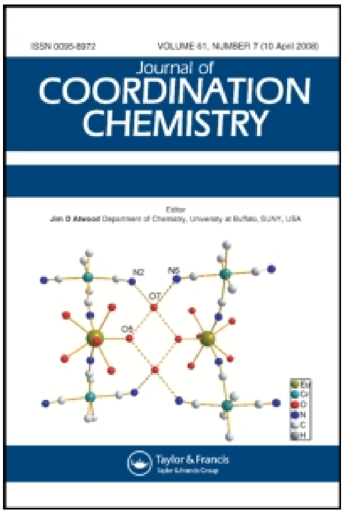

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, Structure and Spectroscopic Properties of the Dimer μ-Bis[2(1H)-Tetrahydropyrimidinone] Octakis[2(1H)-Tetrahydropyrimidinone] Dicopper(II) Perchlorate

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To cite this Article Kováčik, I. , Kožíšek, J. , Hanušík, J. , Langfelderová, H. , Voronkova, V. K. , Mosina, L. V. and Yablokov, Yu. V.(1992) 'Synthesis, Structure and Spectroscopic Properties of the Dimer μ-Bis[2(1H)-Tetrahydropyrimidinone] Octakis[2(1H)-Tetrahydropyrimidinone] Dicopper(II) Perchlorate', Journal of Coordination Chemistry, 26: 1, 45 — 57

To link to this Article: DOI: 10.1080/00958979209407910

URL: http://dx.doi.org/10.1080/00958979209407910

J. Coord. Chem. 1992 Vol. 26, pp. 45–57
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SYNTHESIS, STRUCTURE AND SPECTROSCOPIC PROPERTIES OF THE DIMER μ-BIS[2(1H)-TETRAHYDROPYRIMIDINONE] OCTAKIS[2(1H)-TETRAHYDROPYRIMIDINONE] DICOPPER(II) PERCHLORATE

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(*Received 20 September 1991*)

The complex μ-Bis[2(1H)-tetrahydropyrimidinone]octakis[2(1H)-tetrahydropyrimidinone]dicopper(II) perchlorate has been synthesized and its crystal structure has been determined by X-ray diffraction at room temperature. Crystals are triclinic (space group $P\bar{1}$); $a=11.709(8)$, $b=12.750(12)$, $c=12.891(11)$Å, $\alpha=62.98(7)$, $\beta=67.90(6)$, $\gamma=71.75(7)$°, $R=0.0675$ and $R_w=0.0743$. The unit cell contains one centrosymmetric, dimeric cation, $[Cu_2(PU)_{10}]^{4+}$, and four non-coordinated ClO_4^- anions. The nearest environment of the Cu(II) atom consists of a distorted octahedron of oxygen atoms from molecules of the organic ligands. Neglecting the displacement of the Cu–O_t bonds from the equatorial plane of each Cu(II) polyhedron, this complex represents an example of a dimer built from octahedral fragments with parallel planes of equatorial ligands; one of the equatorial ligands of each Cu(II) atom is simultaneously an axial ligand for another. From EPR measurements, the compound belongs to a class for which the noncoincidence of $\{g\}$ and $\{D\}$ tensor axes in the plane perpendicular to the equatorial ligands is characteristic. Magnetic susceptibilities and EPR parameters indicate ferromagnetic interactions between Cu(II) atoms in $[Cu_2(PU)_{10}]^{4+}$ cations.

Keywords: Pyrimidinone, copper(II), X-ray structure, EPR, magnetics

INTRODUCTION

Copper(II) coordination compounds containing pentacoordinated, monomeric complex ions with a homogeneous coordination sphere, are rare. Only compounds with anions $[CuX_5]^{3-}$ ($X=Cl^-, Br^-$) or cations $[Cu(NH_3)_5]^{2+}$ have been described in the literature. Anions $[CuX_5]^{3-}$ are present in the compounds with general formula $[M(NH_3)_6][CuX_5]$ (M = Co(III), Cr(III)).[1–4] From results of X-ray structure analysis at room temperature[1–3] the CuX_5 polyhedra have trigonal-bipyramidal geometry. However, a detailed study of $[Co(NH_3)_6][CuCl_5]$ at lower temperatures showed that the structure of the anion is a dynamic average of elongated square pyramids.[4] Elongated square pyramidal $[CuCl_5]^{3-}$ anions are also in the structure of the compound $[N(2amet)pipzH_3][CuCl_5].H_2O$, where $[N(2amet)pipzH_3]^{3+}$ is N-(2-ammoniomethyl)piperazinium cation.[5] The cation $[Cu(NH_3)_5]^{2+}$, present[6] in

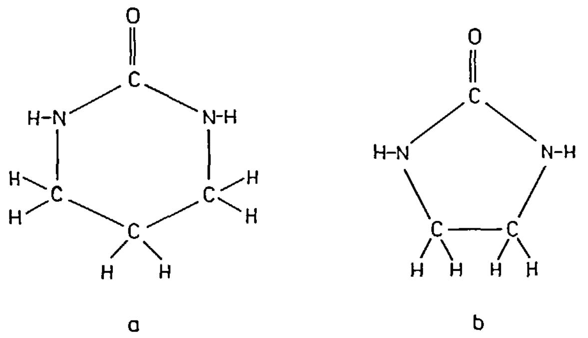

FIGURE 1 2(1H)-tetrahydropyrimidinone (a, PU) and 2-imidazolidinone (b, EU).

