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Transition Metal Complexes with Pentatomic Heterocyclic Ligands Containing Nitrogen, Oxygen and Sulphur.
I. Copper Complexes

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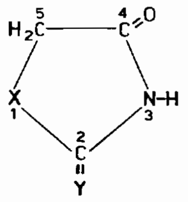
Abstract

The reaction of Cu(II) with the heterocyclic compounds rhodanine, thiohydantoin, pseudothiohydantoin and 2,4-thiazolidinedione were studied in non-aqueous media.

In the complexes obtained, characterized by elemental analysis, solid-state UV-Vis and IR spectroscopy and magnetic measurements, the ligands are present as neutral molecules, monodentate, and as bidentate anions, the donor atoms being sulphur and nitrogen. Structural oligomeric units containing four copper atoms (in the oxidation state +1) are proposed.

Introduction

Ligands of general formula:



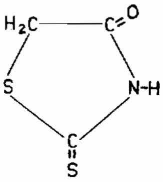
(X = NH, S)
(Y = NH, O, S)

are of great interest in the chemistry of coordination compounds since they can act either as neutral molecules or as deprotonated anions [1–3].

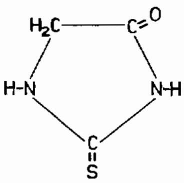
Furthermore, they possess in both forms more than one donor atom being potentially mono- or polydentate in the complexes. In the latter case they can give rise either to a chelate structure, each ligand molecule being coordinated to only one metal atom, or to a polynuclear structure, in which the ligand acts as bridging between two metal ions.

All the above reasons stimulated in the past the interest of many authors toward pentatomic heterocyclic ligands [4–8]. Complexes of several transition-metals have been prepared and characterized; the results obtained are not always unambiguous or in accordance with each other. We thought it therefore worthwhile to get a deeper knowledge of this field, and we started with the synthesis of copper complexes, because a systematic investigation on compounds of this metal was lacking, although other authors had previously prepared some of them [2, 4, 8].

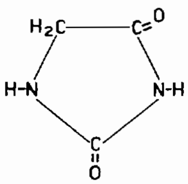
In particular, we studied the coordination reactions in non-aqueous solvents of copper(II) salts with the following ligands:



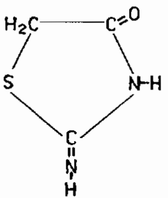
rhodanine



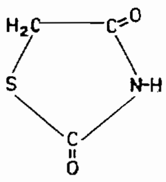
thiohydantoin



hydantoin



pseudothiohydantoin



2,4 thiazolidinedione

These ligands present redox properties [4, 8] wich can be conveniently pointed out by reaction with copper. Another interest of these reactions lies in the biological and pharmacological activity of the ligands [9], also in consideration of the presence and important role of copper in human blood [10].

For a better characterization of the electronic structure of these heterocyclic molecules we recently carried out a UV photoelectron spectroscopic (UPS) investigation [11], the results of which will be useful in the discussion of the bonding situation in the complexes.

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Experimental

Materials and Manipulations

All the ligands (Fluka and B.H.S.) and the solvents were of reagent grade and were purified before use [4].

Copper(II) toluenesulphonate was preferred to other Cu(II) salts because of the relatively low complexing ability of this anion. It was prepared as reported in the literature [12].

Preparation of Complexes

All syntheses were carried out at room temperature in air.

The rhodanine and thiohydantoin complexes were prepared by refluxing the anhydrous copper(II) toluensulphonate and the ligands in 1:2 molar ratio in absolute ETOH for 4 h. After cooling and filtering the solution, the residue obtained (black in each case) was washed with the solvent and dried *in vacuo.* Yield 60%; m.p. >300 °C; analytical data for the complexes of:

(a) rhodanine ($Cu_2C_{13}H_{12}N_2O_5S_5$)

Calcd. (%): Cu, 22.55; C, 27.70; H, 2.13; N, 4.97; O, 14.20; S, 28.41.

Found (%): Cu, 22.25; C, 27.40; H, 2.12; N, 5.03; O, 13.97; S, 29.08.

