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Complexes of chelates of amides and thioamides

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Abstract - Some complexes of planar oxamides, dithiooxamides and monothiooxamides with general formula RHNCXCYNHR' (where X and Y are S and for O, R and R' are H and/or alkyl groups) are described.
The synthesis, chemical properties, N.M.R. and T.G.A. results are given. Special attention is given to the vibrational spectra.

INTRODUCTION

The advantages of F.T.I.R. over Dispersive Infrared Spectroscopy are well known (Jacquinot, Felgett). These advantages when combined with a series of specially designed accessories (DRIFTS Diffuse Reflectance Infrared Fourier Transform Spectroscopy) have allowed many new and novel applications of infrared spectroscopy.

Conventional laser Raman spectroscopy has significant limitations. The main problem is that fluorescence often occurs, and even if weak it is sometimes enough to obscure the Raman signals which are extremely weak. A second problem is excessive heating and photochemical dissociation with absorbing samples. Calibration and the low resolution are other problems in the conventional laser Raman spectroscopy. These problems can now be addressed by Fourier transform Raman spectroscopy, using near infrared excitation (Nd-YAg laser).

The introduction of F.T. infrared and Raman spectroscopy must result in a RENAISSANCE of vibrational spectroscopy. This technique is much more than a method for specification. We want to emphasize that a throughough analysis of the combined spectra allows important structural and chemical data to be obtained.

Most molecular geometries of the complexes under investigation have been predicted from the vibrational spectra, where other possible structures could be excluded. The vibrational spectra also give important information on the nature of the chemical bonding (bond strenght, hydrogen bonding, trans-effect) in these complexes.

DESCRIPTION OF COMPLEXES

NN' dihydroxy ehtyldithiooxamide [$HO(CH_2)_2NHCSCSNH(CH_2)_2OH$] exhibits two ν(OH) bands in the infrared spectrum. This is in agreement with the crystallographic structure, which proposes that the unit cell of the compound consists of two independent molecules with two different O---O distances (2.721 Å and 2.785 Å). (1)

This molecule exhibits both intra- and intermolecular hydrogen bonding. The N–H---S hydrogen bonding is intramolecular and practically no change is observed in the different aggregation states. The O–H---O hydrogen bonds are intermolecular and O–H---dioxane associations are observed in dioxane solution, whilst in CS_2 the free ν(OH) is observed). The infrared spectra of the high frequency region is given in Fig. 1.
Even when the product is not at all soluble we can distinguish between the different hydrogen bonds by taking the infrared spectra at different temperatures. Fig. 2 shows the high frequency region of this ligand at 20°C and -200°C. The intermolecular O–H---O hydrogen bands shift to lower frequency by cooling, whilst the intramolecular N–H---S band at about 3200 cm^{-1} is unaffected.

Dithiooxamides form $M(LH)_2$ complexes with Pd^{2+} and Pt^{2+} in neutral media. The structure of the $Pd(LH)_2$ (LH_2 = NN' dicyclohexyldithiooxamide) is given in fig. 3. (2) The molecule has crystallographically-imposed C_i symmetry with the metal atom lying at the inversion centre, which requires the PdS_4 moiety to be planar in a nearly idealized D_{4h} symmetry. The thioamide groups in the ligand are nearly coplanar with very small torsional angles (0.8° to 2.7°) about the central carbon-carbon bond. (3) (4)
This planar conformation of the ligand is indeed the most suitable for an intramolecular hydrogen bonding between the thioamide nitrogen atoms, which has been confirmed by the infrared spectrum (νNH = 3190 cm^{-1}). (5)

Proton and ^{13}C n.m.r. spectra were used previously (6) to prove that, in these 2/1 complexes, the ligand is coordinated through both sulfur atoms. The ^{13}C n.m.r. spectra of the complex in the solid state exhibits two signals for the four C atoms (191 ppm for the protonated and 168 ppm for the deprotonated thioamide C-atom) and only one signal for the complex in solution (180.5 ppm). From this we can assume that a rearrangement of the hydrogen atom in the fluxional complex occurs rather fast in solution. This indicates that the energy barrier between the undeprotonated and deprotonated thioamide forms is lowered in solution and we can consequently consider the unique thioamide proton as located at both nitrogen atoms with half occupancy factors.

