Scientific paper

Solid State EPR Studies on Bis(1,2-dithiosquarato) cuprates(II): a Structure – Spectroscopy Relationship

Katja Bellin,[a] Duha Jawad,[b] Barbara Wenzel[c] and Peter Strauch[b]*

[a] *GKSS-Research Center, Institute of Polymer Research; Kantstr. 55, D-14513 Teltow*

[b] *University of Potsdam, Institute of Chemistry, Karl-Liebknecht-Str. 24-25, 14476 Golm; e-mail: ps@chem.uni-potsdam.de*

[c] *Institute of Interdisciplinary Isotope Research e. V. (IIF), Permoserstraße 15, D-04318 Leipzig*

** Corresponding author: E-mail: ps@chem.uni-potsdam-de*

Received: 31-03-2008

Dedicated to the memory of Professor Ljubo Golič

Abstract

1,2-Dithiosquaratometalates (M = Cu, Ni) are available by direct synthesis from metal salts with dipotassium-1,2-dithiosquarate and the appropriate counter cations. For EPR measurements in solid state (powder or single crystals) a diamagnetic dilution of the paramagnetic centers by isostructural host lattices is necessary to separate the magnetic centers from each other to prevent interactions. The X-ray structures of two potential diamagnetic hosts $(Ph_4P)_2[Ni(dtsq)_2]$ **1** and $[(Ph_3P)_2N]_2[Ni(dtsq)_2]$ **2** as well as the structures of two paramagnetic$[Cu(dtsq)_2]^{2-}$ complexes with sterically demanding counter cations $[(Ph_3P)_2N]_2[Cu(dtsq)_2]$ **4** and $[p\text{–}C_6H_4(CH_2Ph_3)_2][Cu(dtsq)_2]$ **5** are discussed. The copper complexes **4** and **5** as well as $(Ph_4P)_2[Cu(dtsq)_2]$ **3** were studied by solid state EPR spectroscopy as powders or single crystals and the parameters are compared to those of related complexes in diamagnetic host lattices. Metal-metal distances of 11–13 Å in the copper complexes separate the paramagnetic centres sufficiently and reduce the interactions to enable a well resolved hyperfine structure and to determine the tensor parameters of the magnetic g- and A^{Cu}-tensors.

Keywords: 1,2-dithiosquarate, X-ray, EPR, copper(II), nickel(II)

1. Introduction

1,2-Dithiolenes and 1,2-dithiolates belong to the best investigated classic ligand systems due to their interesting properties[1–6]. During the last few years they have gained a renewed interest to study their transition metal complexes as building blocks e.g. for conducting or magnetic materials[7–12]. To tune these properties an exact knowledge of the electronic structure and the shape and parameters of the magnetic tensors would be of essential interest. EPR spectroscopy is a powerful tool to investigate paramagnetic transition metal centres and to describe their paramagnetic properties. For such studies copper(II) complexes have been established as a workhorse in the field, due to their simple spin state of S = ½ with a nuclear spin of I = 3/2. Other advantages are the moderate spin density localization in the coordination sphere, making these systems sensitive for modifications in the coordination sphere, and the fact that copper(II) complexes usually do not require low temperatures. During the last decades there has been an ongoing debate on the nature of paramagnetic "through bond" and "through space" interactions. The nonbonding separation of paramagnetic centres in a structurally well defined surrounding is a possibility to study these effects by means of EPR spectroscopy.

Bis(1,2-dithiosquarato)metalates(II), $[M(dtsq)_2]^{2-}$ (M = Fe^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, VO^{2+}, Pd^{2+}), are structurally well described[13–18] and the EPR parameters for $[Cu(dtsq)_2]^{2-}$ in structurally not distorted square planar host lattices[15, 16] as well as the influence of nonplanar host systems[18] are known and understood. Therefore, they are suited to act as a probe for more detailed studies of direct interactions.

In this work we describe the preparation, crystal and molecular structures and paramagnetic properties of some square planar 1,2-dithiosquarato complexes as two potential diamagnetic hosts $(Ph_4P)_2[Ni(dtsq)_2]$ **1** and $[(Ph_3P)_2N]_2[Ni(dtsq)_2]$ **2** as well as three paramagnetic $[Cu(dtsq)_2]^{2-}$ complexes with sterically demanding counter cations $(Ph_4P)_2[Cu(dtsq)_2]$ **3**, $[(Ph_3P)_2N]_2[Cu(dtsq)_2]$ **4** and $[p–C_6H_4(CH_2Ph_3)_2][Cu(dtsq)_2]$ **5** in order to vary the distances and the orientation of the paramagnetic complex dianions in the crystal structure. The structures of coordination compounds with those large counter ions once have been named by Ljubo Golič himself as "Rubens-type structures". These results might give some input for the ongoing discussion of "through space" and "through bond" interactions of paramagnetic centres.

