

## Synthesis and Properties of a Trinuclear Copper(II) Complex with Trithiocyanurate Bridge

by P. Kopel<sup>1</sup>, Š. Čermáková<sup>1</sup>, K. Doležal<sup>2</sup>, B. Kalińska<sup>3</sup>,  
A. Bieńko<sup>3</sup> and J. Mroziński<sup>3\*</sup>

<sup>1</sup>Department of Inorganic Chemistry, Palacký University,  
Křížkovského 10, CZ-771 47 Olomouc, Czech Republic

<sup>2</sup>Laboratory of Growth Regulators, Institute of Experimental Botany ASCR & Palacký University,  
Šlechtitelů 11, CZ-783 71 Olomouc, Czech Republic

<sup>3</sup>Faculty of Chemistry, University of Wrocław, 14 F. Joliot-Curie, PL-50 383, Wrocław, Poland

(Received November 21st, 2006; revised manuscript January 22nd, 2007)

Mixed-ligand trinuclear Cu(II) complex involving trithiocyanurate(3<sup>-</sup>) anion (ttc<sup>3-</sup>) and N,N,N',N'',N''-pentamethyldiethylenetriamine (pmdien) in the coordination sphere of composition [Cu<sub>3</sub>(pmdien)<sub>3</sub>(μ-ttc)](ClO<sub>4</sub>)<sub>3</sub> has been prepared. The complex has been characterized by EA, IR, UV-Vis, and mass spectroscopy. We can assume, that the complex is trinuclear with central atoms connected by trithiocyanurate(3<sup>-</sup>) bridges. Each central atom is in deformed trigonal bipyramidal arrangement formed by chelating S,N atoms of ttc(3<sup>-</sup>) and by three N atoms of pmdien. Temperature dependence of magnetic susceptibility and EPR spectroscopy have also been employed to characterize the compound. Magnetic susceptibility measurements over the 1.8–300 K temperature range revealed antiferromagnetic interactions among central atoms. The antitumor activity *in vitro* against G-361 (human malignant melanoma), HOS (human osteogenic sarcoma), K-562 (human chronic myelogenous leukaemia) and MCF-7 (human breast adenocarcinoma) tumor cell lines have been tested but unfortunately the complexes showed no cytotoxic activity against the four cell lines.

**Key words:** copper(II), trithiocyanuric acid complexes, magnetic properties, EPR, cytotoxicity

Much attention has been paid to preparation and characterization of polynuclear transition metal complexes connected by monoatomic and polyatomic bridges. The complexes are studied for their interesting magnetic and spectral properties and they can also serve as potential models of biological systems. Many of them show magnetic exchange interactions, antiferromagnetic or ferromagnetic, and thus the materials can further find their industrial applications [1–3]. In contrast with frequently studied dinuclear copper(II) complexes, much less studied are triangular trinuclear copper(II) clusters. In such complexes one or more hydroxy groups serve as bridging ligands among three copper(II) atoms [4–6]. Very often carboxylate bridged complexes are studied as they are able to connect metal ions in different manners. When dicarboxylic or tricarboxylic acids are used, the situation is more complicated and structural data are necessary to find the precise manner of carboxylate groups coordi-

\*Corresponding author Tel/fax.: +48-71-3757307; E-mail address: jmroz@wchuwr.chem.uni.wroc.pl

nation. In our previous works we have focused our attention to thiodiglycolic acid, which is a dicarboxylic compound containing sulfur atom, which can also be coordinated [7–8]. Previously we have prepared and obtained magnetic data of iron(III) Schiff base complexes, with 1,3,5-benzenetricarboxylato bridge, which showed weak antiferromagnetic interactions among central atoms [9]. Unfortunately the compounds have not been structurally characterized.

Trithiocyanuric acid (ttcH<sub>3</sub>), also referred as trimercaptotriazine, attracted our attention as well. This symmetric compound has got potentially six donor atoms suitable for formation of coordination compounds. In our previous papers we have structurally characterized series of mononuclear nickel(II) and zinc(II) complexes with chelating N,S mode or N only coordinated ttcH<sup>2-</sup> anion. The complexes are of compositions [Ni(bapen)(ttcH)]·2H<sub>2</sub>O (bapen = N,N'-bis(3-aminopropyl)ethylenediamine), [Ni(bappn)(ttcH)]·1.5H<sub>2</sub>O (bappn = N,N'-bis(3-aminopropyl)-1,3-propanediamine), [Ni(taa)(ttcH)] (taa = tris-(2-aminoethyl)amine), [Ni(dpta)(ttcH)(H<sub>2</sub>O)]·H<sub>2</sub>O (dpta = dipropylenetriamine), [Ni(pmdien)(ttcH)] and [Zn(bapen)(ttcH)]·EtOH [10–15].

