BIS(DISELENOCARBAMATO)COPPER(II) COMPLEX.
SOME PECULIARITIES IN SYNTHESIS, ELECTRONIC STRUCTURE,
THERMAL AND PHOTOCHEMICAL REACTIONS AS STUDIED
BY EPR AND ELECTRONIC SPECTROSCOPY

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The paper is a review on the present data about the structure, properties and reactivity of bis(diselenocarbamate)copper(II), Cu(dsc)₂, complexes which are significantly different from the remaining chelates with chromophores CuO₄, CuN₄ and CuS₄ known up to now. The marked differences of Cu(dsc)₂ are attributed to its specific electronic structure with dominating donor properties of the ligands atoms in the chromophore CuSe₄ and strongly suppressed acceptor properties of Cu(II). As a result its reaction products are unpredictable on the basis of the present knowledge on the other copper(II) chelates. These facts, as well as the very limited number of studies on Cu(dsc)₂ suggest that the complex could be considered as a challenge for future investigations in the field of coordination chemistry.

Key words: bis(diselenocarbamate)copper(II); EPR spectroscopy; electronic spectroscopy; coordination chemistry

INTRODUCTION

In the last decades the metal complexes of dithiocarbamates, [M(dtc)n], have found wide applications in different areas of science and technology [1–3]. At the same time, their selenium analogues, metal diselenocarbamates M(dsc)n, were considered as potential materials efficient and useful as selective reagents in analytical chemistry [4–7], as photostabilizer [8] and antioxidant additives to hydrocarbons [9–11] or motor oil [12], metal deactivators [13], pesticides and fungicides [14, 15], flotation agents [16], precursors in preparation of solar cell materials [17–27], etc. Independently of their advantages, the use of M(dsc)n still remains much limited compared to M(dtc)n and the literature data on their structure, properties and reactivity are quite limited most probably because of the complicated synthesis of diselenocarbamate ligands. The poorly studied chemistry of M(dsc)n encouraged us to summarize our studies in the last few years in order to find a relation between structure, properties and reactivity of bis(diethyl-diselenocarbamate)copper(II), Cu(dsc)₂. The studies are performed with the methods of EPR and electronic spectroscopy and the obtained results are compared with the available data for bis(dialkyl-dithiocarbamate)copper(II) complexes, Cu(dtc)₂, which are much more widely studied.

EXPERIMENTAL

Principles of dithiocarbamate and diselenocarbamate ligands synthesis

The starting materials for the syntheses of both ligands are secondary amines, R₂NH, and CS₂ or CSe₂ following the reaction (1):

R₂NH + CS₂ (or CSe₂) → R₂NC(S)SH
(or R₂NC(Se)SeH)  \( (1) \)

The obtained products are R₂-dithio- resp. R₂-diseleno-carbamic acids (R = alkyl or aryl). Since both acids are unstable, the syntheses are carried...
out in alkali media to give Na(dtc)$_2$, or Zn(dtc)$_2$, and Zn(dsc)$_2$ respectively. The obtained salts are further used as precursors in the preparation of other metal complexes. From our point of view the reason for the limited use and studies of M(dsc)$_n$ are the lack of commercially available CSe$_2$ and its complicated synthesis [28].

**Synthesis of Cu(dtc)$_2$ and peculiarities in the case of Cu(dsc)$_2$**

The complex Cu(dtc)$_2$ is prepared by mixing aqueous Na(dtc) and copper(II) salt solutions (CuSO$_4$, CuCl$_2$, CuBr$_2$, etc.) to precipitate Cu(dtc)$_2$ according to the reaction (2).

$$2\text{Na(dtc)} + \text{Cu}^{2+} \rightarrow \text{Cu(dtc)}_2 + \text{Na}^+ \quad (2)$$

The same product is obtained by shaking aqueous copper(II) solution with Zn(dtc)$_2$ in toluene.

Synthesis of Cu(dsc)$_2$ is carried out according to reaction (3) by shaking aqueous Cu(II) solution with Zn(dsc)$_2$ in toluene:

$$\text{Zn(dsc)}_2 + \text{Cu}^{2+} \rightarrow \text{Cu(dsc)}_2 + \text{Zn}^{2+} \quad (3)$$

but the product depends on the used copper(II) salt [29]. The use of CuSO$_4$ yields Cu(dsc)$_2$ [29, 30] with an absorption at 20 200 cm$^{-1}$ in toluene (Fig. 1a) and strong, stable with the time EPR signal.

The product obtained with CuCl$_2$ [29] shows an absorption maximum at 22 600 cm$^{-1}$ with a shoulder at 20 200 cm$^{-1}$ (Fig. 1b) and a very weak EPR spectrum. A small part of the obtained crystals are soluble in toluene giving the spectral features of Cu(dsc)$_2$. The main (insoluble in toluene) portion gives EPR silent CHCl$_3$ solution with an absorption at 22 600 cm$^{-1}$. Toluene insoluble material is not the product of a redox reaction [29] because the EPR spectrum of Cu(dsc)$_2$ remains unchanged for at least 5 months. The formation of a chloride-bridged dimmeric complex of the type (dsc)Cu$^{10}$Cl$_4$Cu$^{10}$(dsc) in which copper ions are strongly antiferromagnetically coupled was confirmed by the addition to its CHCl$_3$ solution of equivalent amounts of Zn(dsc)$_2$, stoichiometrically yielding Cu(dsc)$_2$, i.e. the same product as obtained by the use of CuSO$_4$.

