

EPR STUDY OF THREE COPPER(II) SCHIFF BASE COMPLEXES

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Three copper Schiff bases have been investigated by the electron paramagnetic resonance (EPR) method in the 90-310 K temperature range. The EPR spectra are compared and analyzed. A detailed picture of magnetic interactions is deduced from the temperature dependence of the EPR parameters (g-factors, integrated intensities). The optimization of the spin-Hamiltonian parameters was achieved by using the software package SIMPOW.

INTRODUCTION

There is continuous interest in the investigation of Schiff base metal complexes obtained by condensation between aldehydes and imines. They are able to coordinate many different metals such as rare-earths and transition metals, and to stabilize them in various oxidation states. This permits the use of Schiff base metal complexes for a large variety of useful catalytic transformations (Cozzi, 2004). Also, large accessibility of the substituent groups display a wide range of physical and chemical properties used in a variety of fields, e.g. in medicine (Sun, Kong, Yang and You, 2006; Roy, 2009; Kukawska-Tarnawska, Leś, Dziembowska and Rozwadowski, 2009).

Schiff base Cu(II) complexes display a wide range of geometric arrangements around the copper ion, from the square planar to deformed tetrahedral geometry. Complexes of CuL(NCS) typically exhibit different axial distortions of their coordination polyhedral and a great variety of structural ordering effects. These phenomena are reflected in their spectral properties.

Electron paramagnetic resonance (EPR) is a suitable tool for the study of paramagnetic metal ion complexes and may provide useful information about the oxidation states, modes of coordination, geometry and type of ligand sites (Leniec, Kaczmarek, Typek, Kołodziej, Grech and Schilf, 2006; Leniec, Kaczmarek, Typek, Kołodziej, Grech and Schilf, 2007; Leniec, Typek and Kaczmarek, 2008; Leniec, Kołodziej, Przybylski, Kaczmarek, Typek, Brzeziński and Grech, 2009; Kaczmarek and Leniec, 2009).

In this paper we analyze powder EPR spectra of three copper Schiff bases based on some results derived from their structural analysis. We focused our interest on three different copper(II) complexes: CuL₁(NCS) (L₁ : C₆H₄(OH)CH=N-(CH₂)₂-N(CH₃)₂), CuL₂(NCS) (L₂ : C₆H₃(OH)BrCH=N-(CH₂)₂-N(CH₃)₂) and CuL₃(NCS)·H₂O (L₃ : C₆H₃(OH)(OCH₃)CH=N-(CH₂)₂-N(CH₃)₂) with the aim to understand the magnetic interactions between the copper ions and to find some magneto-structural correlations (Leniec, Kaczmarek, Typek, Tomaszewicz and Szady-Chelmienicka, 2010a, b).

EXPERIMENTAL

The CuL₁(NCS), CuL₂(NCS), and CuL₃(NCS)·H₂O complexes were prepared by the same procedure as that described for [Cu₂L₂(NCS)₂] complex, where L=2-[(2-dimethylaminoethylimino)methyl] phenolate, using a Schiff base and NCS⁻ ion as the ligands (Sun *et al.*, 2006). The preparation details and some results on the crystallographic structure of the mononuclear copper(II) complexes with Schiff bases are given in (Szady-Chelmienicka, Makal, Grech and Woźniak, submitted).

The EPR spectra were recorded on a conventional X-band Bruker ELEXSYS E 500 CW-spectrometer operating at 9.5 GHz with 100 kHz magnetic field modulation. The investigated samples were in fine powder form. The first derivative of the power absorption spectra has been recorded as a function of the applied magnetic field. Temperature dependence of the EPR spectra of the powder sample in the 90-310 K

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temperature range was recorded using an Oxford Instruments EPR helium-flow cryostat. The optimization of the spin-Hamiltonian parameters and EPR data simulation was achieved by using the software package SIMPOW (Nilges, SIMPOW).

RESULTS AND DISCUSSION

In Fig. 1 the crystal lattices of $\text{CuL}_1(\text{NCS})$ (A), $\text{CuL}_3(\text{NCS})\cdot\text{H}_2\text{O}$ (B) and $\text{CuL}_2(\text{NCS})$ (C) are presented.

