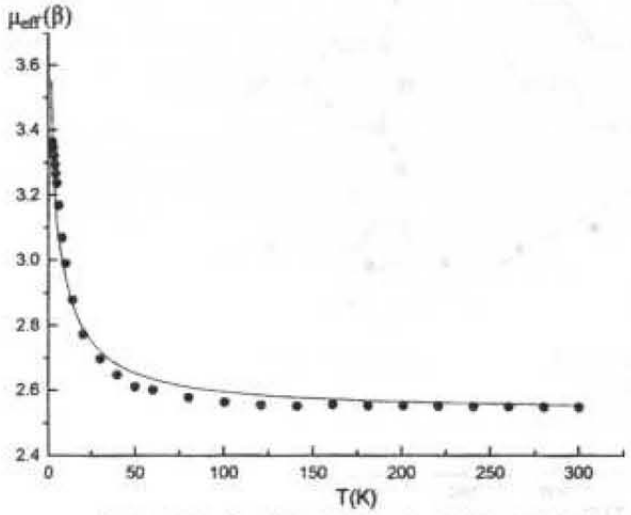

$g = 2.07 \pm 0.02$, $J = 9.7 \pm 1.1$ K, $zJ' = 0.47 \pm 0.07$ K

Рис. 4. Температурная зависимость эффективного магнитного момента соединения 10 (X = O)

βРабота выполнена при финансовой поддержке программы Президиума РАН "Направленный синтез веществ с заданными свойствами и создание функциональных материалов на их основе" (тема 00-04-17), грант РФФИ (06-03-90892-Мол_а. и гранта президента РФ (НШ-4849.2006.3)

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Надійшла до редколегії 30.01.06

J. Jezierska, Prof., V. Kokozay, Prof., A. Ożarowski, Dr.

EPR IN MODERN COORDINATION CHEMISTRY. Spin-Spin interactions within Cu(II) pairs of polynuclear complexes

На примерах поли- и гетерополиядерных комплексов рассмотрены особенности обменных взаимодействий между атомами меди (II). Показаны преимущества ЭПР-спектроскопии при исследовании слабых спин-спиновых взаимодействий.

The peculiarities of the exchange interactions between copper(II) atoms are considered for the case of poly- and heteropolynuclear complexes. EPR-spectroscopy has been shown to have advantages for the investigation of weak shin-spin interactions.

EPR spectroscopy is a much more sensitive technique than the measurements of static magnetic susceptibility for investigating the spin-spin interactions smaller than 1 cm^{-1}. Interactions weaker even by three orders of magnitude (of $10^{-2} - 10^{-3}$ cm^{-1}) still lead to a characteristic EPR spectrum distinctly different than that for the individual paramagnetic centers.

The splitting of the S = 1 levels in zero magnetic field (ZFS) measured by parameter D, for the simplest case of two interacting Cu(II) centers with spins $S_1 = 1/2$ and $S_2 = 1/2$, is demonstrated schematically in fig. 1 for parallel orientation of molecular axis towards the magnetic field direction. Spectra of this kind, consisting of the so-called fine structure lines, are interpreted in terms of the spin Hamiltonian that includes the ZFS parameters D and E:

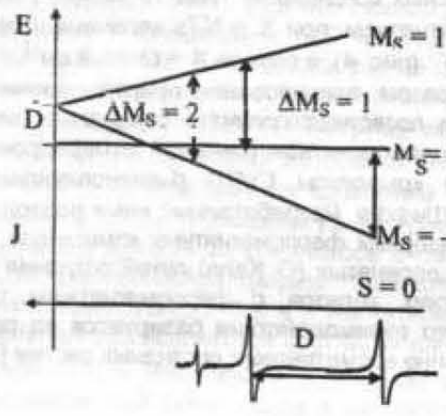


Fig. 1

$$\mathbf{H} = \beta \mathbf{B}\cdot\mathbf{g}\cdot\mathbf{S} + \mathbf{S}\cdot\mathbf{A}\,\mathbf{I} + \mathbf{D}\{(S_z^2 - (1/3)S(S+1)\} + \mathbf{E}(S_x^2 - S_y^2)\},$$

where $S = S_1 + S_2 = 1$

$$D = D^{dip} + D^{ex};$$

$$D^{ex} = 1/32\,\Delta g_z^2/J_{x2\text{-}y2,xy} - 1/16\,\Delta g_x^2/J_{x2\text{-}y2,yz} - 1/16\,\Delta g_y^2/J_{x2\text{-}y2,xz}$$

$$D^{dip} = -(g_z^2 + 1/4 g_y^2 + 1/4 g_x^2) / \beta^2 r^3$$

When the isotropic exchange $\mathbf{H} = \mathbf{J}\mathbf{S}_1\cdot\mathbf{S}_2$ between two Cu(II) ions is weak, D parameter is usually dominated by dipolar interactions and experimental D value allow to calculate Cu-Cu separation.

Unfortunately, the EPR measurements at common frequencies (corresponding to X- and Q-band) give often the line overlapping because the resonances are too close; some of them are not observed because of limited magnetic field range and ZFS being too large compared to the microwave quantum energy. Such effects, that are especially onerous for systems with S > 1, lead to ambiguous results of the experimental spectra simulation.

