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On the Synthesis of M(LH)$_2$ Complexes of Planar Dithiooxamides by Solid State Reactions of (M(LH$_2$)$_2$X$_2$ Salts in NaF

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Introduction

Planar dithiooxamides form stable M(LH$_2$)$_2$X$_2$ complexes [M = Pd, Pt [1], M = Ni [2]] in acid media. In neutral media non-electrolyte M(LH)$_2$ complexes [M = Pd, Pt [3]] and polymeric nickel complexes [4, 5] are formed. In this article we present a method for preparing neutral M(LH)$_2$ complexes with planar dithiooxamides such as H$_2$NCSCSNH$_2$ (D.T.O.), RHNCSCSNH$_2$ (R.D.T.O.) and RHNCSCSNHR (R.R.D.T.O.) by reacting solid (M(LH$_2$)$_2$X$_2$ complexes with solid NaF.

Experimental

The ^{13}C-NMR spectra were obtained with a J.E.O.L. INM PFT-100 spectrometer operating at 25.15 MHz and equipped with a Texas Instrument 980 B computer for operating in the Fourier Transform mode.

Saturated CDCl$_3$ solutions of the compounds were used with TMS as internal standard, 8 K interferograms were accumulated with a spectral width of 6250 Hz, pulse width of 9 μs (45° flip angle) and pulse delay time of 2 s in the noise decoupling mode.

The i.r. spectra were recorded on a Perkin-Elmer 580 instrument. The compounds were pressed in KX-pellets and kept at different temperatures, spectra were taken directly after pressing the pellet, after one hour, four hours and eight hours. The halide substitution is complete after four times regrinding and repressing the original pellet at room temperature or keeping the original pellet at 80 °C for about 8 hours.

The i.r. measurements of the M(LH$_2$)$_2$X$_2$ compounds performed in nujol (1350–200 cm^{-1}) and perfluorolube (4000–1350 cm^{-1}), in KX disks (X the same halide as in the M(LH$_2$)$_2$X$_2$ complex) and in saturated CDCl$_3$ solutions are practically identical, proving that the same structures and associations prevail in those different phases. I.R. spectra from diluted CDCl$_3$ solutions give totally different i.r. spectra, due to different association and dissociation of the complexes [7].

TABLE I. ^{13}C N.M.R. Chemical Shifts of M(LH$_2$)$_2$Cl$_2$ and M(LH)$_2$ Complexes (LH$_2$ = iC$_4$H$_9$HNCSCSNHiC$_4$H$_9$) in Saturated CDCl$_3$ Solutions.

	CH$_3$	CH$_2$	CH	C=S (p.p.m. downfield from internal TMS
Ligand (LH$_2$)	20.38	54.80	27.47	184.63
Pd(LH$_2$)	20.58	56.01	28.44	180.41
Pd(LH$_2$)$_2$Cl$_2$	20.69	56.97	26.63	186.98
Pt(LH)$_2$	20.58	56.69	28.44	179.68
Pt(LH$_2$)$_2$Cl$_2$	20.57	57.64	26.57	186.74
Ni(LH$_2$)$_2$Cl$_2$	20.69	57.76	26.88	187.77

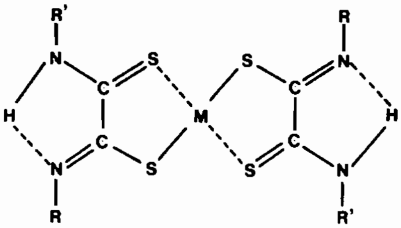

Fig. 1. Structure of the complexes and other mesomeric forms, H$_2$NCSCSNH$_2$ (D.T.O.) R = R'=H, R'HNCSCSNH$_2$ (R.D.T.O.) R = H; R' = alkyl. R'HNCSCSNHR (R.R.'.D.T.O.) R = R' = alkyl.

Results and Discussion

We have already reported on the novel structure of planar neutral dithiooxamide complexes with Pd(II) and Pt(II). ^{13}C-NMR [6], infra-red and electronic spectra [7] indicate a planar MS$_4$ symmetry and consequently a geometry as given in Fig. 1.

(M(LH$_2$)$_2$X$_2$ (M = Pd, Pt, Ni) complexes also show identical NMR shifts for the corresponding atoms in the four thioamide groups [7]. As an example we give the NMR data for L = iC$_4$H$_9$HNCSCSNHiC$_4$H$_9$ in Table I, the isobutyl group being chosen for solubility reasons. The MS$_4$ symmetry and the appearance of IR bands indicating an ammonium association of the type N$^+$–H···X$^-$ [7],

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TABLE II. I.r. Bands Liable to Hydrogen Bonding in Some $Pd(RHNCSCSNHR')X_2$ Complexes (in cm^{-1}).

