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Tetranuclear copper complexes with new β-diketone and β-iminoketone-containing ligands

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Summary

Novel tetranuclear copper complexes, $Cu_4(OH)_2(ClO_4)_3(HA) \cdot H_2O$ *(1)* and $Cu_4(ClO_4)_5(H_3B) \cdot 3H_2O$ *(2)*, were synthesized by reacting 1,5-bis(1′-phenyl-3′-methyl-5′-pyrazolone-4′)-1,5-pentanedione with 1,3-propanediamine and 2-hydroxyl-1,3-propanediamine in the presence of a template reagent copper ion. New [2 + 2] type open cyclic multidentate ligands are also obtained from the reaction (H_4A and H_6B stand for new compounds from 1,3-propanediamine and 2-hydroxyl-1,3-propanediamine, respectively). They each contain five C=O, three C=N and one NH_2 groups. The complexes were characterized by elemental analyses, conductivity, FT-i.r. (micro-i.r., deconvolution technique), FAB-MS, e.s.r., electronic spectra and extended X-ray absorption fine structure (EXAFS). Copper ions in *(1)* are basically four coordinate with tetragonal geometry. The average coordination bond distances of Cu—N and Cu—O are 1.91 Å and 2.05 Å. In *(2)*, copper ions are primarily five coordinate with square-based pyramidal geometry. The average coordination bond distances of Cu—N and Cu—O are 1.93 Å and 2.08 Å. Four copper atoms in molecules may be arranged tetragonally. Both the ligand field and the coordination bonds in complex *(1)* are stronger than those in *(2)*. Investigations on variable temperature susceptibilities show that some antiferromagnetic exchange interaction exist in the complexes. The plots of χ^{-1} *versus* T obey the Curie-Weiss law only at low temperature. Preliminary results of a bioassay indicate that the two complexes have some antitumour activity *in vitro*.

Introduction

Polynuclear complexes play an important role in molecular materials and in supramolecular chemistry(1–3). Design and syntheses of new ligands and complexes with special structures and properties are attracting more and more interest in recent years(4–6). Of course, the multidentate ligand is a critical factor in structure-controllable synthesis. Bispyrazolones (containing two β-diketone groups) are a new type multidentate ligand(7–8), which can form different coordination compounds(9,10) and show fascinating chemistry in the context of rare earth elements. Their rare earth complexes strongly fluoresce and can be used in luminescent materials(10–12). Antitumor activity is also observed for some complexes(13). However the ligand may change its coordination behavior to metal ions and form varies types of metal complexes, when modified by other functional groups. To further our studies on fluorescent materials and molecule-based magnetic properties, modifying the bispyrazolone with diamines was attempted. The introduced imine or amine groups provide a more flexible and variable means of adjusting the interaction between the metal ions. A better selectivity for chelating metal ions can also be achieved(14). Recently we investigated the reaction of bispyrazolone with a series of ω-diamines. It is interesting to note that the length of the alkyl diamine chain may significantly affect the products of the condensation with the tetraketone. Thus the structure of the complex can be designed and its properties then may be tuned. For 1,4-butanediamine, a new [1 + 1] type chain ligand-containing C=O, C=N, NH_2 groups is obtained from the condensation(15). Interestingly, new [2 + 2] type macrocycles containing C=O, C=N groups are obtained when bispyrazolone react with 1,2-ethylenediamine and 1,2-propanediamine(16). The reactions with 1,3-propanediamine and 2-hydroxyl-1,3-propanediamine are also of the 2 + 2 type, but acquired [2 + 2] open cyclic compounds with an amine group in the molecules. This paper reports the results of the condensation of the tetraketone, 1,5-bis (1′-phenyl-3′-methyl-5′-pyrazolone-4′)-1,5-pentanedione, with 1,3-propanediamine and 2-hydroxyl-1,3-propanediamine using copper ion as the template reagent. The ligands and their complexes are reported for the first time.

Experimental

Reagents

1,5-Bis(1′-phenyl-3′-methyl-5′-pyrazolone-4′)-1,5-pentanedione (BPMPPD, H_2L) was synthesized by the literature method(8). $Cu(ClO_4)_2 \cdot 6H_2O$ was prepared in our laboratory. Other reagents used for synthetic experiments and measurements were of commercial analytical grade.