The aim of this report is to present our previous and recent results on application of X-band and modern HF (high field and high frequency) EPR spectroscopy to discriminate between separate Cu(II) ions and coupled pair of Cu(II) ions coordinated to the same ligands, to observe small differences in the interactions within the pairs of Cu(II) ions in dimeric or tetrameric (homo- and heteronuclear) compounds as well as to find unique structural characteristics of the coordination centers.

1. EPR DIFFERENTIATION OF Cu-Cu PAIRS FORMED BY $[Cu_2(\beta\text{-ALANINE})_4CL_2]CL_2{\cdot}H_2O$ IN ONE UNIT CELL [4]

The unit cell of the title compound contains two different binuclear $[Cu_2(\beta\text{-alanine})_4Cl_2]Cl_2{\cdot}H_2O$ entities, (a) and (b) that have only slightly different coordination polyhedra; a shorter Cu-Cu distance of 2.6331(10) Å and Cu-Cl bond length of 2.4511(10) Å for (a) in comparison with 2.6608(10) Å and 2.4387(10) Å, respectively, for (b). No difference between isotropic exchange integrals in (a) and (b) can be revealed by magnetic susceptibility measurements. The carboxylate-type interactions are strongly antiferromagnetic with J value of 320 cm^{-1}. On other hand the complexes exhibit two distinct overlapping spin-triplet EPR spectra (fig. 2) with different Spin Hamiltonian parameters: $g_x = 2.061$, $g_y = 2.063$, $g_z = 2.352$, $D = 0.3389$, $E = 0.0027$ cm^{-1} for (a) and $g_x = 2.059$, $g_y = 2.061$, 2.353, $D = 0.3318$, $E = 0.0035$ cm^{-1} for (b) and very well resolved hyperfine splitting from two equivalent copper nuclei in each coupled pair with $A_z = 0.0067$ cm^{-1} for (a) and 0.0074 cm^{-1} for (b). Taking into account the Cu-Cu distances and g parameters for (a) and (b) dimers, the values of $D^{dip} = -0.182$ and -0.176 were calculated giving a rare possibility to determine the contribution of $D^{ex} = +0.521$ cm^{-1} and $+0.508$ cm^{-1}, respectively, to total D values derived from the EPR spectra.

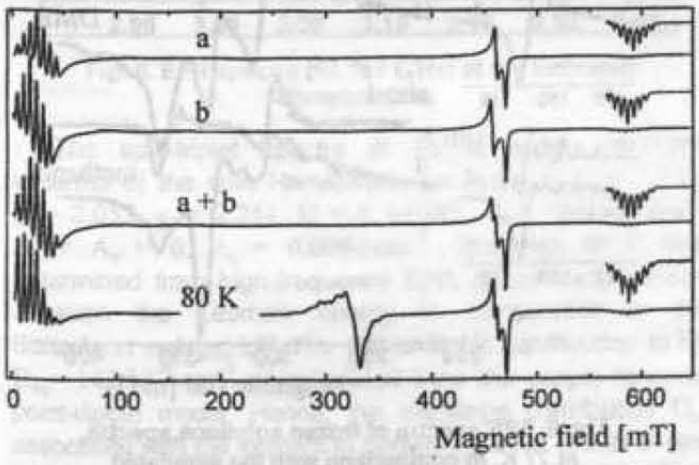
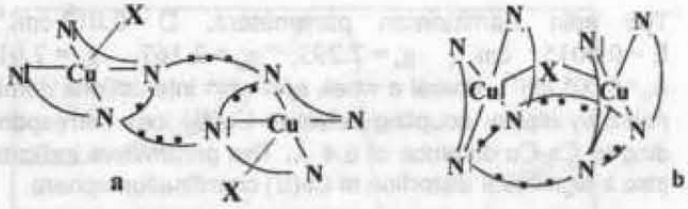


Fig. 2. EPR spectra: (a), (b), (a + b) dimmers and measured for polycrystalline $[Cu_2(\beta\text{-alanine})_4Cl_2]Cl_2{\cdot}H_2O$ at 80 K

Structural differences between the dimeric centres which exist only in case of chlorine derivative of Cu(II) dimer with β-alanine affect significantly the Zero – Field splitting parameter D.

2. EPR DETECTION OF Cu-Cu PAIRS FORMED IN SOLUTIONS [5]

The Cu(II) complexes with the ligand N,N',N'',N'''-Tetrakis(2-pyridyl-methyl)-1,4,8,11-tetraazacyclotetradecane (tpmc), have various coordination modes: the chair-type (a) for $Cu_2(tpmc)(ClO_4)_4$, $[Cu_2(N_3)_2(tpmc)](ClO_4)_2$ and boat-type (b) for anion-bridged complexes $[Cu_2X(tpmc)](ClO_4)_3{\cdot}n$ with X = F, $n = 2CH_3CN$, $X = NO_2$, X = OH, $n = 2H_2O$. The Cu-Cu distance is 5.74 Å for complex (a) with X = Br and 3.712 or 3.99 Å. for (b) with X = OH or F.



The antiferromagnetic exchange is weak $J = 2.0$ and 3.4 cm^{-1} for $[Cu_2N_3(tpmc)](ClO_4)_3$ and $[Cu_2(N_3)_2(tpmc)](ClO_4)_2$, respectively and strong, $J = 80$ cm^{-1} for $[Cu_2OH(tpmc)](ClO_4)_3$ [9].

