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Electronic Spectra of Cu(II) Crystal Complexes with S-methylthiosemicarbazones

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Electronic spectra for a series of coordination compounds of copper(II) with tridentant ligands of salicyl aldehyde S-methylthiosemicarbazone and 8-quinoline aldehyde S-methylthiosemicarbazone were investigated. Coordinations of central ions were determined on the basis of X-ray data and IR spectra. Electronic transitions were detected by processing the diffusion-reflection spectra according to the *Kubelka-Munk* theory. Identifications proved the presence of bands corresponding to intraligand transition, charge transfer spectra and the transition of d-d type which are the result of the elimination of d-orbital degeneration for Cu(II) ions in the crystal field. The effect of the symmetry of coordination polyhedrons is discussed.

[*Keywords: Copper(II); Crystal complexes; Electronic spectra*]

Elektronenspektren von Cu(II) *Kristall-Komplexen mit S-Methylthiosemicarbazonen*

Es wurden Elektronenspektren einer Serie von Koordinationsverbindungen des Kupfer(II) mit tridentaten Liganden (Salizylaldehyd-S-methylthiosemicarbazon und 8-Chinolinylaldehyd-S-methylthiosemicarbazon) untersucht. Die Zentralionkoordination wurde durch Röntgenstrahlenuntersuchungen und auf Grund der IR-Spektren festgestellt. Die Elektronenübergänge wurden nach der *Kubelka-Munk*-Theorie aus den diffusen Reflexionsspektren ermittelt. Die Banden wurden den Intraligandübergängen, dem charge-transfer-Spektrum und den d-d-Typ-Übergängen, die als Resultat der Entartungsbeseitigung der Cu(II)-d-Orbitale im Kristallfeld verschiedener Symmetrie entstehen, zugeschrieben.

Introduction

Synthesis of the coordination compounds of copper with tridentant ligands [salicyl aldehyde S-methylthiosemicarbazone (H_2*thsa*) and 8-

quinoline aldehyde S-methylthiosemicarbazone (H *thqua*)] was previously published [1–3].

Numerous detailed structural investigations undertaken during the past several years [4–7] have shown that the results published by *Malik* and *Philips* [8] were faulty concerning the way of coordination. Namely, tridentity of these ligands is not realized by means of the sulphur atom but exclusively by three nitrogen atoms for H *thqua* and by two nitrogen and the one of oxygen for H_2 *thsa.*

Results of spectral investigations of the following complexes are given in this paper:

Cu(H *thsa*)$X \cdot nH_2O$ (X = Cl, Br, NO_3, ClO_4);
Cu(H *thsa*)*Py*NO_3; Cu(H *thsa*) (*o-phen*)NO_3;
Cu(*thsa*)$NH_3 \cdot H_2O$ (1); Cu(H *thqua*) $(NO_3)_2$;
Cu(H *tqua*) (*o-phen*)$ClO_4 \cdot H_2O$; Cu(*thqua*)NH_3ClO_4;
Cu(H *thsa*) · $(H_2O\, NO_3) \cdot 0.5\, H_2O$

Copper(II) with its nine electrons in d-orbital allows (from the aspect of the theory of crystal field), to be treated as uni-hole model. Thus the effect of surrounding on the elimination of 3 d level degeneration could be more simply treated. This series of measurements has given great possibilities for the investigations of the characteristics of electronic transition bearing in mind the estimates for the point groups of symmetry obtained by the other methods.

Experimental

Diffusion-reflection spectra were measured on a monochromator SPM-2 (Zeiss-Jena) and reflection cell of the type R 45/0 at room temperature and within the interval 10 000 to 45 000 cm^{-1}. Samples were prepared to comply with the hypothesis of *Kubelka-Munk* [9]. MgO was used as white standard.

The diffusion reflection spectra are shown in Fig. 1 and Fig. 2. The obtained values of the *Kubelka-Munk* function for complexes are shown in Fig. 4 and Fig. 5.

IR spectra were recorded with a Carl-Zeiss model Specol IR 75 in KBr. X-ray diffraction of crystal powder was recordered with a PW 1965/50 (Philips) diffractometer using CuKα radiation.