$Cu_4(OH)_2(ClO_4)_3(HA) \cdot H_2O$ (1)

A solution of 1,3-propanediamine (0.5 mmol) in EtOH (20 cm^3) was added to a hot EtOH (50 cm^3) solution of BPMPPD (0.5 mmol) and the mixture was heated under reflux for 5 h, then an EtOH (20 cm^3) solution of Cu $(ClO_4) \cdot 6H_2O$ (1 mmol) was added with stirring. The mixture was then stirred under reflux for another 17 h, the resulting solid was washed thoroughly with EtOH and dried in vacuum at room temperature over P_2O_5. The

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complex was obtained as a light green solid. (Found: C, 42.0; H, 4.0; N, 10.6; Cu, 15.9. $C_{56}H_{63}N_{12}O_{20}Cu_4Cl_3$, calcd.: C, 42.4; H, 4.0; N, 10.6; Cu, 16.0%). Molar conductivity, Λ_M(DMF) = 115 S·cm^2·mol^{-1}. *Caution:* the complex is explosive at 285 °C!

$Cu_4(ClO_4)_5(H_3B)\cdot 3H_2O$ (2)

The blue green complex *(2)* was obtained by a method similar to that described for complex *(1)* using 2-hydroxyl-1,3-propanediamine instead of 1,3-propanediamine. (Found: C, 36.8; H, 3.5; N. 9.2; Cu, 14.5. $C_{56}H_{65}N_{12}O_{30}Cu_4Cl_5$, calcd.: C, 37.0; H, 3.6; N. 9.3; Cu 14.0 %). Λ_M(DMF) = 108 S·cm^2·mol^{-1}. *Caution*: the complex is explosive at 265 °C!

Measurements

Elemental analyses were carried out on a Carlo-Erba 1102 analyzer. The conductivities were measured on a DDS-11A conductometer. FT-i.r. spectra were recorded on a Magna 750 IR spectrometer. Micro i.r. spectra were performed with Nic-Plan microscopy. Electronic spectra were carried out on a Shimadzu UV-3100 UV-visible spectrophotometer. E.s.r. spectra were recorded on a JES-FEIXG spectrometer at the X-band frequency with manganese scale [Mn(MgO)] determining the magnetic field. Fast bombardment atomic mass spectra were carried out on a ZAB-HS mass spectrometer. Variable temperature magnetic susceptibilities were performed on an extracting sample magnetometer CF-1. Di-magnetic corrections were made using Pascal's constants, and the effective magnetic moments of complex were calculated with $\mu_{eff} = 2.828(\chi_A T)^{1/2}$.

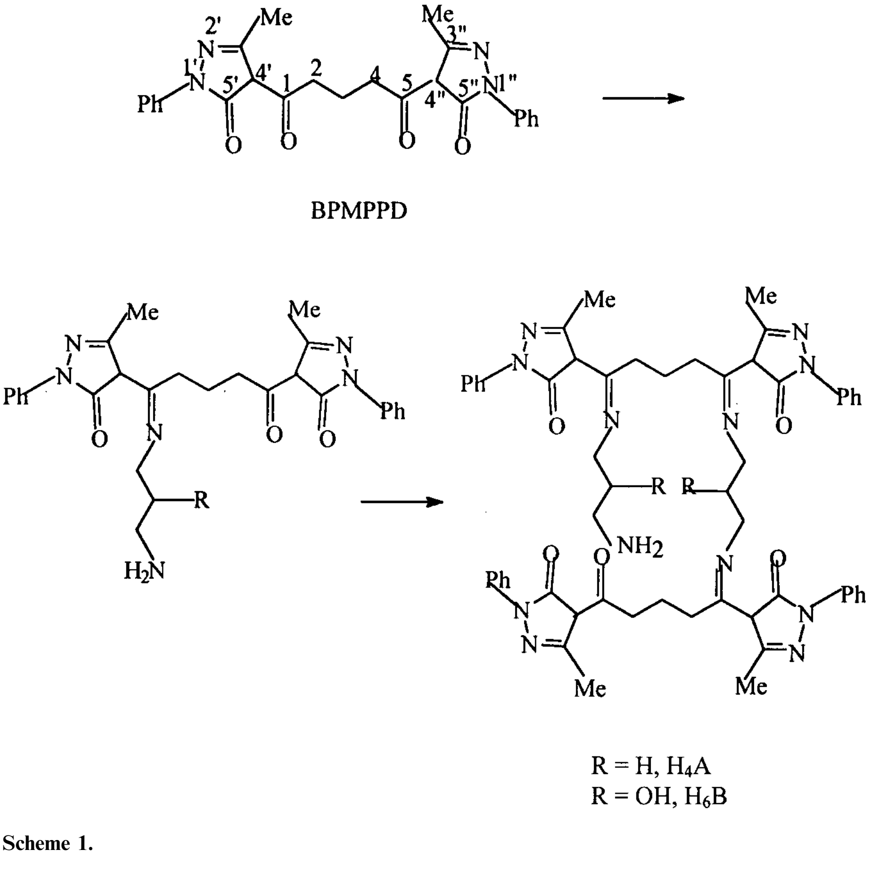
The extended X-ray absorption fine structure (EXAFS) measurement was carried out in the transmission mode for Cu K-edge at the EXAFS station using a Si(111) double-crystal monochromator on 4W1B beamline of Beijing Synchrotron Radiation Factory (BSRF), Institute of High Energy Physics. The storage ring ran at 2.2 GeV with a current of 40–70 mA. Copper oxide chosen as the model compound. Data acquisition was accomplished by an IBM PC/XT, and data processing was performed on a Micro VAX computer using the EXCURV 88 program of Daresbury, UK.