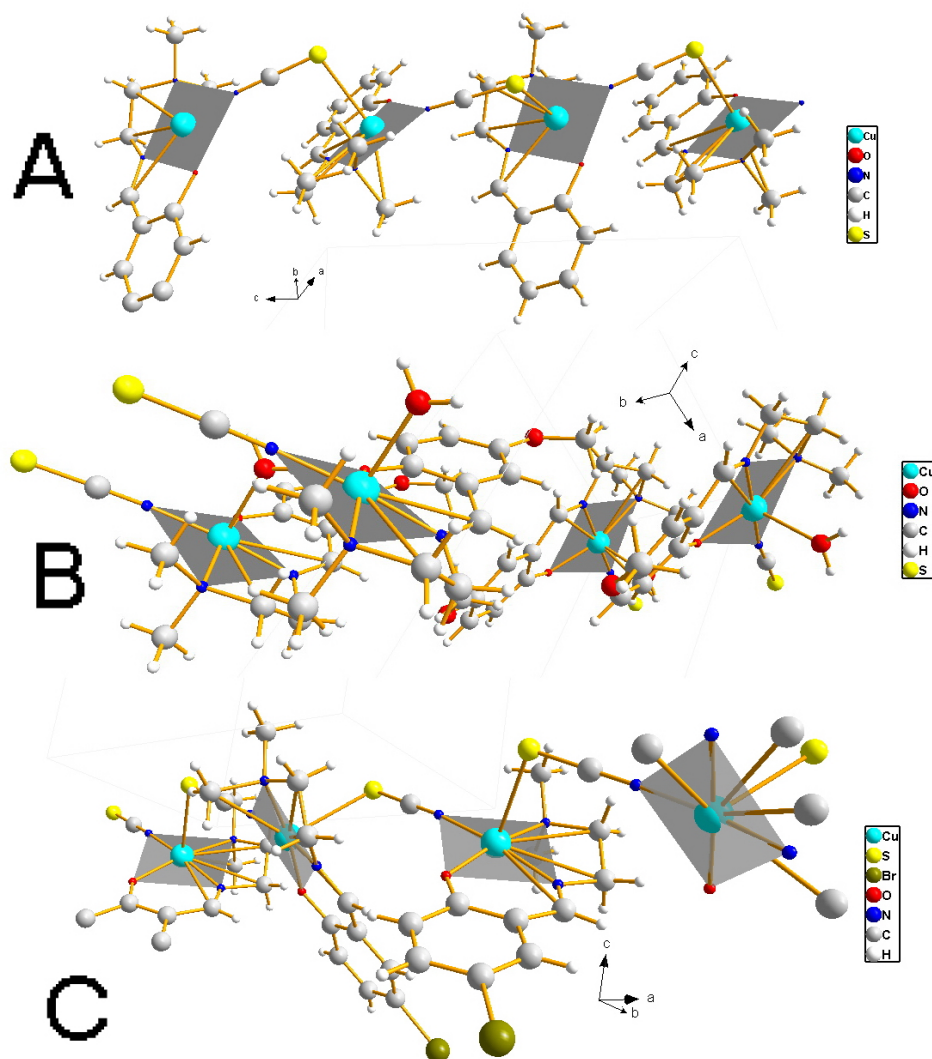


Fig. 1. The crystal lattices of $\text{CuL}_1(\text{NCS})$ (A), $\text{CuL}_3(\text{NCS})\cdot\text{H}_2\text{O}$ (B) and $\text{CuL}_2(\text{NCS})$ (C).

This figure has been generated by DIAMOND-3 program based on XRD data (Szady-Chelmeniecka *et al.*, submitted). The complex molecule is characterized by an axially elongated square-pyramidal $\text{Cu}(\text{II})$ coordination ($4 + 1$). Three nitrogen ions (blue balls) and one oxygen ion (red ball) occupy the basal plane of the pyramid. Additionally, in $\text{CuL}_3(\text{NCS})\cdot\text{H}_2\text{O}$ complex a weakly coordinating O2 atom of an adjacent water molecule is located at the apical site. The copper ion in one molecule is well separated from the metal ions in

surrounding moieties - the distance between two nearest Cu ions is the following: in $\text{CuL}_1(\text{NCS})$ it is 5.77 Å (along c-axis), in $\text{CuL}_3(\text{NCS})\cdot\text{H}_2\text{O}$ it is 5.63 Å (along b-axis), and in $\text{CuL}_2(\text{NCS})$ it is 6.02 Å (along a-axis).