Results and Discussion

In order to carry out detailed analyses of electronic spectra, the most probable structural formulae was first established for all investigated compounds applying some other methods. Complete structures of the compounds Cu(H *thsa*)*Py*NO_3; Cu(H *thsa*)(*o-phen*)NO_3; Cu(H *thsa*)Cl; Cu(H *thqua*)$(NO_3)_2$ and Cu(H *thsa*)$NO_3 \cdot H_2O$ were determined by diffraction investigations of monocrystalline forms [4–7, 10].

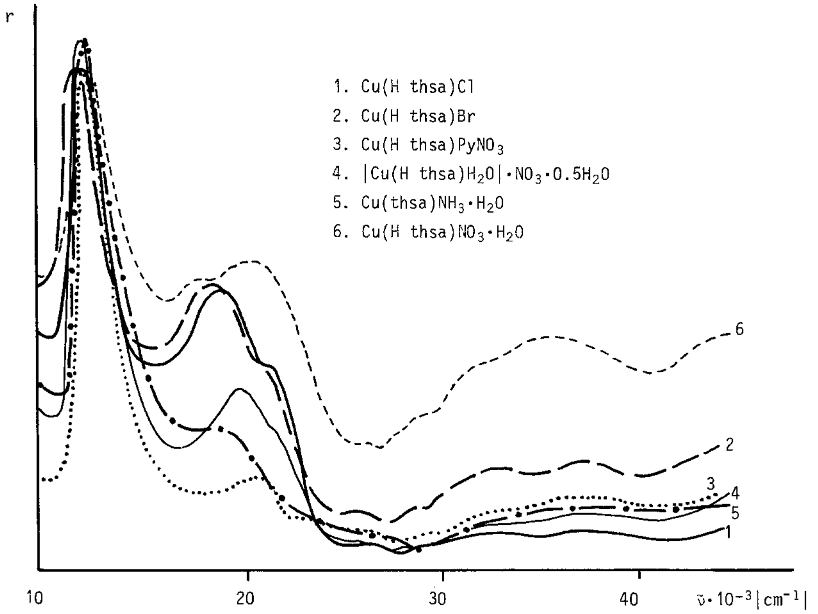


Fig. 1. Reflection spectra of square planar complexes; ordinate: $r = R_{\text{sample}}/R_{\text{stand.}}$

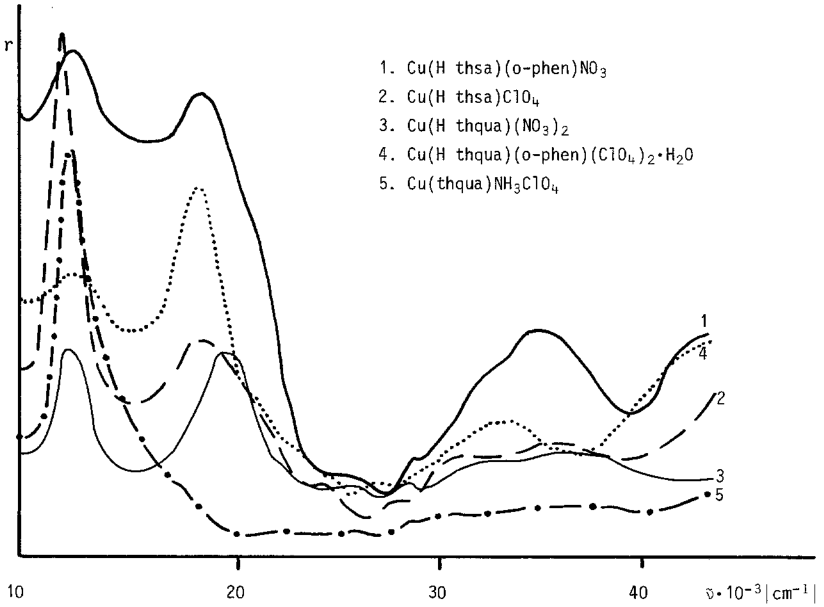


Fig. 2. Reflection spectra of square pyramidal complexes; ordinate: $r = R_{\text{sample}}/R_{\text{stand.}}$