In the literature, we can find further examples of ttc bonding proved by X-ray analyses. Bis-chelating N,S mode of ttc occurs in binuclear complex [ $\{\text{Co}(\text{en})_2\}_2(\text{ttc})(\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$  (en = ethylenediamine) [16], whereas complexes of composition [ $\{\text{Au}(\text{PPh}_3)\}_3(\text{ttc})$ ], [ $\{\text{HgMe}\}_3(\text{ttc})$ ], [ $\{\text{SnMe}_3\}_3(\text{ttc})$ ] and [ $\{\text{SnPh}_3\}_3(\text{ttc})$ ] are examples of trinuclear species with ttc anion bonded by S atoms to metal centres [17–19]. Quite recently, Kar *et al.* have prepared a series of trinuclear Ru(II) complexes of composition [ $\{\text{Ru}(\text{bpy})_2\}_3(\text{ttc})(\text{ClO}_4)_3$ ], [ $\{\text{Ru}(\text{phen})_2\}_3(\text{ttc})(\text{ClO}_4)_3$ ] and [ $\{\text{Ru}(\text{L})_2\}_3(\text{ttc})(\text{ClO}_4)_3$ ], where bpy = 2,2'-bipyridine, phen = 1,10-phenanthroline and L = phenylazopyridine, which contain trithiocyanurate(3-) bridge among Ru(II) centers by S,N chelating donor sets of the anion [20,21]. X-ray study of the later complex proved that ruthenium atoms are further coordinated by two bidentate nitrogen ligands (phenylazopyridine) in deformed octahedral surrounding. The complexes are diamagnetic and in addition to the electrochemical and spectral study, interaction of the complexes with the circular and linear forms of p-Bluescript DNA is reported. Three tested complexes reduce fluorescence intensity of both circular and linear DNA but the nature of these interactions is still unknown.

The aim of this work was to prepare trinuclear copper complex with trithiocyanurate bridge and terdentate ligand pmdien, that is used to block coordination sites of central atoms and thus to prevent formation of polymers. Further we have studied its magnetic properties and also we tried to prepare single crystals for X-ray analysis to confirm stereochemistry of the compound but until now good quality crystal has not been obtained. The complex must be isolated immediately because contamination can occur by a product appearing as yellow precipitate. Other goal of our study has been to test possible cytotoxic activity against selected cell lines.

## EXPERIMENTAL

**Materials and methods**

**Safety note:** *Caution!* Perchlorate salts of metal complexes with organic ligands are potentially explosive. Even a small amount of these materials should be handled with great caution.

The chemicals and solvents were supplied from Aldrich and Lachema (Czech Republic). The C, H, N, and S analyses were carried out on an EA 1108 instrument (FISONS). IR spectrum ( $400\text{--}4000\text{ cm}^{-1}$ ) was recorded on a FT-IR Spectrometer Spectrum One (Perkin Elmer) using KBr pellet and diffuse-reflectance spectrum ( $9000\text{--}35000\text{ cm}^{-1}$ ) was obtained on an UV/VIS Spectrometer Lambda 35 (Perkin Elmer) using KBr pellets. The magnetization measurements of the powdered sample were accomplished over the temperature range 1.8–300 K using a Quantum Design SQUID – based MPMSXL–5-type magnetometer. The superconducting magnet was generally operated at a field strength ranging from 0 to 5 T. Measurements were made at magnetic field 0.5 T. The SQUID magnetometer was calibrated with the palladium rod sample. Corrections are based on subtracting the sample-holder signal and contribution  $\chi_D$  estimated from the Pascal constants equal to  $-698 \times 10^{-6}\text{ cm}^3\text{ mol}^{-1}$  [22]. The TIP per copper ion was assumed to be  $60 \times 10^{-6}\text{ cm}^3\text{ mol}^{-1}$ . The effective magnetic moment was calculated from the equation,  $\mu_{\text{eff}} = 2.83(\chi_M T)^{1/2}$  (B.M.). EPR spectra were recorded at room temperature, 77 K and 4.5 K, on the spectrometer Bruker ESP 300, operating at X-band equipped with an ER 035M Bruker NMR gaussmeter and a HP 5350B Hewlett Packard microwave frequency counter. The EPR measurements at 4.5 K were performed on a conventional X-band reflection spectrometer equipped with an Oxford Instruments ESR-900 helium flow cryostat. The ESI<sup>+</sup> mass spectra were recorded on a Waters ZMD 2000 mass spectrometer. The mass-monitoring interval was  $m/z$  10–1500. The spectra were collected using 3.0 s cyclical scans and applying the sample cone voltages 20, 30 or 40 V, at the source block temperature 80°C, desolvation temperature 150°C and desolvation gas flow rate 200 l/h. The mass spectrometer was directly coupled to a MassLynx data system. All  $m/z$  interpretations were based on <sup>35</sup>Cl and <sup>63</sup>Cu, respectively.