(b) thiohydantoin ($Cu_2C_{13}H_{14}N_4O_5S_3$)

Calcd. (%): Cu, 24.00; C, 29.48; H, 2.64; N, 10.58; O, 15.12; S, 18.14.

Found (%): Cu, 23.70; C, 29.24; H, 2.70; N, 10.50; O, 15.39; S, 18.09.

The 2,4-thiazolidinedione complex was prepared by refluxing the anhydrous Cu(II) toluensulphonate and pseudothiohydantoin in 1:2 molar ratio in ethylene dichloride and absolute ETOH (50:20cc) for 8 h. The resulting solution was cooled and filtered and the residue obtained (black) was washed with boiling ethylene dichloride and dried *in vacuo.* Yield 20%; m.p. >300 °C. *Anal.* Calcd. for $Cu_4C_{16}H_{14}N_3O_9S_4$: Cu, 32.85; C, 24.83; H, 1.60; N, 5.44; O, 18.60; S, 16.56. Found: Cu, 32.70; C, 24.04; H, 2.04; N, 5.81; O, 18.31; S, 16.56.

Attempts to prepare this compound starting from 2,4-thiazolidinedione were not successful.

We were unable to prepare hydantoin complex.

The same results were obtained in all cases by using different molar ratios (ligand/Cu > 2).

Measurements

Chemical analyses were performed by Alfred Bernhardt, Mikroanalytisches Laboratorium, Elbach, West Germany.

IR spectra were recorded on a Perkin-Elmer model 580 spectrophotometer using sodium chloride optics. For the far infrared region, cesium iodide optics were used. The spectra were recorded in Nujol in the region 4000–200 cm^{-1} and repeated in Fluorolube in the region 4000–2500 cm^{-1}.

Reflectance spectra were measured by a Beckman DK 1-A spectrophotometer.

The UV photoelectron spectra (He I) were recorded on a Perkin-Elmer PS-18 spectrometer. The samples, all solid at room temperature, were heated at temperatures ranging from 90 to 200 °C to get reasonably intense spectra of their vapours. Calibration was formed by Ar, CH_3I and self-ionizing He.

Magnetic susceptibilities were measured by the Gouy method at room temperature, using mercury(II)-tetrathiocyanato-cobalt(II) as a standard.

Properties

The obtained complexes are diamagnetic, consistent with a d^{10} configuration, and can be handled in air without evident decomposition. They decompose in water and are insoluble in common organic solvents, which suggests that they are polymeric with coordination of more than one ligand molecule to the metal atom. Stereochemistry of the complexes cannot be derived easily from diffuse reflectance spectra owing to the lack of d–d transitions. The general insolubility of the complexes precluded their study by means of NMR, molecular weight determinations etc.

Results and Discussion

Cu/Rhodanine

The results of the elemental analysis suggest for this compound the formula $[Cu_2(L)(LH)]A$, where A is the *p*-toluensulphonic anion, and L the deprotonated rhodanine anion. This implies that copper is present in the complex in the +1 oxidation state, as confirmed by experimental data. In fact, the complex is diamagnetic, and the visible spectrum run in solid state does not show any d–d band. Both results are consistent with the d^{10} electronic structure of Cu(I).

As a consequence of the 2:1 molar ratio between Cu and A, one of the two ligands present in the molecule of the complex is deprotonated, as requested by electroneutrality. On the other hand, the presence of the ligand in two different forms is confirmed both by UPS and IR measurements. In the experimental condition of the photoelectron spectroscopy (high temperature, low pressure) the complex decomposes, giving rise to a spectrum which we could unambiguously attribute to the rhodanine molecule previously studied in UPS [11]. The temperature at which such a spectrum appeared was close to the melting point of rhodanine; the spectrum was persistent and reproducible, ruling out the

TABLE I: The Major IR Absorption Bands (cm^{-1}) in the Range 4000–600 cm^{-1}.