The EPR powder spectra of the three investigated complexes consist of a line with dominating Lorentzian shape. Representative spectra at two selected temperature for all complexes are shown in Fig. 2.

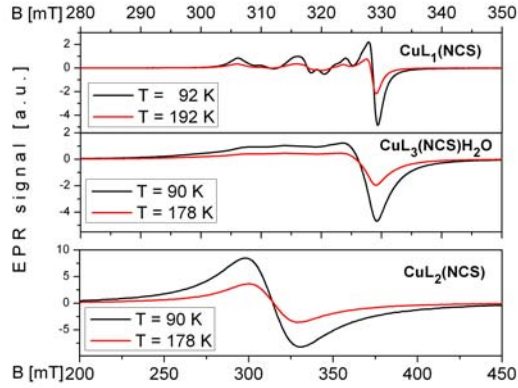


Fig. 2. The spectra $\text{CuL}_1(\text{NCS})$, $\text{CuL}_3(\text{NCS})\cdot\text{H}_2\text{O}$ and $\text{CuL}_2(\text{NCS})$ at two different temperatures.

The spectra of $\text{CuL}_1(\text{NCS})$ and $\text{CuL}_3(\text{NCS})\cdot\text{H}_2\text{O}$ demonstrate a typical powder pattern of an axially compressed copper complexes with hyperfine structure. These spectra are attributed to Cu^{2+} ion, for which effective values of electron and nucleus spins are $S=1/2$ and $I=3/2$, respectively. The double component lines in the hyperfine structure of EPR spectrum of the Cu^{2+} centres in $\text{CuL}_1(\text{NCS})$ in the parallel orientation corresponds to stable isotopes ^{63}Cu and ^{65}Cu (natural abundance – 69.1 % of ^{63}Cu and 30.9 % of ^{65}Cu , nuclear spin $I = 3/2$ for both isotopes). Since the linewidth is broad, different kinds of copper hyperfine lines are not clearly resolved. The spectrum can be described in terms of a spin-Hamiltonian containing only Zeeman and hyperfine terms of the following form:

$$H = \beta[g_{\parallel}B_zS_z + g_{\perp}(B_xS_x + B_yS_y)] + [A_{\parallel}I_zS_z + A_{\perp}(I_xS_x + I_yS_y)] \quad (1)$$

where $g_{\parallel} = g_z$ and $g_{\perp} = g_x = g_y$ are g -factors, β - Bohr magneton, S is the electron spin, I is the nucleus spin, B is the resonance magnetic field, and A_{\parallel} and A_{\perp} are the parallel and perpendicular components of the hyperfine tensor A .

EPR spectra of $\text{CuL}_2(\text{NCS})$ complex have been registered in the 90-300 K temperature range. As an example, two of the obtained spectra are presented in Fig. 1. The observed single, symmetric lines without hyperfine structure display little or no magnetic anisotropy. For generation of the EPR spectrum the following spin Hamiltonian was used:

$$H = \beta[g_{\parallel}B_zS_z + g_{\perp}(B_xS_x + B_yS_y)], \quad (2)$$

The spin-Hamiltonian contains only the Zeeman term and all symbols in the above equation have their usual meaning.

SIMPOW computer program enabled decomposition of the powder spectrum on lines observed for a single crystal. The observed powder spectra could be satisfactory simulated assuming only two g_{\parallel} and g_{\perp} factors in the whole temperature range. For $\text{CuL}_1(\text{NCS})$ and $\text{CuL}_3(\text{NCS})\cdot\text{H}_2\text{O}$ complexes the hyperfine parameters A_{\parallel} and A_{\perp} were extracted. The values of spin Hamiltonian parameters are presented in Tab. 1. There are not separately described parameters for ^{63}Cu and ^{65}Cu isotopes because corresponding EPR lines cover each other.