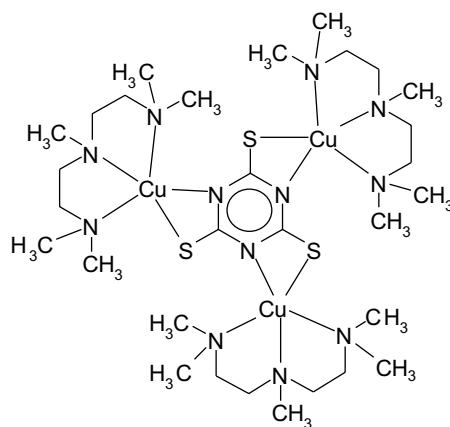
The cytotoxic activity of prepared compound and ttcNa<sub>3</sub> was assayed *in vitro* against four cell lines G-361, HOS, K-562 and MCF-7 as described in the literature [23,24]. The tumor cells were maintained in 75 ml plastic tissue culture flasks (TPP) and grown on Dulbecco's modified Eagle's cell culture medium (DMEM) containing 1 g l<sup>-1</sup> glucose, 4 mmol glutamine, 100 IU ml<sup>-1</sup> penicillin, 100 µg ml<sup>-1</sup> streptomycin, 10% foetal bovine serum and 3.7 g l<sup>-1</sup> sodium bicarbonate. The cell suspension of approximate density  $1.25 \times 10^5$  cells/ml was redistributed into 96-well microtitre plates (Nunc, 80 µl per well). After preincubation (12 h at 37°C, 5% CO<sub>2</sub>), the test compounds, in six-fold dilutions, were added (20 µl per well). Incubation of cells with the tested compound, with maximum concentrations 12.5 µM and 100 µM (ttcNa<sub>3</sub>), lasted for 72 h at 37°C in 5% CO<sub>2</sub> atmosphere, 100% humidity. At the end of this period, the cells were incubated for 1 h with calcein AM and the fluorescence of the live cells was measured at 485 nm/538 nm (ex/em) with a Fluoroscanner Ascent (Labsystems, Finland). IC<sub>50</sub> values, the drug concentrations lethal to 50% of the tumor cells, were estimated.

**Preparation of [Cu<sub>3</sub>(pmdien)<sub>3</sub>(µ-ttc)](ClO<sub>4</sub>)<sub>3</sub>.** Pmdien (0.2 cm<sup>3</sup>, 1 mmol) was added to a solution of Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.37 g, 1 mmol) in water (50 cm<sup>3</sup>), yielding a violet solution. Consecutively, a solution of ttcNa<sub>3</sub>·9H<sub>2</sub>O (0.14 g, 0.33 mmol) in water (2 cm<sup>3</sup>) was slowly added with stirring at room temperature. Colour of the solution turned green and soon the green microcrystalline material appeared. The crystals were collected on a frit, washed with small amounts of water and dried in air. Yield: 78%. Anal. calcd.: C, 30.4; H, 6.0; N, 14.2; S, 8.1; found: C, 30.2; H, 5.6; N, 14.1; S, 7.9%. IR (cm<sup>-1</sup>): 498m, 585w, 627s, 753w, 762m, 777s, 806s, 892s, 921m, 936s, 966m, 1042s, 1228s, 1286m, 1377s, 1633m, 2015m, 2170w, 2409w, 2812w, 2900s, 2977s, 3593s. UV-Vis (cm<sup>-1</sup>): 12270, 25320, 36000. ESI<sup>+</sup> MS ( $m/z$ ): 1182, 1083, 984, 885 [Cu<sub>3</sub>(pmdien)<sub>3</sub>(ttc)H]<sup>+</sup>, 711 [Cu<sub>3</sub>(pmdien)<sub>3</sub>H]<sup>+</sup>, 648 [Cu<sub>2</sub>(pmdien)<sub>3</sub>H]<sup>+</sup>, 237 [Cu(pmdien)H]<sup>+</sup>, 178 [ttcH]<sup>+</sup>, 175 [pmdienH]<sup>+</sup>.