The observed effects in the synthesis of Cu(dsc)$_2$ are unknown for other copper(II) chelates.

**RESULTS AND DISCUSSION**

**Structure of Cu(dsc)$_2$ and Cu(dtc)**

*a) Crystal and molecular structure*

The X-ray data about the crystal and molecular structure of Cu(Et$_2$dsc)$_2$ [31, 32] and Cu(Et$_2$dtc)$_2$ [33, 34] show good similarity between them since both complexes belong to the space group – P2$_1$/c with two molecules per unit cell. The parameters of their unit cell are collected in Table 1 and the bond lengths (Å) and angles (°) – in Table 2. Each Cu atom is surrounded by five S (Se) atoms in an approximately tetragonal pyramidal geometry (Fig. 2). The four donor atoms are lying roughly in a plane forming the base of a pyramid with copper atom slightly above it, the fifth (long) bond, Cu–D(4$'$) being approximately perpendicular to the plane.
Thus, X-ray investigations prove very close similarity in the crystal and molecular structure of both Cu(dsc)_2 and Cu(dtc)_2 complexes.

**Table 1**

<table>
<thead>
<tr>
<th>Parameters of the unit cell</th>
<th>Cu(dtc)_2 [31, 32]</th>
<th>Cu(dsc)_2 [33, 34]</th>
</tr>
</thead>
<tbody>
<tr>
<td>pm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>990.7</td>
<td>988.3</td>
</tr>
<tr>
<td>b</td>
<td>1062.7</td>
<td>1086.0</td>
</tr>
<tr>
<td>c</td>
<td>1659.1</td>
<td>1717.3</td>
</tr>
<tr>
<td>β</td>
<td>113°52'</td>
<td>113°12'</td>
</tr>
</tbody>
</table>

| Space group                  | P2_1/c             | P2_1/c             |

**Table 2**

**Distance (pm) and angles (°) in the first copper neighbors of Cu(Et_2dtc)_2; Cu(Et_2dsc)_2**

**Angles (°) in the copper coordination sphere in Cu(Et_2dtc)_2 [31, 32]**

<table>
<thead>
<tr>
<th>Bond</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S(1)-Cu-S(2)</td>
<td>77°19'</td>
</tr>
<tr>
<td>S(1)-Cu-S(3)</td>
<td>101°29'</td>
</tr>
<tr>
<td>S(2)-Cu-S(4)</td>
<td>102°16'</td>
</tr>
<tr>
<td>S(2)-Cu-S(4)</td>
<td>76°27'</td>
</tr>
<tr>
<td>Cu-S(1)-C(1)</td>
<td>83°43'</td>
</tr>
<tr>
<td>Cu-S(2)-C(1)</td>
<td>84°18'</td>
</tr>
<tr>
<td>Cu-S(3)-C(6)</td>
<td>86°10'</td>
</tr>
<tr>
<td>Cu-S(4)-C(6)</td>
<td>84°22'</td>
</tr>
</tbody>
</table>

**Angles (°) in the copper coordination sphere in Cu(Et_2dsc)_2 [33, 34]**

<table>
<thead>
<tr>
<th>Bond</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S(1)-Cu-Se(2)</td>
<td>79°41'</td>
</tr>
<tr>
<td>S(1)-Cu-Se(3)</td>
<td>99°11'</td>
</tr>
<tr>
<td>S(2)-Cu-Se(4)</td>
<td>99°61'</td>
</tr>
<tr>
<td>S(2)-Cu-Se(4)</td>
<td>79°11'</td>
</tr>
<tr>
<td>Cu-Se(1)-C(1)</td>
<td>83°46'</td>
</tr>
<tr>
<td>Cu-Se(2)-C(1)</td>
<td>84°15'</td>
</tr>
<tr>
<td>Cu-Se(3)-C(6)</td>
<td>84°86'</td>
</tr>
<tr>
<td>Cu-Se(4)-C(6)</td>
<td>83°66'</td>
</tr>
</tbody>
</table>

**b) Electronic structure**

Single-crystal EPR studies of Cu(dtc)_2 and Cu(dsc)_2

Single crystal EPR on Cu^{II}(dsc)_2 [35–39] and Cu^{II}(dtc)_2 [37, 40] doped in the isomorphous Ni(II) or Zn(II) matrices show that contrary to the similarity in crystal and molecular structures their electronic structures differ significantly [37]. The EPR studies of Cu/Ni(dtcd)2 single crystal [38–40] indicate that Cu(dtcd)2 molecule exhibits a planar structure of D_{2h} symmetry with coinciding axes of the g- and hyperfine- (hf) splitting tensors — a typical structure for all other copper(II) chelates studied up to now. Contrary, the single crystal studies of Cu/Ni(dsc)_2 [35–38] or Cu/Zn(dsc)_2 [39] show that the g- and hf-splitting tensors do not coincide (Fig. 3). The EPR investigations of Cu(dsc)_2 in liquid crystals also prove this phenomenon [41]. The principal values of the g- and hf (A-) tensors of both Cu(dtcd)2 and Cu(dsc)_2 complexes are shown in Table 3.