$K[Cu(NH_3)_5](PF_6)_3$, is square pyramidal as well. This is somewhat surprising as a slightly higher stability was predicted[7] for elongated trigonal bipyramidal structures.

According to the crystal structure[8] of the compound $Cu(EU)_5(ClO_4)_2$ (EU = 2-imidazolidinone, or *N*,*N'*-ethyleneurea), the cation $Cu(EU)_5^{2+}$ can be regarded as constituting a tetragonal pyramid. However, two monomeric units are connected *via* hydrogen bonds to give centrosymmetric dimers and perchlorato oxygen atoms are located as near as 3Å to each copper(II) atom (opposite the apical Cu–EU bond).

Before had thought that the greater steric demands of 2(1H)-tetrahydropyrimidinone (Fig. 1) would have prevented the formation of hydrogen bonds between neighbouring $Cu(PU)_5^{2+}$ cations in the compound $Cu(PU)_5(ClO_4)_2$, as well as preventing the coordination of perchlorato anions to Cu(II) atoms. If this idea were to be fulfilled, the compound $Cu(PU)_5(ClO_4)_2$ would belong to the class of Cu(II) compounds containing isolated CuL_5 entities. However, the compound does not contain isolated $Cu(PU)_5^{2+}$ cations; it does contain dimeric $[Cu_2(PU)_{10}]^{4+}$ cations build up from two monomeric $Cu(PU)_5^{2+}$ fragments. We report here the synthesis of $Cu(PU)_5(ClO_4)_2$, its crystal and molecular structure, as well as relevant spectral properties.

EXPERIMENTAL

Starting materials

The ligand 2(1H)-tetrahydropyrimidinone was prepared from 1,3-propylenediamine and urea.[9] Copper perchlorate was used as supplied.

Synthesis of the complex

The complex was prepared from a saturated ethanolic solution of copper perchlorate and a saturated ethanolic solution of the organic ligand. For the synthesis of the complex of composition $Cu(PU)_5(ClO_4)_2$, the molar ratio (copper to ligand) 2:5 was used. The two alcoholic solutions were mixed, the solvent was partly evaporated, and after the cooling of the concentrated solution to −10°C, precipitation of complex occurred. The crystals were collected, washed with ethanol and diethylether and finally dried at room temperature *in vacuo*. *Anal*; calcd. for $Cu(PU)_5(ClO_4)_2$: Cu, 8.32; C, 31.48; N, 18.35; H, 5.28%. Found: Cu, 8.12; C, 31.55; N, 18.31; H, 5.27%.

Physical measurements

Infrared spectra were recorded on a Carl Zeiss Jena M-80 Spectrophotometer in the region 400–4000 cm^{-1}, in nujol mulls. Electronic spectra were recorded (diffuse reflectance) on a Cary 14 instrument.

EPR investigations were carried out using an ERS-230 radiospectrometer in the X ($\nu_1 = 9.3$ GHz)- and Q ($\nu_2 = 35.7$ GHz)-bands. The measurements were carried out in the temperature range 15–300K as well as at 4.2K in the X-band, and at 300K in the Q-band. Magnetic susceptibilities were determined by the Gouy method, using a Newport instrument. The measurements were performed at eight different temperatures, from room temperature to 93K at four field strengths in the range *ca* 4.6–6.6 kOe.

Crystal structure determination

Crystal data

$C_{20}H_{40}CuN_{10}O_{13}Cl_2$: $M_r = 763.0$, triclinic, space group $P\bar{1}$, $a = 11.709(8)$, $b = 12.750(12)$, $c = 12.891(11)$ Å, $\alpha = 62.98(7)$, $\beta = 67.90(6)$, $\gamma = 71.75(7)°$, $V = 1564(2)$ Å^3, $D_x = 1.62$ gcm^{-3}, $z = 2$, $F(000) = 793.97$, $\lambda = 0.71069$ Å, $\mu(MoK\alpha) = 0.938$ mm^{-1}.

