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# 1,10-Phenanthroline-dithiolate mixed ligand transition metal complexes. Synthesis, characterization and EPR spectroscopy

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#### ABSTRACT

A series of new  $N_2S_2$  mixed ligand transition metal complexes, where  $N_2$  is phenanthroline and  $S_2$  is 1,2dithiooxalate (dto) or 1,2-dithiosquarate (dtsq), has been synthesized and characterized. IR spectra reveal that the 1,2-dithiolate ligands are coordinated via the sulfur atoms forming a  $N_2S_2$  coordination sphere. The copper(II) complex [Cu(phen)(dto)] was studied by EPR spectroscopy as a diamagnetically diluted powder. The diamagnetic dilution resulted from doping of the copper complex into the isostructural host lattice of the nickel complex [Ni(phen)(dto)]. The electronic situation in the frontier orbitals of the copper complex calculated from the experimental data is compared to the results of EHT and DFT calculations. Furthermore, one side product, chlorobis(1,10-phenanthroline)copper(I) ethanol solvate hydrate [(phen)<sub>2</sub>CuCl]·C<sub>2</sub>H<sub>5</sub>OH·H<sub>2</sub>O, was formed by a reduction process and characterized by X-ray diffraction. In the crystal packing one-dimensional columns of dimers are formed, stabilized by significant  $\pi$ - $\pi$ interactions.

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# 1. Introduction

Mixed ligand complexes with a diimine/dithiolate ligand combination have attracted an increasing interest over the last decades because of their properties [1], e.g. as conducting and superconducting materials [2–4], optical materials [5,6] and solar cell dyes [7–9]. Some of these complexes have also shown very promising anti-tumor activities (in vitro and in vivo) in *cis*-platin-resistant model systems [10].

Copper as an essential element is always interesting to study in nature related compounds. With its d<sup>9</sup> electron configuration and the well separated ground state (S = 1/2) and a nuclear spin of I = 3/2, Cu<sup>2+</sup> is also very well suited to be studied by EPR spectroscopy. The blue copper enzymes of type 1 are an interesting group of transition metal centered enzymes with a  $N_2S_2$  coordination sphere. The distorted coordination geometry between the typical square planar coordination of copper(II) and the tetrahedral of copper(I) is known as an entatic state, ready to switch easily between both oxidation states. In the present paper we have synthesized and studied a series of phenanthroline  $N_2S_2$  coordinated mixed ligand complexes. To get more insight into the electronic situation, EPR spectroscopic measurements were performed, and the experimental spin density distribution is compared with the results of quantum chemical calculations on different levels (EHT and DFT). A chlorobis(phenanthroline)copper(I) complex as a reduced by-product was isolated and structurally characterized.

#### 2. Experimental

### 2.1. Synthesis

1,10-Phenanthroline and the transition metal chlorides were used as purchased without any further purification. For the palladium complexes,  $Pd(CH_3-CN)_2Cl_2$  was used as starting material, prepared by dissolving  $PdCl_2$  in acetonitrile and evaporation of the excess solvent [11], whereas  $K_2PtCl_4$  was used for the platinum complexes.

The dithiolate ligands dipotassium-1,2-dithiooxalate ( $K_2$ dto) [12] and dipotassium-1,2-dithiosquarate [13] were synthesized as described in the literature.

Dipotassium-1,2-dithiooxalate (K<sub>2</sub>dto): decomposes > 200 °C; IR [KBr, cm<sup>-1</sup>]:  $v_{(C-O)} = 1514$ ,  $v_{(C-C-O)} = 1371$ ,  $v_{(C-C-S)} = 1113$ ,  $v_{(C-S)} = 875$ ; Elemental *Anal.* Calc.: C, 12.11; O, 16.13; S, 32.33. Found: C, 11.67, 12.33; O, 13.78, 13.92; S, 32.14%, 32.26%.

Dipotassium-1,2-dithiosquarate (K<sub>2</sub>dtsq): decomposes > 200 °C; IR [KBr, cm<sup>-1</sup>]:  $\nu_{(C-O)}$  = 1707, 1623,  $\nu_{(C-C-O)}$  = 1343,  $\nu_{(C-C-S)}$  = 1209,  $\nu_{(C-S)}$  = 923; Elemental *Anal.* Calc.: C, 21.61; O, 14.39; S, 28.84. Found: C, 21.83, 21.33; O, 16.60, 18.49; S, 26.98%, 26.84%.