**Table 3**

**Single-crystal EPR parameters of Cu(Et_2dtc)_2 and Cu(Et_2dsc)_2 diamagnetically diluted in the corresponding Ni(II) complexes**

<table>
<thead>
<tr>
<th>EPR parameters</th>
<th>Cu(Ni(Et_2dtc)_2)</th>
<th>Cu(Ni(Et_2dsc)_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>g_x ± 0.002</td>
<td>2.020</td>
<td>2.051</td>
</tr>
<tr>
<td>g_y ± 0.002</td>
<td>2.025</td>
<td>2.020</td>
</tr>
<tr>
<td>g_z ± 0.002</td>
<td>2.084</td>
<td>1.994</td>
</tr>
<tr>
<td>A_x ± 0.1 mT</td>
<td>3.6</td>
<td>3.6</td>
</tr>
<tr>
<td>A_y ± 0.1 mT</td>
<td>4.2</td>
<td>2.8</td>
</tr>
<tr>
<td>A_z ± 0.1 mT</td>
<td>15.9</td>
<td>6.20</td>
</tr>
<tr>
<td>Ref.</td>
<td>40</td>
<td>35 – 39</td>
</tr>
</tbody>
</table>
Another very important observation is that the magnitudes of the g-tensor of Cu(dsc)\(_2\) (Table 3) are the lowest known up to now for Cu(II) complexes [35–39] suggesting approximately 100% covalent character of the Cu–Se bond [36–38, 42].

**EPR studies on powdered Cu(dsc)\(_2\) and Cu(dtc)\(_2\) samples**

The described anomaly of the g- and hf-splittting tensors orientation found in Cu(dsc)\(_2\) affects the features of glassy (powder or frozen solution) EPR spectra of Cu(dsc)\(_2\) [35, 36, 39, 42]. Typical powder EPR spectra of Cu(dtc)\(_2\) and Cu(dsc)\(_2\), diamagnetically diluted in corresponding Ni(II) matices or recorded as frozen (at 77 K) solutions are presented in Fig. 4.

Whereas powder EPR spectrum of Cu(dtc)\(_2\) (Fig. 4a) is typical for complexes with axial symmetry, Cu(dsc)\(_2\) powder EPR spectrum (Fig. 4b) is obviously different. It is worth to note that the EPR spectrum of frozen (at 77 K) toluene solution of bis(di-iso-propyl-diselenophosphato)copper(II) (Cu(dsp)\(_2\)) has the shape as in Fig. 5 [45].

The marked “anomaly” in the electronic structure of Cu(dsc)\(_2\), compared to other copper(II) chelates with chromphores (CuO\(_4\), (CuN\(_4\)), or (CuS\(_4\)), is attributed [35–38, 42] to the fact that in Cu(dsc)\(_2\) or Cu(dsp)\(_2\) complexes the magnitude of the spin-orbit coupling constant of ligand’s donor atoms is larger than that of Cu(II) \(\lambda(Cu) = 828 \text{ cm}^{-1} \) [46], \(\lambda(Se) = 1690 \text{ cm}^{-1} \) [47], \(\lambda(S) = 382 \text{ cm}^{-1} \) [48] and \(\lambda(N) = 76 \text{ cm}^{-1} \) [48] and \(\lambda(O) = 151 \text{ cm}^{-1} \) [49].

EPR spectrum typical [30, 35, 43, 44] of Cu(dsc)\(_2\) solution at the room temperature is shown in Fig. 6. The spectrum consists of four hf lines due to the interaction of the unpaired electron with
63,65Cu (nuclear spin \(I = 3/2\)). Furthermore, by the natural abundance of \(^{77}\text{Se}\) (\(I = 1/2\)) which is 7.5% and assuming equal distribution of this isotope among all complex molecules we can expect that ca. 30% of Cu(dsc)_2 molecules contain one \(^{77}\text{Se}\) atom expected to give a superhyperfine (shf) splitting. The remaining 70% of Cu(dsc)_2 should not exhibit \(^{77}\text{Se}\) shf splitting. The narrow lines of Cu(dsc)_2 spectrum are the reason to observe two additional satellites in both high- and low-field lines of the spectrum (Fig. 6) by the splitting due to copper isotopes.

\[ \begin{align*}
\text{63}^{65}\text{Cu} & \\
\text{65}^{63}\text{Cu} & \\
\text{Se} & \\
A & \\
\end{align*} \]

\[ \begin{align*}
\text{100 G} & \\
\end{align*} \]

Fig. 6. Typical room temperature EPR spectrum of Cu(dsc)_2 complex dissolved in organic solvents

Table 4

Isotropic EPR parameters of Cu(Et_2dtc)_2 and Cu(Et_2dsc)_2 dissolved in the used solvents

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Solvent</th>
<th>EPR parameters</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(g) (\pm 0.002)</td>
<td>(c_A) (\pm 0.1\text{ mT})</td>
</tr>
<tr>
<td>Cu(Et_2dtc)_2</td>
<td>heptane, hexane, CH_2Cl_2, CHCl_3, CCl_4, DMFA, C_6H_6, acetone pyridine</td>
<td>2.046 8.0</td>
<td>—</td>
</tr>
<tr>
<td>Cu(Et_2dsc)_2</td>
<td>heptane, hexane, CH_2Cl_2, CHCl_3, CCl_4, DMFA, C_6H_6, acetone pyridine</td>
<td>2.022 8.0</td>
<td>4.6</td>
</tr>
</tbody>
</table>