2. Experimental

2. 1. Synthesis

The ligand 1,2-dithiosquarate (dtsq) was synthesized following a modified method as described by Eggerding and West[19]. A solution of 1.5 g potassium in 60 ml dry ethanol was saturated with H_2S. To this solution of K_2S/KHS was added 1 g of 1,2-diethoxy-squarate (3,4-diethoxy-3-cyclobutene-1,2-dione). This solution was stirred in an argon atmosphere for 4 hours. After standing overnight the precipitated ligand was isolated by filtration. Decomposition starts at 200 °C; IR [cm^{-1}] : $\nu_{C–O}$ 1707, 1622 , $\nu_{C–C–O}$ 1348, $\nu_{C–C–S}$ 1208, $\nu_{C–S}$ 921.

$(Cat)_2[M(dtsq)_2]$ (Cat = cation; M= Cu, Ni). For the syntheses of the complexes 112 mg (0,5 mmol) K_2dtsq and 0,25 mmol of the appropriate metal(II) salt were dissolved in 10 ml water and the solution of the ligand is added slowly to the solution of the metal salt with stirring. The rapid complex formation was indicated by the colour change of the solution. After 1 hour an equimolar solution of the counter cation (according to the dtsq ligand) as onium chloride in 10 ml water was added very slowly and the crystalline complexes started to precipitate. The micro crystalline products were washed with water and cold methanol. The complexes are air stable and soluble in polar solvents e.g. dichloromethane, dimethylformamide, acetonitrile.

$(Ph_4P)_2[Ni(dtsq)_2]$ 1: from $Ni(ac)_2 \cdot 4\ H_2O$; yellow brown, melting point: 254–256 °C ; IR [cm^{-1}] : $\nu_{C–O}$ 1822, 1727, 1683, $\nu_{C–C–O}$ 1437, $\nu_{C–C–S}$ 1167 cm^{-1}, $\nu_{C–S}$ 910, 756 cm^{-1}, diamagnetic.(see also Coucouvanis et al.[14])

$[(Ph_3P)_2N]_2[Ni(dtsq)_2]$ 2: from $Ni(ac)_2 \cdot 4\ H_2O$; yellow brown; melting point: 200–205 °C ; IR [cm^{-1}] : $\nu_{C–O}$ 1825, 1724, 1691, $\nu_{C–C–O}$ 1436, $\nu_{C–C–S}$ 1114, $\nu_{C–S}$ 918, 750, diamagnetic.

$(Ph_4P)_2[Cu(dtsq)_2]$ 3: from $CuCl_2 \cdot 2\ H_2O$; dark green (solution violet); melting point: 182 – 185 °C (dec.), IR [cm^{-1}]: $\nu_{C–O}$ 1823, 1730, 1695, 1667, $\nu_{C–C–O}$ 1401 $\nu_{C–C–S}$ 1107, $\nu_{C–S}$ 917, 738, paramagnetic $\mu_{eff} = 1{,}7^{0.2}$ B.M.

$[(Ph_3P)_2N]_2[Cu(dtsq)_2]$ 4: from $CuCl_2 \cdot 2\ H_2O$; dark green (solution violet); melting point: 230–240 °C (dec.), IR [cm^{-1}]: $\nu_{C–O}$ 1826, 1726, 1696, $\nu_{C–C–O}$ 1397, $\nu_{C–C–S}$ 1118, $\nu_{C–S}$ 918, 746, paramagnetic $\mu_{eff} = 1{,}8^{0.2}$ B.M.

$[p–C_6H_4(CH_2Ph_3)_2][Cu(dtsq)_2]$ 5: from $CuCl_2 \cdot 2\ H_2O$; dark green (solution violet); melting point: 228–231 °C (dec.), IR [cm^{-1}]: $\nu_{C–O}$ 1825, 1728, 1695, $\nu_{C–C–O}$ 1398 $\nu_{C–C–S}$ 1111, $\nu_{C–S}$ 910, 744, paramagnetic $\mu_{eff} = 1{,}7^{0.2}$ B. M. The elemental analyses confirm the assumed compositions for all compounds.

For the diamagnetic dilution the nickel complex **2** was doped with copper by adding a solution of an equivalent of approximately 1–3% of the related copper complex **4** to a concentrated solution of the isostructural nickel complex and slow crystallization as described above.

2. 2. Methods

The **IR-spectra** were recorded on a Perkin Elmer Spectrum 200 in range between 4000 and 400 cm^{-1} as KBr-pellets (reference KBr).

The **X-ray** data set has been collected on a SIEMENS diffractometer system CCD Smart. The experimental data of the structure determination are summerized in tables 1 and 2. The structures have been solved by direct methods[19] and refined with anisotrope temperature factors[20]. The refinement has been performed on F^2. Crystals of diffractometer quality have been grown by covering of a concentrated solution of the complex in acetonitrile or dichloromethane by propanol-2 and slow interdiffusion of the solvents.

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif or by e-mail: deposit@ccdc.cam.ac.uk on quoting the deposition numbers CCDC 696179 (**1**), 696178 (**2**), 696177 (**4**), and 696176 (**5**).