Accurate cell dimensions and the crystal orientation matrix were determined on a SYNTEX P2$_1$ diffractometer by least-squares treatment of the setting angles of 15 reflections in the range $5.5 < \Theta < 11.5°$. Crystal dimensions were 0.10 × 0.20 × 0.30 mm; intensities of reflections with indices h 0 to 14, k −15 to 15, l −15 to 15, with $2 < \Theta < 27°$ were measured; $\Theta - 2\Theta$ scan; graphite-monochromized MoKα radiation; intensities of two reflections ($\bar{1}21$, $\bar{1}\bar{2}0$) were measured every 98 reflections; no significant systematic fluctuation was found. Some 6866 reflections were measured, 2648 of which with $F_o > 6\sigma(F_o)$ were considered observed; $R_{int} = 0.031$ for 644 unique reflections before absorption correction. Empirical absorption correction was based on intensity measurements at different azimuthal angles; transmission ranged from 0.2–1.2. The structure was solved by Patterson methods using SHELXS86[10] and refined on F by least-squares methods, with SHELX76.[11] A difference map of the partially refined structure gave the positions of some hydrogen atoms. The rest were positioned on geometric grounds (C–H, N–H 1.08 Å). Refinement was continued using all 538 positional and thermal parameters (anisotropic for non-H atoms; positional parameters for H-atoms constrained). In the final cycle $R = 0.0675$ and $R_w = 0.0743$ for 2648 observed reflections (14 of the strongest reflections (F_o differed from F_c by about 10%) were considered to be poorly measured and were excluded from the final refinement), $w^{-1} = k\sigma^2(F)$, $k = 2.98$; max. $\Delta/\sigma = 0.033$ and max. and min. heights in final $\Delta\rho$ map +0.55 and −0.35 eÅ^{-3}. The scattering factors for neutral atoms were taken from International Tables for X-ray Crystallography.[12] Lists of hydrogen positions, anisotropic temperature factors and observed and calculated structure factors are available from Jozef Kožíšek upon request.

RESULTS AND DISCUSSION

The first results which suggested that the structure of $Cu(PU)_5(ClO_4)_2$ was exceptional, were associated with EPR spectroscopy of polycrystalline samples.

EPR spectra at room temperature in the X- and Q-bands, respectively, are given in Figures 2a and 3a. The intensity of all signals increased with lowering temperature to 4.2K. The measured shapes, frequencies and the temperature dependence of the $Cu(PU)_5(ClO_4)_2$ spectra allow two interpretations.

With respect to the first, in the X- and Q-band spectra, one may distinguish signals with effective g-factors not changing with the frequency. These are signals with $g_{ef}=2.095$ ($B=0.32T$ in the X-band; $B=1.22T$ in the Q.band) and $g'y=2.52$ ($B=0.27T$ and $1.01T$ in the X- and Q-bands, respectively), $\Delta g=\pm 0.005$. Due to the form and position of these signals and their frequency independence, the signals would be attributed to the $S=1/2$ transitions state of a mononuclear Cu(II) complex ($g_{\perp}=g_{ef}=2.095$; $g_{\parallel}=g'_{ef}=2.52$). The form, as well as the frequency and temperature dependences of other signals in the EPR spectrum would enable one to conclude that they are due to transitions between $S=1$ triplet levels.[13,14] This state results from the exchange interaction JS_1S_2 ($J<0$) between two Cu(II) ions and is realized by a definite location of ions and molecular fragments in the crystal structure. The position of the observed signals can be satisfactorily described by the spin Hamiltonian with $S=1$

$$H=\mu_B\vec{B}\{g\}\hat{\vec{S}}+\hat{\vec{S}}\{D\}\hat{\vec{S}} \qquad (1)$$

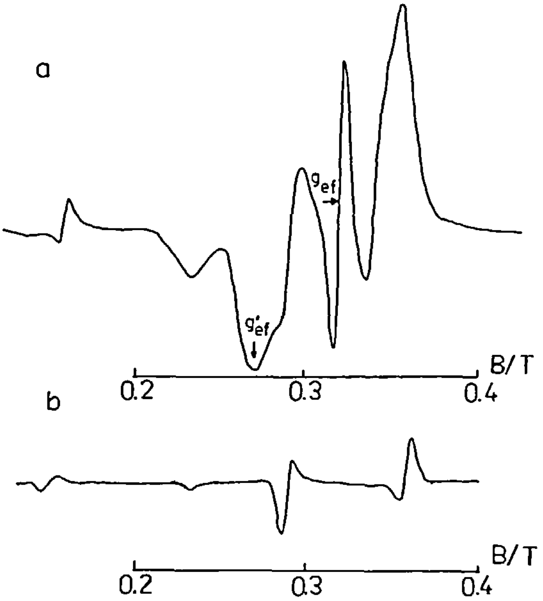

FIGURE 2 EPR spectrum of a polycrystalline sample of $Cu(PU)_5(ClO_4)_2$ at $\nu_1=9.3$ GHz (a); spectrum simulated for $S=1$, $g_{\perp}=2.07$, $g_{\parallel}=2.26$, $D=0.07\,cm^{-1}$, $h\nu=0.31\,cm^{-1}$ (b).