	$\nu_{(NH)}$	$\nu_{(C=O)}$	$\nu_{(C=S)}$	$\nu_{(C=S)}$	$\nu_{(C-S)}$
rhodanine	3170ms 3080ms	1775ms 1710vs	1082s	820ms 784ms	680ms
Cu/rhodanine	2980w	1765sb 1710sb	1065w	818w 785w 725w 710sh	680ms
thiohydantoin	3282s 3195ms	1780m 1712s	1045m	890ms 765m	
Cu/thiohydantoin	3300w 3080ms	1780m 1750m 1700sh 1660s		880w 818m 765w 710s	

presence of free rhodanine as an impurity only. This result indicates the presence of at least one ligand in neutral form in each molecule of complex.

From the analysis of the IR spectrum of the complex in comparison with that one of the free ligand, already known [6, 7, 8, 13] but repeated in the present work, several important facts were obtained.

(i) In the IR spectrum of free rhodanine there are two $>$NH stretching bands, at 3170 and 3080 cm^{-1}, the latter being due to differential influences of hydrogen-bonds or other local interactions in the crystal lattice. This band disappears upon complexation, while the former one shifts 190 cm^{-1} to lower frequencies and decreases in intensity relative to the other bands: the negative shift points out that the $>$NH group is involved in coordination to the metal, and the decrease in intensity is probably due to the fact that part of the ligand is deprotonated in the complex.

(ii) The C=S stretching bands at 820 and 784 cm^{-1}, in the free ligand, are each split into two components in the complex, one remaining roughly at the same frequency, the other being shifted to lower frequencies (see Table I). This is a clear indication that in only one of the two forms of the ligand is the thiocarbonylic sulphur coordinated, giving rise to the negative shift of $\nu_{C=S}$. The bands remaining at the original frequencies arise from the uncoordinated C=S groups. The constancy of these frequencies with respect to those in free rhodanine suggests that the species which is not coordinated through the thionic sulphur is the neutral molecule: in the opposite case, in fact, $\nu_{C=S}$ should change due to the inductive effect following the deprotonation.

(iii) The stretching frequencies of the C=O group, at 1775 and 1710 cm^{-1}, practically do not change on passing from the free ligand to the complex, but a broadening of the bands is observed. The substantial constancy of $\nu_{C=O}$ suggests that this group is not involved in the coordination, which should imply a negative shift. Actually, a negative shift should occur anyway because of the deprotonation of the $>$NH group, but it is likely to be compensated by an opposite shift due to the coordination through the thionic sulphur. The broadening of these bands confirms the existence of the ligand in two different forms in the complex. The ν_{C-S} stretching involving cyclic sulphur is at 680 cm^{-1}, both in the free ligand and in the complex, ruling out the possibility that this atom acts as a donor towards copper.

From the experimental findings conclusions can be drawn on the bonding situation in the copper complex: nitrogen is involved in the coordination in the neutral species, as indicated by the negative shift of $\nu_{>N-H}$. Thiocarbonyl sulphur is involved in the coordination only in one of the two forms of the ligand, which from the experimental data we assume to be the anionic one (see point ii). This form is also coordinated through nitrogen, which shares with thionic sulphur the highest electron density. In the complex the neutral ligand molecule acts as monodentate coordinating through nitrogen, while the anion is bidentate, having nitrogen and exocyclic sulphur as donor atoms.

Cu/Thiohydantoin

This compound is analogous to Cu/rhodanine. In fact, elemental analysis indicates the same stoichiometry, with copper present as Cu(I), as confirmed by the magnetic measurements and the solid state UV–Vis. spectra.

Also the IR spectra (see Table I) present many

TABLE II. The Major IR Absorption Bands (cm^{-1}) in the Range 4000–600 cm^{-1}.

	$\nu(\rangle NH)_{cycl.}$	$(\nu_{=NH})_{exocycl.}$	$\nu_{(C=O)}$	$\nu_{(C-S)}$
2,4-thiazolidinedione	3130ms 3045ms		1775m 1735s 1680s 1650s	720s
pseudothiohydantoin	3385m 3100sb	3230ms	1690m 1655s	710s
Cu/2,4-thiazolidinedione			1780m 1745s 1680s 1650m	680s