EPR spectra have been recorded in X-band at 9.5 GHz with a Bruker ESP 300E spectrometer at room temperature. For the collection of the 3D single crystal data the crystal has been mounted on a goniometer and the spectra have been recorded in 10° steps in three perpendicular planes.

3. Results and Discussion

3. 1. X-ray Structures

The experimental details of the X-ray structure determination are summarized in tables 1 and 2. Figure 1 shows the Ortep plots of the two complex anions $[Ni(dtsq)_2]^{2-}$ and $[Cu(dtsq)_2]^{2-}$. Complexes of this type are structurally well studied[13–18], some characteristic bond distances and angles are collected in table 3. As expected these parameters of the symmetric complex molecu-

les do not differ much from each other and correspond also to the other reported structures. The aim of the present paper is not a detailed discussion of individual structures but more the influence of the sterically demanding counterions on the separation of the M^{2+} centres.

Table 1: Experimental details of the X-ray structure determination of **1** and **2**.

	$[(Ph_3P)_2N]_2[Ni(dtsq)_2]$ **2**	$[Ph_4P]_2[Ni(dtsq)_2]$ **1**
Formula	$C_{80}H_{60}N_2NiO_4P_4S_4$	$C_{56}H_{40}NiO_{46}P_2S_4$
Formula weight	1424,13	1025
Temperature	293(2) K	295(2) K
Wavelength	0.71073 Å, MoK_α	0.71073 Å, MoK_α
Crystal system	monoclinic	monoclinic
space group	C2/c	$P2_1/c$
a / Å	13.7867(3)	10.9587(8)
b / Å	22.3201(3)	15.2523(12)
c / Å	23.2067(2)	17.4462(13)
α / °	90 °	90 °
β / °	92.4730(10)	124.174 (4)
γ / °	90 °	90 °
V / Å ^{3}	7134.53(19)	2412.6(3)
Z	4	2
$D_{calc.}$ / g/cm^3	1.326	1.412
μ / mm^{-1}	0.531	0.689
Theta range / °	2.43 – 25.00	1.94 – 25.00
Refl. collected	20230	14063
Refl. Unique	6273	4240
Refined parameters	429	385
Goodness-of-fit on F^2	1.035	0.979
R_1/wR_2 (obs. data)	0.0489 / 0.0882	0.0368 / 0.0609
R_1/wR_2 (all data)	0.0966 / 0.1052	0.0549 / 0.0642
Electron density / e/Å^3	0.231 and –0.309	0.192 and –0.190

Table 1: Experimental details of the X-ray structure determination of **4** and **5**.

	$[p\text{-}C_6H_4(CH_2Ph_3)]_2[Cu(dtsq)_2]$ **(5)**	$[(Ph_3P)_2N]_2[Cu(dtsq)_2]$ **(4)**
Formula	$C_{56}H_{38}CuO_4P_2S_4$	$C_{80}H_{60}CuN_2O_4P_4S_4$
Formula weight	1028.58	1428.96
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å, MoK_α	0.71073 Å, MoK_α
Crystal system	monoclinic	monoclinic
space group	$P2_1/n$	C2/c
a / Å	11.4636(3)	13.7637(9)
b / Å	13.63320(10)	22.2901(15)
c / Å	15.6639(3)	23.1792(15)
α / °	90	90
β / °	104.9340(10)	92.4840(10)
γ / °	90	90
V / Å ^{3}	2365.35(8)	7104.6(8)
Z	2	4
$D_{calc.}$ / g/cm^3	1.444	1.336
μ / mm^{-1}	0.751	0.567
Theta range / °	1.98 – 28.03	1.74 – 26.17
Refl. collected	12933	15551
Refl. Unique	5136	6278
Refined parameters	286	430
Goodness-of-fit on F^2	1.012	1.046
R_1/wR_2 (obs. data)	0.0587 / 0.1017	0.0463 / 0.0841
R_1/wR_2 (all data)	0.1295 / 0.1299	0.0794 / 0.0954
Electron density / e/Å^3	0.475 and –0.526	0.285 and –0.298

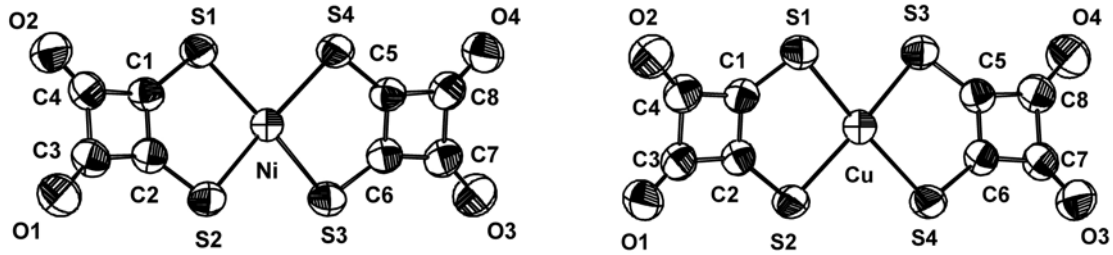

Figure 1: Molecular structures of the complex anions bis(1,2-dithiosquarato)-nickelate(II), $[Ni(dtsq)_2]^{2-}$ and bis(1,2-dithiosquarato)cuprate(II), $[Cu(dtsq)_2]^{2-}$.