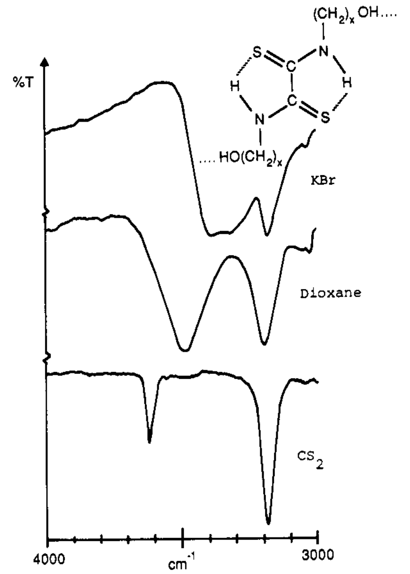


Fig. 1

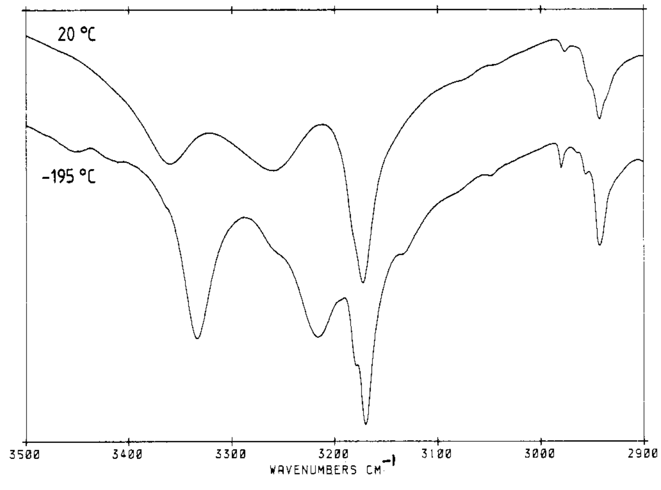


Fig. 2

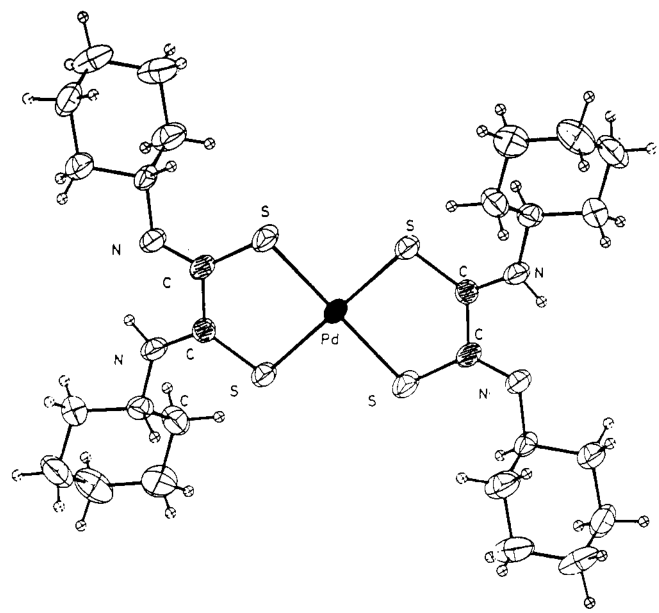


Fig. 3

$M(LH_2)_2X_2$ complexes are formed with Pd^{2+}, Pt^{2+}, Cu^{2+}, Ni^{2+} in strong HX media. The structure of $Cu(LH_2)_2(ClO_4)_2$ (LH_2 = NN' dibenzyldithiooxamide) is given in Fig. 4.