The EPR spectra of frozen solutions of both type (a) and type (b) compounds in DMF and NMF are characteristic for ZFS caused mainly by dipolar interaction (fig. 3). The signals corresponding to $\Delta M_S = 1$ and $\Delta M_S = 2$ transitions are distinctly resolved due to hyperfine interaction with two weakly coupled Cu(II) nuclei. The D parameters, covering the range from 0.0318 to 0.0187 cm^{-1}, for these compounds in DMF solutions correspond to Cu-Cu distances between 4.6 and 5.5 Å. These distances may be correlated with the presence or absence of a bridge in the solid state complexes. For NMF solutions the D parameters (about 0.0250 cm^{-1}) are similar, suggesting that this solvent forces all compounds into the same boat conformation with copper ions separated by about 5 Å. The results indicate the loosening, removal or substitution of the anions in dimers of both types by solvent molecules, leading to a structure intermediate between (a)- and (b)-type.

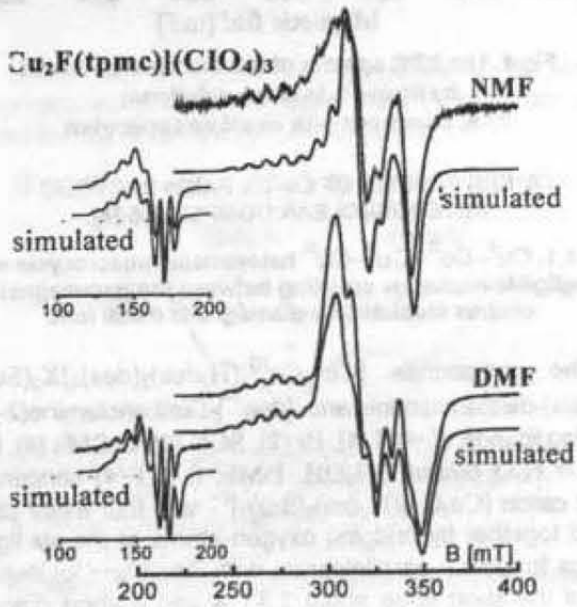


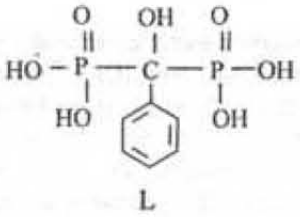
Fig. 3. EPR spectra of frozen solutions of $[Cu_2F(tpmc)](ClO_4)_3{\cdot}2CH_3CN$ (2) in NMF and DMF compared with simulated spectra

3. EPR IDENTIFICATION OF DIMERIC AND MONOMERIC Cu(II) COMPLEXES WITH POLYFUNCTIONAL LIGAND [3]

Observation of the changes in EPR spectra as a function of pH is an important method for structural identification of Cu(II) complexes formed by polyfunctional ligands; it allows to detect formation of different complexes and to observe equilibria between them.

For a Cu(II)-L system (where L=1-phenyl-1-hydroxymethylene bisphosphonate) the EPR spectra at pH lower than 5 or higher than 8 (fig.4) indicate the presence of monomeric Cu(II) complexes with tetragonal geometry. In the pH range 5 to 8 a very specific spectrum is observed with distinctly resolved hyperfine splitting due to two copper nuclei.

The spin Hamiltonian parameters, $D = 0.012\ cm^{-1}$, $E = 0.0015\ cm^{-1}$, $g_z = 2.293$, $g_y = 2.167$, $g_x = 2.01$, $A_z = 0.005\ cm^{-1}$, reveal a weak spin-spin interactions dominated by dipolar coupling between Cu(II) ions corresponding to Cu-Cu distance of 6.4 Å. The parameters indicate also a significant distortion of Cu(II) coordination sphere.



L

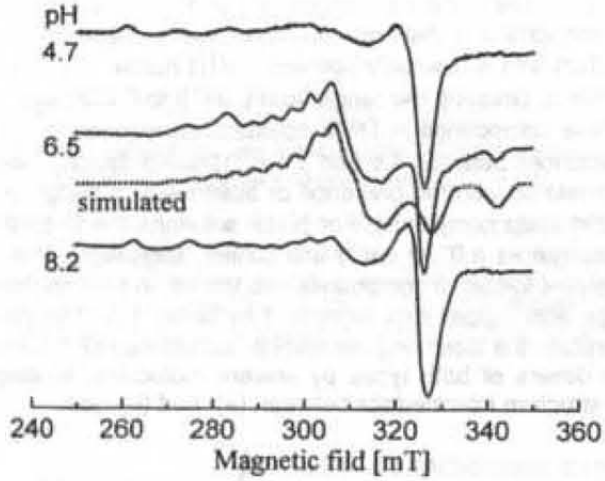


Fig 4. The EPR spectra of the complexes formed by ligand L in water solutions; 77 K compared with simulated spectrum

4. EPR STUDIES OF Cu-Cu PAIRS IN CYCLIC HETERONUCLEAR COMPLEXES [8]

4.1. Cu^{II}–Co^{III}–Cu^{II}–Co^{III} heterometallomacrocycle with negligible exchange coupling between the paramagnetic centres mediated by diamagnetic metal ions

The compounds $[Cu^{II}_2Co^{III}_2(H_2dea)_2(dea)_4]X_2(Solv)_n$ [(H_2dea)-diethanolamine and (dea^{2-})-Diethanolamine(2-) as bridging ligands, X = Cl (**1**), Br (**2**), SCN (**3**), O_2CMe (**4**), I (**5**); Solv = H_2O or/and CH_3OH, DMF, n = 1–4] contain the cyclic cation $[Cu_2Co_2(H_2dea)_2(dea)_4]^{2+}$ with four metal atoms linked together by bridging oxygen atoms of the six ligand groups to form a parallelogram with the (Cu···Co) separation of the short edge about 2.83 Å and a short diagonal (Cu···Cu) distance about 3.23–3.29 Å. Variable-temperature magnetic susceptibility measurements show no significant exchange coupling between the copper centres.

