_6: $\delta = 1.38$ (t), $^3J_{HH} = 7.2$ Hz; $\delta = 1.48$ (t), $^3J_{HH} = 7.2$ Hz (12H, methyl groups); $\delta = 3.51$ (multiplet, 6H, methylene protons); $\delta = 4.43$(dq), $^3J_{HH} = 7.2$ Hz; $^2J_{gem} = 13.5$ Hz (2H; methylene protons); $\delta = 6.94$ (m) (6H, meta and para aromatic protons); $\delta = 7.39$ (m), $^3J_{PtH} = 83.5$ Hz (4H, orto aromatic protons).

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