The complex has the $Cu(LH_2)_2^{2+}$ cation and two ClO_4^- anions each interacting through hydrogen bonds. (7, 8, 9) The coordination is closely related to that observed for the neutral $M(LH)_2$ complexes. The closest approach to the octahedral coordination sites of the copper ion is 3.07 Å and is consequently too great to be involved in even weak coordination to the metal atom. Similar spectra and the fact that the halide ions can be exchanged in a matrix let us conclude that also the halide ions are not involved in the coordination to the metal (10). The SS geometry in the undeprotonated complex requires a torsional mode about the carbon-carbon bond between the two planar thioamide groups (θ = 36.3°). The intense ν(CC) observed for the planar $M(LH_2)$ complexes at about 1050 cm^{-1} shifts to the 850 cm^{-1} region when the ligand is no more planar. A completely planar complex for the $M(LH_2)_2X_2$ would result in a non-bonded H---H distance of about 1.40 Å between the two thioamide protons. As a consequence there is relevant distorsion of the five-membered chelate ring (-0.159 to 0.173 Å). The corresponding deviations in the completely planar $M(LH)_2$ complexes are in the range -0.044 to 0.082 Å .

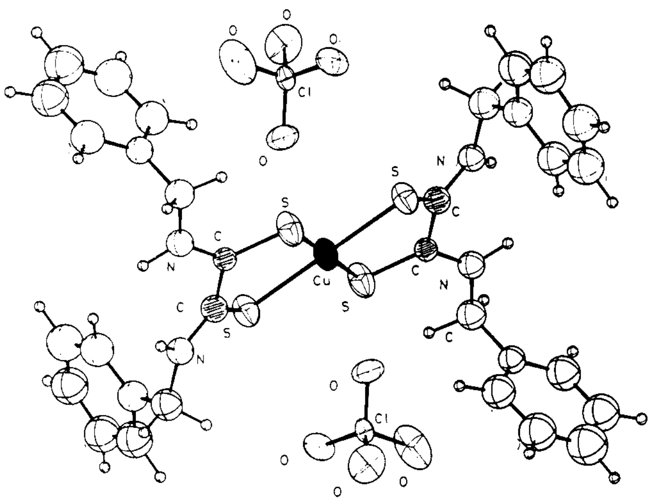


Fig. 4

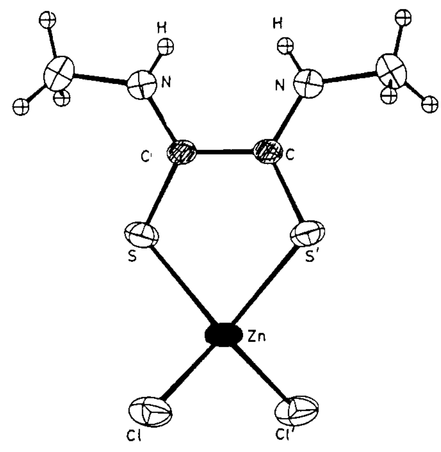


Fig. 5

Infrared spectra in the solid state and in highly concentrated $CDCl_3$ solutions are practically identical, proving that the same structures and associations previal in these different phases. The fact that hydrogen bonding stabilises these structures is indicated by the decomposition in dilute solutions according following reactions :

$$n\,M(LH_2)_2X_2 \rightarrow (ML)_n + nLH_2 + 2n\,HX \quad (M = Ni^{2+}, Cu^{2+})$$
$$M(LH_2)_2X_2 \rightarrow MX_2 + 2LH_2 \quad (M = Pt^{2+}, Pd^{2+})$$

From the infrared study we can also learn that in these $M(LH_2)_2X_2$ complexes we can substitute the counter ion, simply by pressing the product in another alkali halide matrix. (10)

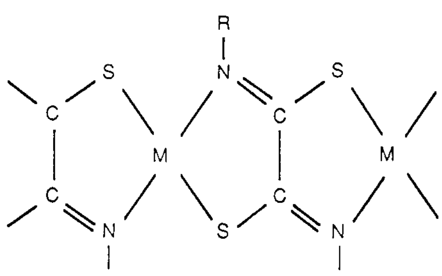
$$M(LH_2)_2X_2 + 2KX' \rightarrow M(LH_2)_2X_2' + 2KX$$

This halide exchange is solely dependent on the ratio of the solid reactants, in approximately hundred fold excess in the KX. When $Pd(LH_2)_2X_2$ was pressed in NaF matrix we expect the $Pd(LH_2)_2F_2$ to be formed with exceptionally strong N^+–H---F^- associations, but instead we observe the spectrum of $Pd(LH)_2$ an $NaHF_2$. When $Ni(LH_2)_2X_2$ was pressed in NaF matrix the polymer $(NiL)_x$ $NaHF_2$ and the ligand LH_2 werd formed. These different reactions between Ni^{2+} and Pd^{2+} are explained by the fact that the $M(LH)_2$ complex is not stable for the Ni^{2+} as the Ni^{2+} is harder than Pd^{2+} and Pt^{2+}, so the MS_4 coordination is no more selfevident and the S, N coordination, giving a harder interaction with Ni^{2+} results in the formation of the polymer.