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# 2.2. Preparation of the dichlorophenanthroline complexes of [*M*(phen)Cl<sub>2</sub>] type (general procedure)

Metal-1,10-phenanthroline-dichloro complexes were synthesized according to the method described by Jäger and van Dijk [14]. An ethanolic solution of 1,10-phenanthroline was added slowly to a well stirred warm ethanolic solution of the appropriate metal chloride (MCl<sub>2</sub> . nH<sub>2</sub>O) (M = Ni, Cu, Zn) or the appropriate bis(acetonitrile)dichloro complex [(AN)<sub>2</sub>PdCl<sub>2</sub>] or tetrachloroplatinate(II) complex [PtCl<sub>4</sub>]<sup>2–</sup>. After 1 h the reaction mixture was allowed to cool to room temperature. The micro crystalline products were filtered off, washed with ethanol and dried in vacuum. For the platinum complex the method was slightly modified: water with some drops of HCl was used as solvent and the mixture was refluxed for 1 day [15]. These 1,10-dichlorophenanthroline metal(II) complexes were directly used for the synthesis of the dithiolate complexes without further purification.

# 2.3. Preparation of the phenanthroline-dithiolate complexes [M(phen)(dto)] and [M(phen)(dtsq)] (general procedure)

To a well stirred solution of the appropriate dichloro-1,10-phenanthroline metal(II) complex in an ethanol/water mixture (3:1) was added an aqueous solution of the equimolar amount of the potassium dithiolate,  $K_2$ dto or  $K_2$ dtsq. After 1 h (for the Pt-complex one day) the colored micro crystalline products were filtered off, washed with ethanol and dried in vacuo. The yield is practically quantitative.

[Cu(phen)(dto)]; dark green, decomposes at 160 °C; elemental *Anal.* Calc. for C<sub>14</sub>H<sub>8</sub>N<sub>2</sub>S<sub>2</sub>O<sub>2</sub>Cu: C, 46.21; H, 2.22; N, 7.70; S, 17.62; O, 8.79. Found: C, 44.21; H, 1.77; N, 7.52; S, 16.72; O, 9.00%. Susceptibility:  $\mu_{\text{eff}} = (1.8 \pm 0.5)$  B.M.

[Cu(phen)(dtsq)]: brown, decomposes at 230 °C; elemental *Anal.* Calc. for C<sub>16</sub>H<sub>8</sub>N<sub>2</sub>S<sub>2</sub>O<sub>2</sub>Cu: C, 49.54; H, 2.08; N, 7.22; S, 16.53; O, 8.25. Found: C, 46.29; H, 1.88; N, 7.17; S, 14.73; O, 8.15%. Susceptibility:  $\mu_{\text{eff}}$  = (2.0 ± 0.5) B.M.

[Ni(phen)(dto)]; brown, decomposes at 242 °C; elemental *Anal.* Calc. for C<sub>14</sub>H<sub>8</sub>N<sub>2</sub>S<sub>2</sub>O<sub>2</sub>Ni: C, 46.83; H, 2.25; N, 7.80; S, 17.86; O, 8.91. Found: C, 45.19; H, 2.14; N, 7.53; S, 17.73; O, 8.75% (9.25). Susceptibility:  $\mu_{\text{eff}} = (1.3 \pm 0.5)$  B.M.

[Ni(phen)(dtsq)]:dark green, decomposes at 245 °C; elemental *Anal.* Calc. for  $C_{16}H_8N_2S_2O_2Ni$ : C, 50.17; H, 2.11; N, 7.31; S, 16.74; O, 8.35. Found: C, 51.36; H, 2.17; N, 7.77; S, 14.29; O, 8.05%. Susceptibility: (2.7 ± 0.5) B.M.

[Zn(phen)(dto)]; yellow, decomposes at 202 °C; elemental *Anal.* Calc. for C<sub>14</sub>H<sub>8</sub>N<sub>2</sub>S<sub>2</sub>O<sub>2</sub>Zn: C, 45.98; H, 2.20; N, 7.66; S, 17.53; O, 8.75. Found: C, 45.07; H, 2.17; N, 7.59; S, 16.90; O, 8.62%.

[Zn(phen)(dtsq)]: yellow, decomposes at 309 °C; elemental *Anal.* Calc. for  $C_{16}H_8N_2S_2O_2Zn$ : C, 49.31; H, 2.07; N, 7.19; S, 16.45. Found: C, 46.10; H, 2.04; N, 6.79; S, 16.35%.

[Pd(phen)(dto)]; light yellow, decomposes at 274 °C; elemental *Anal.* Calc. for  $C_{14}H_8N_2S_2O_2Pd$ : C, 41.34; H, 1.98; N, 6.89; S, 15.76; O, 7.87. Found: C, 39.53; H, 1.97; N, 6.49; S, 15.41; O, 8.79%.