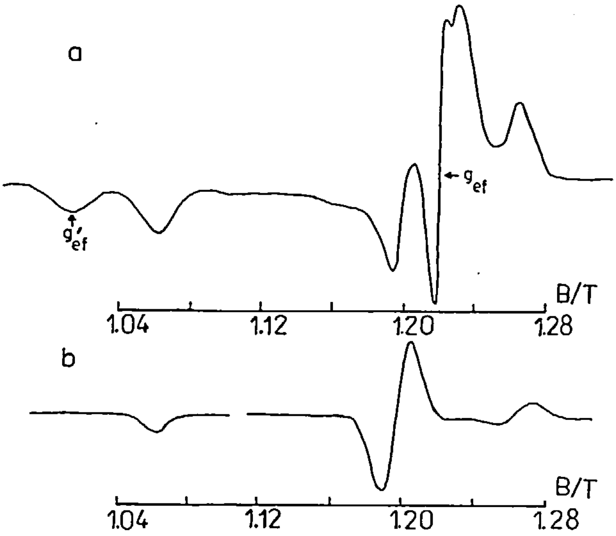

FIGURE 3 EPR spectrum of a polycrystalline sample of $Cu(PU)_5(ClO_4)_2$ at $\nu_2 = 35.7$ GHz (a); spectrum simulated for $S = 1$, $g_\perp = 2.07$, $g_\parallel = 2.26$, $D = 0.07\,cm^{-1}$, $h\nu = 1.2\,cm^{-1}$ (b).

where the principal axes of {g}- and {D}-tensors coincide, and $g_\perp = 2.07$, $g_\parallel = 2.26$ and $D = 0.07\,cm^{-1}$. EPR spectra simulated by means of the program EXCHANGE[15] are given in Figures 2b and 3b. The relation of the intensities of $S = 1/2$ and $S = 1$ signals, practically does not change from synthesis to synthesis. Thus it does not seem reasonable to attribute the signals with $S = 1/2$ to minor admixture of a monomeric Cu(II) complex. The value of $g_\parallel = 2.52$ as compared with typical g-factors for mononuclear Cu(II) would be explained by unusual coordination of the magnetic centre and electronic properties of the ligands.

In the second case, it is not necessary to invoke the simultaneous presence of mononuclear and binuclear centres in the crystal structure of the compound. Neglecting the signal with $g_{ef} = 2.095$, one can satisfactorily describe all signals observed in the X- and Q-bands by transitions within the levels of a triplet state with $S = 1$, and by using the spin Hamiltonian (*1*) with somewhat different estimates of spin Hamiltonian parameters in the X- and Q-bands ($D \sim 0.07\,cm^{-1}$). This difference could be due to the non-coincidence of the principal axes of {g}- and {D}-tensors.[16]

It should be noted that in this case the signals with $g'_{ef} = 2.52$ in the X- and Q-bands correspond to the transitions within the $S = 1$ state for the different canonical orientations of the magnetic field respective to the principal axes of the {D} tensor; the signal with $g_{ef} = 2.095$ may be due to the so-called double quantum transitions in the three level system.[17]

It was impossible to make a final choice based on the data for the polycrystalline samples. It was also impossible to answer the question concerning whether the clusters are intermolecular dimers or if they are distinguished by specific contacts between

TABLE I
Basic crystallographic data for $[Cu_2(PU)_{10}](ClO_4)_4$.

Space group: $P\bar{1}$	a/pm = 1170.9(8)
$z=1$	b/pm = 1275.0(12)
$R=0.0675$	c/pm = 1289.1(11)
$R_w=0.0743$	$\alpha=62.89(7)°$
	$\beta=67.90(6)°$
	$\gamma=71.75(7)°$

mononuclear molecules. Both cases are possible, and examples are found in the literature.[14–15] The existence of the clusters as well as the ferromagnetic nature of the exchange interactions, $J<0$, were however doubtless.

For unambiguous interpretation of structural and EPR spectral properties it was thus necessary to solve the crystal and molecular structure. Basic crystallographic data are given in Table I. Final atomic coordinates and equivalent isotropic temperature factors are given in Table II and selected bond lengths and angles[18] in Tables III and IV. The molecular structure[19] with atom numbering is shown in Figure 4.