Results and discussion

Ligands

It is known that Schiff-bases can be created by reacting a ketone with an amine. For the tetraketone BPMPPD, the first Schiff-base should form at one of the four positions (Scheme 1, 1 and 5, 5′ and 5″ are isopositions). Several kinds of products can be predicted for the 1 + 1 reaction. A single crystal analysis of the reaction of 1,4-butanediamine with BPMPPD (1/1 ratio) shows that the [1 + 1] type reaction occurs and that a chain compound is obtained. It contains one NH_2 group. The Schiff-base formation occurs at position 1, not at 5′ of BPMPPD (Scheme 1)$^{(17)}$.

The enolization tendency of ketones in the [1 + 1] reaction product of 1,4-butanediamine with BPMPPD (1/1) indicates that the second Schiff-base should be created at position 5 (Scheme 1, if the first Schiff-base is at position 1) in the 1 + 1 product$^{(17)}$. The formation of a pyrazole ring (from the enol form of the ketone) lowers the energy of the system. Thus when



Scheme 1.

the [1 + 1] product undergoes further intermolecular condensation between two molecules, the [2 + 2] compound can be formed.

Due to the similarity of the alkyl diamines, the reaction of BPMPPD with 1,3-propanediamine or 2-hydroxyl-1,3-propanediamine should be similar to that with 1,4-butanediamine. When using a rare earth ion as a template reagent, we indeed obtained [1 + 1] products for the three diamines. However, fast atomic bombardment mass spectra investigations of the new copper complexes reveal that 2 + 2 type condensations occur in both reactions with 1,3-propanediamine and 2-hydroxyl-1,3-propanediamine. Furthermore, the reaction does not stop at the [1 + 1] stage and additional intermolecular condensation occurs. Thus [2 + 2] products are achieved. FT-i.r. spectra show the presence of an NH_2 group in the two new copper complexes. Thus the resulting new 2 + 2 ligands must be acyclic with the molecular structures show in Scheme 1 (In H_4A, H_6B, the easily broken bonds are also present in the molecular structure). Recently we also obtained a similar [2 + 2] type new acyclic compound from the direct condensation of 1,4-butanediamine with bis-pyrazolone BPMPPD (1/1 starting molar ratio). This result is also verified the speculation showed in Scheme 1.

Constituents of the complexes

The components of the complexes were determined by elemental analyses and the results are in accord with calculations. FAB-MS spectra (in DMF) also confirmed the tetranuclear complex formation.

In the FAB-MS spectra of complex *(1)*, the largest mass number (m/e), 1465, can be assigned to $Cu_4(OH)_2(ClO_4)_2(HA)$ (M−1 peak) fragment. This peak has the characteristic copper isotope pattern. The mass number 983 is assigned to ligand H_4A (MW 982, M + 1 peak), 927 to fragment H_4A-$(CH_2)_3NH_2$ {M + 3 peak, H_4A-$(CH_2)_3NH_2$ represents the ligand H_4A lost $(CH_2)_3$-NH_2 group}. These mass peaks reveal that the BPMPPD reacting with 1,3-propanediamine is 2 + 2 condensation to form a [2 + 2] type acyclic new complex (producing three water molecules and one remaining NH_2 group).