## RESULTS AND DISCUSSION

**Preparation, infrared and UV-Vis spectra.** The title complex is readily prepared by reaction of copper perchlorate, pmdien and ttcNa<sub>3</sub> in water or ethanol in molar ratio 3 : 3 : 1. It is necessary to collect crystalline material immediately. When reaction time is prolonged, the product can be contaminated by a byproduct. It is very probable that reduction of product to some copper(I) species of unknown composition takes place and thus a yellow precipitate can be obtained from filtrate. The title complex was characterized by the combination of elemental analysis and mass spectroscopy. The ESI<sup>+</sup> mass spectra display an intense peak at  $m/z = 885$ , corresponding to the trinuclear molecular ion of the composition  $[\text{Cu}_3(\text{pmdien})_3(\text{ttc})\text{H}]^+$ . It shows also several minor peaks at  $m/z = 984$ , 1083 and 1182, which can be attributed to the  $\text{ClO}_4^-$  - adduced multiply protonated species  $[\text{Cu}_3(\text{pmdien})_3(\text{ttc})\text{H}_2]^{2+}$ ,  $[\text{Cu}_3(\text{pmdien})_3(\text{ttc})\text{H}_3]^{3+}$  and  $[\text{Cu}_3(\text{pmdien})_3(\text{ttc})\text{H}_4]^{4+}$  respectively. Such  $\text{ClO}_4^-$  adduct formation was previously reported for similar complex ions [25]. Other observed peaks at lower  $m/z = 711$ , 648, 237, 178 and 175 correspond to different fragments of the trimer and its organic parts.

The trinuclear structure of the complex was also proved by single crystal X-ray analysis but the data are not sufficient for deposit. The structure is somewhat similar to  $[\{\text{Ru}(\text{L})_2\}_3(\text{ttc})](\text{ClO}_4)_3$ , where L = phenylazopyridine [21]. The copper atoms in title complex are also bridged by trithiocyanurate(3-) ion in tris S,N chelating mode (see Fig. 1). Coordination polyhedron of copper atoms is completed by three N atoms of pmdien like in complex  $[\text{Ni}(\text{pmdien})(\text{ttcH})]$  [12]. In comparison with the nickel complex, where coordination polyhedron is rather an intermediate between pyramid and trigonal bipyramid, copper centres in  $[\text{Cu}_3(\text{pmdien})_3(\mu\text{-ttc})](\text{ClO}_4)_3$  are in a slightly distorted trigonal bipyramidal arrangement with basal plane formed by S,N atoms of ttc and central N atom of pmdien.



**Figure 1.** The scheme of complex cation  $[\text{Cu}_3(\text{pmdien})_3(\mu\text{-ttc})]^{3+}$ .

The vibrational frequencies with their relative intensities are given in *Experimental Section*. IR spectrum of the complex contains broad bands with maxima at 2900 and 2977  $\text{cm}^{-1}$  that can be connected with  $\nu_s(\text{CH}_2)$  and  $\nu_{as}(\text{CH}_2)$  vibrations whereas that broad band with maximum observed at 3593  $\text{cm}^{-1}$  region can be attributed to  $\nu(\text{C-H})$  and  $\nu(\text{N-H})$  vibrations [26]. The bands attributable to vibrations of uncoordinated perchlorate groups are observed at 627, 936 and 1042  $\text{cm}^{-1}$ . When we compare the spectrum of  $[\text{Cu}_3(\text{pmdien})_3(\mu\text{-ttc})](\text{ClO}_4)_3$  with a spectrum of  $[\text{Ni}(\text{pmdien})(\text{en})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$  (with the main peaks at 512(w), 626(vs), 778(w), 802(w), 932(m), 1018(m), 1091(vs), 1289(w), 1481(m), 1597(m), 2893(m), 3314(s)), we can unambiguously assign the peaks that belong to trithiocyanurate anions. Thus the peaks connected with  $\nu(\text{C-N})$  vibrations of triazine ring appear in the spectrum of the complex at 1228, 1377 and 1633  $\text{cm}^{-1}$ . They can overlap some peaks attributable to  $\nu(\text{C-H})$  and  $\nu(\text{N-H})$  of *pmdien* but in comparison with the spectrum of the former mentioned complex, they are much more intensive. The peak that belongs to  $\nu(\text{C-S})$  vibrations of *ttc* anion is at 892  $\text{cm}^{-1}$ . These assignments are in good agreement with infrared frequencies calculations for *ttc* anions [27].