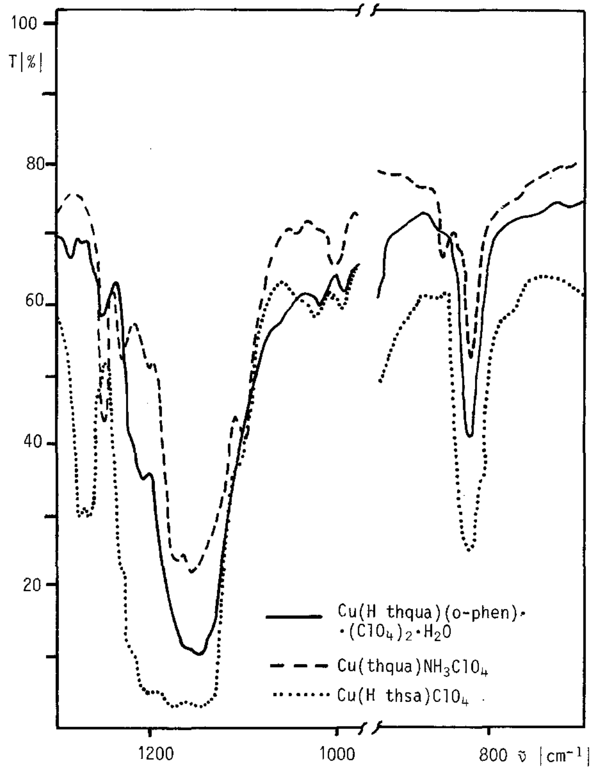


Fig. 3. IR spectra of [Cu(H *thqua*)(*o-phen*)]$(ClO_4)_2 \cdot H_2O$, Cu(H *thqua*)NH_3ClO_4, and Cu(H *thsa*)ClO_4 in the characteristic range

Diffractograms obtained for the powders of Cu(H *thsa*)Cl and Cu(H *thsa*)Br indicated two isostructural complexes. It was obvious that they were not completely isomorphic, but it is possible to conclude with some confidence that their structural formulae are analogous.

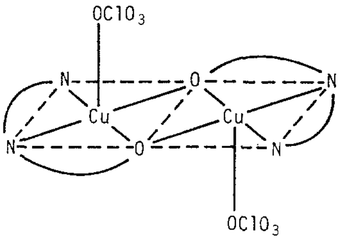
As the reflection spectrum of the complex [Cu(H *thsa*)H_2O]$NO_3 \cdot 0.5\,H_2O$ indicated square planar coordination of the central copper ion, there were two possibilites for the occupation of the fourth coordination position. It was necessary to decide whether the nitrate group or the water molecule was the one that occupied this coordination position beside the tridentant ligand (H *thsa*).

According to IR spectra of Cu(H *thsa*)*Py*$\cdot NO_3$ and Cu(H *thsa*)$H_2ONO_3 \cdot 0.5\,H_2O$ the position of the characteristic bands at 1 385 cm^{-1}, 1 042 cm^{-1}, and 827 cm^{-1} indicated the ionic feature of the nitrate group for both compounds.

In the case of [(Cu(H *thqua*)(*o-phen*)]$(ClO_4)_2 \cdot H_2O$, Cu(H *thqua*)NH_3ClO_4, and Cu(H *thsa*)ClO_4 the question arises whether the ClO_4 group participates in the coordination or not. IR spectra in the characteristic range of these complexes are given in Fig. 3.

Characteristic absorption bands for the ClO_4 group were at 1 040–1 150 cm^{-1} and 600–630 cm^{-1}. Intensive wide bands for [Cu(H *thqa*) (*o-phen*)]$ClO_4 \cdot H_2O$ indicate the characteristics of ionically bound ClO_4 group. On the other hand, an extremely remarkable resolution of the basic band for Cu(*thqua*)NH_3ClO_4 suggests that the ClO_4 group participates the coordination. Taking into account all these moments, as well as the fact that the electronic spectra indicate that the shape of the coordination polyhedron is the square pyramide, it was concluded that the fifth coordinative position is occupied by one oxygen atom of the ClO_4 group.