[Pd(phen)(dtsq)]:dark orange, decomposes at 300 °C; elemental *Anal.* Calc. for  $C_{16}H_8N_2S_2O_2Pd$ : C, 44.61; H, 1.87; N, 6.50; S, 14.88; O, 7.43. Found: C, 40.58; H, 2.23; N, 6.36; S, 8.93/8.56<sup>\*</sup>); O, 7.45%.

[Pt(phen)(dto)]; light orange, decomposes > 300 °C; elemental *Anal.* Calc. for  $C_{14}H_8N_2S_2O_2Pt$ : C, 33.94; H, 1.63; N, 5.65; S, 12.94; O, 6.46. Found: C, 33.19; H, 1.58; N, 5.62; S, 9.61<sup>\*</sup>); O, 6.12%.

[Pt(phen)(dtsq)]: orange, decomposes at 310 °C; elemental *Anal.* Calc. for  $C_{16}H_8N_2S_2O_2Pt$ : C, 37.00; H, 1.55; N, 5.39; S, 12.34; O, 6.16. Found: C, 33.79; H, 1.78; N, 5.51; S, 6.14/5.97<sup>\*</sup>); O, 6.13%. <sup>\*)</sup> We have often observed that especially Pd- and Pt-dithiolate complexes gave abnormal results for the determination of sulfur.

#### 2.4. Methods

EPR spectra were recorded at 9.4 GHz (X-band) with a Bruker CW Elexsys E500 spectrometer as powders. The Q-band spectra were recorded at  $\sim$ 36 GHz with a Bruker EMX spectrometer at 295 K. The spectra were simulated with the experimental parameters using the program WIN-Simfonia [16].

The program CACAO (Computer Aided Composition of Atomic Orbitals) by Mealli and Proserpio [17] has been used for the EHT calculations (Extented Hückel Theory). For the DFT-Calculations the program package GAUSSIAN 03 and the basis set B3LYP/6-31G<sup>\*</sup> was applied [18].

IR-Spectra were recorded on a Perkin–Elmer type 16 PC FT-IR spectrophotometer in the region between 4000 and 400  $cm^{-1}$  as KBr-pellets (reference KBr).

The magnetic susceptibilities of the synthesized complexes were measured with Gouy method using a magnetic balance type MSB-Auto (Sherwood Scientific Ltd.).

Diffraction data were collected at 210 K on a STOE Imaging Plate Diffraction System IPDS-II using graphite monochromatized Mo Ka radiation ( $\lambda$  = 0.71 073 Å). The data were corrected by a spherical absorption correction using the program X-Area (STOE, 2004) as well as for Lorentz, polarization and extinction effects. The solution of the crystal structure was performed using the program SHELXS-97 by direct methods (Sheldrick, 1997) [19], and refined using the program SHELXL-97 (Sheldrick, 1997) [20]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from the difference Fourier map and allowed to ride on their parent atoms with  $U_{iso}(H) = 1.2 U_{eq}(C)$ . The crystal structure contains disordered water and ethanol as solvate molecules. In spite of several attempts, the electronic density in this area could not be resolved satisfactory. Therefore the contribution of the disordered solvent species was subtracted from the structure factor calculations by the SQUEEZE instruction of the program PLATON [21].

#### 3. Results and discussion

The series of complexes was synthesized by a straight forward synthesis (see Scheme 1) via the dichloro-1,10-phenanthroline metal(II) species followed by an exchange of the chloro ligands by the dithiolates 1,2-dithiooxalate (dto:  $K_2C_2O_2S_2$ ) and 1,2-dithiosquarate (dtsq:  $K_2C_4O_2S_2$ ). The problem of the synthesis is the poor solubility of the final complexes, reducing the chance of purification by recrystallization. Also all attempts to grow single crystals of diffractometer quality for the M(II) complexes failed.

#### 3.1. IR spectroscopy

A comparison of the IR spectra of the series of diimine/dithiolate complexes (Tables 3 and 4) as well as the dichlorophenanthroline intermediates (Table 2) show that all these complexes have the same structure with only some slight differences in the absorption energies due to the different metal centers. The IR-results give also a clear evidence of the coordination of the two dithiolate ligands (1,2-dithiooxalate and 1,2-dithiosquarate) via their sulfur atoms being reflected by a shift of the carbonyl absorptions (dto:  $v_{(C-O)} = 1514 \text{ cm}^{-1}$ , dtsq:  $v_{(C-O)} = 1707 \text{ cm}^{-1}$ ) towards higher wave numbers in the complexes.