The structure of $Cu(PU)_5(ClO_4)_2$ consists of discrete dimeric species $Cu_2(PU)_{10}^{4+}$ formed by two complex cations, $Cu(PU)_5^{2+}$, related by a centre of symmetry and bridged by oxygen O1 and O1* atoms of the PU ligand with noncoordinated perchlorato anions. On this basis it is more convenient to write the chemical formula of the complex as $[Cu_2(PU)_{10}](ClO_4)_4$. Each Cu(II) atom is pseudooctahedrally

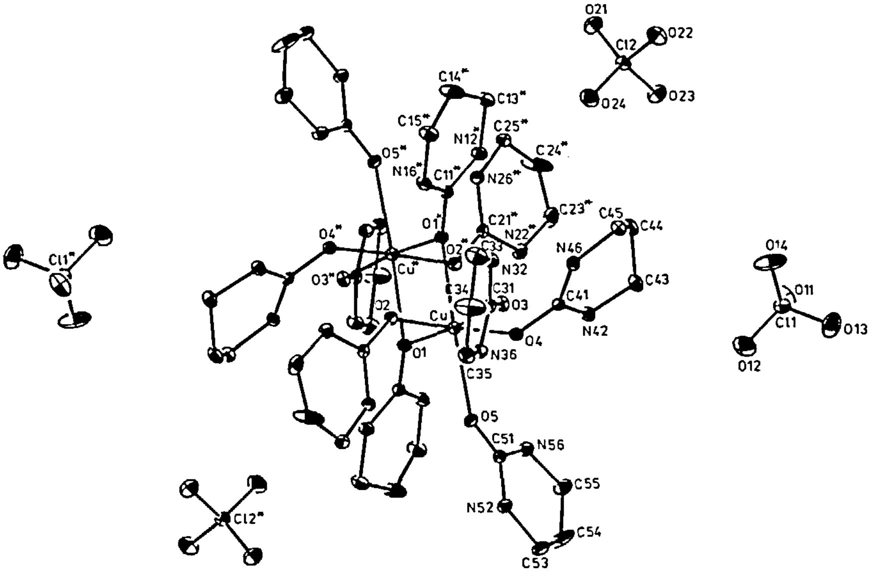

FIGURE 4 Contents of the unit cell for $Cu(PU)_5(ClO_4)_2$.

TABLE II

Final atomic coordinates for non-hydrogen atoms (×10^4) and equivalent isotropic thermal parameters U_{eq} (×10^4 Å^2) with e.s.d.'s in parentheses; $U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* a_i a_j$.

Atom	*x/a*	*y/b*	*z/c*	U_{eq}
Cu	1509(1)	231(1)	4496(1)	652(7)
C11	2164(3)	4742(3)	6871(3)	963(19)
C12	2844(3)	−1008(3)	−881(3)	889(17)
O1	206(6)	507(6)	3726(6)	730(37)
O2	2136(6)	−1340(5)	4431(6)	705(39)
O3	2677(6)	−128(6)	5421(6)	778(41)
O4	793(6)	1772(5)	4646(6)	704(40)
O5	2945(6)	1243(6)	2680(6)	773(40)
O11	967(10)	5352(11)	6963(10)	1736(103)
O12	2622(13)	4553(12)	5813(12)	1968(107)
O13	2883(11)	5420(13)	6801(15)	2117(127)
O14	2227(12)	3752(12)	7771(13)	2305(103)
O21	3944(9)	−539(8)	−1440(9)	1344(70)
O22	2231(9)	−703(9)	−1734(9)	1361(70)
O23	3134(8)	−2251(8)	−359(9)	1261(63)
O24	2072(10)	−589(9)	15(9)	1482(71)
N12	803(8)	995(7)	1715(8)	817(50)
C13	778(11)	1810(10)	515(9)	1061(80)
C14	129(14)	2972(10)	422(10)	1673(124)
C15	−843(11)	3115(9)	1423(10)	1130(87)
N16	−673(8)	2253(8)	2566(7)	837(51)
N22	3281(8)	−2858(7)	3912(7)	864(57)
C23	4227(10)	−3370(10)	3091(13)	1208(106)
C24	4800(16)	−2566(13)	1963(12)	2281(156)
C25	4356(11)	−1314(11)	1621(9)	1142(97)
N26	3382(8)	−941(6)	2504(7)	811(53)
N32	3799(8)	−1760(8)	6436(7)	924(61)
C33	4891(12)	−2650(11)	6513(11)	1383(114)
C34	5905(12)	−2494(13)	5438(13)	2162(154)
C35	5714(9)	−1637(11)	4328(10)	1018(90)
N36	4562(7)	−790(7)	4392(7)	766(52)
N42	−192(8)	3180(7)	5381(7)	835(55)
C43	−613(11)	3611(8)	6324(10)	1030(93)
C44	−667(10)	2683(10)	7474(9)	1069(83)
C45	421(10)	1797(9)	7509(8)	915(75)
N46	823(7)	1422(7)	6529(8)	728(49)
N52	3923(7)	2665(7)	1065(8)	824(50)
C53	4082(9)	3883(9)	376(10)	1060(78)
C54	3004(11)	4728(9)	541(13)	1942(134)
C55	2028(11)	4402(8)	1628(10)	1121(84)
N56	2013(7)	3159(7)	2285(7)	878(56)
C11	141(8)	1244(8)	2691(9)	645(54)
C21	2915(9)	−1699(8)	3630(9)	688(62)
C31	3661(9)	−892(8)	5402(9)	693(61)
C41	486(9)	2102(8)	5517(9)	665(54)
C51	2959(8)	2312(9)	2045(9)	668(59)

TABLE III
Selected bond distances (pm) with standard deviations in parentheses.