Table 1. Spin-Hamiltonian parameters for three investigated complexes at room temperature.

complex	g_{\parallel}	g_{\perp}	A_{\parallel} [mT]	A_{\perp} [mT]
$\text{CuL}_1(\text{NCS})$	2.111(2)	2.062(1)	8.8(3)	-
$\text{CuL}_2(\text{NCS})$	2.139(3)	2.136(3)	0	-
$\text{CuL}_3(\text{NCS})\cdot\text{H}_2\text{O}$	2.184(2)	2.064(1)	8.6(1)	-

Temperature dependence of the calculated g -factors (g_{\parallel} , g_{\perp}) for all complexes is presented in Fig. 3.

For $(\text{CuL}_1(\text{NCS}))$ complex the obtained g_{\parallel} and g_{\perp} are typical for an axially elongated $d_{x^2-y^2}$ ground state which is consistent with the d-orbital population derived from the experimental charge density presented in (Szady-Chelmeniecka *et al.*, submitted). On lowering the temperature from RT, the values of g -factors slightly diminish and the intensity of the EPR spectrum increases. Small value of A could be explained by considering the admixture of d_z^2 (excited state) orbital to $d_{x^2-y^2}$ ground state and covalent character of the metal – ligand bond (Natarajan, Mithira, Deepa and Sambasiva, 2008).

For the $(\text{CuL}_2(\text{NCS}))$ complex, taking into account uncertainties in calculated values of g -factors (± 0.003), it could be assumed that for $T > 200$ K $g_{\parallel} \approx g_{\perp} = g_0$ and is temperature independent. Below $T \sim 150$ K, $g_{\parallel} > g_{\perp}$ and on lowering temperature the magnetic anisotropy is getting more pronounced. As the hyperfine interaction lines were not observed for this complex it could be assumed that the exchange interaction was stronger than the hyperfine interaction and the hyperfine lines were washed away by a stronger interaction.

For the $(\text{CuL}_3(\text{NCS})\cdot\text{H}_2\text{O})$ complex the obtained g_{\parallel} and g_{\perp} values ($g_{\parallel} > g_{\perp} \approx 2.0023$) are typical for axially elongated $d_{x^2-y^2}$ ground state. Kivelson and Neiman (Kivelson and Neiman, 1961) have reported that g_{\parallel} values less than 2.3 indicates considerable covalent character of the metal-ligand bonds, while a value greater than 2.3 indicates an ionic character. As the g_{\parallel} value of $\text{CuL}_3(\text{NCS})\cdot\text{H}_2\text{O}$ complex is found to be less than 2.3 it implies a significant covalent character of the metal-ligand bonds.

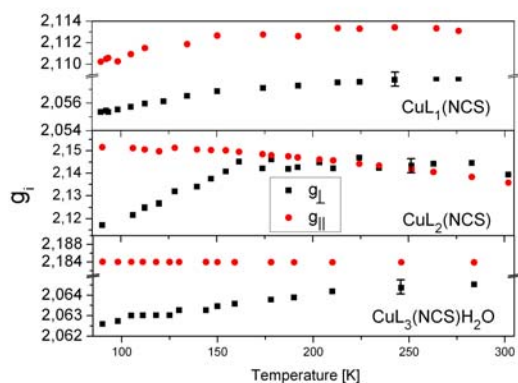


Fig. 3. Temperature dependence of the calculated g -factors (g_{\parallel} , g_{\perp}) for three investigated complexes.

The integrated EPR intensity I_{int} is an important spectroscopic parameter that can be calculated from the EPR spectrum. It is defined as the area under the absorption resonance line and is proportional to the imaginary part of the complex magnetic susceptibility of the investigated spin system. Study of the temperature dependence of I_{int} reveals the magnetic interactions between spin species. Fig. 4 displays the results of the temperature studies of I_{int} for all studied copper complexes. Temperature dependence of the integrated intensity has a similar character for all studied complexes. In all cases, this dependence is described by the Curie-Weiss law in the temperature range below 175 K, $I_{int}(T) = C/(T - \theta_{CW})$, where T is temperature and θ_{CW} the Curie-Weiss constant.