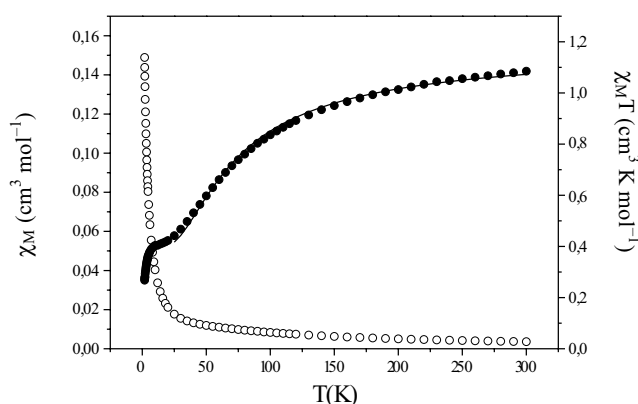
The band at 12270  $\text{cm}^{-1}$  which appears in diffuse-reflectance spectrum belongs to a d-d transition whereas the bands at 25320 and 36000  $\text{cm}^{-1}$  are probably connected with metal-to-ligand charge transfer (MLCT) transitions [28].

The cytotoxic activity of the complex and sodium salt of trithiocyanuric acid ( $\text{ttcNa}_3$ ) were studied on G-361, HOS, K-562 and MCF7 cancer cell lines. The complex at concentration of 12.5  $\mu\text{M}$  and  $\text{ttcNa}_3$  shows no activity against the tested lines. The reason that the complex is not active can be caused by its very low solubility and probably low stability of the complex in solution. Stability of the complex in solution has not been studied, but on the base of our previous findings on Zn(II), Fe(II), Mn(II) and Ni(II) complexes with *ttc* [29], we can conclude that inactivity towards tumor cell lines is due to low solubility of the complex.

#### Magnetic susceptibility and EPR study of $[\text{Cu}_3(\text{pmdien})_3(\mu\text{-ttc})](\text{ClO}_4)_3$ .

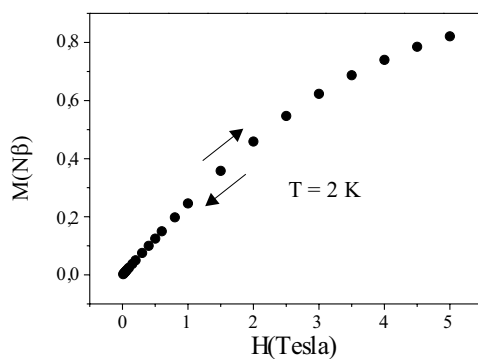
The temperature dependence of the product  $\chi_M T$  and  $\chi_M$  in the field of 0.5 Tesla for trimer ( $\chi_M$  is the susceptibility per  $\text{Cu}_3$  unit) is shown in Figure 2. The Curie-Weiss behavior is observed on the reciprocal susceptibility curve in the temperature range 200–300 K only with Curie constant  $C = 1.26 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  and Weiss constant  $\Theta = -48 \text{ K}$ . The compound reveals the magnetic behavior which is characteristic of antiferromagnetic spin coupling. The  $\chi_M T$  value decreases gradually with lowering of the temperature from 1.08  $\text{cm}^3 \text{ mol}^{-1} \text{ K}$  at 300 K to 0.268  $\text{cm}^3 \text{ mol}^{-1} \text{ K}$  at 1.8 K and the effective magnetic moment decreases from 2.95 B.M. at 300 K to 1.47 B.M. at 1.8 K.