Cu-O1	197.1(9)	Cu-O5	237.2(6)
Cu-O2	193.5(7)	Cu-O1*	243.6(6)
Cu-O3	196.0(9)	Cu-Cu*	341.7(3)
Cu-O4	194.7(7)		

TABLE IV
Selected bond angles (degrees) with standard deviations in parentheses.

O1-Cu-O1*	79.1(3)	O1*-O1-C5	170.7(3)
O1-Cu-O2	90.6(3)	O2-Cu-O3	88.8(3)
O1-Cu-O3	174.0(3)	O2-Cu-O4	176.5(3)
O1-Cu-O4	88.6(3)	O2-Cu-O5	96.6(3)
O1-Cu-O5	95.6(3)	O3-Cu-O4	91.6(3)
O1*-Cu-C2	91.2(3)	O3-Cu-O5	90.4(3)
O1*-Cu-C3	94.7(3)	O4-Cu-O5	86.9(3)
O1*-Cu-C4	85.4(3)	Cu-O1-Cu*	100.9(3)

coordinated. There are three terminally bonded ligands through the O2, O3 and O4 atoms and one bridging ligand (coordinated through the O1 atom) in the equatorial plane. The axial positions are completed by the second bridging atom O1* of a ligand belonging to the second monomer fragment Cu(PU)$_5^{2+}$ and one terminally bonded ligand (through the O5 atom). The Cu–O distances in the equatorial plane are in the range 1.94(1)–1.98(1)Å and may be considered as being equivalent, while the axial interactions are different (2.372(6) and 2.436(6)Å). The equatorial bond distances Cu–O$_i$ are similar to those in the compound[8] Cu(EU)$_5$(ClO$_4$)$_2$ (ranging between 1.94(1)–1.95(1)Å). On the other hand, the length (2.372(6)Å) of the axial bond, Cu–O5, is considerably greater than in Cu(EU)$_5$(ClO$_4$)$_2$: 2.239(6)Å. This is probably caused by the greater steric effects of PU ligands coordinated in axial positions as compared with the case in Cu(EU)$_5$(ClO$_4$)$_2$.

As mentioned above, Cu(EU)$_5$(ClO$_4$)$_2$ contains[8] a pair of hydrogen bonds between two adjacent Cu(EU)$_5^{2+}$ cations. One of the bonds is between a coordinating carbonyl oxygen atom of one copper(II) cation and a nitrogen atom of a ligand in the adjacent cation. The other bond is complementary. Thus the molecules pack as centrosymmetric hydrogen-bonded dimers.

In the case of Cu(Cu(PU)$_5^{2+}$(ClO$_4$)$_2$ there are no hydrogen bonds between the two monomeric fragments. On the other hand, strong hydrogen bonds are formed between ligands of Cu(PU)$_5^{2+}$ monomeric fragment; of a related nature to the above, bonding distances and angles for which are given in Table V. In addition, others are located between donors on the ligand and oxygen atoms of the perchlorato anions. Close contacts also exist between NH-groups of neighbouring ligands coordinated to the same Cu(II) atom. It is interesting that the bridging atoms O1 and O1* are not involved in any hydrogen bonds.

TABLE V

Hydrogen bonding distances and angles (in pm and degrees) with standard deviations in parentheses.

Atom 1	*Atom 2*	*Atom 3*	*2–3*	*1–3*	α(*1–2–3*)
N26	H26	O5	186.6(3)	276.8(1)	147.81(2.68)
N36	H36	O5	232.0(4)	317.0(1)	141.72(1.62)
N46	H46	O3	204.9(5)	286.4(1)	137.09(3.31)
N56	H56	O4	193.4(5)	280.2(1)	142.99(3.62)
N16	H16	O2	255.8(2)	338.2(1)	139.13(3.68)