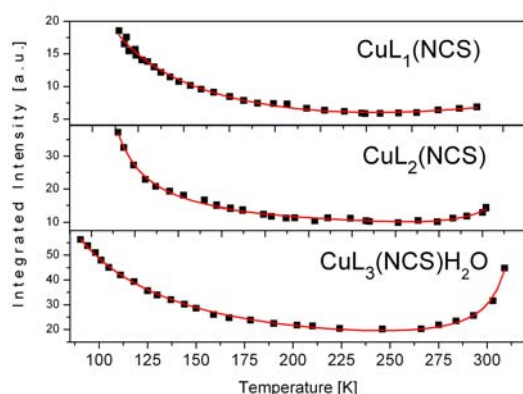


Fig. 4. Temperature dependence of the integrated EPR intensity I_{int} and fitting by the Bleaney-Bowers expression.

The least-square fits of the experimental points to that function gave the values of θ_{CW} presented in Tab. 2. The positive sign of the Curie-Weiss constant indicates on the existence of a rather strong ferromagnetic interaction between the paramagnetic centres.

Table 2. The value of parameters θ_{CW} , $-2J$, ρ in Eq. (4)

complex	θ_{CW} [K]	$-2J$ [cm ⁻¹]	ρ
CuL ₁ (NCS)	36.1	540	0.9
CuL ₂ (NCS)	62.6	1850	0.55
CuL ₃ (NCS)·H ₂ O	30.5	160	0.96

Unexpectedly, in the high-temperature range ($T > 250$ K) the integrated intensity increases with temperature increase. In general, the product of temperature and integrated intensity, $T \cdot I_{int}$ is proportional to the square root of an effective magnetic moment. For all of complexes the effective magnetic moment decreases with temperature decrease in high-temperature range ($T > 250$ K), but increases in low-temperature range, below 175 K. Thus the dominating antiferromagnetic interaction at high temperature changes to the ferromagnetic interaction at low temperatures.

The literature devoted to the magneto-structural correlations of copper complexes - including mono- and di-nuclear complexes - is very large. In many cases magnetic properties of copper(II) complexes were found to be very similar to what was registered for our complexes (Tandon, Thompson, Bridson and Bubenik, 1993; Getova, Bontchev, Mehendjiev and Bontchev, 2006; Yuste, Bentama, Stirba, Armentano, De Munno, Lloret and Julve, 2007; Guskos, Papadopoulos, Likodimos, Majszczyk, Typek, Wabia, Grech, Dziembowska, 2001). All three complexes displayed ferromagnetic interaction in the low temperature range, although with different values of the Curie-Weiss constant (see Table 2). This difference of interaction strength could not arise due to the difference in distances of the two nearest neighbors copper ions (5.76 Å, 5.63 Å and 6.03 Å, respectively) that is not very significant. Also the bridging -NCS- unit and its geometry in both complexes is the same. The only difference is in an arrangement of (3N+1O) deformed "squares" surrounding the copper ions. In the CuL₁(NCS) and CuL₃(NCS)·H₂O complexes the planes of these squares form an angle 30° and 0°, respectively while in the CuL₂(NCS) complex this angle is 90°.

In the high temperature range the antiferromagnetic interaction is detected in all complexes. The switch of interaction type is usually interpreted in terms of two-component system. The first is a paramagnetic one, present as a monomeric impurity. The second component is an antiferromagnetic one, formed as a result of an intermolecular indirect exchange interaction between copper(II) centers. Antiferromagnetic type interaction at high temperatures is usually described by the Bleaney-Bowers (Bleaney and Bowers, 1952) expression resulting from the isotropic (Heisenberg) exchange Hamiltonian ($\hat{H} = -2J\hat{S}_1\hat{S}_2$) for two interacting $S=1/2$ centers and given by

$$I = \frac{C_1}{T} \left[1 + \frac{1}{3} \exp\left(-\frac{2J}{kT}\right) \right]^{-1} \quad (3)$$

where C_1 is a constant. We have fitted the high temperature part of our integrated intensity I_{int} measurements by the following function, containing the contribution of dimers (first term) and the monomers (second term):

$$I_{int} = \frac{C_1}{T} \left[1 + \frac{1}{3} \exp\left(-\frac{2J}{kT}\right) \right]^{-1} (1 - \rho) + \frac{C_2}{T - \theta_{CW}} \rho \quad (4)$$

where ρ is the fraction of monomeric copper(II) centers. In Fig. 4 the results of the least-squares fits to the experimental points I_{int} are presented. The obtained values are presented in Tab. 2. They confirmed that the antiferromagnetic interaction is much stronger in the $\text{CuL}_2(\text{NCS})$ complex (1850 vs. 540 cm^{-1}) and in consequence the percentage of monomeric paramagnetic copper(II) complexes is much higher in the $\text{CuL}_1(\text{NCS})$ complex (90% vs. 55%). In the $\text{CuL}_3(\text{NCS}) \cdot \text{H}_2\text{O}$ complex the antiferromagnetic interaction is weak (160 cm^{-1}) and the highest is the percentage of monomeric paramagnetic copper(II) complexes (96%). The difference in a value of the J parameter in all complexes must be correlated with the very different arrangement of two (3N+1O) 'squares' connected by the NCS bridge.