$M(LH_2)X_2$ complexes are formed with Pd^{2+}, Pt^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Hg^{2+} and Cd^{2+}.
The structure of $Zn(LH_2)Cl_2$ (LH_2 = NN' dimethyldithiooxamide) is given in Fig. 5.

The molecule has crystallographically-imposed C_2 symmetry with the metal ion lying on the two-fold axis which bisects the S–Zn–S and Cl–Zn–Cl angles. The metal exhibits tetrahedral geometry, being bonded to two chlorine atoms and one chelate which acts as SS donor. As the thioamide groups are not deprotonated, the chelate is more planar and a dihedral angle of 36.9° is observed between the two thioamide groups. Both the thioamide functions are involved in intermolecular hydrogen bonds with the chlorine atoms of other molecules. This intermolecular hydrogen bonding links the molecules into linear chains which parallel the b-axis. These chains are further separated by normal Van der Waals distances.

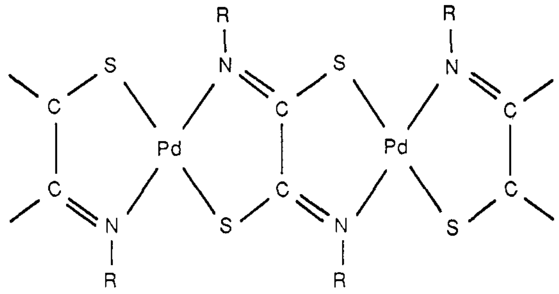
Infrared spectra indicate the following structure for the Ni^{2+} and Cu^{2+} polymeric complexes. (11) (12) (13)



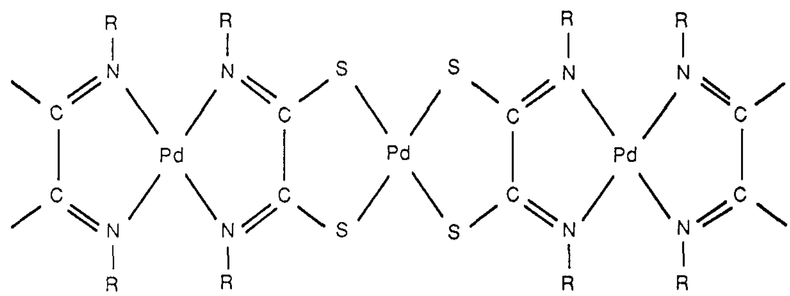
These proposed structures have further been confirmed by structural analysis. (14)

For Pd^{2+}, three different complexes can be prepared.

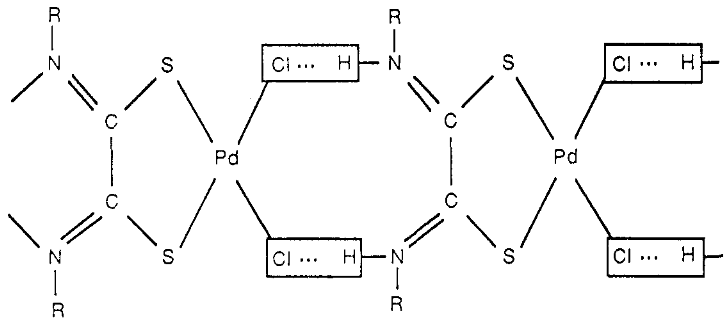
1. $Pd(ClO_4)_2$ forms with LH_2 at pH = 7 polymeric complexes which resemble the polymers formed for Ni^{2+} and Cu^{2+}.