Therefore, the EPR spectrum of Cu(dsc)_2 (Fig. 6) is a superposition of four signals from the molecules of \(^{63}\text{Cu}\) and \(^{65}\text{Cu}\), each of them giving two different spectra (one consisting of four Cu hf lines only and the other with each Cu hf line split into two shf lines by the nuclear spin of \(^{77}\text{Se}\)). The stick spectrum with all four signals is given at the bottom of Fig. 6. Typical EPR parameters of Cu(dsc)_2 dissolved in benzene, toluene, CHCl_3, acetone or DMFA are given in Table 4 [30, 35, 43]. Comparison of these parameters with the data of Cu(dtc)_2 in the same solvents (Table 4) shows negligibly small solvent influence on the electronic structure of Cu(dsc)_2.

**Intermolecular interactions of Cu(dsc)_2**

It is well known that metal chelates exhibit donor or acceptor properties [50] due to the remaining donor or acceptor properties of the atoms in their chromophore. Therefore, they can interact with donor (Lewis bases) or acceptor (Lewis acids) molecules. Copper(II) chelates give the following order of chromophores (4) [50]:

\[
\text{Cu(O}_4\text{)} < \text{Cu(O}_2\text{N}_2\text{)} < \text{Cu(N}_4\text{)} < \text{Cu(N}_2\text{S}_2\text{)} < \text{Cu(S}_4\text{)} < \text{Cu(S}_2\text{Se}_2\text{)} < \text{Cu(Se}_4\text{)}
\]

in which the covalent character of the \(\sigma\)-copper-equatorial ligand bond increases, decreasing the remaining positive charge on the metal ion. Thus, the acceptor properties of the complexes (due to the metal ion) decrease and their donor properties (due to the ligand’s donor atoms in the chromophores) increase from left to right. (The same order is also found for Ni(II) complexes [51].)

The recently published [30, 52] first investigation on the interaction of Cu(dsc)_2 with some commonly used solvents or compounds consider the following three groups:

- “inert” solvents (heptane, hexane, benzene);
- donor solvents (DMFA, DMSO, pyridine);
- acceptor molecules \([\text{CH}_2\text{Cl}_2, \text{CHCl}_3, \text{CCl}_4\text{ and CuX}_2 (\text{X} = \text{Cl, Br, NO}_3)]\).

The EPR parameters and the electronic absorption of Cu(dsc)_2 dissolved in inert solvents are used as a basis for comparing the data obtained with other solvents (or compounds).

**Interactions with Lewis bases**

The interactions of the complexes in the right side of order (4) with Lewis bases increase the
magnitude of the isotropic g-value and decrease the magnitudes of the hf structure [50, 53–56] and batochromic shift in their electronic spectra is observed [50, 53]. Both effects are connected with the corresponding change in the electronic structure of the complex and are attributed [50, 53–56] to the formation of an adduct with axial coordination of Lewis base molecule(s) along the z-axis of the complex. The adduct formation is a reversible process (eq. 5) and the stronger equilibrium (5) is shifted to the right i.e. the higher is the equilibrium constant the higher are the changes in the EPR parameters.

\[
\text{CuL}_2 + B \leftrightarrow \text{CuL}_2.B \quad (5)
\]

Independently of the donor properties of DMFA and DMSO [57] and the possibility of axial adduct formation, the isotropic EPR parameters of Cu(dsc)₂ in these solvents remain unaffected. From the studied donor solvents only pyridine (which is stronger Lewis base than DMFA and DMSO) [57] changes the parameters of the room temperature EPR spectra of Cu(dsc)₂ (Table 4). The observed effect suggests a strong decrease of the remaining positive charge on copper ion in Cu(dsc)₂ because of the strong donor properties of Se atoms from the equatorial ligands forming ca. 100 % covalent Cu – Se bond.

The main conclusion from these studies is that the strong donor properties of Se atoms make Cu(dsc)₂ very insensitive to interactions with Lewis bases.

**Interactions with Lewis acids**

*a) Interactions with copper(II) salts*

Interaction of Cu(dtc)₂ with metal salts (MXₙ or MYₙ where X = Cl or Br and Y = NO₃ or ClO₄), acting as Lewis acids [50, 58–60], yields mixed-ligand complexes of the type Cu(dtc)Xₙ (n = 1 or 2) or Cu(dtc)⁺...Y⁻. Parallel studies on the interaction of Cu(dsc)₂ with some copper (II) salts – CuCl₂, CuBr₂ and Cu(NO₃)₂ [30] gave the following results:

- The EPR spectra obtained by mixing DMFA solutions of Cu(dsc)₂ and Cu(NO₃)₂ (Fig. 7) indicate that the increase of Cu(NO₃)₂/Cu(dsc)₂ molar ratio is accompanied by the appearance of a new EPR spectrum with parameters given in Table 5. This new EPR spectrum was attributed to a mixed-ligand Cu(dsc)⁺...NO₃⁻ complex with the chromophore given in Scheme 1 following which a shf splitting from the NO₃⁻ is not observed because of the ionic bonding of NO₃⁻ (¹⁶O nuclear spin I = 0). The complex is completely analogous to the product obtained in Cu(dtc)₂ reaction with Cu(NO₃)₂ [50, 59, 60].