In the FAB-MS spectra of complex *(2)*, the largest mass number (m/e) is 1270 which can be assigned to fragment Cu_4B (M^+ peak), 1253 to fragment $Cu_4(H_6B$-$NH_2)$ (M−1 peak). These two peaks exhibit the characteristic copper isotope pattern. Peak 1015 is assigned to a new ligand H_6B (MW 1014, M + 1 peak), 997 to fragment H_6B-NH_2 (M−1), 983 to fragment H_6B-CH_2NH_2 (M−1), 944 to fragment H_6B-$C_3H_6ONH_2$ (M + 4). These results also indicate that the reaction of BPMPPD with 2-hydroxyl-1,3-propanediamine is similar to that of BPMPPD with 1,3-propanediamine (1/1 molar ratio reaction). A new acyclic 2 + 2 compound is obtained with NH_2, C=N, C=O, OH as the coordination groups.

The complexes are insoluble in water. They dissolve in mixed methanol/acetonitrile, hot ethanol and DMF. The molar conductivity of the complexes in DMF show that the two copper complexes are 1:1 electrolytes[18], which means one ClO_4^- group must be outside the coordination sphere in the complexes and the other ClO_4^- group is coordinated to the metal ions.

FT-i.r. spectra

FT-i.r. spectra of the two copper complexes are similar. A broad should peak at *ca.* 3200 cm^{-1} (KBr pellet) in complexes *(1)* and *(2)* indicates the existence of the NH_2 group. A strong broad peak at *ca.* 1100 cm^{-1} is assigned to the ν(Cl—O) vibration in ClO_4. The splitting of the peak (into four absorption bands: at *ca.* 1143, 1120, 1109, 1091 cm^{-1}) reveals the existence of coordinated perchlorate ions[19]. Stretching vibrations related to ν(C=O) and ν(C=N) (imine) are listed in Table 1. The peak at *ca.* 1525 cm^{-1} originates from the stretching vibration of ν(C=C), which is present in the enol tautomer of a β-diketone or β-iminoketone[19]. That means the ligands coordinate to copper ions *via* the enol form. Unsymmetrical absorption bands at *ca.* 3442, 3428 cm^{-1} for complexes *(1)* and *(2)* respectively can be assigned to ν(OH). Since KBr may influence this peak, we recorded the micro, i.r. spectra of the complexes.

Micro-i.r. spectra (4000–650 cm^{-1}) require no sample preparation. The spectra in the 1700–650 cm^{-1} range are similar to those recorded with KBr Pellets. The vibrations related to ν(C=O), ν(C=N) are at *ca.* 1606s. 1582s 1506s and 1494s for complex *(1)* and 1608s, 1586s, 1525m, 1506s and 1498s cm^{-1} for complex *(2)*. The ν(C=O) and ν(C=N) frequencies provide evidence that the coordination bonds between copper and the ketone or imine in complex *(1)* are stronger than those in complex *(2)*. Several peaks at the 3700–3000 cm^{-1} range appear in the micro i.r. spectra of complexes: 3528vs, br, 3318w, 3257m, 3160m for complex *(1)*; 3506vs, br, 3337m, 3276m, 3175m for complex *(2)*. The peaks in the 3300–3000 cm^{-1} range can be assigned to ν(NH_2). The absorption at *ca.* 3300–3400 cm^{-1} may relate to coordinated water in the molecules.

The strong broad unsymmetrical peak at *ca.* 3500 cm^{-1} in the micro i.r. can be assigned to the ν(O—H) stretching vibration. It clearly consists of several peaks. Thus the second order derivative and deconvolution techniques are applied to this peak. The result shows that this peak contains three bands, 3608, 3518, 3428 for complex *(1)* and 3607, 3522, 3437 cm^{-1} for complex *(2)*. These absorptions are related to the vibrations of hydroxyl and the water molecules in complexes[20]. Micro-i.r. and the deconvolution spectra also indicate that the ligands in the two complexes should exist as similar enol tautomers. The OH group of 2-hydroxyl-1,3-propanediamine may coordinated to the metal ion.