#### 3.2. EPR spectroscopy

Copper(II) with a d<sup>9</sup> electron configuration is well suited to be studied by EPR spectroscopy. Fig. 1 shows the EPR-spectrum of a pure powdered sample of dichloro-1,10-phenanthrolinecopper(II) at 150 K as a glass (frozen solution). The spectrum is of axial



Scheme 1. Synthesis of the 1,10-phenanthroline-dithiolate mixed ligand complexes [M(phen)(dto)] and [M(phen)(dtsq)].

Table 1

Crystal data and details of structure determination of [Cu(phen)<sub>2</sub>Cl]·C<sub>2</sub>H<sub>5</sub>OH·H<sub>2</sub>O.

Formula <sup>a</sup>	C24H16ClCuN4
Formula weight <sup>a</sup>	459.41
Crystal size (mm)	$0.15\times0.22\times1.00$
Temperature (K)	210(2)
Crystal system	Monoclinic
Space group	C2/c
a (Å)	16.5080(13)
b (Å)	15.8475(15)
c (Å)	17.6002(12)
β (°)	95.379(6)
$V(Å^3)$	4584.1(6)
Ζ	8
$D_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.331
$\mu$ (mm)	1.086
F(0 0 0)	1872
θ (°)	1.8-25.0
Collected reflections (R <sub>int</sub> )	14 490
Unique reflections (R <sub>int</sub> )	4016 [0.061]
Observed data $[I > 2\sigma(I)]$	2884
Data/restraints/parameters	4016/0/320
$R_1$ , $wR_2^{b}$ (all data)	0.0683, 0.1068
$R_1, w R_2^{b} [I > 2\sigma(I)]$	0.0480, 0.1014
Goodness of fit (GOF) on $F^2$	1.014
Minimum/maximum resd. dens. (eÅ <sup>-3</sup> )	-0.479/0.351

<sup>a</sup> Data only reflect known cell content.

<sup>b</sup>  $w = 1/[\langle s^2(F_o^2) + (0.0571P)^2]$ , where  $P = (F_o^2 + 2F_c^2)/3$ .

symmetry with the parameters  $g_{||} = 2.284 \pm 0.002$  and  $g_{\perp} = 2.067 \pm 0.002$ . The hyperfine structure due to the coupling of the electron spin (*S* = 1/2) with the nuclear spin of the two copper isotopes (<sup>63</sup>Cu: *I* = 3/2 natural abundance 69.2% and <sup>65</sup>Cu: *I* = 3/2 natural abundance 30.8%) is not resolved. This indicates that the metal

Table 2	2
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Characteristic IR absorptions of dichloro-1,10-phenanthroline metal(II) complexes of type [M(phen)Cl<sub>2</sub>].

Table	3
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Characteristic IR absorptions of 1,10-phenanthroline-1,2-dithiooxalato(S,S') metal(II) complexes of type [M(phen)(dto)].

Assignment	IR-frequency (cm <sup>-1</sup> )					
М	Cu	Ni	Zn	Pd	Pt	
$V_{C-H}$ $V_{C=0}$ $V_{ring}$ $V_{ring} + \delta_H$ $\delta_H$ (in plane) $V_{C-C-S}$ $V_{C-S}$ $\delta_H$ (out of plane) $\delta_{rior}$	3052 1620 s 1517 m 1426 s 1146 m 1106 w 870 w 723 m 644 w	3058 1629 s 1515 s 1426 s 1142 w 1105 w 870 w 724 m 646 w	3055 1621 m 1517 s 1426 s 1143 m 1103 m 868 s 726 s 642 w	3061 1623 s 1515 m 1426 s 1150 m 1110 m 876 w 716 s 650 w	3083-3058 1632 s 1516 m 1428 s 1152 m 1112 m 880 w 710 s 655 w	
Ring torsion	428 w	426 w	422 w	421 w	417 w	

m: medium, s: sharp, w: weak.

centers are not sufficiently separated by the solvent and the complex is only suspended and not dissolved.