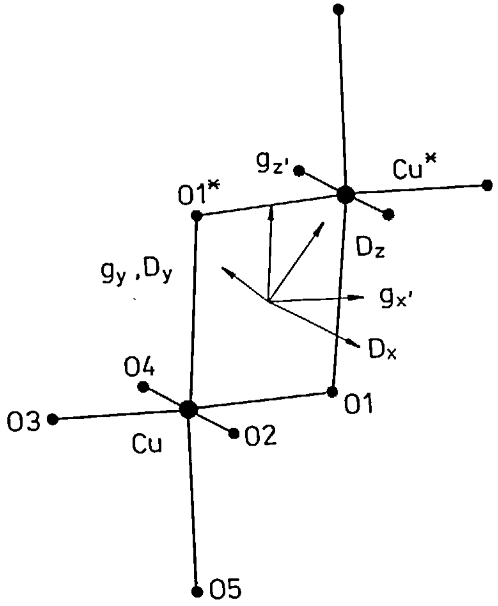

FIGURE 5 Orientation of the {g} and {D} tensors in the dimeric cation $[Cu_2(PU)_{10}]^{4+}$.

The second interpretation of the EPR spectra is thus correct, although accurate parameters could not be determined. This would require single-crystal EPR measurements the results of which will be published in detail elsewhere.[20] In accordance with the structural data, the single-crystal EPR show the presence of one centre with $S=1$. The principal values and orientations of {g} and {D} tensors were obtained;[20] g_y and D_y are coincident within experimental error and rotation of {g} and {D} axes is observed only in the plane perpendicular to y. The angle between g_x, (g_z) and D_x (D_z) is 36°. The orientation of {g} and {D} tensors is given in Figure 5. Comparison with structural data shows that the principal axes of the {g} tensor are close to the Cu–O_i directions. It was also possible to obtain, from the fine structure, information on anisotropy of the exchange interaction between the two Cu(II) atoms of $[Cu_2(PU)_{10}]^{4+}$. The main contribution to the values of the fine structure tensor

{D} arises from dipole-dipole interactions. The peculiarities of the polycrystalline spectra dependence on the frequency, and the {g} and {D} non-coincidence angle were analyzed.[20] It was shown that such a situation is possible when at different frequencies signals corresponding to different orientations are detected. Most noticeable changes of orientation occur for $D/h\nu < 0.2$ and are observed even for a small non-coincidence angle. Analysis of EPR spectra for these compounds may lead to erroneous conclusions.

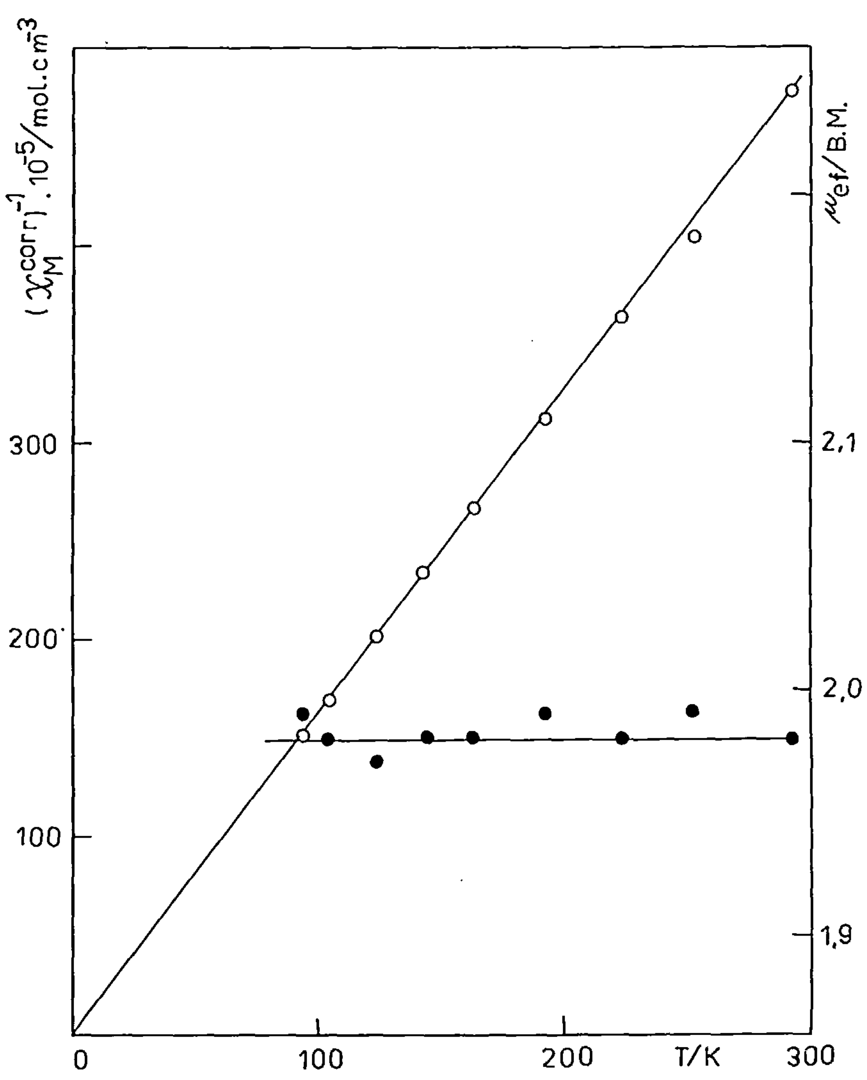

FIGURE 6 Dependence of reverse-corrected molar susceptibility (○) and of magnetic moment (●) on temperature for $Cu(PU)_5(ClO_4)_2$.