The triplet state (S = 1) EPR spectra are observed at 77 K (fig. 5 and 6), with spin Hamiltonian parameters for the compounds in frozen-solutions and solid-state being similar, which proves that the structure remains unchanged under the polar solvent influence. The spectra were interpreted with the assumption of noncoaxiality between the *g* and D tensors of about 30°, and the ZFS parameters D=0.0560 (**2–5**) and D = 0.0710, E = 0.0028 cm^{-1} (**1**) were obtained. The dominant contribution to the ZFS is presumed to be dipole-dipole in origin, and corresponds to Cu-Cu separations of 3.4 (**2–5**) and 3.2 Å (**1**), which are very close to those observed in crystal structures. The angle of noncoaxiality seems to be justified by the X-Ray structure studies; namely the plane of N,O,O,O donor set around Cu(II) makes an angle of ca. 30° with the axis joining the two copper centers.

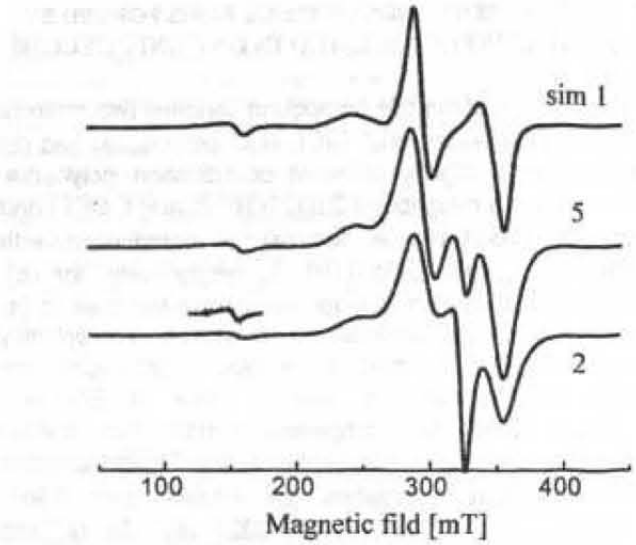


Fig. 5. EPR spectra of polycrystalline complexes, at 77 K, compared with the simulated (sim1) spectrum

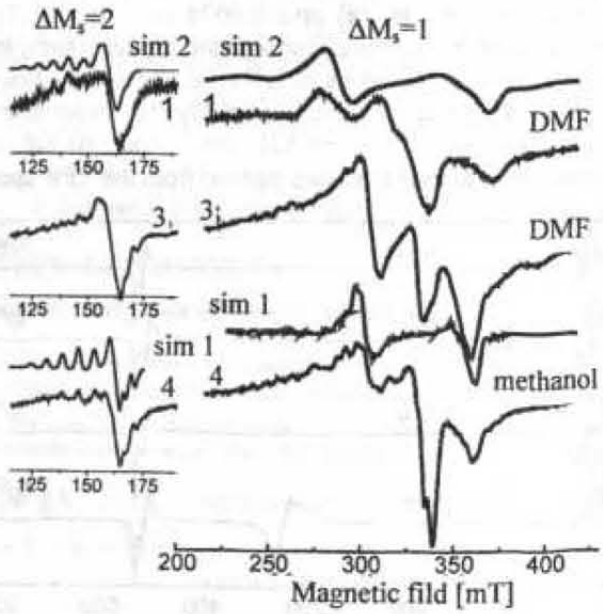


Fig. 6. EPR spectra of frozen solutions spectra, at 77 K, in comparison with the simulated (sim1 and sim2) spectra

4.2. Cu-Zn-Cu-Zn heterometallomacrocycle with significant antiferromagnetic coupling between paramagnetic centers mediated by diamagnetic metal [1]

An unprecedented antiferromagnetic exchange mediated by two -O-Zn-O- bridges, with singlet–triplet splitting $J = 35.0\ cm^{-1}$ occurs between two copper centers separated by 5.7062 Å in $Cu^{II}_2Zn^{II}_2(NH_3)_2Br_2(Hdea)_4]Br_2 \cdot CH_3OH$ (1) complex with diethanolamine (H_2dea) as bridging ligand. The X-band EPR spectrum at 77 K do not provide any evidence of Cu-Cu interaction (fig. 7). Although, the temperature lowering to 10 K reveals a hyperfine splitting due to two coupled Cu(II) ions; its interpretation is not possible because of the extensive overlap of the 'parallel' and 'perpendicular' features (fig. 7). Fortunately, application of high-frequency EPR resolved that difficulty. At 10 K a spin-triplet spectrum appeared (fig. 8) with its 'parallel' part split into eight lines separated by about 85 Gauss. Below 4 K, the 8-line structure was replaced by a 4-line hyperfine pattern with a splitting of 174 Gauss, characteristic of a single-copper impurity.