Electronic spectra

The d-d electronic spectra of the complexes in DMF were recorded. For a four coordinate Cu^{2+} complex

Table 1. Spectral data of complexes *(1)* and *(2)*

Complex	I.r. spectra ν(C=O) (cm^{-1})	 ν(C=N) (cm^{-1})	d-d spectra λ (nm)	 ε (M^{-1} cm^{-1})	e.s.r. *g* (ΔMs = 1)
(1)	1605vs	1581vs	610.5	392	2.110
	1520sh	1493vs			
(2)	1606vs	1583vs	642.5	506	2.044, 2.328
	1525m	1499vs			

(EXAFS), copper may be in tetrahedral or square coordination geometry. The d-d transition in the tetrahedron usually appears at low frequency. The transition energy of d-orbital in complex *(1)* is *ca.* 16380 cm^{-1}, which is at the range of that for tetragonal geometry copper compounds (usual 13000–20000 cm^{-1})(21).

Complex *(2)* is primarily five coordinated (EXAFS). There are two extreme structures for five coordinate cu^{2+} complexes: the square pyramid and the trigonal bipyramid. The trigonal bipyramid usually exhibits a strong low energy and is followed by a weaker band or shoulder at higher energy(22). The transition energy of the d-orbital in complex *(2)* is a broad symmetric band at *ca.* 15560 cm^{-1}. Thus the square-based pyramidal geometry for the complex is proposed(23). The d-d transition can be assigned to $^2E \leftarrow {}^2B_1$. The e.s.r. spectra also confirm this speculation. The stronger d-d transition energy in *(1)* reveals that the ligand field of this complex is stronger; a result which is also consistent with the i.r. spectral results and the EXAFS.

E.s.r. spectra

The solid state e.s.r. spectrum of compound *(1)* shows a basically broad symmetric $\Delta Ms = 1$ resonance signal and a very weak $\Delta Ms = 2$ signal (half-field line) with $g = 4.18$ (amplified by 100 times). Since the zero field splitting effect can be observed only for the $S \geq 1$ system and Cu^{2+} is d^9 configuration with $S = 1/2$, the appearance of a half field line in the e.s.r. spectra indicates that the complex is multinuclear(24).

Complex *(2)* has a broad unsymmetrical $\Delta Ms = 1$ resonance signal in the solid state e.s.r. spectrum and the superfine structure can be observed ($A_{\|} = 178$ G). The spectra indicate that the single electron in Cu^{2+} (d^9) should be in $d_{x^2\text{-}y^2}$ orbital ($g_{\perp} > g_{\|}$) not dz^2 ($g_{\perp} < g_{\|}$). The coordination geometry of copper may be square-based pyramid (single electron in $d_{x^2-y^2}$ orbital) with distorted C_{4V} geometry, which is in accord with the results of the electronic spectra(25). Though no $\Delta Ms = 2$ signal is observed for complex *(2)*, the unsymmetrical signal of $\Delta Ms = 1$ also indicates that the complex is multinuclear. Figure 1 shows $\Delta Ms = 1$ resonance signals at room temperature.

Solid state e.s.r. spectra were also measured at low temperature. The intensities of the $\Delta Ms = 1$ signal decrease at low temperature (−150 °C) in both complexes, which means that the $\Delta Ms = 1$ resonance signal comes from the $|\pm 1> \rightarrow |0>$ transition and some antiferromagnetic interaction exists between copper ions in the complexes. The magnetic properties are also identified in the result.

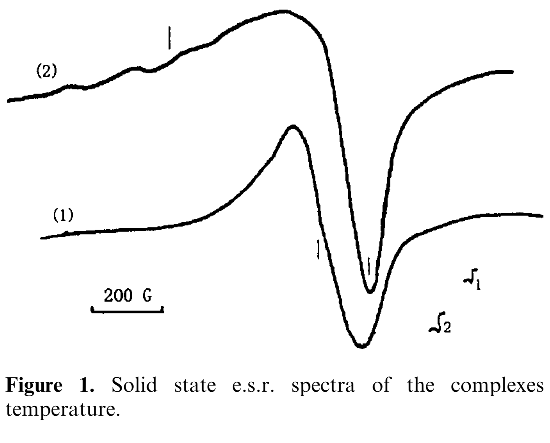


Figure 1. Solid state e.s.r. spectra of the complexes at room temperature.

Extended x-ray absorption fine structure (EXAFS)

EXAFS is a useful tool for investigating the coordination structure of powder or microcrystalline compounds(26). Though the EXAFS can not give the whole image of the coordination geometry of compounds, it can provide the average coordination number and the average coordination bond distances for the local atom. These data can also give some useful information on the coordination structures. Since it is very difficult to obtain the single crystal at present, the EXAFS technique is applied to study the nearest neighboring coordination environment of the copper ions in the complexes.