There is a plateau between 20 and 10 K with small slope with  $\chi_M T \approx 0.41 \pm 0.01 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ . The observed plateau corresponds to the Curie law expected for a doublet ground state and magnetic moment stabilizes approximately at 1.81 B.M. This value of magnetic moment is characteristic for a single copper(II) center with one unpaired electron and it is a result of antiferromagnetic coupling among copper centers inside the trimer molecule [4–6]. For the further temperature lowering, decreasing of the  $\chi_M T$  values was observed, that is indicative of intermolecular antiferromagnetic



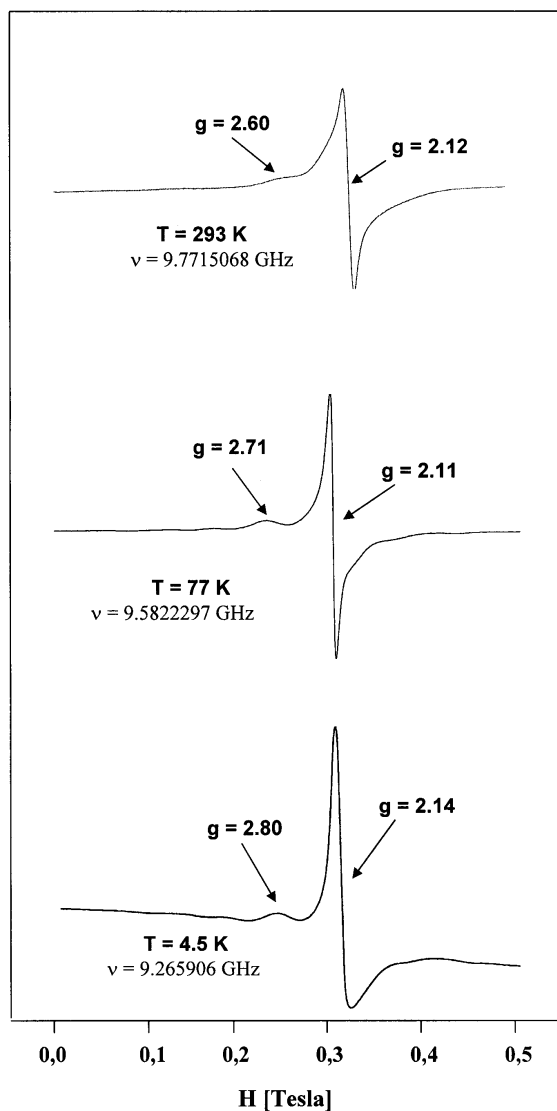
**Figure 2.** The plot of the experimental  $\chi_M$  (•) and  $\chi_M T$  (o) product *versus* temperature. Solid line represents the theoretical curve (see text).

interactions only between single unpaired electrons from the trimer molecules in the crystal lattice. Magnetization measurement *versus* magnetic field at 2 K (Fig. 3) strongly support this suggestion. Magnetization increases gradually, reaching only the value of  $M = 0.82 N\beta$  at 5 Tesla. No differences were observed between  $M(H)$  curves measured with increase or decrease of magnetic field strength.



**Figure 3.** The plot of the magnetization per trimer molecule *versus* applied field.

EPR spectrum of powdered sample of the trimeric complex [see Fig. 4] indicates lines related to  $\Delta m = \pm 1$ ,  $\pm 2$  and  $\pm 3$  transitions [30–34] dependent on the temperature. At room temperature the main symmetrical line at  $g = 2.12$  and a peak-to-peak linewidth ( $\delta H_{pp}$ )  $\cong 130$  G and additional bump at  $g = 2.60$ , at 77 K are observed with the main signal at  $g = 2.11$  with  $\delta H_{pp} \cong 140$  G and bump at  $g = 2.71$ . From magnetic



**Figure 4.** The EPR spectra of powdered sample of  $[\text{Cu}(\text{pmdien})_3(\mu\text{-ttc})](\text{ClO}_4)_3$ .

point of view at the lowest temperatures only one unpaired electron exists on the whole trimer molecule. EPR spectrum of the trimer at 4.5 K indicates intensive asymmetric line with  $g = 2.14$  and  $\delta H_{pp} \cong 140$  G, and additional weak bumps at  $g = 2.80$  is also observed. Recorded EPR spectra of the trimer in the temperatures 4.5, 77 and 293 K can be related to a doublet ( $S = 1/2$ ) species and to a higher spin state generated by spin coupling within units becoming thermally populated at higher temperatures.