Fig. 2 shows the room temperature EPR-spectrum of a powdered sample of 1,10-phenanthroline-1,2-dithiooxalatocopper(II), [Cu(phen)(dto)], diamagnetically diluted in the isostructural [Ni(phen)(dto)] host lattice measured at 295 K in X-band (9.4 GHz). The spectrum reflects the axial symmetry of the *g*-tensor and the Cu hyperfine interaction tensor  $A^{Cu}$ . The hyperfine structure quartet due to the coupling with the nuclear spin of the copper (I = 3/2) is well resolved in the parallel part (lower field) as well as the super hyperfine structure due to the coupling with the two nitrogen atoms (<sup>14</sup>N: I = 1, natural abundance 99.6%). The perpendicular part is only poorly resolved because of some overlap. Overall 80 lines could be expected in the axial symmetric spectrum. The

Assignment	IR-frequency (cm <sup>-1</sup> )	IR-frequency (cm <sup>-1</sup> )				
М	M Cu		Zn	Pd	Pt	
$v_{C-H}$ $v_{ring}$ (C=C, C=N) $v_{ring}$ $v_{ring} + \delta_H$ $\delta_H$ (in plane) $\delta_H$ (out of plane) $\delta_H$ (out of plane) $\delta_{\Lambda}$	3079–3010 1606 m 1584 s 1516 s 1423 s 1145 m 1107 m 856 s 722 s 644 m	3050-3006 1605 m 1583 s 1516 s 1425 s 1144 m 1106 m 849 s 725 s 644 m	3054 1602 m 1583 s 1519 s 1427 s 1145 m 1105 m 853 s 726 s 647 m	3077-3058 1602 m 1581 s 1515 s 1425 s 1151 m 1109 m 842 s 724 s 651 m	3082–3059 1604 m 1578 s 1515 s 1427 s 1153 m 1112 m 841 s 725 s 656 w	
Ring torsion	429 m	427 m	427 m	434 m	419 w	

m: medium, s: sharp, w: weak.

<sup>a</sup> As [Ni(phen)(H<sub>2</sub>O)<sub>2</sub>Cl<sub>2</sub>];  $v_{(O-H)} = 3357 \text{ cm}^{-1}$ .

 Table 4

 Characteristic
 IR absorptions of 1,10-phenanthroline-1,2-dithiosquarato(*S*,*S'*) metal(II) complexes of [M(phen)(dtsq)] type.

Assignment	IR-frequency (cm <sup>-1</sup> )					
М	Cu	Ni	Zn	Pd	Pt	
v <sub>C-H</sub>	3061	3058	3057	3058	3082-3058	
$v_{c} = 0$	1822 w	1817 w	1726 s	1816 w	1820 w	
	1743 s	1723 s	1687 w	1744 s	1748 s	
	1706 s	1681 m	1663 m	1710 s	1708 s	
		1658 m				
vring	1601 m	1583 m	1584 w	1600 m	1603 w	
Vring	1518 m	1514 m	1518 m	1515 m	1516 m	
$v_{ring} + \delta_H$	1425 s	1423 s	1427 m	1426 s	1428 s	
$v_{ring} + \delta_H$	1317 w		1317 w	1311 w	1309 w	
V <sub>C-C-S</sub>	1224 w	1368 s	1360 s	1220 m	1220 m	
		1182 s	1182 s 1191 s			
$\delta_{\rm H~(in~plane)}$	1158 s	1143 w	1142 w	1152 m	1154 w	
V <sub>C-S</sub>	909 w	897 w	898 w	913 m	910 w	
$\delta_{\rm H}$ (out of plane)	720 s	725 s	725 s	713 s	709 s	
$\delta_{ring}$	644 w	641 w	642 w	651 w	654 w	
Ring torsion	428 w	423 w	424 w	433 w	418 w	

m: medium, s: sharp, w: weak.



Fig. 1. EPR-spectrum of [Cu(phen)Cl<sub>2</sub>] in water at 150 K.



**Fig. 2.** EPR-spectrum of a powdered sample of [(phen)Cu(dto)] diamagnetically diluted in the isostructural [(phen)Ni(dto)] host lattice at 295 K (X-band).



**Fig. 3.** EPR-spectrum of the same powdered sample of [(phen)Cu(dto)] diamagnetically diluted in the isostructural [(phen)Ni(dto)] host lattice at 295 K (Q-band).

hyperfine coupling to the two other magnetic nuclei, <sup>33</sup>S and <sup>15</sup>N, that are present in the complex structure, cannot be observed because of their low natural abundance of 0.75 and 0.367%, respectively. Not all of the 80 lines are resolved due to the partial overlapping of the two line quintets for the two copper isotopes, resulting in a seven line pattern in the parallel part and a not fully resolved perpendicular part. For a better resolution namely of this perpendicular part we have also measured the same sample at higher frequency in Q-band (32 GHz). The Q-band-spectrum is depicted in Fig. 3. The parallel part and the perpendicular part are well separated but likewise the perpendicular part is not better resolved as at X-band frequencies. Obviously a slightly rhombic distortion of the g-tensor is observed at higher frequency preventing a better resolution of this spectral part in the Q-band spectrum. The spectra can be explained with the following effective spin Hamiltonian:

$$H_{\rm sp} = g\mu_e SB_0 + SA^{\rm Cu}I^{\rm Cu} + \sum_i SA_i^{\rm N}I^{\rm N} \tag{1}$$

All symbols have their usual meaning. The quadrupole and the nuclear Zeeman terms have been neglected because they only influence the EPR-spectrum in higher order perturbation theory.