In the case of the Cu(H *tsa*)ClO_4 complex the situation is far more complex. The IR spectrum indicates the probable coordination of ClO_4, although this conclusion may be criticised. However, an electronic spectrum indicates characteristics of coordination number five, which could be the result of one specific effect. Namely, the value of the magnetic moment of only 1.01 μB indicates that the copper atoms are mutually coupled.



The appearance of one remarkable peak for Cu(H *tsa*)$NO_3 \cdot H_2O$ at 1 357 cm^{-1} gives the basis for NH_3 group to be considered coordinated [11].

According to these considerations it is possible to conclude that the investigated complexes have a surrounding with the coordination numbers 4 and 5.

Figure 4 gives the *Kubelka-Munk* functions for the complexes with the coordination number 4.

Distribution of the maxima and the intensities of individual bands indicate the same types of coordination polyhedrons for all these compounds. Taking into account that the deformed square planary coordination of these central ions is explicitely determined for Cu(H y*thsa*)Cl, Cu(H *thsa*)*Py*NO_3, and Cu(H *thsa*)$NO_3 \cdot H_2O$, such

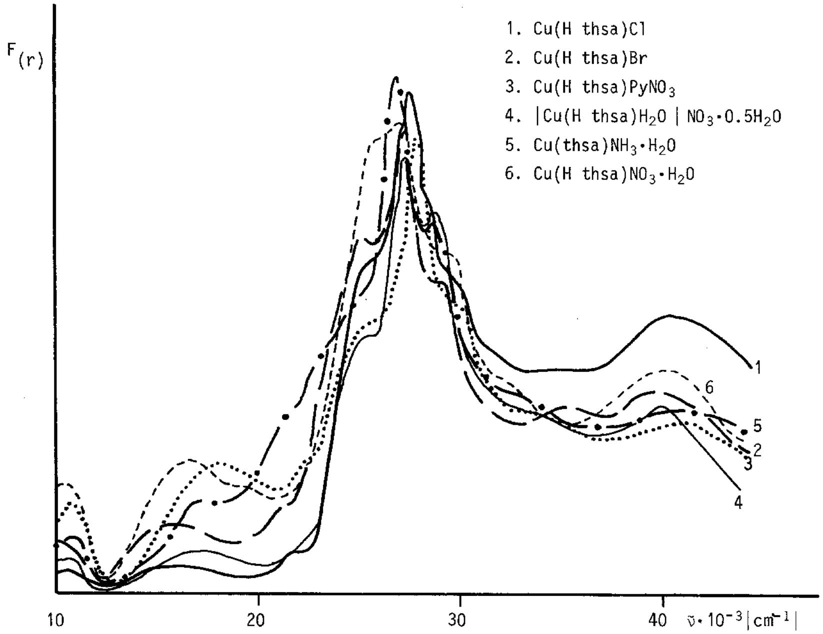


Fig. 4. *Kubelka-Munk* function $F_{(r)}$ for the square planar complexes: $F_{(r)} = (1-r)^2/2r$

coordination could be also ascribed to the other compounds of this group: Cu(H *thsa*)Br, [Cu(H *thsa*)$\cdot H_2O$]$\cdot NO_3 \cdot 0.5\,H_2O$, and Cu(*thsa*)$NH_3 \cdot H_2O$.

Figure 5 shows the *Kubelka-Munk* function for the complexes with the coordination number 5.

Distribution of the maxima and the intensities of individual bands indicate for all these compounds the same types of coordination polyhedrons, but this time (according to X-ray investigations Cu(H *thsa*)(*o-phen*)NO_3 [4] and Cu(H *thqua*)$(NO_3)_2$ [5] in the shape of a deformed square pyramide.

X-ray investigations gave the detailed data on some of the mentioned coordination polyhedrons.

Cu(II) is located in the basic plane at square planary coordination with a deviation smaller than 0.02 Å. When the polyhedron is a square pyramide, the central atom is transfered toward the top of pyramide for maximally 0.15 Å [4].