The temperature dependence of the inverse molar magnetic susceptibility of the compound (Figure 6) follows the Curie-Weiss law over the whole temperature range of the measurements; the constants $C=6.197\,\mathrm{cm^3\,K\,mol^{-1}}$ and $\theta=0.33\,\mathrm{K}$ were calculated using least-square analyses of the function $(\chi_M^{corr})^{-1}$ *versus* T. The small temperature variation of the magnetic moment (Figure 6) is characteristic of an intramolecular ferromagnet. Results of both magnetic and EPR measurements show that the exchange interaction between the Cu(II) atoms of $[Cu_2(PU)_{10}]^{4+}$ cations is of ferromagnetic nature.

Comparison of the IR spectrum of the complex with that of the free ligand[21] shows differences characteristic of the carbonyl stretching and the NH bending changes. These (Table VI), are in good agreement with preliminary studies and predictions[21,22] concerning 2(1H)-tetrahydropyrimidinone coordinated to metal cations through

TABLE VI

Carbonyl stretching and NH bending frequencies for free 2(1H)-tetrahydropyrimidinone and the complex*.

Compound	$\nu(CO)/cm^{-1}$	$\delta(NH)/cm^{-1}$
PU	1686 (s)	1540 (s)
$Cu(PU)_5(ClO_4)_2$	1636 (s), 1622 (sh)	1548 (s)
	1602 (s)	1541 (s)

* Abbreviations: s = strong, sh = shoulder.

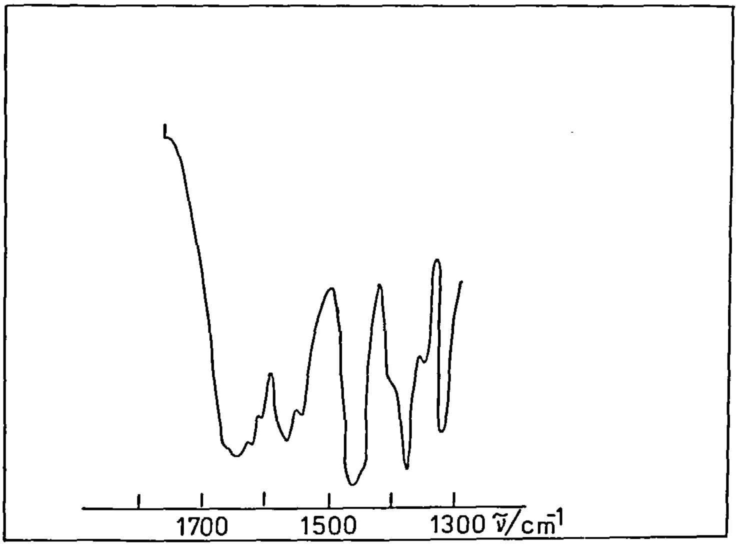

FIGURE 7 Infrared spectrum of $Cu(PU)_5(ClO_4)_2$ in the region 1800 – 1300 cm^{-1}.

TABLE VII
Ligand field data for $Cu(PU)_5(ClO_4)_2$ and its related compounds.[22,23]

Compound	$\nu_{max}(d-d)/cm^{-1}$
$Cu(PU)_5(ClO_4)_2$	12300, 9900(sh)
$Cu(EU)_5(ClO_4)_2$	12400, 10700(sh)
$Cu(EU)_4(ClO_4)_2$	13400, 11200(sh)

oxygen donor atoms.[21] A decrease of the carbonyl stretching frequency in the complex as compared with that of the free PU ligand is caused by coordination of oxygen. Increase in the NH bending frequencies is caused by increased C–N double bond character resulting from Cu–O_t complexing. Doublets (Figure 7), found in the IR spectra of the complex for CO stretching and NH bending frequencies, arise from the non-equivalent ligands (terminal and bridging).

The ligand field spectrum of the complex is very similar in band width and shape (Table VII) to the ligand field spectra of $Cu(EU)_4X_2$ and $Cu(EU)_5X_2$ ($X^- = ClO_4$, BF_4).[22,23] These similarities suggest that the Cu(II) coordination polyhedra in all compounds have a similar geometry, namely tetragonal bipyramidal.

Acknowledgements

The authors wish to thank Mr. M. Nádvorník for carrying out magnetic susceptibility measurements.

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