\[
\text{Cu(dsc)Cl} + \text{DMFA} \rightarrow \text{NO}_3^- \quad (5)
\]

![Fig. 7. Several room temperature EPR spectra taken after mixing of Cu(dsc)₂ with Cu(NO₃)₂. The ratio Cu(dsc)₂/Cu(NO₃)₂ is: (a) 1:0; (b) 3:2; (c) 1:1; (d) 3:4; (e) 1:2; Solution DMFA](image)

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**Table 5**

Isotropic EPR parameters of the mixed-ligand copolymers obtained by the interaction of Cu(dsc)₂ with Cu(II) salts

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Solvent</th>
<th>EPR parameters</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(dsc)Cl</td>
<td>acetone</td>
<td>g 2.063 ±0.002</td>
<td>7.8 0.8 – 30</td>
</tr>
<tr>
<td></td>
<td>CHCl₃/EtOH (1:1)</td>
<td>2.064 7.6</td>
<td>0.8 30</td>
</tr>
<tr>
<td></td>
<td>DMFA</td>
<td>2.066 7.5</td>
<td>0.8 30</td>
</tr>
<tr>
<td></td>
<td>pyridine</td>
<td>2.074 6.6</td>
<td>0.8 30</td>
</tr>
<tr>
<td>Cu(dsc)⁺...Cl⁻</td>
<td>DMFA</td>
<td>2.076 7.3</td>
<td>0.8 30</td>
</tr>
<tr>
<td>Cu(dsc)⁺...NO₃⁻</td>
<td>DMFA</td>
<td>2.073 7.3</td>
<td>5.0 30</td>
</tr>
<tr>
<td></td>
<td>EtOH</td>
<td>2.067 8.0 0.4</td>
<td>30</td>
</tr>
</tbody>
</table>

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- Mixing acetone, CHCl₃/EtOH, or pyridine solutions of Cu(dsc)₂ and CuCl₂ yields the EPR spectrum in Fig. 8a, Table 5, with two significant features: (i) much lower intensity compared to the parent Cu(dsc)₂ signal and (ii) additional splitting of the high field copper hf lines (with m_I = –1/2...
and $-3/2$) into four shf lines with $1:1:1:1$ intensity (Fig. 8a). The shf splitting indicates interaction of Cu(II) unpaired electron with one $^{35,37}$Cl nucleus ($I = 3/2$). Therefore, spectra in Fig. 8a suggest one covalently bound Cl$^-$ ion in the plane $xy$ giving a mixed-ligand Cu$^{II}$(dsc)Cl complex (Scheme 2) the fourth equatorial coordination place being occupied by a solvent molecule.

The EPR parameters (Table 5) of Cu$^{II}$(dsc)Cl in different solvents show increasing $g_o$-value and decreasing $A_o$ with increasing donor properties of the solvents in the order (6)

$$\text{acetone} < \text{EtOH} < \text{pyridine}$$

(6)

The observed strongest deviation of the EPR parameters in pyridine (Table 5) could be explained by the coordination of two pyridine molecules: one in the plane $xy$ and the other along the $z$-axis of the complex, which is in good agreement with the discussion on the EPR parameters of axial Cu(dsc)$_2$·B adducts.

Two EPR spectra of mixed-ligand complexes appear in Fig. 8b on mixing Cu(dsc)$_2$ and CuCl$_2$ solutions in DMFA. One of them is characterized by a shf splitting from one $^{35,37}$Cl nucleus and fully coincides with the signal of the mixed-ligand Cu$^{II}$(dsc)Cl complex (Scheme 2), whereas the other one appears at lower magnetic field without any shf feature. The magnitudes of the EPR parameters (Table 5) suggest that the second signal is due to the bis-solvated Cu$^{II}$(dsc)(DMFA)$_2$ complex (Scheme 1).

According to the above results mixing Cu(dsc)$_2$ and copper(II) solutions (see Table 5) yields mixed-ligand complexes. However, the observed ca. 100 fold lower EPR intensity of copper(II)diselenocarbamate mixed-ligand complexes compared to the parent Cu(dsc)$_2$ spectrum suggests that the following equilibrium (7) is shifted to the side of the antiferomagnetic dimmer:

$$\text{Cu}^{II}(\text{dsc})_2 + \text{Cu}^{II}X_2 \leftrightarrow 2\text{Cu}^{II}(\text{dsc})X \leftrightarrow (\text{dsc})\text{Cu}^{II}_2X\text{Cu}^{II}(\text{dsc})$$

(7)

Equilibrium in reaction (7) is also affected by the counter-ion of the copper(II) salts, its shifting to the right being forced in the following order of anions (8)

$$\text{NO}_3^- < \text{Cl}^- < \text{Br}^-$$

(8)

It is worth to note that contrary to the interaction of Cu(dtc)$_2$ with CuBr$_2$ giving the mixed-ligand Cu(dtc)Br [59] complex with well resolved shf splitting, only gradual decrease in Cu(dsc)$_2$ EPR intensity is observed on addition of small portions of CuBr$_2$ to Cu(dsc)$_2$ solution without a new EPR signal indicating that only the complex complex...
is obtained with Br⁻ [30]. The observed specific behaviour of Cu(dsc)₂ could be used to explain the peculiarities observed during its synthesis [30].