The EXAFS results for the two copper complexes are shown in Table 2. A two shell fit is better than a one-shell fit. The Debye-Waller factor (DWF) is small. For nitrogen and oxygen atoms having similar X-ray deflections, it is not easy to identify which bond distance belongs to Cu—N or Cu—O, but two kinds of bond distance exist. The shorter coordination bond distance in complex *(1)* indicates a stronger coordination bond. this is in accordance with the i.r. data and electronic spectra. The average total coordination number for copper ion in complex *(1)* is *ca.* 4 and in complex *(2)* *ca.* 5. The two complexes have different coordination geometry. Figure 2 shows the EXAFS spectra of complex *(2)*.

From the coordination numbers, compositions, conductance of complexes, spectral data and the signal crystal structures of rare earth and transition metal complexes with H_2L(13), we can draft the possible structures for complexes. One of the speculation structures is shown in Figure 3.

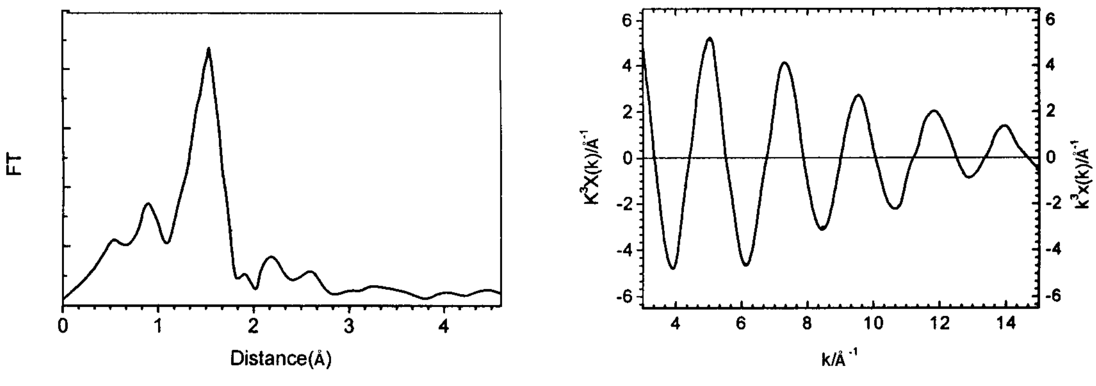
In the molecular structures of complexes, the three β-iminoketones of ligands are in the deprotonated enol tautomer. Each copper ion coordinates one keto-form (β-diketone) or one deprotonate enol form (β-iminoketone). Hydroxyl groups act as bridging ligands connecting two copper ions. Water molecules and partial perchlorates are also coordinated to copper ions. The longer coordination bonds may be Cu—NH_2, Cu—ClO_4, Cu—H_2O and the shorter bonds can be assigned to Cu—β-imiketone, Cu—β-diketone and the bridging Cu—OH. Four copper atoms, arranged tetragonally, make the molecular structure of complexes with a large hole.

Magnetic properties

The temperature dependence of the effective magnetic moment μ_{eff} per copper atom is depicted in Figure 4.

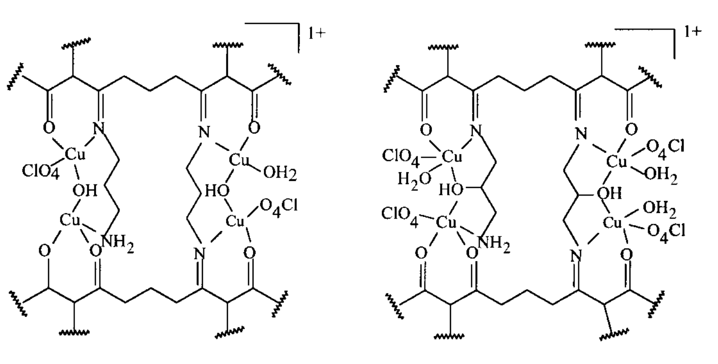
Table 2. EXAFS results for complexes *(1)* and *(2)*

Complex	Coordination no.	Bond distances, r(Å), Cu—O, Cu—N	DWF (Å)
(1)	3.2 ± 0.3	1.91 ± 0.01	0.0035
	1.0 ± 0.1	2.05 ± 0.01	0.013
(2)	3.6 ± 0.4	1.93 ± 0.01	0.0044
	1.9 ± 0.2	2.08 ± 0.01	0.011