Table 3: Selected bond distances (Å) and angles (°) of the complex anions.

	(1)	(2)	(4)	(5)
M–S1	2.2194(5)	2.3211(11)	2.3180(11)	2.2983(12)
M–S2	2.2226(5)	2.3212(11)	2.3193(11)	2.3468(11)
C1–S1	1.700(2)	1.686(4)	1.680(4)	1.686(4)
C2–S2	1.697(2)	1.687(3)	1.691(3)	1.689(4)
C3–O1	1.209(2)	1.215(4)	1.208(4)	1.208(5)
C4–O2	1.207(2)	1.209(4)	1.205(4)	1.211(5)
C1–C2	1.380(3)	1.388(4)	1.385(5)	1.378(5)
C2–C3	1.478(3)	1.474(5)	1.480(5)	1.478(6)
C3–C4	1.538(3)	1.524(5)	1.527(6)	1.520(6)
C4–C1	1.474(3)	1.483(5)	1.470(5)	1.478(5)
S1–M–S2	94.47(2)	93.34(3)	93.33(3)	91.94(4)

Square planar coordinated nickel(II) complexes are usually diamagnetic and well suited as host lattices for EPR investigations of the isostructural copper(II) complexes. From that point of view the crystal system is of importance, because depending on the crystallographic symmetry the presence of one or two magnetically independent orientations are possible. This might be demonstrated with the two presented nickel complexes (**1** and **2**). $(Ph_4P)_2[Ni(dtsq)_2]$ **1** crystallises in the monoclinic space group $P2_1/c$ and due to this symmetry two different orientations of the complex molecules are the result (see figure 2), which are important for single crystal EPR studies (see below). The other nickel complex $[(Ph_3P)_2N)]_2[Ni(dtsq)_2]$ **2**, crystallises also in a monoclinic space group but C2/c with an unique orientation of the complex molecules as it can be clearly seen in figure 3. In a single crystal EPR spectrum of $(Ph_4P)_2[Cu(dtsq)_2]$ **3** diamagnetically diluted in the host lattice **1** two different parameter sets as the effect of the crystal symmetry might be detected. This effect can make the exact evaluation of the spectra and the determination of the orientation of the tensor main axis in relation to the crystallographic axes more complicate. Therefore, the second system **2** with an unique orientation of the complex molecules and only one parameter set would be more welcomed as host lattice from a spectroscopical point of view.

For the use of sterically demanding counter ions as spacers to separate the metal centres not only the orientation but also the direct metal-metal distances are of significant importance. Large counter ions enable also larger distances between the metal centres, giving rise to a sufficient separation of the paramagnetic centres. We have studied two pure copper(II) systems as single crystals, $[(Ph_3P)_2N)]_2[Cu(dtsq)_2]$ **4** and $[p\text{-}C_6H_4(CH_2Ph_3)_2][Cu(dtsq)_2]$ **5**. The first (**4**) is isostructural to the corresponding nickel complex **2** (figure 3), whereas the second (**5**) (figure 4) crystallises in the monoclinic space group $P2_1/n$ and due to this crystallographic symmetry one would again expect two different orientations of the complex molecules (see figure 5), and consequently two parameter sets in a single crystal EPR spectrum.

In the nickel complex $(Ph_4P)_2[Ni(dtsq)_2]$ **(1)** the separation of the metal centres is already almost effective. The shortest metal-metal distances are 13.0985(9) and 13.7637(9) Å in the layer according to the square planar

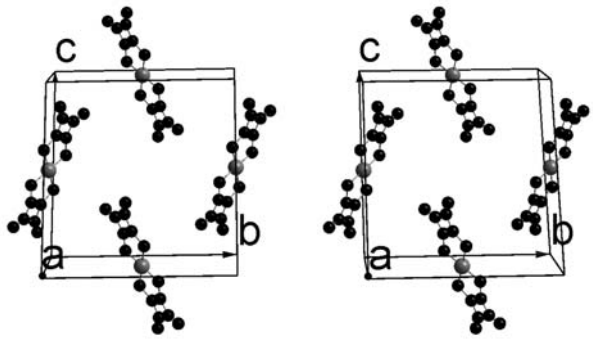

Figure 2: Stereoscopic view on the packing diagram of $(Ph_4P)_2[Ni(dtsq)_2]$ **1.** (The cations are omitted for clarity.)