CONCLUSIONS

Copper(II) ion is in the same square-pyramid coordination in all three complexes but they have different apex ions: oxygen in case of $\text{CuL}(\text{NCS}) \cdot \text{H}_2\text{O}$, sulphur in $\text{CuL}_1(\text{NCS})$ and $\text{CuL}_2(\text{NCS})$. However, there are also important differences that might influence the magnetic properties of these compounds: two crystallographic different sites of copper in $\text{CuL}_1(\text{NCS})$ and $\text{CuL}_2(\text{NCS})$ structures, but only one site in $\text{CuL}(\text{NCS}) \cdot \text{H}_2\text{O}$. This fact makes direct comparison of the values of the spin-Hamiltonian parameters not feasible (Tandon *et al.*, 1993). Besides, there are infinite chains of molecules in $\text{CuL}_1(\text{NCS})$ and $\text{CuL}_2(\text{NCS})$ structures, but separated molecular moieties in $\text{CuL}(\text{NCS}) \cdot \text{H}_2\text{O}$ complex. Yet another important factor that should reflect itself in the temperature dependence of EPR spectrum is the presence of water molecule in the nearest neighbourhood of magnetic Cu(II) ion. Despite the indicated differences comparison of magnetic properties in the low temperature range shows

a remarkable similarity: domination in all three complexes of an effective ferromagnetic interaction of comparable strength, $T_c \approx 35$ K. On the other hand in all three complexes in the high temperature range the antiferromagnetic interaction prevails. There is also a similar separating temperature, $T \approx 175$ K between these temperature ranges. The value of the J parameter is not correlated with the distance between copper ions, but most likely with the different arrangement of two neighbouring (3N+1O) 'squares'.

REFERENCES

- Bleaney B. and Bowers K. D. (1952). Anomalous Paramagnetism of Copper Acetate. *Proc. R. Soc. London A*, **214**, 451-465.
- Cozzi P. G. (2004). Metal-Salen Schiff base complexes in catalysis: practical aspects. *Chem. Soc. Rev.* **33**, 410-415.
- Getova V. T., Bontchev R. P., Mehandjiev D. R. and Bontchev P. R. (2006). Temperature dependence of the magnetic susceptibility of Cu^{2+} complexes. *Polyhedron*, **25**, 2254-2260.
- Guskos N., Papadopoulos G.J., Likodimos V., Majszczyk J., Typek J., Wabia M., Grech E., Dziembowska T., Perkowska A. and Aidinis K. (2001). Electronic structure of polycrystalline polyamine copper dinitrate complexes investigated by photoacoustic and electron paramagnetic resonance spectroscopy. *J. Appl. Phys.*, **90**, 1436-1441.
- Kaczmarek S. M. and Leniec G. (2009). Spectral and magnetic properties of macroacyclic and macrobicyclic Schiff base RE complexes. *J. Non-Cryst. Sol.*, **355**, 1325-1332.
- Kivelson D. and Neiman R. (1961) ESR Studies on the Bonding of Copper Complexes. *J. Chem. Phys.*, **35**, 149-155.
- Kukawska-Tarnawska I., Leś A., Dziembowska J. and Rozwadowski Z. (2009). Tautomeric forms of N-(5-nitrosalicylidene)-2-butylamine: Experimental and theoretical DFT study. *J. Mol. Struct.*, **928**, 25-31.
- Leniec G., Kaczmarek S. M., Typek J., Kołodziej B., Grech E. and Schilf W. (2006). Spectroscopic and magnetic properties of gadolinium macrobicyclic cryptate complex. *J. Phys.: Cond. Matter*, **18**, 9871-9880.
- Leniec G., Kaczmarek S. M., Typek J., Kołodziej B., Grech E. and Schilf W. (2007). Magnetic and spectroscopic properties of gadolinium macroacyclic Schiff base complex. *Solid State Sciences*, **9**, 267-273.
- Leniec G., Typek J. and Kaczmarek S. M. (2008). Magnetic properties of a new Er (III) macrobicyclic complex studied by EPR. *Applied Mag. Res.*, **35**, 197-203.
- Leniec G., Kołodziej B., Przybylski P., Kaczmarek S. M., Typek J., Brzeziński B. and Grech E. (2009). FTIR, ESI and EPR studies of a Dy(III) Schiff base podand complex. *J. Non-Cryst. Sol.*, **355**, 1355-1359.
- Leniec G., Kaczmarek S. M., Typek J., Tomaszewicz E. and Szady-Chelmienicka A. (2010a). EPR study of Schiff base $\text{CuL}(\text{NCS}) \cdot \text{H}_2\text{O}$ complex (L is $\text{C}_6\text{H}_3(\text{OH})(\text{OCH}_3)\text{CH}=\text{N}-(\text{CH}_2)_2-\text{N}(\text{CH}_3)_2$). *Rev. Adv. Mat. Sci.*, in the print.
- Leniec G., Typek J., Kaczmarek S. M. and Szady-Chelmienicka A. (2010b). EPR study of two Schiff base complexes: $\text{CuL}_1(\text{NCS})$ (L_1 is $\text{C}_6\text{H}_4(\text{OH})\text{CH}=\text{N}-(\text{CH}_2)_2-$