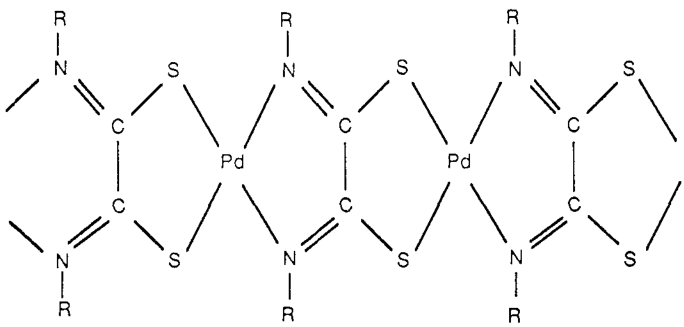


2. The planar $Pd(LH)_2$ complex reacts in alcalic media with Pd^{2+} with further deprotonation to give the following polymer.



3. $Pd(LH_2)X_2$ forms linear chains with intermolecular hydrogen bonds ; by heating these complexes two HX molecules are formed and a polymer different from 1 or 2 is formed.

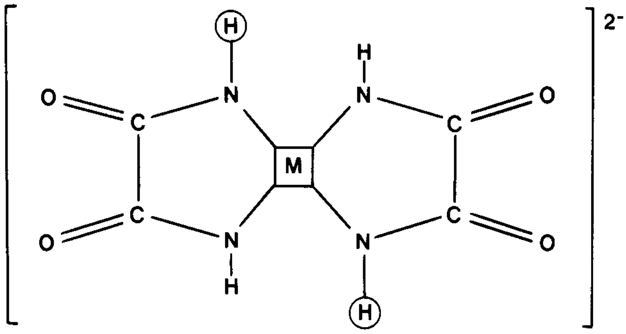




The growing interest in complexes of oxamic acid, oxamide and other simple amides and amino acids results from the fact that some have anti-tumor activity. For these complexes, structural studies (15) again confirm the molecular geometries proposed from the vibrational spectra. (16-20)

The planar oxamides generally form K_2ML_2 complexes for LH_2 = oxamide, only the "cis-secondary amide" functional group could be observed. From the i.r. and Raman spectra an inversion centre of the molecule could be derived so the following structure exhibiting the "cis" secondary amide group and having an inversion centre was proposed (Fig. 6).

Fig. 6



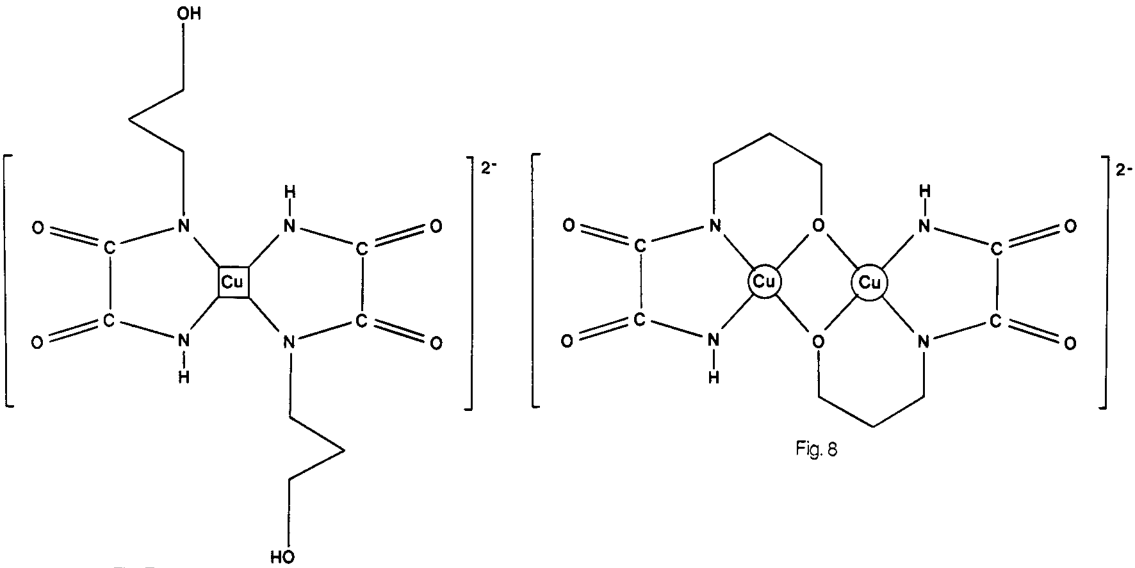
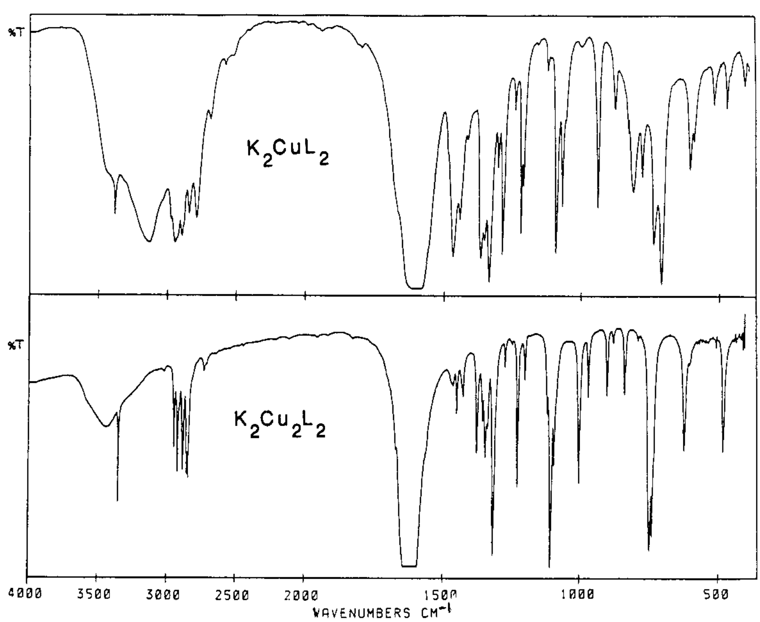