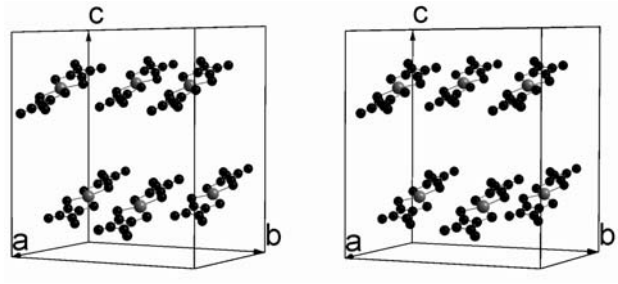

Figure 3: Stereoscopic view on the packing diagram of the isostructural complexes $[(Ph_3P)_2N)]_2[Ni(dtsq)_2]$ **2** and $[(Ph_3P)_2N)]_2[Cu(dtsq)_2]$ **4**. (The cations are omitted for clarity.)

coordination sphere and 13.2988(7) and 13.8089(7) Å between the layers, means perpendicular to the coordination plane. For the Cu(II) complex $[(Ph_3P)_2N)]_2[Cu(dtsq)_2]$ (**4**) these distances are even longer, 13.2988(7) and 13. 8089(7) Å. The other crystal system $[p–C_6H_4(CH_2Ph_3)_2][Cu(dtsq)_2]$ (**5**) with the large counter cation p-tolylbis(triphenylphosphonium) (see figures 4 and 5) has due to the crystal packing rather short metal-metal distances. The copper ions are placed on a special position and occupy the corners of the unit cell with distances according to the unit cell axes a, b, and c. Another complex ion with a crystal symmetry caused different orientation is located in the centre of the unit cell. The distances between the centre and the positions on the unit cell corners are 10.8407(1) and 12.7983(2) Å. For more structural details see supplementary material.

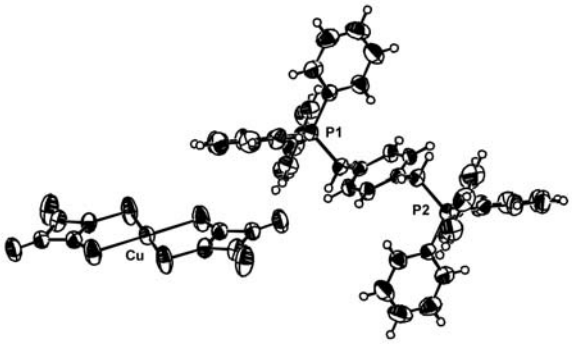

Figure 4: Molecular structure of p-xylylbis(triphenylphosphonium)(1,2-dithioquadra-tato)cuprat(II), $(p–C_6H_4(CH_2Ph_3)_2$ $[Cu(dtsq)_2]$ (**5**).

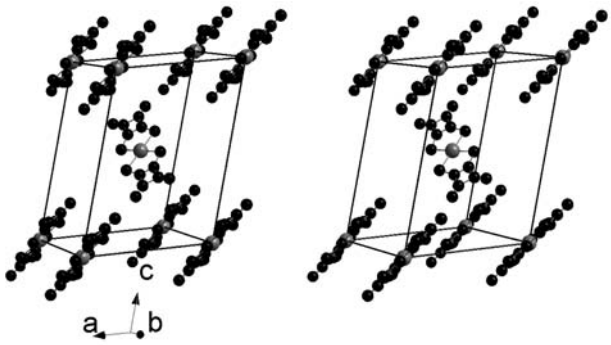

Figure 5: Stereoscopic view on the packing diagram of $[p–C_6H_4(CH_2Ph_3)_2][Cu(dtsq)_2]$ **5**.(The cations are omitted for clarity.)

3. 2. EPR Spectroscopy

The main goal of this paper is the investigation of these Cu(II)-systems with means of EPR spectroscopy in solid state as diamagnetically diluted guests in the corresponding nickel host lattice and as pure Cu(II)-complexes with exclusively the large counter ions as "diamagnetic medium" to separate the paramagnetic Cu^{2+} centres from each other. The EPR parameter of these square planar "$Cu(dtsq)^{2–}$ complexes are already well studied in solution, as polycrystalline powders and as paramagnetic hosts in several host lattices[15–18]. Single crystal studies of the pure compounds are new to our knowledge. For the comparison the orientation of the tensor main axes of the paramagnetic tensor should be defined as depicted in figure 6.

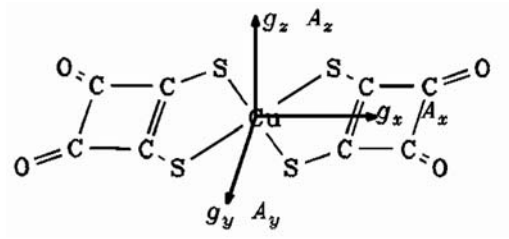

Figure 6: Orientation of the magnetic hfs-tensor main axes in bis(1,2-dithio-squarato)cuprates(II).

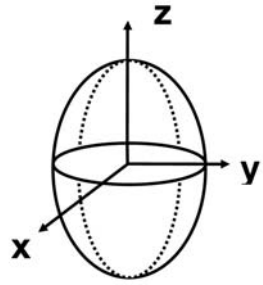

Figure 7: Principle shape of the paramagnetic tensor of square planar CuS_4-complexes.

The anisotropy of these parameters give the axial symmetric tensor the shape of a cigar demonstrated in the scheme of figure 7. The parameter sets of some $Cu(dtsq)^{2–}$ complexes are summarised in Table 4, demonstrating the anisotropy of the g- as well as the A-tensors .