- $N(CH_3)_2$ and $CuL_2(NCS)$ (L_2 is $C_6H_3(OH)BrCH=N-(CH_2)_2-N(CH_3)_2$). *J. Non-Cryst. Sol.*, in the print.
- Natarajan B., Mithira S., Deepa S. and Sambasiva P. Rao, (2008). Single-Crystal EPR Identification of a Low Hyperfine Value and Interstitial Position of Copper Impurity in Diaquabis[malonato(1-)- κ^2O,O'] Zinc(II). *Appl. Magn. Reson.*, **35**, 57-71.
- Nilges M. Program SIMPOW, Illinois ESR Research Center NIH, Illinois, IL, Division of Research Resources Grant No. RR0181.
- Roy G. P. (2009). Synthesis and study of physico-chemical properties of a new chiral Schiff base ligand and its metal complex. *Inorg. Chim. Acta*, **362**, 1709-1714.
- Sun Y.-X., Kong D.-S., Yang G. and You Z.-L. (2006). Synthesis, Crystal Structures and Antibacterial Activities of a Pair of Isostructural Dinuclear Schiff Base Nickel(II) and Copper(II) Complexes. *Polish J. Chem.*, **80**, 1457-1463.
- Szady-Chelmeniecka A., Makal A., Grech E. and Woźniak K. (2010). Experimental charge density analysis of a model Schiff base complex: $CuLNCS$ ($L=C_{11}H_{15}N_2O$). submitted to *Mat. Chem. Phys.*
- Tandon S. S., Thompson L. K., Bridson J. N and Bubenik M. (1993). Synthesis and structural and magnetic properties of mononuclear, dinuclear, and tetranuclear copper(II) complexes of a 17-membered macrocyclic ligand (HM3), capable of forming endogenous phenoxide and pyridazino bridges. X-ray crystal structures of $[Cu_2(M_3)(\mu_2-OMe)(NO_3)_2]$, $[Cu_4(M_3)_2(\mu_3-OMe)_2(\mu_2-Cl)_2Cl_2]$, $[Cu_4(M_3)_2(\mu_3-OEt)_2(\mu_2-N_3)_2(N_3)_2](MeOH)$, $[Cu_4(M_3)_2(\mu_3-OMe)_2(NCS)_4](DMF)$, and $[Cu(M_3)(NCS)_2]$. *Inorg. Chem.*, **32**, 4621-4631.
- Yuste C., Bentama A., Stirba S. E., Armentano D., De Munno G., Lloret F. and Julve M. (2007). Ligand effects on the structures and magnetic properties of tricyanomethanide-containing copper(II) complexes. *Dalton Trans.*, **44**, 5190-5200.