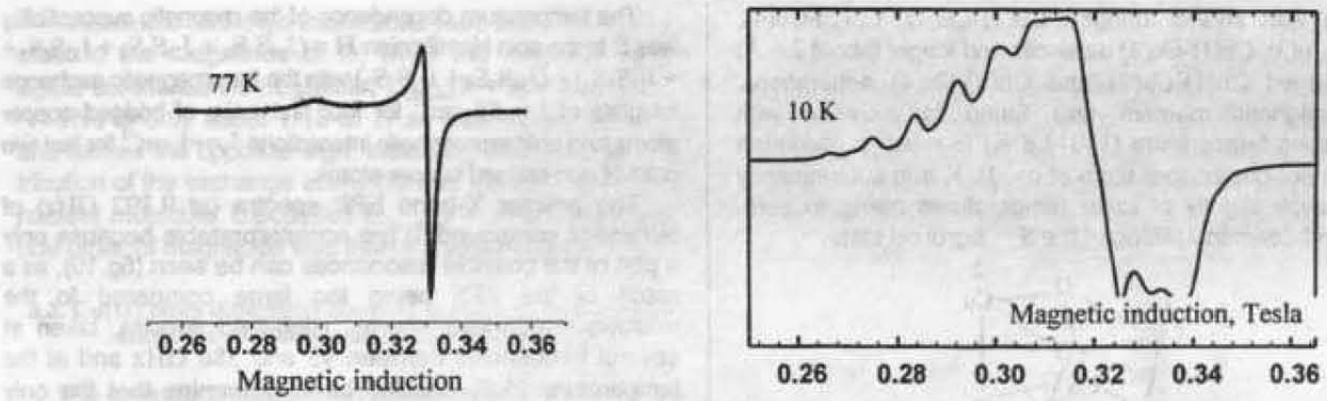


Fig. 7. X-band (9.5 GHz) EPR spectrum of polycrystalline compound (1) at 77 and 10 K

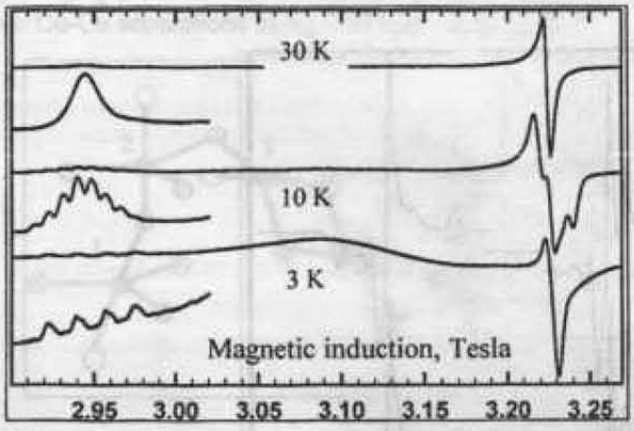


Fig. 8. EPR spectra (92.767 GHz) at the indicated temperatures

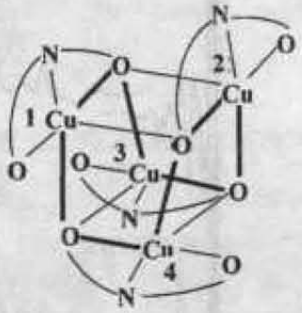
The spin-triplet spectra at 10 K were interpreted in terms of the spin Hamiltonian parameters: $g_x = 2.053$, $g_y = 2.055$, $g_z = 2.251$, D = k 0.0101, E = –0.0006 cm^{-1}, $A_x = A_y = 0$, $A_z = 0.0094 \cdot cm^{-1}$. The sign of D was determined from high-frequency EPR at low temperatures because the Zeeman energy is comparable to the Boltzmann energy, kT. The dipole-dipole contribution to D, $D_{dip} = 142 \cdot 10^{-4}$ cm^{-1} as calculated from the copper-centered point-dipole model. Hence, the exchange contribution D_{ex} associated with the interaction between a x^2-y^2 orbital of one copper atom and a *xy* orbital of another copper atom is about $-130 \cdot 10^{-4}$ cm^{-1}. Nevertheless, the interaction between x^2-y^2 orbitals of both copper ions, determining the magnitude of the isotropic exchange integral, J, seems to be transmitted through a system of bonds in the $Cu_2Zn_2O_4$ macrocycle. It appeared that the system of strong σ-bonds makes the -O-Zn-O- bridges surprisingly efficient in enabling the communication between copper atoms.

5. EPR STUDIES OF POLYNUCLEAR Cu(II) COMPLEXES

5.1. Cu_4O_4 cubane-like tetramer of Cu(II) complexes with tridentate Schiff bases [6]

In our previous magnetic susceptibility studies on tetrameric Cu(II) complexes with Schiff bases derived from two isomeric α-aminoalkohols, [Cu(acac-amino-2-propanol)]$_4$, (**a**), [Cu(acac-DL-2-amino-1-propanol)]$_4$, (**b**), the magnetic moments per one copper atom increased with temperature decrease (from about 2.20 BM at the room temperature to about 2.45 BM at 10 K) indicating the quintet ground state in the systems.