It was established that the distances between the central ion Cu(II) and the coordinated atoms are in an interval from 1.888 Å up to 2.230 Å for square planary complexes [7, 10]. In the case of surrounding in the shape

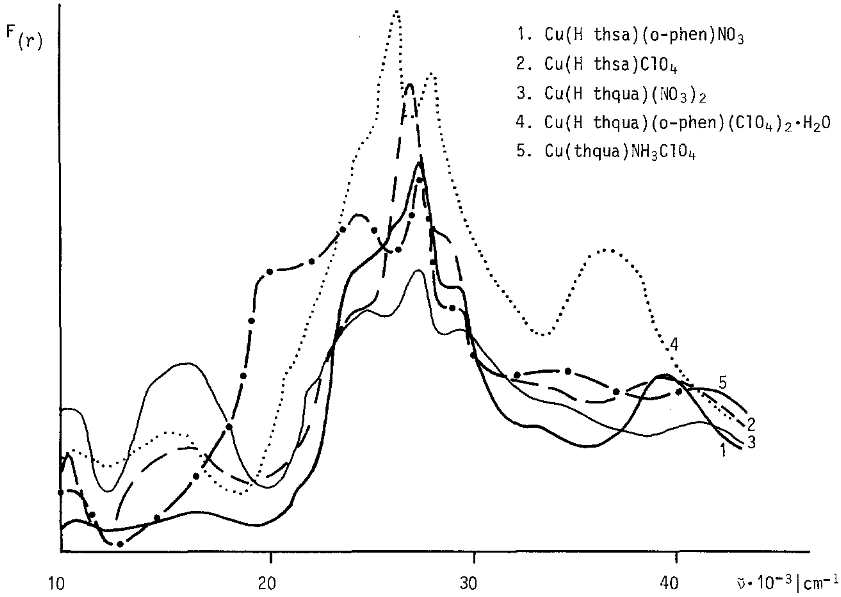


Fig. 5. *Kubelka-Munk* function $F_{(r)}$ for the square pyramidal complexes: $F_{(r)} = (1-r)^2/2r$

of a square pyramide the coordinated atoms in the basal plane were at a distance of 1.927 Å–2.022 Å from Cu(II) [4].

N atoms which are on the top of pyramides are at a distance of 2.261 Å [4] and 2.312 Å [5] from the central metal ion.

Considering the determined values for distances and angles it could be established that both types of the coordination polyhedrons are significantly deformed. Therefore, instead of D_{4h}, C_{4v} as a lower point group of symmetry was effectively present. From the analyses of electronic spectra it was concluded that the number of absorption maxima corresponds to the one obtained by the symmetry of C_{2v} according to the selection rules. It was assumed that this point group was approximatively present both at square planary and square pyramidal complexes, because all electronic spectra were obviously of the same type.

By means of electronic spectra obtained for the investigated complexes (Fig. 4 and Fig. 5) it is possible to assign three types of transitions: 1) d-d transitions, 2) charge transfer (CT) and 3) intraligand transition (IL).

Maxima that correspond to intraligand transitions were identified by comparing the spectra of this complex with the one formerly registered for the free ligand [12]. It is obvious from Tables 1 and 2 that the position of intraligand bands for all complexes are very close.

Spectra of the Square Planary Complexes

d-d transitions for the square planary complexes of Cu(II) were interpreted in accordance with the separation scheme for 3 d orbitals at successive lowering the symmetry from the point group D_{4h} to C_{2v}. According to the selection rules, transitions from the lowest level $d_{x^2-y^2}$ to d_{z^2} (1), d_{xz} (2), and d_{yz} (3) are expected and in electronic spectra they are registered by three bands. Positions of these bands for the square planary complexes (Fig. 4) are given in Table 1.