Equation (7) is also in accordance with the results obtained by the electronic spectra, indicating the appearance of a new band at 22 600 cm⁻¹ on mixing Cu(dsc)₂ and CuX(Y)₂ solutions (Fig. 9) simultaneously with the decreasing intensity of Cu(dsc)₂ absorption at 20 200 cm⁻¹.

The new band is attributed to the dimmeric (dsc)CuIICl₂CuII(dsc) complex which is also obtained in the synthesis of Cu(dsc)₂ with CuCl₂ instead of CuSO₄. The isobestic point at 21 000 cm⁻¹ also supports reaction scheme (7). Fig. 9 shows that the band at 22 600 cm⁻¹ is twice as high as that at 20 200 cm⁻¹ which may be used for increasing the sensitivity of spectrophotometric estimations of Cu(dsc)₂.

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**b) Interactions with chloromethanes**

EPR parameters of Cu(dsc)₂ in some acceptor solvents like CH₂Cl₂ and CHCl₃ [30, 52] are equal to the data obtained in inert solvents (Table 4) suggesting identical electronic structure and their EPR intensity remains unchanged for at least 30 days at room temperature. Contrary to CH₂Cl₂ and CHCl₃, the EPR intensity of Cu(dsc)₂ gradually decreases when CCl₄ is used as a solvent (Fig. 10) and temperature increase up to 60 °C is enough for the complete destruction of Cu(dsc)₂ within several hours in it. Under the same experimental conditions Cu(dtc)₂ complex is stable (Fig. 10).

In fact, Cu(dsc)₂ is the only copper(II) chelate known up to now which is destroyed in CCl₄. The explanation of this effect is based on the large magnitude of the remaining negative charge on Se-atoms in the chromophore CuSe₄, much higher than in other copper(II) chelates (eq. 4), providing stronger donor properties of CuSe₄. As a result, the electron-acceptor molecule of CCl₄ coordinates to selenium atom of the chromophore yielding strong donor-acceptor (D-A) complex with Cu(dsc)₂. This assumption is in a good agreement with the order of decreasing dissociation energy of C-Cl bond in chloromethanes (eq. 9) making CCl₄ the strongest acceptor among them [61, 62]:

\[ \text{CH}_2\text{Cl}_2 > \text{CHCl}_3 > \text{CCl}_4 \]  

(Eq. 9)

**Fig. 10.** Dependence of the intensity of the EPR spectra of Cu(Et₂dtc)₂ and Cu(Et₂dsc)₂, dissolved in CCl₄, as a function of time (days). The intensity is taken as the ratio of the intensity of the EPR spectra of the complexes, and the intensity of Mn/MgO used as a standard.

Electron reorganization in the frames of the obtained D-A Cu(dsc)₂·CCl₄ complex further yields the mixed-ligand CuII(dsc)Cl complex and dsc-CCl₂ ester.

Analogous D-A complex between bis(dithiophosphato)copper(II), Cu(dtp)₂, and CHCl₃ is detected by ENDOR spectroscopy [63, 64], but the EPR parameters of Cu(dtp)₂ remain unchanged because of the weak D-A interaction suggesting formation of very weak D-A complex. Another example is the formation of D-A complex between CCl₄ (or CHCl₃) and Cu(dtc)₂ (or Cu(dtp)₂) [65] explaining the reaction between their adducts with Lewis bases and CCl₄ (or CHCl₃).
Photochemical studies on Cu(dsc)$_2$

Charge-transfer (CT) photochemistry of Cu(dsc)$_2$ has been studied in 1:1 CH$_2$Cl$_2$/EtOH and CHCl$_3$/EtOH [66]. As pointed out, Cu(dsc)$_2$ is stable in these solvents at temperatures up to 50 °C. The electronic and EPR spectra of the complex change upon UV-irradiation. As a result, the visible absorption of Cu(dsc)$_2$ at 20 200 cm$^{-1}$ gradually decreases (Fig. 9) with the appearance of an isobestic point at 21 000 cm$^{-1}$ and a corresponding strong increase in absorption at 22 600 cm$^{-1}$. Under the same experimental conditions the intensity of the initial EPR spectrum of the complex decreases and a low intensity EPR signal appears with EPR parameters completely identical with the data given in Table 5 for Cu$^{II}$(dsc)Cl. Irradiation of Cu(dsc)$_2$ in toluene results in only gradual decrease in intensity of the initial EPR spectrum of the complex and the absorption band at 20 200 cm$^{-1}$ without any intermediate EPR signal or absorption band. UV-irradiation in 1:1 toluene/EtOH yields the EPR and electronic spectral changes described above.