Fig. 7

Fig. 8

Special complexes have been synthesized for substituted oxamides where R = $-(CH_2)_n$ - OH or $-(CH_2)_n$ - NH_2.
When LH_2 = $RHNCOCONH_2$ (R = $-(CH_2)_3$ - OH) two different complexes can be formed.
K_2CuL_2 (Fig. 7) where the -OH group has no ineraction with the metal and the $K_2Cu_2L_2$ (Fig. 8) where the Cu is also coordinated through the oxygen by deprotonation. The difference between the two structures can clearly be observed in the infrared spectra (Fig. 9).

Fig. 9



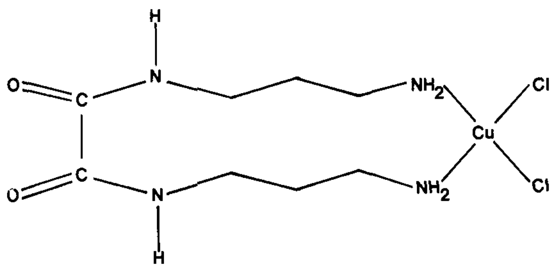


Fig. 10

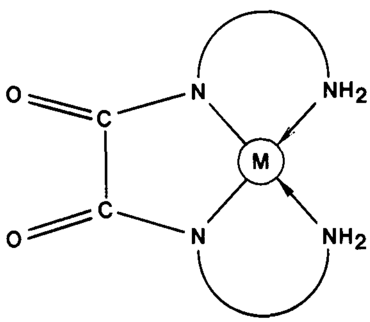


Fig. 12

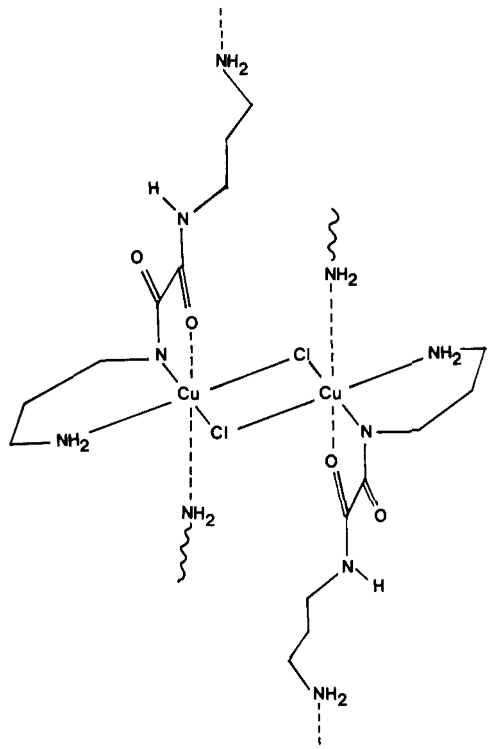


Fig. 11

With LH_2 = RHNCOCONHR (R–$(CH_2)_4$ - NH_2) three different complexes can be obtained in the solid state.
The LH_2CuCl_2 is given in Fig. 10. This complex is formed without deprotonation, the infrared spectrum shows the "cis secondary amide" group and the coordinated –NH_2 group.
The $(LH)_2Cu_2Cl_2$ complex is given in Fig. 11. This complex is formed in more alcalic media and gives one deprotonation per ligand. In the infrared spectrum we observe two different NH_2 groups (one free, one coordinated) Cu-halogen bridges, "trans-secondary amide" groups, coordinated carbonyl group.

The CuL complexes given in Fig. 12; This complex is formed in strong alcalic media and gives two deprotonations per ligand. In the infrared spectrum we observe coordinated NH_2 groups, no NH bands and the tertiary amide group.

Monothiooxamides can coordinate through the nitrogen and/or oxygen of the amide group and the sulfur and/or nitrogen of the thioamide group according the ligand, the pH and the metal, forming generally 2/1 or 1/1 polymeric complexes. (20)

REFERENCES