Table 1. *Maxima of electronic spectra for square planary complexes*

	$\tilde{\nu} \times 10^{-3}$ [cm^{-1}]							
	d-d			CT			IL	
Complex	1	2	3	CT_1	CT_2	CT_3	I	II
Cu(H *thsa*)Cl	10.1	15.8	21.9	25.2	29.4	33.9	27.4	40.2
Cu(H *thsa*)Br	10.3	15.6	22.1	25.2	29.4	34.0	27.5	40.2
Cu(H *thsa*)*Py*NO_3	10.6	17.7	23.5	23.8	29.6	34.6	27.6	40.2
[Cu(H *thsa*)H_2O]$\cdot NO_3 \cdot 0.5\,H_2O$	10.5	17.4	23.4	24.4	29.9	34.6	27.7	40.5
Cu(*thsa*)$NH_3 \cdot H_2O$	10.4	17.6	23.3	24.4	29.4	34.5	27.6	40.8
Cu(H *thsa*)$NO_3 \cdot H_2O$	10.7	16.5	19.5	25.5	29.6	32.6	27.0	40.0

An interpretation of the charge transfer spectra has to consider some ligand orbitals too beside the 3 d orbitals of Cu(II).

Charge transfer bands CT_1, CT_2, CT_3 (positions are given in Table 1) could be explained by electronic transition from the ligand π_L orbital to d_{z^2}, d_{xz}, and d_{yz} respectively. The π_L orbital corresponds most probably to the ligand N, i.e. N and O atoms which enter the coordination as already has been explained in [13]. CT $\pi_L \rightarrow d_{x^2-y^2}$ was not detected because it affords an energy below 10000 cm^{-1}. Analyzing the Table 1 it was possible to notice that the distance between CT bands CT_1, CT_2, and CT_3, is equivalent to the distances of d-d bands, which implies the probable correctness of this model.

Spectra of the Square Pyramidal Complexes

Interpretation of d-d spectra of these complexes was given according to the separation scheme for 3 d levels in point group C_{2v} obtained by lowering the symmetry from C_{4v}.

The lowest d-level is now d_{z^2}, whereas d-d transitions are now d_{x-y} (1), d_{yz} (2), and d_{xz} (3). Positions of the corresponding spectral bands from Fig. 5 are given in Table 2.

Table 2. *Maxima of electronic spectra for square pyramidal complexes*

	$\tilde{\nu} \times 10^{-3}$ [cm^{-1}]							
	d-d			CT			IL	
Complex	1	2	3	CT_1	CT_2	CT_3	I	II
Cu(H *thsa*)(*o-phen*)NO_3	10.4	15.9	21.6	24.9	30.1	34.2	27.7	39.9
Cu(H *thsa*)ClO_4	10.3	15.9	21.8	24.6	29.7	34.1	27.6	40.4
Cu(H *thqua*)$(NO_3)_2$	10.2	15.8	22.3	25.1	30.0	34.9	27.4	40.6
Cu(H *thqua*)(*o-phen*)$(ClO_4)_2 \cdot H_2O$	10.4	15.6	21.8	24.8	29.6	34.1	27.6	39.5
Cu(*thqua*)NH_3ClO_4	10.4	16.4	22.0	24.8	29.6	34.3	27.7	40.4

CT spectra CT_1, CT_2, CT_3 (Table 2) for these complexes are interpreted by electron transition from ligand π_L orbital to $d_{x^2-y^2}$, d_{yz}, and d_{xz}, respectively.

Therefore is possible to conclude generally that the effective point group of symmetry in all samples could be reduced to C_{2v}, concerning orbital symmetry and the corresponding selection rules. However, the level distribution involves also the characteristics of slightly higher symmetries, which approximatively correspond to the point groups D_{4h} and C_{4v}, i.e. the characteristic point groups for the regular square-planar and square pyramidal coordination.

It is noticed that d-d transitions, designated by 2 and 3, indicate slightly greater energies at square planarity than at square pyramidal coordination. Exceptions are the complexes Cu(H *thsa*)Cl and Cu(H *thsa*)Br where the effect of halogenic elements causes a significant deviation from the basic symmetry D_{4h}, which, in principle, indicates maximum splitting.

No consequences for electronic transitions were noticed when in the course of coordination the oxygen atom was substituted by an atom of nitrogen, since there are no effects in the electronic spectra caused by the changes of ligands H_2 *thsa* (NNO-coordination) with the ligands H *thqua* (NNN-coordination).

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