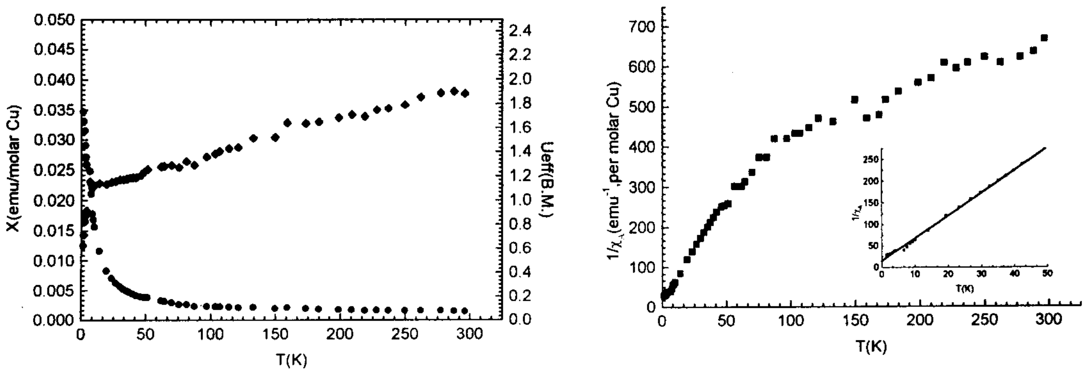
(a) (b)

Figure 2. Cu K-edge EXAFS spectra of complex *(2)*; (a) Fourier transform uncorrected for the phase shifts; (b) κ^3 Weighted EXAFS experimental (...) an best fit (——) spectra.



Complex *(1)* Complex *(2)*

Figure 3. Speculation coordination structures for the complexes.



(a) (b)

Figure 4. Temperature dependence of magnetic properties for complex *(2)*: (a) magnetic susceptibility ($\chi \sim$ T) and moment ($\mu_{eff} \sim$ T); (b) plot of $1/\chi \sim$ T, per molar copper ion.

The μ_{eff} value at room temperature, 1.88 B.M., is near to the spin-only value of 1.73 B.M. for the mononuclear system, where the spin-only value was calculated by assuming g value of $g_{Cu} = 2.0$. On lowering the temperature, μ_{eff} gradually decreases to 1.12 B.M. at 10 K and decreases rapidly below 10 K, which indicates the existence of antiferromagnetic interaction in the multinuclear complex. The rapidly decrease of μ_{eff} at low temperature may be due to an intermolecular antiferromagnetic interaction. The plot of $1/\chi$ *versus* T does not obey the Curie-Weiss law [$1/\chi_A = (T - \theta)/C$] in the test temperature range (Figure 5). At low temperature it agrees well with a negative Weiss constant of $\theta = -2.9$ K, indicating the presence of a weak antiferromagnetic interaction. The interaction between metal ions in the complex may be complicated. Similar plot of $1/\chi$ *versus* T is also observed in the polynuclear complex of copper with BPMPPD. Theoretical approach of the interaction is not available at present.

Table 3. Antitumor activities *in vitro* (inhibition %, in DMSO)

Complex	Conc. μmol/L	ESCL	K562	Bel-7402	KB	BGC-823
(1)	1	21.26	49.86	26.04	−8.76	−3.99
	10	28.50	68.71	69.30	3.30	32.56
	100	49.77	91.43	94.82	80.76	77.48
(2)	1	20.91	21.43	19.82	6.39	2.83
	10	28.97	49.29	60.88	18.09	28.96
	100	61.10	80.43	94.82	53.91	79.41

Antitumour activities in vitro

The antitumour activities of the complexes *in vitro* were determined using the MTT methods(27). The samples used were ESCL human carcinoma of the oesophagus, human hasopharyngeal carcinoma KB and K562, human carcinoma ventriculi BGC-823, Human hepatocellular carcinoma Bel-7402. Some results are listed in Table 3. The preliminary bioassay shows that the new complexes have some antitumor activities *in vitro*. Complex *(1)* has remarkable inhibiting activities for K562 and Bel 7402 cells and complex *(2)* for Bel-7402 cells. It is interesting that complex *(1)* stimulates the growth of KB and BGC-823 carcinoma cells in lower concentration (minus inhibition) and inhibits it at higher concentration. Detailed results are not available at this time.

Acknowledgments

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