common features. Of the two $\nu_{\rangle N-H}$ present in the spectrum of free thiohydantoin, the latter one at 3195 cm^{-1}, due to differential interactions in the lattice, disappears upon complexation, like in Cu/rhodanine. The former one, at 3282 cm^{-1}, is split into two components, one at practically the same frequency (3300 cm^{-1}), the other one at lower frequency (3080 cm^{-1}). The negative shift of this component is clearly due to the complexation of one of the two $\rangle$N–H groups, the former component accounting for the uncoordinated one. The observed decrease in intensity of this component with respect to free thiohydantoin is consistent with the above interpretation and with the partial deprotonation of the ligand in the complex, suggested by the stoichiometry. The $\nu_{C=S}$ and $\nu_{C=O}$ bands display a behaviour similar to that one in Cu/rhodanine, leading therefore to the same conclusions.

The experimental data indicate therefore that the bonding situation in Cu/thiohydantoin is analogous to that in Cu/rhodanine, with the metal bonded to the deprotonated ligand through nitrogen and sulphur and to the neutral ligand through nitrogen only.

Cu/2,4-thiazolidinedione

The analysis of the product obtained by reaction of Cu toluensulphonate with pseudothiohydantoin indicated the formula $[Cu_4L_3]A$, where copper is present as Cu(I) and L is 2,4-thiazolidinedione anion. The presence of this ligand in the complex molecule is confirmed also by the IR spectra (see Table II). In fact these do not show any stretching of either exo or endo-cyclic NH groups. Furthermore, there are four $\nu_{C=O}$ bands, at the same frequencies as in 2,4-thiazolidinedione, at variance with the pseudothiohydantoin, whose IR spectrum shows only two $\nu_{C=O}$ bands. These two observations strongly suggest that the exocyclic =NH group is hydrolysed in the complex into a C=O group, and that endocyclic $\rangle$NH is deprotonated upon coordination. The $\nu_{C=S}$ band shifts 40 cm^{-1} to lower frequencies, suggesting that sulphur is involved in the coordination. We conclude therefore that in this molecule the anionic ligand acts as bidentate, having sulphur and nitrogen (the latter for the reasons already discussed for the other complexes) as donor atoms.

A possible explanation for the formation of this complex by the pseudothiohydantoin, while it is not directly obtained by 2,4-thiazolidinedione, lies in the initial formation of the copper compound of the former ligand, followed by a rapid hydrolysis of the =N–H group, whose double bond is weakened by the electron-withdrawing activity of the neighbouring atoms involved in the coordination. The hydrolysing agent is in this case ethanol, which adds to the carbon atom bearing the =NH group with subsequent formation of $\rangle$C=O. It is significant that this complex is not obtained by direct reaction between the copper salt and 2,4-thiazolidinedione, which confirms that hydrolysis occurs not on the ligand but on the complex.

Conclusions

From the analysis of the experimental results a common behaviour of the ligands in these complexes is evident: they act as reducing agents towards copper, the oxidation product being unidentified.

As for the structure of the synthesized compounds, their insolubility in practically all the common organic solvents prevents crystallization, and therefore also precludes the possibility of clear-cut structural evidence. Hypotheses can however be put forward, starting with the following considerations:

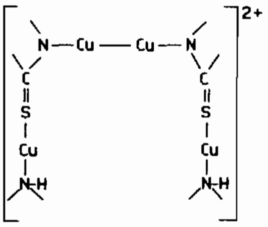
(i) the insolubility suggests a polymeric or oligomeric structure.

(ii) the ligands act in different ways according to their neutral or anionic state, *i.e.* as monodentate, respectively bidentate.

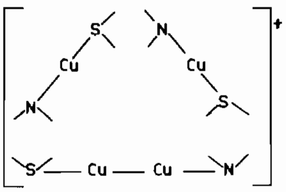
(iii) the rigid structure of the ligand molecules favours linear sp hybridization of copper.

(iv) it is unlikely that copper presents in the same molecule different coordination numbers.

For Cu/rhodanine and Cu/thiohydantoin we propose the existence of the structural unit:



For Cu/2,4-thiazolidinedione the structural unit of the complex can be formulated as:



In both cases the structural unit contains four copper atoms with coordination number 2, each bonded to donor atoms of different ligand molecules or, in one case, to another copper atom.

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