1. P. Geboes, H. Hofmans, H.O. Desseyn, R. Dommisse, A.T.H. Lenstra, Spectrochimica Acta 43A, 35 (1987).
2. L. Antolini, A.C. Fabretti, G. Franchini, L. Menabue, G.C. Pellacani, H.O. Desseyn, R. Dommisse, H.C. Hofmans, J. Chem. Soc. Dalton Trans., 1921 (1987).
3. H. Hofmans, H.O. Desseyn, A.T.H. Lenstra, Bull. Soc. Chim. Belg. 94, 705 (1985).
4. H. Hofmans, H.O. Desseyn, R. Dommisse, P. Van Nuffel, A.T.H. Lenstra, Transition Met. Chem. 9, 213 (1984).
5. H. Hofmans, H.O. Desseyn, A.J. Aarts, M.A. Herman, Bull. Soc. Chim. Belg. 91, 19 (1982).
6. R. Dommisse, A.J. Aarts, H.O. Desseyn, F.C. Alderweireldt, Bull. Soc. Chim. Belg. 88, 109 (1979).
7. H. Hofmans, H.O. Desseyn, M. Herman, Spectrochim. Acta 38A, 12, 1307 (1982).
8. H. Hofmans, H.O. Desseyn, R. Dommisse, Bull. Soc. Chim. Belg. 91, 3, 175 (1983).
9. H. Hofmans, H.O. Desseyn, Thermochimica Acta 85, 67 (1985).
10. H. Hofmans, H.O. Desseyn, J. Shamir, R. Dommisse, Inorganic Chim. Acta 54, L227 (1981).
11. H. Desseyn, W. Jacob, M.A. Herman, Spectrochim. Acta 25A, 1685 (1969).
12. H. Hofmans, H. Desseyn, M.A. Herman, Spectrochim. Acta 38A, 1213 (1982).
13. B. Slootmaekers, S.P. Perlepes, H.O. Desseyn, Spectrosc. Int. J. 4, 265 (1985).
14. M. Abboudi, A. Mosset, J. Galy, Inorganic Chemistry 24, 2091 (1985).
15. W. Van Riel, H. Desseyn, W. Van de Mieroop, A.T.H. Lenstra, Transition Met. Chem. 5, 330 (1980).
16. H. Desseyn, W. Van Riel, L. Van Haverbeke, A. Goeminne, Transition Met. Chem. 5, 88 (1980).
17. F. Quaeyhaegens, S.P. Perlepes, H. Desseyn, Spectrochim. Acta 43A, 917 (1987).
18. G. Schoeters, H.O. Desseyn, Spectrochim. Acta 39A, 71 (1983).
19. H. Desseyn, G. Schoeters, Bull. Soc. Chim. Belg. 95, 13 (1986).
20. S.P. Perlepes, P. Jacobs, H. Desseyn, J.M. Tsangaris, Spectrochim. Acta 43A, 771 (1987) ; 43A, 1007 (1987).