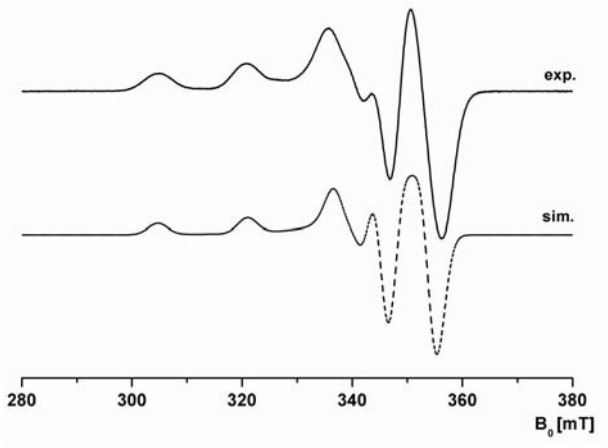

Figure 8: Experimental (exp.) and simulated (sim.) EPR spectrum of a polycrystalline powder sample of pure $(Ph_4P)_2[Cu(dtsq)_2]$ **3.**

In figure 8 the spectrum of a polycrystalline powder sample of pure $(Ph_4P)_2[Cu(dtsq)_2]$ **3** is presented. The spectrum is very related to the powder spectrum measured in the isostructural $(Ph_4P)_2[Pd(dtsq)_2]$ host lattice reported by Arrizabalaga et al. in 1987[15]. Due to the efficient separation of the paramagnetic centres the characteristic hyperfine structure of the Cu(II) is resolved but as a result of remaining weak interactions the line broadening effects are still significant. A total isolation of the paramagnetic metal centres as it is usually the case in diamagnetically well diluted systems gives typical single crystal spectra with small line width as for example in the $[(Ph_3P)_2N)]_2[Ni/Cu(dtsq)_2]$ system. Figure 9 shows a randomly oriented single crystal EPR spectrum of $[(Ph_3P)_2N)]_2[Cu(dtsq)_2]$ diamagnetically diluted in the $[(Ph_3P)_2N)]_2[Ni(dtsq)_2]$ host lattice. The typical hyperfine structure of two sets of four lines due to the coupling of the unpaired electron with the nuclear spins of the two copper isotopes (^{63}Cu: I = 3/2, natural abundance 30,8%; ^{65}Cu: I = 3/2, natural abundance 69,2%) is well resolved.

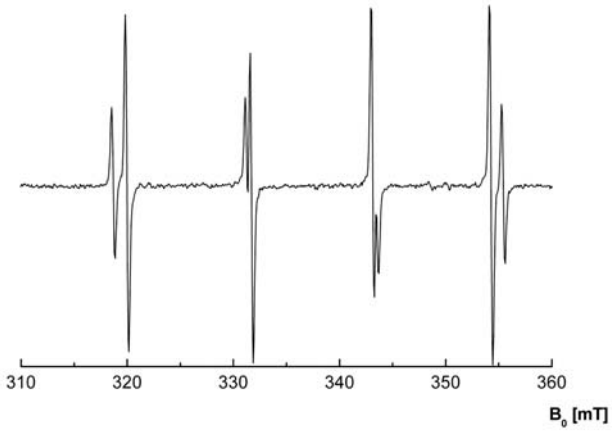

Figure 9: Single crystal EPR spectrum of $[(Ph_3P)_2N)]_2[Cu(dtsq)_2]$ **4** diamagnetically diluted in the $[(Ph_3P)_2N)]_2[Ni(dtsq)_2]$ **2** host lattice (randomly oriented).

A direct comparison of the EPR parameters of $[Cu(dtsq)_2]^{2-}$ in solution, as pure complexes with different cations (**3**, **4**) and as paramagnetic guests in three different host lattices shows that the g- as well as the A^{Cu}-tensor parameters do not differ significantly (table 4). This indicates that the chemical and structural situation for all complexes is in principle the same and the square planar coordination geometry is only slightly distorted. A distortion towards a more tetrahedral arrangement in the coordination sphere would give higher g-values and smaller coupling constants for complexes of this type[18]. The smaller coupling constant in the isotropic solution spectra might be attributed to solvent effects.

It follows from the parameters summarized in table 4 that in the pure complexes (**3**, **4**) the two cations $(Ph_4P)^+$ and $[Ph_3P)_2N]^+$ are large enough to separate the paramagnetic centers sufficiently. There is no paramagnetic interaction indicated in the parameters but there is still a small influence as it is reflected by the broadening of the line width (figure 8). Whereas the single crystal EPR spectrum $[(Ph_3P)_2N)]_2[Cu(dtsq)_2]$ diamagnetically diluted in the $[(Ph_3P)_2N)]_2[Ni(dtsq)_2]$ host lattice in figure 9 shows very small lines and the two copper isotopes are well resolved. The single crystal spectra of **4** have a much broader line width without resolution of the isotope splitting, but the typical four lines of the hyperfine splitting is still well resolved (see figure 10).