X-ray analysis indicated that the Cu(II) centers form regular triangle. Isotropic exchange model and the Hamiltonian of the trimer can be written as follows:

$$\hat{H} = -2J(\hat{S}_1\hat{S}_2 + \hat{S}_2\hat{S}_3 + \hat{S}_1\hat{S}_3)$$

where  $S_i = 1/2$  and  $J$  is an exchange parameter.

A closed-form solution of the magnetic susceptibility derived from the susceptibility takes the form [35–39]:

$$\chi = \frac{Ng^2\mu_B^2}{4kT} \frac{1 + 5e^{3J/kT}}{1 + e^{3J/kT}}$$

where  $N$ ,  $g$ ,  $\beta$ ,  $k$  and  $T$  have their usual meanings and both  $J$  and  $g$  factors were calculated for the temperature range 25–300 K (off the plateau region) in the fitting processes. The best least-squares fit was obtained for the following values:  $J = -23 \text{ cm}^{-1}$ ,  $g = 2.08$  and  $R = 3.23 \times 10^{-5}$ .

$$R = \sqrt{\left\{ \sum_{i=1}^n \left[ \left( \chi_M^{\text{exp}} \right)_i - \left( \chi_M^{\text{calc}} \right)_i \right]^2 / \left( \chi_M^{\text{exp}} \right)_i^2 \right\} / \sum_{i=1}^n 1 / \left( \chi_M^{\text{exp}} \right)_i^2}$$

In order to obtain value of exchange parameter for the lowest temperature range 1.8–10 K model of magnetic interactions for the trimer with a molecular field correction was applied [40]:

$$\chi_M^{\text{corr}} = \frac{\chi_M}{1 - \frac{2zJ'\chi_M}{Ng_{\text{av}}^2\beta^2}}$$

where  $zJ'$  is intermolecular exchange parameter,  $z$  is the number of nearest neighbouring trimers and  $g_{\text{av}}$  is average spectroscopic splitting factor obtained in the fitting process. The best least-squares fit was obtained for the following values:  $zJ' = -1.8 \text{ cm}^{-1}$ ,  $g = 2.22$  and  $R = 4.43 \times 10^{-4}$ . All obtained data very well confirm that the trinuclear complex can be seen as practically isolated units and the magnetism mainly results from the spin coupling within them.

#### Acknowledgments

Authors wish to thank Prof. Zdeněk Trávníček for X-ray data collection and calculations. Authors thank the Ministry of Education of the Czech Republic (MSM 6198959218) and the Polish Ministry of Science and Higher Education Grant No. 1 T09A 124 30.

#### REFERENCES

1. Gatteschi D., Kahn O. and Willet R.D., *Magneto-Structural Correlations in Exchange Coupled Systems*, Reidel, Dordrecht, 1984.
2. Kahn O., *Molecular Magnetism*, VCH Publishers, New York, 1993.
3. Mroziński J., *Coord. Chem. Rev.*, **249**, 2534 (2005).