$R = R', = CH_3$	(N^+H)	(N^+H)	Reference band
X = Cl	2800 ↑	845 ↑	637
Br	2835	802	637
I	2900	750	636
$R = H, R' = CH_3$			
X = Cl	2850 ↑	790 ↑	630
Br	2880	760	632
I	2970	737	633
R = R' = H			
X = Cl	2910		611
Br	3000		614

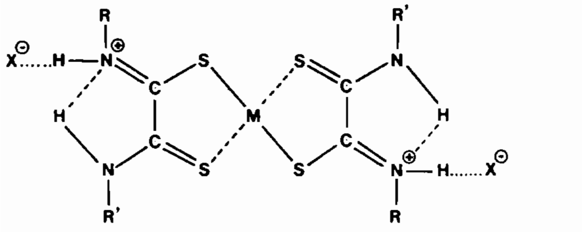

Fig. 2. Structure of hydrogen bonded forms (and other mesomeric forms).

allows us to propose a structure for the $M(LH_2)_2X_2$ complexes as given in Fig. 2. Table II summarizes some pure NH frequencies as observed in the IR, the very same vibrations in the different halides are observed at different frequencies and also vary in their relative intensities; their trend of change is given in Table II by the arrow indicating the increasing intensity. The strength of the H bonds is reflected in the extent of the shifting stretching vibrations, as expected, to lower frequencies whereas the bending modes are shifted to higher frequencies. It can indeed be noticed from Table II that the strength of the H bonds is in the sequence $I^- < Br^- < Cl^-$ and similarly the weakest for the dithiooxamides (D.T.O.) and strongest for the disubstituted ones (R'.R.D.T.O.). The spectra of the deuteriated complexes [7] indicate pure vibrations for the bands assigned to the $\nu(N^+H)$ and $\pi(N^+H)$ modes and mixed vibrations for the bands with high $\delta(N^+H)$ character. In Table II we only show the data for the pure vibrations. The intensities are measured relative to the sharp intense band appearing for all the products in the 600–650 cm^{-1} region, assignable to a vibration with high νCS character. From the i.r. spectra it can be seen that in the $M(LH_2)_2X_2$ compounds, we can substitute the halide anion at room temperature simply by pressing the product in another alkali halide matrix, according to the following reaction:

$$M(LH_2)_2X_2 + 2KX' \rightarrow M(LH_2)_2X'_2 + 2KX$$

LH_2 = [RHNCSCSNHR', R,R' = H or alkyl] (X, X' = Cl, Br, I). The halide exchange is solely dependent on the ratio of the solid reactants, in approximately hundred fold excess in the KX. Nothwithstanding the type of the halogen, a heavier halide can be exchanged by a lighter one and *vice versa.* When $Pd(LH_2)_2X_2$ was pressed in NaF matrix, we expected the $Pd(LH_2)_2F_2$ to be formed with exceptionally strong $N^+–H\cdots F^-$ associations, but instead we observed in the IR the spectrum of $Pd(LH)_2$.

The complex has been extracted with $CHCl_3$ from the grinded powder of the pellet, in order to perform analytical determination of the metal and the halide. In the extracted compound no halides were found.

The formation of the neutral $Pd(LH)_2$ can be explained by assuming as a first step the formation of a fluoride, $Pd(LH_2)_2F_2$. However the $F^-\cdots H–N^+$ bonds are so strong that HF is formed and eliminated. The HF is then captured by NaF forming $NaHF_2$. The formation of $NaHF_2$ is proved by observing in the IR spectrum the typical frequencies of this compound, namely the 2100 cm^{-1}, the broad 1600 cm^{-1}, the 1200 cm^{-1} and the weak 730 cm^{-1} bands [8].

$$M(LH_2)_2X_2 + 2NaF \rightarrow [M(LH_2)_2F_2] + 2NaX$$

$$[M(LH_2)_2F_2] \rightarrow M(LH)_2 + 2HF$$

$$2HF + 2NaF \rightarrow 2NaHF_2$$

The IR bands of $NaHF_2$ disappear from the spectrum on heating the pellet at about 80 °C. The formation of $Pd(LH)_2$ proceeds faster at higher temperatures, or for products with the strongest hydrogen bonds. So the reaction proceeds faster in the following sequences $I^- < Cl^- < Br^-$ and D.T.O. < R.D.T.O. < R.R.D.T.O.

The Pd(II) and Pt(II) Complexes

$M(LH)_2$ complexes can be formed by adding the metal to an alcoholic solution of the ligand (LH_2) at pH = 7.

The identical N.M.R. and i.r. spectra obtained for $M(LH)_2$ where M = Pd, Pt and LH_2 = D.T.O., R.D.T.O. and R.R'.D.T.O., whether prepared at pH = 7 or prepared from the electrolyte $M(LH_2)_2X_2$ by reaction with NaF, prove that this method can indeed be applied for synthesizing planar dithiooxamide complexes.

The Ni(II) Complexes

Hitherto to $Ni(LH)_2$ complexes have been formed with planar dithiooxamides. In acid media the $Ni(LH_2)_2X_2$ complexes are formed. The NMR data in Table I and the i.r. spectra, which are practically identical to the spectra of the Pd and Pt complexes permit us to propose an analogous structure. However in neutral and basic media, polymeric complexes and no $Ni(LH)_2$ compounds are formed [4, 5].

NMR, infrared and conductivity measurements [7] indicate an equilibrium dissociation of the complex in dilute solutions; this has also been observed for the Pd- and Pt-compounds. The complex dissociates according to the following reaction:

$$M(LH_2)_2X_2 \underset{\text{dilution}}{\rightleftarrows} MX_2 + 2LH_2$$

On heating the $Ni(LH_2)_2X_2$ complex we obtained the acid, the free ligand LH_2 and the polymer $(NiL)_x$ and no $Ni(LH)_2$. The pure $Ni(LH)_2$ complex formed from $Ni(LH_2)_2X_2$ in the NaF pellets could not be extracted from the NaF pellet with $CDCl_3$, as the product decomposes to form the ligand LH_2 and the polymeric $(NiL)_x$ complex. This can be explained by the fact that Ni is a harder acid than Pd and Pt, so the MS_4 coordination is no more self evident and an S,N coordination, giving a harder interaction with nickel, results in the formation of the polymer form [4].

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