Similar magnetic behaviour was observed for β-form of [Cu(acac-ethanolamine)]$_4$, a cubane-like tetramer built up from two rectangle dimers whose planes are perpendicular to each other, with inter-dimer Cu(1)-Cu(2) and Cu(3)-Cu(4) distances longer by about 0.2 Å than the intra-dimer Cu-Cu distances.



Hence, the magnetic susceptibilities of (**a**) and (**b**) tetramers were analyzed using spin Hamiltonian appropriate for the simplified cubane structure:

$$H = J_1(S_1S_2 + S_3S_4) + J_2(S_1S_3 + S_1S_4 + S_2S_3 + S_2S_4).$$

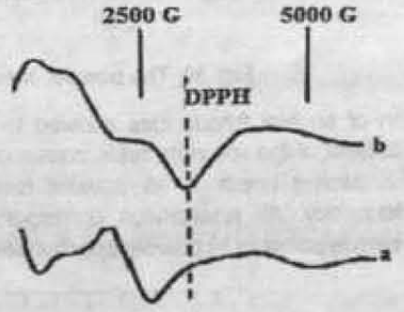


Fig. 9. X-band EPR spectra of (a) and (b) etramers

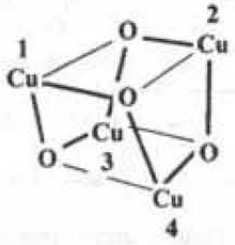
The results indicate domination of out-off plane ferromagnetic interactions between Cu(II) ions of different dimers, $J_2 = -63.2$ cm^{-1} (**a**), -136.6 cm^{-1} (**b**), and antiffero-magnetic interactions in pairs of Cu(II) ions of each dimer, $J_1 = 23.6$ cm^{-1} (**a**), 62.2 cm^{-1} (**b**).

Application of X-band and Q-band frequency to EPR measurements gave highly overlapped signals, and in addition, many transitions expected within the S=2 state were not observed because of limited magnetic field range. These effects made practically impossible the analysis of the spectra.

5.2. Cu_4O_4 cubane-like tetramer of Cu(II) complexes with diethanoleamine(-1) as bridging ligands [2]

A tetranuclear cubane-type cation $[Cu_4(NH_3)_4(HL)_4]^{4+}$ is present in the heterometallic complex $[Cu_4(NH_3)_4(HL)_4][CdBr_4]Br_2 \cdot 3dmf \cdot H_2O$ (**I**). In the cation, four copper atoms occupy vertices of a distorted tetra-

hedron with shorter bridged Cu(1)-Cu(4), Cu(2)-Cu(4), Cu(2)-Cu(3), Cu(1)-Cu(3) distances and longer (about 2.5 Å) non-bridged Cu(1)-Cu(2) and Cu(3)-Cu(4) separations. The magnetic moment was found to increase with decreasing temperature (300–1.8 K) to reach a maximum of 2.60 per one copper atom at ca. 10 K and subsequently to diminish slightly at lower temperatures owing to zero-field and Zeeman splitting of the S = 2 ground state.



The temperature dependence of the magnetic susceptibility was fit to the spin Hamiltonian $\mathbf{H} = (J_{14}S_1S_4 + J_{24}S_2S_4 + J_{32}S_3S_2 + J_{13}S_1S_3) + (J_{34}S_3S_4 + J_{12}S_1S_2)$ with the ferromagnetic exchange integrals of J_1=–65 cm^{-1} for four first pairs of bridged copper atoms and antiferromagnetic interactions J_2=+1 cm^{-1} for last two pairs of non-bridged copper atoms.

The powder X-band EPR spectra (at 9.392 GHz) of tetrameric compound (I) are noninterpretable because only a part of the possible resonances can be seen (fig.10), as a result of the ZFS being too large compared to the microwave quantum energy. High-field spectra, taken at several frequencies between 95 and 380 GHz and at the temperature 15 K enabled us to determine that the only spin state observed was the quintet, S = 2.

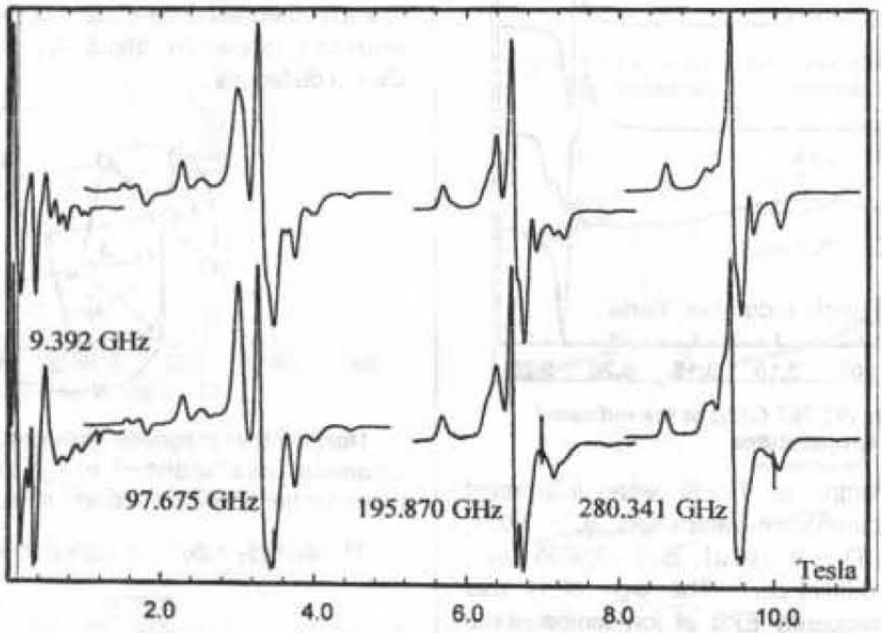


Fig. 10. The powder X-band and High-frequency EPR spectra of compound (I)