4. Ferrer S., Haasnoot J.G., Reedijk J., Muller E., Cingi M.B., Lanfranchi M., Lanfredi A.M.M. and Ribas J., *Inorg. Chem.*, **39**, 1859 (2000).
5. Ferrer S., Lloret F., Bertomeu I., Alzuet G., Borrás J., Garcia-Granda S., Liu-Gonzalez M. and Haasnoot J.G., *Inorg. Chem.*, **41**, 5821 (2002).
6. Mirica L.M. and Stack T.D.P., *Inorg. Chem.*, **44**, 2131 (2005).
7. Kopel P., Trávníček Z., Marek J., Korabik M. and Mroziński J., *Polyhedron*, **22**, 411 (2003).
8. Kopel P., Trávníček Z., Marek J. and Mrozinski J., *Polyhedron*, **23**, 1573 (2004).
9. Kopel P., Šindelář Z. and Klička R., *Transition Met. Chem.*, **23**, 139 (1998).
10. Kopel P., Trávníček Z., Kvítek L., Panchártková R., Biler M., Marek J. and Nádvorník M., *Polyhedron*, **18**, 1779 (1999).
11. Kopel P., Trávníček Z., Kvítek L., Černošek Z., Wrzeszcz G. and Marek J., *J. Coord. Chem.*, **56**, 1 (2003).
12. Kopel P., Trávníček Z., Panchártková R., Biler M. and Marek J., *Transition Met. Chem.*, **24**, 239 (1999).
13. Kopel P., Trávníček Z., Panchártková R., Šindelář Z. and Marek J., *J. Coord. Chem.*, **44**, 205 (1998).
14. Kopel P., Trávníček Z., Kvítek L., Biler M., Pavlíček M., Šindelář Z. and Marek J., *Transition Met. Chem.*, **26**, 282 (2001).
15. Marek J., Kopel P. and Trávníček Z., *Acta Cryst.*, **C59**, m558 (2003).
16. Yamanari K., Kushi Y., Yamamoto M., Fuyuhiko A., Kaizaki S., Kawamoto T. and Kushi Y., *J. Chem. Soc. Dalton. Trans.*, 3715 (1993).
17. Hunks W.J., Jennings M.C. and Puddephatt R.J., *Inorg. Chem.*, **38**, 5930 (1999).
18. Cecconi F., Ghilardi C.A., Midollini S. and Orlandini A., *J. Organomet. Chem.*, **645**, 101 (2002).
19. Haiduc I., Mahon M.F., Molloy K.C. and Venter M.M., *J. Organomet. Chem.*, **627**, 6 (2001).
20. Kar S., Miller T.A., Chakraborty S., Sarkar B., Pradhan B., Sinha R.K., Kundu T., Ward M.D. and Lahiri G.K., *Dalton Trans.*, 2591 (2003).
21. Kar S., Pradhan B., Sinha R.K., Kundu T., Kodgire P., Rao K.K., Puranik V.D. and Lahiri G.K., *Dalton Trans.*, 1752 (2004).
22. König E., *Magnetic Properties of Coordination and Organometallic Transition Metal Compounds*, Springer, Berlin, 1966, p. 1.
23. Trávníček Z., Maloň M., Šindelář Z., Doležal K., Rolčík J., Kryštof V., Strnad M. and Marek J., *J. Inorg. Biochem.*, **84**, 23 (2001).
24. Trávníček Z., Maloň M., Zatloukal M., Doležal K., Strnad M. and Marek J., *J. Inorg. Biochem.*, **94**, 307 (2003).
25. Pavlishchuk V.V., Kolotilov S.V., Addison A.W., Prushan M.J., Butcher R.J. and Thompson L.K., *Inorg. Chem.*, **38**, 1759 (1999).
26. Pouchert C.J., *The Aldrich Library of Infrared Spectra* (3rd Ed.), Aldrich Chemical Company, Milwaukee, Wisconsin, 1981.
27. Kopel P., Trávníček Z., Zbořil R. and Marek J., *Polyhedron*, **23**, 2193 (2004).
28. Lever A.B.P., *Inorganic Electronic Spectroscopy*. Elsevier, Amsterdam, 1984.
29. Kopel P., Doležal K., Machala L. and Langer V., *Polyhedron*, (2006), (in press).
30. Costes J-P., Dahan F. and Laurent J-P., *Inorg. Chem.*, **25**, 413 (1986).
31. Kothe G., Ohmes E., Brickmann J. and Zimmermann H., *Angew. Chem. Int. Ed. Engl.*, **10**, 938 (1971).
32. Hudson A. and Luckurst G.R., *Mol. Phys.*, **13**, 409 (1967).
33. Kothe G., Naujok A. and Ohmes E., *Mol. Phys.*, **32**, 1215 (1976).
34. Kothe G., Neugebauer F.A. and Zimmermann H., *Angew. Chem. Int. Ed. Engl.*, **11**, 830 (1972).
35. Tsukerblat B.S., Kuyarskaya B.Ya., Belinski M.I., Ablov A.V., Novotvortsev V.M. and Kalinnikov V.T., *Theoret. Chim. Acta* (Berlin), **38**, 131 (1975).
36. Inoue M. and Kubo M., *J. Coord. Chem.*, **6**, 157 (1977).
37. Butcher R.J., O'Connor C.J. and Sinn E., *Inorg. Chem.*, **20**, 537 (1981).
38. Costes J.P., Dahan F. and Laurent J.P., *Inorg. Chem.*, **25**, 413 (1986).
39. Nakao Y., Nakamura H., Mori W., Samurái T., Suzuki S. and Nakahara A., *Bull. Chem. Soc. Jpn.*, **59**, 2755 (1987).
40. Smart J.S., *Effective Field Theories of Magnetism*, W.B. Saunders Comp., Philadelphia and London, 1966.