According to the scheme of Cu(dsc)$_2$ CT-photolysis proposed on the ground of the obtained results (Scheme 3) the primary photoprocess proceeds within the D-A complex between CHCl$_3$ and Cu(dsc)$_2$ as an electron transfer from an equatorially bound Se-atom of the chromophore CuSe$_4$ to Cu(II). The primary photoproducts Cu$^{I}$(dsc) and (dsc) are obtained as a result of the homolytic Cu–Se bond cleavage in the CT excited state [RX·Cu$^{I}$(dsc)··(dsc)]. The electronic and EPR parameters of the complex are given in Table 5 for Cu$^{II}$(dsc)Cl. Irradiation of Cu(dsc)$_2$ in toluene results in only gradual decrease in intensity of the initial EPR spectrum of the complex and the absorption band at 20 200 cm$^{-1}$ without any intermediate EPR signal or absorption band. UV-irradiation in 1:1 toluene/EtOH yields the EPR and electronic spectral changes described above.

![Scheme 3](image)

Ligand-exchange reaction between copper(II) chelates

The exchange interaction between different chelate complexes yielding mixed-chelate complexes is an important reaction since the product exhibits typical properties of one or both the parent complexes important for some special applications. In view of this, ligand-exchange equilibrium reaction (10):

$$\text{CuL}_2^{+} + \text{CuL}^{2-} \leftrightarrow 2\text{CuL}^L$$  (10)

is relatively well studied on the basis of electronic and EPR spectral data for oxygen, nitrogen and sulphur containing copper (II) chelates [68]. All available data show that depending on the nature of the parent complexes equilibrium (10) is partially or completely shifted to the mixed-chelate complex (Cu$L$.‘). Unambiguous evidence of mixed-chelate Cu$L$.‘ complex formation is the recorded shf splitting coming from atom(s) of only one of the ligand molecules from the parent complexes. Another significant feature of the EPR parameters ($g_0$ and $A$) of the mixed- chelate complexes are their value, which are the average of the corresponding parameters of the parent complexes satisfying the rule of “additivity” (11) [69].

$$g_{\text{CuL}'\text{L}''} = \left( g_{\text{CuL}^2} + g_{\text{CuL}^2}^{2-} \right)/2$$  (11)
$$A_{\text{CuL}'\text{L}''} = \left( A_{\text{CuL}^2} + A_{\text{CuL}^2}^{2-} \right)/2$$

The explanation of the effect of “additivity” is based on the fact that the unpaired electron in the parent complexes occupies a group orbital formed by the atomic orbitals (AO) of four orbitals of ligand’s donor atoms and copper(II). In mixed-chelate complexes the group orbital is formed by the AO of copper(II) and two donor atoms from each of the ligands of the parent complexes. Initially applied for EPR recently was found [70] that “additivity” rule may also be extended on the position of the CT absorption band in the electronic spectra of the parent and mixed-chelate complexes.

Ligand-exchange reaction between Cu(dsc)$_2$ and Cu(dtc)$_2$ complexes

The available literature data show that mixing Cu(dsc)$_2$ (chromophore CuSe$_4$) and Cu(dtc)$_2$ (chromophore CuS$_4$) in a mixture of chloroform and other non-halogen containing solvents yields the simultaneous appearance of the EPR spectra of three mixed-chelate complexes. On the basis of the
“additivity” rule these mixed-chelate complexes were proposed to have the chromophores Cu(S₂Se₂), Cu(SSe₃) and Cu(S₃Se) [71–73]. Kinetic studies with stopped-flow techniques show that reaction between Cu(dsc)₂ and Cu(dtc)₂ is very fast, with a second order rate constant \( k \) about \( 10^4 \text{ mol}^{-1} \text{·s}^{-1} \) [74]. However, the mechanism of formation of mixed-chelate complexes is not explained up to now [71–78].

It is worth to note that such reaction products take place only with Cu(dsc)₂, not with other chelates where their reaction product satisfies eq. (10). Detailed investigation of this phenomenon was an important point in the studies on the relation between structure and reactivity of Cu(dsc)₂ because of the possibility for new additional information about reaction mechanism and structure of mixed-ligand complexes. In view of this, the ligand-exchange reaction between Cu(dsc)₂ and Cu(dtc)₂ was studied in several solvents – “inert” (heptane, hexane, toluene and benzene), with the electron acceptor (CH₂Cl₂, CHCl₃, CCl₄) and donor (DMFA, DMSO, acetone) properties [70].

Typical isotropic EPR spectra recorded immediately after mixing equimolar solutions of the parent complexes (Fig. 11) exhibit EPR signals of three complexes – the parents (Fig. 11a and 11b) and the mixed-chelate Cu(dtc)(dsc) complex (Fig. 11c) suggesting partial shifting to the right of equilibrium (10). The sticks diagram of all spectra is shown at the bottom of Fig. 11.

Further changes in the EPR spectrum \( c \) in Fig. 11 were observed with the time and manifested by the appearance of a different mixed-ligand complex definitely depending on the solvent nature. The following three cases were found:

- Spectrum \( c \) in Fig. 11 yielded on mixing the parents Cu(dtc)₂ and Cu(dsc)₂ in heptane, hexane, toluene, benzene, DMFA, DMSO, acetone or CH₂Cl₂ remains unchanged for one month monitoring;
- When CCl₄ or CHCl₃ are used as a solvent, the EPR spectrum \( a \) in Fig. 12 appears immediately after mixing equimolar solutions of Cu(dtc)₂ and Cu(dsc)₂. Obviously it is a superposition of the parents and the mixed-ligand Cu(dtc)(dsc) complex signals (compare with spectrum \( c \) in Fig. 11c). However, keeping the CCl₄ reaction mixture for one hour at room temperature (or 5 minutes at 60 °C) or in case of CHCl₃ – two days or 1 h at 60 °C spectrum \( b \) in Fig. 12 is obtained, which is a superposition of the EPR signals of two parents and three mixed-ligand complexes. The parameters of the new EPR spectra (ML-2 and 3) are equal to those reported above and are given in Table 6.