Application of several frequencies allowed to find a two-dimensional dataset of the resonant fields corresponding to the X, Y, and Z turning points in all powder spectra versus microwave frequency. All resonances corresponding to the X, Y, and Z turning points in all powder spectra were treated as one dataset. Spin Hamiltonian parameters g_x = 2.138, g_y = 2.142, g_z = 2.067, D= –0.3529 cm^{-1}, E = – 0.0469 cm^{-1} were obtained by a simultaneous fit to all experimental points. Individual powder spectra are nicely simulated with these parameters (fig. 11).

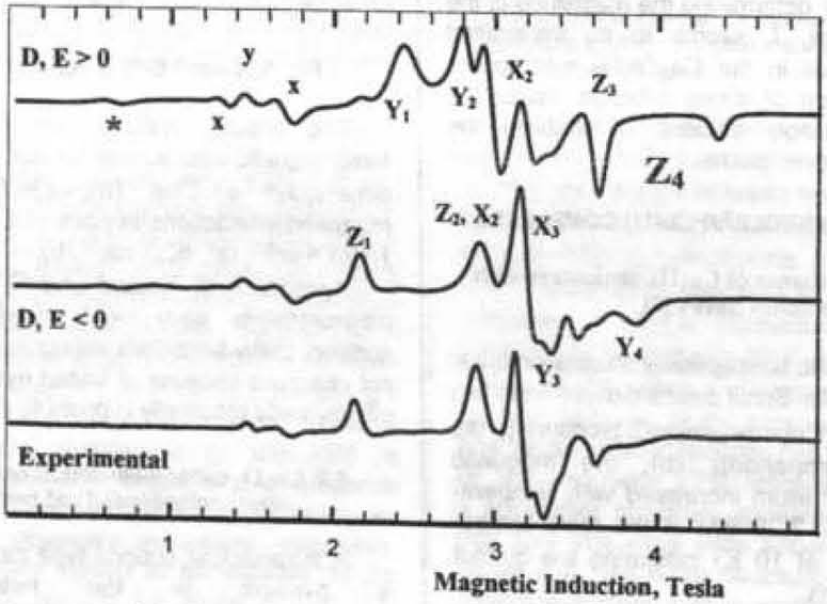


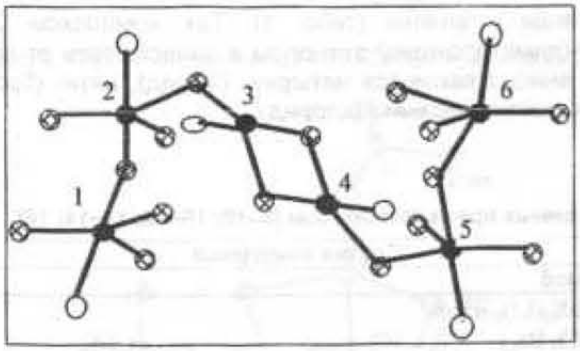
Fig. 11. Experimental powder EPR spectrum of compound (I) at 4.0 K and 93.654 GHz (bottom) and spectra simulated with either D = –0.3529 cm^{-1} and E = –0.0469 cm^{-1} (center) or D = +0.3529 cm^{-1} and E = +0.0469 cm^{-1} (top)

Anisotropic exchange interactions were found to contribute most to the magnitude of D, while the magnetic dipole-dipole contribution is negligible, $D_{dipole}(S = 2) = 0.02\ cm^{-1}$.

This is only about 1/18 of D as determined from EPR and carries the opposite sign, indicating overwhelming contribution of the exchange interactions to the ZFS in the tetranuclear molecule. Calculated $E_{dipole}(S = 2)$ is $-0.005\ cm^{-1}$, one order of magnitude less than the experimental E value.

5.3. Cu(II) pairs differently coupled in hexa-copper complex with triethanolamine as bridging ligands [7]

The compound $[Cu_3CdI_2(TeaH)_3]_2 \cdot 4dmf$ (H_3Tea – triethanolamine) has a peculiar topology with 6 copper atoms joined by bridging O atoms from the ligands to form a zig-zag chain with Cu-Cu separations being 2.937(2) – 2.405(2)Å.



The molecular symmetry implies that there are only three different next-neighbor exchange integrals and other exchange interactions were neglected. The magnetic moments were fitted with $J_{12} = J_{56} = 68\ cm^{-1}$, $J_{23} = J_{45} = 20\ cm^{-1}$, $J_{34} = -61\ cm^{-1}$ according to spin Hamiltonian $H = \Sigma_i \Sigma_j J_{ij} S_i S_j$. The relations between exchange integrals are in qualitative agreement with the structure. The ground state of the system is a triplet, S=1. This result is confirmed by the high-field, low temperature EPR spectra (fig. 12) in which a signal due to the triplet state was observed.