The angular variation of the EPR parameters g and A^{Cu} reflect the anisotropy of the magnetic tensor very well as it is depicted in the first stacked plot of figure 10 (left). The second stacked plot (right), from a measuring plane perpendicular to the first, is oriented close to the axial plane of the tensor coinciding with the square planar coordination plane of the complex. The axial symmetry is demonstrated by the very small change of the g- and A^{Cu}– parameters in this measuring plane. The effects on the line width dominate in these spectra. The maximum values of the anisotropic EPR parameters g and A^{Cu} can be directly obtained from the spectra of powdered sam-

Table 4: EPR parameters of $[Cu(dtsq)_2]^{2-}$ in solution, as pure substances and in three different host lattices (coupling constants · 10^{-4} cm^{-1}) [a].

	solution ($CHCl_3$)	**(A)**	**(B)**	**(C) [18]**	**(D) [16]**	**(E) [15]**
$g_\parallel$		2.121	2.118	2.122	2.120	2.119
$g_\perp$		2.028	2.027	2.028	2.029	2.020
g_{av} [b]		2.059	2.057	2.059	2.059	2.053
g_0	2.058					
$A_\parallel^{Cu}$		–161	–160	–159	–159	–157
$A_\perp^{Cu}$		–35	–36	–37	–39	–37
A_{av}^{Cu} [b]		–77	–77	–78	–79	–77
a_0^{Cu}	–73					

$(Ph_4P)_2[Cu(dtsq)_2]$ **(A) 3,** $[(Ph_3P)_2N]_2[Cu(dtsq)_2]$ **(B) 4,** diamagnetic hosts lattices: $(BzlEt_3N)_2[Ni(dtsq)_2]$ **(C),** $(BzlPh_3P)_2[Te(dtsq)_2]$ **(D),** $(Ph_4P)_2[Pd(dtsq)_2]$ **(E);**

[a] exp. error g: ±0.005; A: ±1 [b] $g_{av} = (g_\parallel + 2g_\perp)/3$; $A_{av} = (A_\parallel + 2A_\perp)/3$

[[comment: $g_\parallel$,$A_\parallel$ = g and A (parallel); $g_\perp$, $A_\perp$ = g and A (perpendicular)]]

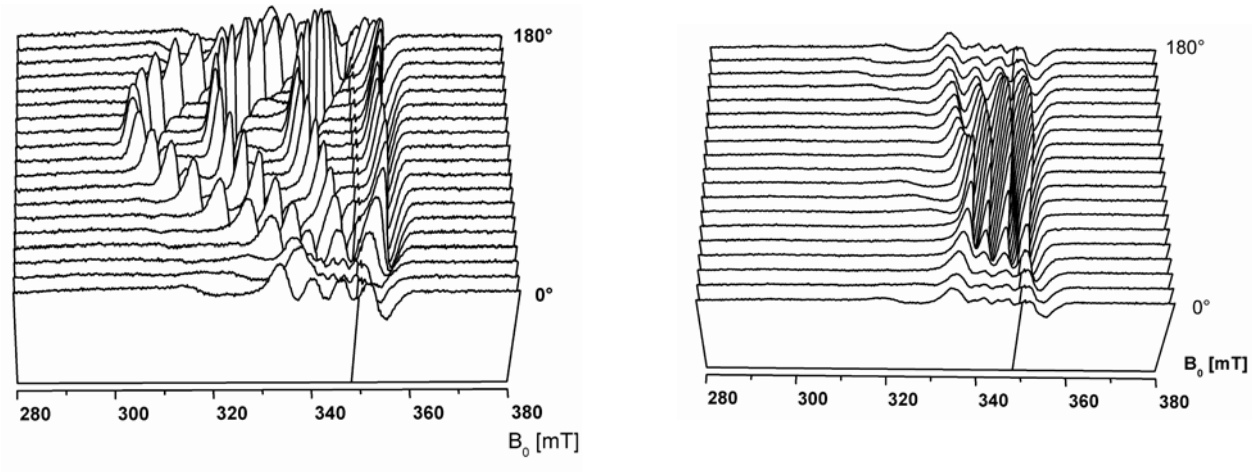

Figure 10: Stacked plot of the angular variations of the single crystal EPR spectra of $[(Ph_3P)_2N)]_2[Cu(dtsq)_2]$ **3** in two perpendicular planes (X-band, 295 K, 10°–steps).

ples with statistically averaged molecular orientations (see table 4).

3. 3. Conclusions

EPR spectroscopy is a suitable tool to monitor the chemical and structural surrounding of paramagnetic centres. The paramagnetic properties are usually exceeding the molecular boundaries making an efficient diamagnetic dilution of the paramagnetic centres necessary. With the presented results we could show that it is possible to separate the paramagnetic complex anions by sterically demanding counter cations without a remarkable influence on the g- and A^{Cu}- tensor parameters. Only the line broadening effects indicate the relatively small distances between the paramagnetic metal centres of approximately 11 – 13 Å. These presented results might give some support for the ongoing discussion of "through space" and "through bond" interactions of paramagnetic centres.