The resulting EPR parameters for [(phen)Cu(dto)] in the [(phen)Ni(dto)] host lattice are  $g_{II} = 2.116 \pm 0.002$ ,  $g_{\perp} = 2.026 \pm 0.002$ ,  $A^{Cu}_{||} = 174.6 \pm 0.5 \times 10^{-4} \text{ cm}^{-1}$   $A^{Cu}_{\perp} = 40 \pm 1.0 \times 10^{-4} \text{ cm}^{-1}$ ,  $A^{N}_{||} = 11 \pm 1.0 \times 10^{-4} \text{ cm}^{-1}$  and  $A^{N}_{\perp} = 11 \pm 1.0 \times 10^{-4} \text{ cm}^{-1}$ . The Q-band spectrum of the same powder indicates a slightly rhombic g-tensor with  $g_{xx} = 2.0275$ ,  $g_{yy} = 2.0310$ ,  $g_{zz} = 2.1170$  derived from Q-band. From these parameters we can calculate the experimental spin density of the unpaired electron in the SOMO at the copper center. This MO is of in-plane- $\pi$  type and has the following composition (Eq. (2)):

$$\psi(b_1)) = \alpha |3d_{xy}(Cu)\rangle - \alpha' |2p_{x,y}(S)\rangle - \alpha'' |2p_{x,y}(N)\rangle$$
(2)

 $\alpha^2$ ,  $(\alpha)^2$  and  $(\alpha'')^2$  are expressions for the covalency of the Cu–S and the Cu–N bonds and can be determined from the Cu-tensor parameters. These are also in correlation with the spin densities  $c_s^2$ ,  $c_p^2$  and  $c_d^2$  in the involved s-, p- and d-orbitals ( $n^2$  is the degree of hybridization between the Cu 4s- and the Cu 3d-orbitals (Eq. (3)).

Cu: 
$$c_s^2 = \alpha^2 (1 - n^2), c_d^2 = \alpha^2 n^2$$
 (3)

Applying the generally accepted formalism of Morton and Preston [22] the individual spin densities can be calculated by the following simple equations (Eqs. (4a), (4b), (4c)):

$$(c_s)^2 = (A_{iso, exp})/(A_{iso, th})$$
 (4a)

$$\left(c_{\rm p,d}\right)^2 = (A_{\rm din\ exp\ })/(A_{\rm din\ th\ }) \tag{4b}$$

$$(A_{\rm dip.exp.} = (A_{\parallel} - A_{\perp})/3 \tag{4c}$$

the theoretical values are for  $A_{\rm iso.th.}^{\rm Cu} = 1999.7 \times 10^{-4} \, {\rm cm}^{-1}$  and for  $A_{\rm dip.th.}^{\rm Cu} = 114.1 \times 10^{-4} \, {\rm cm}^{-1}$ . The experimental parameters of the Cu-hfs tensor allow a determination of the spin density at the copper center atom by using the Eqs. (4a), (4b), (4c). With the values of Morton and Preston we get  $c_{\rm s}^2 = 0.04$ ,  $c_{\rm p,d}^2 = 0.40$  and  $\alpha^2 = 0.44$ . Therefore, 44% of the spin density is located at the copper center (calculated values EHT: 37 (42%); DFT 50%). There are two values from the EHT results given where the 37% is the result for the MO-contributions normalized to 100% and the value in brackets (42%) is the result from the MO-coefficients of the direct EHT output.

The calculated energies as well as the relative atomic contributions to the molecular orbitals of the square planar complex 1,2dithiooxalato-1,10-phenanthrolinecopper(II) with the point group  $C_{2v}$  are summarized in Table 5. The molecular orbital with the unpaired electron (SOMO) is a combination of d (Cu) and p (N, S) atomic orbitals and both the HOMO and the LUMO are mainly located at the diimine and dithiolate ligands, respectively. Fig. 4 presents the drawings of the HOMO, SOMO and LUMO for [Cu(phen)(dto)] as result of the EHT calculation and Fig. 5 shows

#### Table 5

Symmetry, relative energies and MO-coefficients of the frontier orbitals in [(phen)Cu(dto)] (direct from EHT output).