The EPR spectrum exhibits effects due to non-coaxiality of the g and zero-field splitting tensors and probably also due to the antisymmetric (Dzialoshinskii–Moriya) exchange interactions that are possible in the copper pairs 1-2, 2-3, 4-5 and 5-6 where the copper atoms are not symmetry-related. The work on full interpretation of the EPR spectra is in progress.

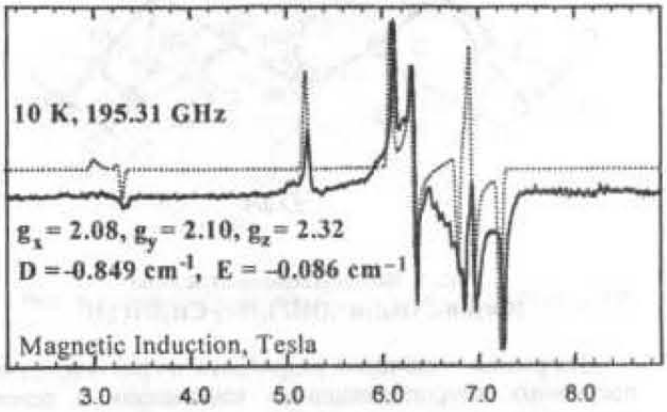


Fig. 12. Spectra of $[Cu_3CdI_2(TeaH)_3]_2$, 4dmf at 10 K and 195.31 GHz; experimental (broad) and the simulated triplet state spectrum (narrow)

1. *Buvaylo E.A., Kokozay V.N., Vassilyeva O.Yu. et el.* // Chem. Commun. – 2005. – P. 4976. 2. *Buvaylo E.A., KokozayV.N., Vassilyeva O.Yu. et el.* // Inorg. Chem. – 2005. – Vol. 44. – P. 206–216. 3. *Gumienna-Kontecka E., Jezierska J., Lecouvey M. et al.* // J. Inorg. Biochem. – 2002. – Vol. 89. – P. 13. 4. *Jezierska J., GłowiakT., Ozarowski A. et el.* // Inorg. Chim. Acta. – 1998. – Vol. 28. – P. 275. 5. *JezierskaJ., Ozarowski A., Vučković G.* // Nukleonika. – 1997. Vol. 42. – P. 475. 6. *Jeżowska-Trzebiatowska B., Jezierska J., Baranowski J., Ozarowski A.* // J. Mol. Structure. – 1980. – Vol. 61. – P. 337. 7. *Kokozay V.N., Ozarowski A.* – prepared for publication. 8. *Makhankova V.G., Vassilyeva O.Yu., Kokozay V.N et el.* // Europ. J. Inorg. Chem. – 2002. – P. 2163. 9. *Voronkova V.K., Vučković G., Jezierska J. et al.* // Inorg. Chim. Acta. – 1997. – Vol. 262. – P. 147.

Надійшла до редколегії 16.02.06

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НОВЫЕ ПОДХОДЫ К СИНТЕЗУ ГЕТЕРОПОЛИЯДЕРНЫХ КОМПЛЕКСОВ

Идея прямого синтеза – использование металлов или их оксидов как исходных веществ для получения координационных соединений – получила дальнейшее развитие в виде "солевого", "аммонийного", "прямого темплатного" и "прямого перманганатного" методов синтеза гетерополиядерных комплексов переходных металлов. На примере комплексов с аминоспиртами, этилендиамином и их производными показаны преимущества предлагаемого подхода при получении гетерополиядерных комплексов переходных металлов. Приведены результаты рентгеноструктурного анализа наиболее интересных соединений. Обсуждаются возможные направления дальнейшего развития методов прямого синтеза гетерополиядерных комплексов.

The idea of direct synthesis of coordination compounds – use of elemental metals or their oxides as starting materials – has been developed into "salt route", "ammonium salt route", "direct template synthesis" and "direct permanganate" methods to synthesize heteropolynuclear complexes of transition metals. The advantages of this approach in obtaining of heteropolynuclear complexes are shown taking complexes of transition metals with aminoalcohols ligands, ethylenediamine and their derivatives as an example. The results of the X-ray crystal structure analysis of the most interesting complexes are presented. The perspectives of the development of the direct synthesis methods for preparation of heteropolynuclear complexes are discussed.

Гетерополиядерные комплексы в последнее время привлекают все большее внимание своими магнитными, электрохимическими и биологическими свойствами [6; 7; 23]. В качестве одного из наиболее интересных примеров гетерополиядерных комплексов можно привести соединение с диэтаноламином $[Cu_2Zn_2(NH_3)_2Br_2(HL^1)_4]Br_2 \cdot CH_3OH$ [3], содержащее макроциклический фрагмент Cu_2Zn_2 (рис. 1).

Из-за довольно большого расстояния между атомами меди (~ 5,7 Å) трудно было предположить наличие между ними обменных взаимодействий. Тем не менее, атомы меди, связанные мостиком -O-Zn-O-, проявляют существенное антиферромагнитное взаимодействие ($J = -35{,}0\ см^{-1}$), которое может передаваться через d-орбитали диамагнитных атомов цинка.