4. Acknowledgement

The authors thank Prof. Joachim Sieler (University of Leipzig/Germany) for collecting the X-ray data.

5. References

1. H. B. Gray, *Trans. Met. Chem*. **1965**, *1*, 239–287.
2. G. N. Schrauzer, *Trans. Met. Chem.* **1968**, *4*, 299–335.
3. J. A. McCleverty, *Progr. Inorg. Chem.* **1968**, *10*, 49–221.
4. R. Eisenberg, *Progr. Inorg. Chem*. **1970**, *12*, 295–369.
5. R. H. Holm, M. J. O´Connor, *Progr. Inorg. Chem*. **1971**, *14*, 241–401.
6. W. Dietzsch, P. Strauch, E. Hoyer, *Coord. Chem. Rev*. **1992**, *121*, 43–130.
7. G. Saito, H. Izukashi, M. Shibata, K. Yoshida, L. A. Kushch, T. Kondo, H. Yamuchi, O. O. Drozdova, K. Matsumoto, M. Kusunoki, K. Sakaguchi, N. Kojima, E. B. Yagubskii, J. *Mater. Chem.* **2000**, *10*, 893–910.
8. H. Yamochi, N. Sogoshi, Y. Simizu, G. Saito, K. Matsumoto, J. Mater. Chem. **2001,** *11*, 2216–2220.
9. Dithiolene Chemistry; K. D. Karlin, E. I. Stiefel (Ed.), *Progr. Inorg. Chem*. **2004**, *52*.
10. H. Alves, D. Simão, I. Cordeiro Santos, V. Gama, R. Teives Henriques, H Novais, M. Almeida*, Eur. J. Inorg. Chem*. **2004**, 1318–1329.
11. K. Ray, T. Weyhermüller, F. Neese, K. Wieghardt, *Inorg. Chem.* **2005**, *44*, 5345–5360.
12. C. J. Adams, P. C. Crawford, A. G. Orpen, T. Podestra, *Dalton Trans.* **2006**, 4078–4092.
13. D. Coucouvanis, F. J. Hollander, R. West, D. Eggerding, J. *Am. Chem. Soc*. **1974**, *96*, 3006–3008.
14. D. Coucouvanis, D. G. Holah, F. J. Hollander, *Inorg. Chem*. **1975**, *14*, 2657–2665.
15. P. Arrizabalaga, G. Bernardinelli, P. Castan, M. Geoffroy, R. Soules, C. R. Acad. Sc. *Paris, t. 304, Serie II*, **1987,** 559–562.
16. U. Drutkowski, P. Strauch, *Inorg. Chem. Commun*. **2001**, *4*, 342–345.
17. B. Wenzel, P. Strauch, Z. Naturforsch. **1999**, *54 b,* 165–170.
18. B. Wenzel, U. Drutkowski, and P. Strauch, *Z. anorg. allg. Chem*. **2001,** *627*, 973–979.
19. D. Eggerding, R. West; *J. Org. Chem*. **1976**, *41*, 3904–3909.
20. a) G. M. Sheldrick, SHELXS-86, Program for solution of X-ray structures, Göttingen **1986**, Acta Crystallogr. **1990**, A 46, 467. b) G. M. Sheldrick, SHELXS-97, Program for solution of X-ray structures, Göttingen **1990**,.
21. a) G. M. Sheldrick, SHELXL-93, Program for refinement of X-ray structures, Göttingen **1993**. b) G. M. Sheldrick, SHELXL-97, Program for refinement of X-ray structures, Göttingen **1997**.

Povzetek

1,2-Ditioskvaratometalati nastanejo z direktno sintezo iz kovinskih soli, dikalijevega-1,2-ditioskvarata in ustreznih kationov. Za EPR meritve v trdnem stanju (prašek ali monokristal) moramo ločiti magnetne centre, da preprečimo interakcije; postopek sestoji iz razredčenja paramagnetnih centrov z diamagnetnim izostrukturalnim ogrodjem. Določili smo rentgenske strukture dveh potencialnih diamagnetskih ogrodij, $(Ph_4P)_2[Ni(dtsq)_2]$ **1** and $[(Ph_3P)_2N]_2[Ni(dtsq)_2]$ **2** in dveh paramagnetnih $[Cu(dtsq)_2]^{2-}$ kompleksov $[(Ph_3P)_2N]_2[Cu(dtsq)_2]$ **4** and $[p\text{-}C_6H_4(CH_2Ph_3)_2][Cu(dtsq)_2]$ **5**. Bakrove komplekse **4** and **5** in $(Ph_4P)_2[Cu(dtsq)_2]$ **3** smo preiskali z EPR metodo v trdnem stanju in primerjali dobljene parameter z ustreznimi parametri v diamagnetnih ogrodjih. Razdalja 11–13 Å med kovinskimi atomi v bakrovih kompleksih ustrezno loči paramagnetne centre ter zmanjša interakcije kar omogoča nastanek dobro ločene hiperfine structure ter določitev tenzorskih parametrov magnetnih g- and A^{Cu}- tenzorjev.