Orbital	Symmetry	$e^{-}$	E (eV)	MO-coefficients		
				Cu	Ν	S
LUMO (42)	<i>b</i> <sub>2</sub>	0	-10.29	0.104 p <sub>z</sub> 0.049 d <sub>xz</sub>	0.017 p <sub>z</sub>	0.388 p <sub>z</sub>
SOMO (43)	$b_1$	1	-10.79	0.015 p <sub>y</sub> 0.650 d <sub>xy</sub>	0.227 p <sub>y</sub> 0.382 p <sub>x</sub>	0.261 p <sub>y</sub> 0.317 p <sub>x</sub>
HOMO (44)	<i>a</i> <sub>1</sub>	2	-12.20	0.128 p <sub>x</sub> 0.069 d <sub>z2</sub>	0.212 p <sub>y</sub> 0.052 p <sub>x</sub>	0.077 p <sub>y</sub> 0.070 p <sub>x</sub>

the graphical result of the SOMO with a square planar coordination sphere (left) and the energy minimum at a twist of 30° (right).

A comparison of the Figs. 4 and 5 (middle) shows, that the molecular orbital with the unpaired electron (SOMO) is qualitatively represented in a similar manner by both methods (EHT and DFT). A structure optimization during the DFT calculations points out, that the energetic ground state is not the square planar arrangement as expected but a slightly twisted configuration with a dihedral angle between the two ligand planes of about 30°. This twist might be the reason for the paramagnetic behavior of the two nickel complexes [(phen)Ni(dto)] and [(phen)Ni(dtsq)] (see Section 2) As it can be seen from Fig. 5 the composition of the molecular orbital does not change significantly.

### 3.3. X-ray structure analysis

Attempts to crystallize the synthesized [(phen)Cu(dtsg)] complex resulted in light blue prism-shaped crystals of the reduced copper(I) complex chlorobis(1,10-phenanthroline-*N*,*N*')copper(I) ethanol solvate hydrate, [(phen)<sub>2</sub>CuCl]·C<sub>2</sub>H<sub>5</sub>OH·H<sub>2</sub>O. Due to the high degree of disorder the atomic positions of the solvent molecules could not be determined. However, a total potential solvent area of 889.5 Å (19.4% of the cell volume) was calculated by the program PLATON [21]. Fig. 6 shows the ORTEP plot and the atom numbering scheme of this complex. The crystallographic and structure refinement data are summarized in Table 1. Selected bond lengths and angles are collected in Table 6. The reduction of Cu(II) to Cu(I) in the presence of the 1,2-dithiosquarato ligand as reducing agent is not surprising and this redox sensibility of Cu(II) with the 1,2dithiosquarato ligand was already observed earlier [23] and is consistent with our laboratory experience over years. The primer oxidation step of the ligand is possibly the formation of a disulfide often followed by desulfurization and decomposition steps. The resulting complex was completely EPR silent due to the reduction of the Cu(II) to Cu(I) (d<sup>10</sup>). The chloro and the two phenanthroline ligands are coordinated to the Cu(I) in a distorted trigonal-bipyra-



Fig. 4. Frontier orbitals of [Cu(phen)(dto)], HOMO (left), SOMO (middle) and LUMO (right) from EHT calculations.



Fig. 5. Shape of the SOMO in a square planar coordination sphere (left) and in the energetic minimum with a twist angle of ~30° (right) from DFT calculations.



Fig. 6. ORTEP plot of the molecular structure and atom labeling scheme of  $[Cu(phen)_2CI]$ .

 Table 6

 Selected bond lengths (Å) and bond angles (°) for [Cu(phen)<sub>2</sub>Cl]-C<sub>2</sub>H<sub>5</sub>OH-H<sub>2</sub>O.

	Cu1-Cl1	2.2811(	(9)	Cu1-N1		2.146(3)
	Cu1-N2	1.995(3)		Cu1-N3		2.096(3)
	Cu1-N4	1.993(3	3)	N1-C1		1.314(5)
	N1-C5	1.362(5	5)	N2-C6		1.352(5)
	N2-C10	1.325(5	5)	N3-C13		1.329(5)
	N3-C17	1.360(4	ł)	N4-C18		1.352(5)
	C5-C6	1.426(6	5)	C17-C18		1.419(5)
	Cl1-Cu1-N1	119.02(8)		N1-Cu1-N3		106.80(10)
	Cl1-Cu1-N2	93.08(9)		N1-Cu1-N4		99.82(13)
	Cl1-Cu1-N4	91.08(9)		N2-Cu1-N3		94.58(12)
	Cl1-Cu1-N3	134.18(8)		N2-Cu1-N4		174.86(13)
	N1-Cu1-N2	80.76(1	3)	N1-Cu1-N2		80.36(12)
	Hydrogen bonds					
		C–H	Cl···H	C(H)· · · Cl	$C{-}H{\cdot}{\cdot}{\cdot}Cl$	Symm.
	C10−H10···Cl1	1.07(4)	2.73(4)	3.660(4)	146(3)°	3_575
	C11-H11···Cl1	0.94(5)	2.69(5)	3.486(4)	143(4)°	7_565
	C14–H14···Cl1	1.00(5)	2.74(5)	3.710(5)	165(4)°	4_574
Tr	anslation of symm	etrv code	to equivale	nt positions:	3 575 = -	-x. 2 - vz