In the last two cases a progressive decrease in signal intensities of the mixed-ligand complexes to full disappearance of their EPR spectra was recorded with the time on keeping the reaction mixture.

**Table 6**

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Chromophore</th>
<th>( g ) ( \pm 0.002 )</th>
<th>( Cu A ) ( \pm 0.1 \text{ mT} )</th>
<th>( Se A ) ( \pm 0.1 \text{ mT} )</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(dtc)₂</td>
<td>CuS₄</td>
<td>2.046</td>
<td>8.0</td>
<td>—</td>
<td>69</td>
</tr>
<tr>
<td>Cu(dsc)₂</td>
<td>CuSe₄</td>
<td>2.022</td>
<td>8.0</td>
<td>4.6</td>
<td>69</td>
</tr>
<tr>
<td>Cu(dtc)(dsc) ML-1</td>
<td>CuS₂Se₂</td>
<td>2.032</td>
<td>8.0</td>
<td>4.6</td>
<td>69</td>
</tr>
<tr>
<td>ML-2</td>
<td>CuS₂Se</td>
<td>exp. 2.042</td>
<td>8.0</td>
<td>—</td>
<td>69</td>
</tr>
<tr>
<td>ML-3</td>
<td>CuSSe₃</td>
<td>exp. 2.029</td>
<td>8.0</td>
<td>—</td>
<td>69</td>
</tr>
</tbody>
</table>

EPR parameters of both parent complexes are given for comparison together with the parameters of the mixed-ligand Cu(dsc)(dtc) in Table 6.
obtained value of $\lambda_{\text{max}} = 21500 \text{ cm}^{-1}$ for all mixed-ligand complexes is just the average of the magnitudes of $\lambda_{\text{max}}$ of the parent complexes thus satisfying the rule of “additivity”. All other time dependent features marked in the EPR spectra are observed also in the electronic spectra. It is worth to note however that the absorption spectra have lower resolution in respect of two new spectra (ML-2 and ML-3) which can not be recorded.

The explanation of the formation of mixed-ligand complexes ML-2 and ML-3 (Scheme 4) is based on the reported reaction of Cu(dsc)$_2$ with CCl$_4$ in the course of which ester of diselenocarbamic acid (dsc-CCl$_3$) is formed [70]. Thus the dsc-CC$_3$ ester, which exhibits strong donor properties may interact with the parent Cu(dtc)$_2$ and the mixed-ligand Cu(dtc)(dsc) complexes (with chromophores CuS$_4$ and CuS$_2$Se$_2$) thus forming ML-2 and ML-3 complexes with chromophores (CuS$_3$Se.S) and (CuSSe$_3$.S). On the ground of the EPR parameters and the rule of “additivity” the fifth donor atom (S) is supposed to be coordinated axially in respect to the plane formed by CuS$_3$Se and CuSSe$_3$ atoms.

**Scheme 4**

CONCLUSIONS

The present review on the data available up to now about the structure, properties and reactivity of bis(diselenocarbamato)copper(II) complexes shows that they are significantly different from all studied complexes with chromophores Cu(O$_4$), Cu(N$_4$), Cu(S$_4$). It is shown that the differences are dictated by the electronic structure of the chromophore in which for the first time donor properties of the ligands atoms are dominating whereas acceptor properties of the Cu(II) are strongly suppressed. As a result Cu(dsc)$_2$ reacts with weak Lewis acids giving intermediate or final reaction products unknown for other complexes which determine further steps of the reaction. These facts combined with the very limited number of studies suggest that Cu(dsc)$_2$ complex can be considered as an attractive challenge for future studies in the field of coordination chemistry.
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Резюме

КОМПЛЕКСОТ НА БИС(ДИСЕЛЕНОКАРБАМАТО)БАКАР(II).

НЕКОИ НЕВООБИЧАЕНОСТИ ВО СИНТЕЗАТА, ЕЛЕКТРОНСКАТА СТРУКТУРА, ТЕРМИЧКИТЕ И ФОТОХЕМИСКИТЕ РЕАКЦИИ ИСПИТУВАНИ СО ЕПР И ЕЛЕКТРОНСКА СПЕКТРОСКОПИЈА

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Ключни зборови: бис(диселенокарбамато)бакар(II); EPR-спектроскопија; електронска спектроскопија; координациона хемија

Овој труд е преглед на постојните податоци за структурата, својствата и реакциевноста на комплексите на бис(диселенокарбамато)бакар(II), Cu(dsc)₂₂, кои се значително различни од другите хелати со хромофори CuO₆, CuN₄ и CuS₂ кои се досега познати. Значителните разлики кај Cu(dsc)₂₂ се припишани на неговата специфична електронска структура со доминантни донорни својства на лигандните атоми кај хромофо-