Translation of symmetry code to equivalent positions:  $3_5/5 = -x$ , 2 - y, -z;  $7_565 = 1/2 - x$ , 3/2 - y, -z;  $4_574 = x$ , 2 - y, -1/2 + z.

midal arrangement (see Fig. 6). The dihedral angle between the planar phenanthroline ligands is 68.65(9)°. As it can be seen from the packing diagram (Fig. 7) intermolecular hydrogen bonds between the chlorine and the hydrogen atoms of the phenanthroline ligands are present stabilizing the molecular packing motif. The complex molecules are arranged in dimers and stabilized by significant  $\pi$ - $\pi$  stacking between two nearly coplanar phenanthroline ligands. The averaged interplanar distance between the two ligand planes is 3.369(5) Å. These dimers are stacked along the crystallographic b-axis (see Fig. 8) by slightly weaker intermolecular  $\pi$ - $\pi$ interactions (averaged interplanar distance of 3.478(5) Å) and the formed one-dimensional columns are interconnected by weak hydrogen bonds (see Table 6). The  $\pi$ - $\pi$  interactions reflected by the interplanar distances are slightly weaker as reported for a polymeric complex  $[Cu_2(phen)_2Cl_2(C_6H_8O_4)] \cdot 4H_2O(3.30 \text{ Å}) [24]$  but significant stronger as reported for some other phenanthroline complexes (3.52–3.79) Å [24–26]. The structure is comparable



**Fig. 7.** Stereo view on the crystal packing of  $[Cu(phen)_2CI]$ , the intermolecular hydrogen bonds from chlorine to hydrogen atoms of the phenanthroline ligands are also depicted.



**Fig. 8.** Unit cell packing of [Cu(phen)<sub>2</sub>Cl]. View along the crystallographic b-axis which coincides with the main axis of the stacked columns.

to the structures reported for chlorobis(1,10-phenanthroline-*N*,*N*')copper(II) hydroxide hexahydrate reported by Ma et al. [27] and recently chlorobis(1,10-phenanthroline-*N*,*N*')copper(I) hexahydrate reported by Zhong et al. [28]. The first complex is reported as a copper(II) complex and the second as copper(I) but both having very related unit cell parameters and the structural details (interatomic distances and angles) slightly differ from herein reported complexes. Therefore, the real oxidation state of the copper in at least one of these complexes might still be questionable.

#### 4. Conclusions

Two series of diimine/dithiolate mixed ligand complexes, 1,2dithiooxalato-1,10-phenanthrolinemetal(II) and 1,2-dithiosquarato-1,10-phenanthrolinemetal(II) are synthetically available for a variety of transition metal ions ( $M^{2+}$  = Ni, Cu, Zn, Pd, Pt). Resulting from the IR spectroscopic results the dithio ligands are coordinated exclusively via their sulfur donor atoms. The poor solubility of these complexes is a clear limitation for further treatment. An EPR spectroscopic study of 1,2-dithiooxalato-1,10-phenanthrolinecopper(II) as polycrystalline sample diamagnetically diluted in the isostructural 1,2-dithiooxalato-1,10-phenanthroline nickel(II) complex as host lattice allows to calculate the spin density distribution at the copper center from the experimental parameters. A comparison with theoretical values from EHT and DFT calculations shows good agreement especially for the EHT results, whereas the DFT calculation slightly overestimate the spin density at the metal center. This proves also that the simple EHT method produces reasonable results in a minimum of computing time at least for complexes of this highly covalent type.

The 1,2-dithiosquarato ligand with its reduction potential tends to reduce Cu(II) to Cu(I). The resulting side product chlorobis(phenanthroline)copper(I) was structurally characterized. The crystal packing motif is stabilized by a variety of  $\pi$ - $\pi$  interactions and hydrogen bonds.

#### 5. Supplementary material

CCDC 745947 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data\_request/cif.

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