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Synthesis, crystal structure and properties of the first trinuclear copper(II) cryptate bridged by an imidazole anion

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The trinuclear copper(II) cryptate $[Cu_3L(im)(Br)_2](ClO_4)_3 \cdot H_2O$ was studied, where im denotes the imidazolate anion and L is a reduced form cryptand which was synthesized by [2 + 3] Schiff-base condensation of tris(2-aminopropyl)amine with 2,6-diformylpyridine followed by reduction with $NaBH_4$. An ES-MS spectrum confirms the presence of a Cu_3L core and its dimer in the cryptate. X-Ray analysis shows that the three copper(II) centers are arranged in an isosceles triangles. Cu(1) is located in a N_4Br coordination environment with a square pyramidal configuration. Cu(2) and Cu(3) showed square planar configurations with N_3Br and N_4 coordination environments, respectively. Two nitrogens of an imidazole anion acting as a bridging ligand link Cu(1) and Cu(3). A weak interaction was found between Cu(2) and Br(1). Both intermolecular hydrogen bonds and the weak interaction between two molecules of cryptates *via* ClO_4^- resulted in the formation of a dimer of the cryptate. The magnetic interaction in the dimer was also studied.

Introduction

Polynuclear copper(II) complexes have received considerable current interest because of their remarkable magnetic coupling behavior[1,2] and important biological significance.[3] Polynuclear copper(II) complexes possess potential applications as new materials[4] such as magnets and as models of metal enzymes.[5,6] The trinuclear copper core is frequently encountered in multi-copper oxidases, such as ascorbate oxidase and laccase *etc.*[7–10] The majority of synthesized trinuclear copper(II) complexes are acyclic complexes showing oxygen or hydroxy bridges between two copper atoms.[11,12] Imidazole is an important ligand in biological systems. There are some examples of structurally and magnetically characterized imidazolate-bridged dinuclear compexes,[13,14] but their trinuclear copper systems are rarely reported.[15,16] The synthesis of trinuclear cryptates are even more difficult and challenging. Up to date, to our knowledge, trinuclear copper cryptates have not been synthesized.

In order to develop the chemistry of cryptates, herein we report the first example of a trinuclear copper(II) cryptate, $[Cu_3L(im)(Br)_2](ClO_4)_3 \cdot H_2O$, (im = imidazole anion, L is a reduced form cryptand) which was synthesized by the following steps: (i) [2 + 3] Schiff-base condensation of tris(2-aminopropyl)amine (trpn) with 2,6-diformylpyridine (dfp) in the presence of Ba^{2+} led to the precursor $[BaL^0](ClO_4)_2$ (L^0 = Schiff-base cryptand); (ii) reduced cryptand L was obtained by reduction of the precursor with $NaBH_4$; (iii) L was then reacted with Cu^{2+} ion. The crystal structure of $[Cu_3L(im)(Br)_2](ClO_4)_3 \cdot H_2O$ demonstrates that the three copper(II) ions are arranged in an isosceles triangle. A quantitative magnetic analysis indicates that an anti-ferromagnetic interaction exists among the three copper(II) ions.

Experimental

Materials

Tris(3-aminopropyl)amine (trpn) was prepared by a modified literature method[17] with a purity of >99% as verified by conductimetric titration, 2,6-diformylpyridine (dfp) was synthesized by a previous method.[18] The precursor $[BaL^0](ClO_4)_2 \cdot MeCN$ (L^0 denotes the cryptand obtained by condensation of trpn with dfp) was synthesized by a published method.[19] Its elemental analysis and spectral data were in agreement with the literature values.

Preparation of the compounds

L (reduced cryptand). A suspension of $[BaL^0](ClO_4)_2 \cdot MeCN$ (1 g, 0.95 mmol) in absolute methanol (50 cm^3) was reduced with an excess of sodium borohydride on an ice-bath. The $NaBH_4$ was added to the stirring suspension in batches. When the reaction was complete, the MeOH was removed under reduced pressure, and the residue was dissolved in 25 cm^3 water. The product was extracted with CH_2Cl_2 (200 cm^3) from aqueous solution in four batches. Anhydrous Na_2SO_4 was added to the CH_2Cl_2 solution and the CH_2Cl_2 was removed under reduced pressure. A pale yellow wax was obtained which was purified in a mixed solution of methanol and ethyl acetate. Yield: 0.391 g (60%). (Found: C, 68.48; H, 9.04; N, 22.73. $C_{39}H_{63}N_{11}$ requires: C, 68.28; H, 9.26; N, 22.46%); ν_{max}/cm^{-1} (KBr). 3250s [ν(N–H)]; 2920s, 2780s [ν(Ar–H)]; 1593s [δ(N–H)]; 1445s[ν(C=C)].

$[Cu_3L(im)(Br)_2](ClO_4)_3 \cdot H_2O$. Imidazole (0.015 g, 0.071 mmol) was added to an EtOH–MeCN (1 : 1, 10 cm^3) solution containing L (0.048 g, 0.071 mmol) and $Cu(ClO_4)_2 \cdot 6H_2O$ (0.0527 g, 0.142 mmol) and the pH of the resultant mixed solution was adjusted to 9 with NaOH. After refluxing for 30 min, the solvent was removed by vaporization and the residue was dissolved in EtOH. Upon slow evaporation of the EtOH solution deep blue crystals were obtained. Yield 0.046 g (65%) (Found: C, 36.10; H, 4.02; N, 13.06. $C_{42}H_{68}N_{13}O_{13}Br_2Cl_3Cu_3$ requires: C, 35.53; H, 4.83; N, 12.82%). ν_{max}/cm^{-1} (KBr). 3420s [ν(O–H)]; 3225s [ν(N–H)]; 2920s, 2780s [ν(Ar–H)]; 1593s [δ(N–H)]; 1445s[ν(C=C)]. UV/VIS [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})] (H_2O): 218 (11 300), 645 (370).

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Table 1 Crystallographic data for $[Cu_3L(Br)_2(im)](ClO_4)_3\cdot H_2O$

Empirical formula	$C_{42}H_{68}Br_2Cl_3N_{13}O_{13}Cu_3$
Formula weight	1419.88
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	13.2283(13)
b/Å	20.941(2)
c/Å	20.875(2)
β/°	94.782(2)
U/Å^3, Z	5762.5(10), 4
μ(Mo-Kα)/mm^{-1}	2.692
Reflections collected	13115
Goodness of fit on F^2	0.786
No. independent reflections, R_{int}	4471, 0.0997
Final $R1$, $wR2$ [$I > 2\sigma(I)$]	0.0653, 0.1530
(all data)	0.1948, 0.1914

Single crystal suitable for X-ray structure analysis were obtained by slow evaporation of the mother-liquor over two months.

Physical measurements

The IR spectrum was measured on a Nicolet 5 DX FT-IR spectrophotometer. The electrospray mass spectrum (ES-MS) was determined on a Finnigan LCQ mass spectrograph. The concentration of the sample was about 0.1 mmol dm^{-3}. The diluted solution was electrosprayed at a flow rate of 2×10^{-4} dm^3 min^{-1} with a needle voltage of +4.5 kV. The mobile phase was an aqueous solution and the sample was run in the positive-ion mode. The variable-temperature magnetic susceptibility of a powder sample was measured on a SQUID-based sample magnetic meter and diamagnetic corrections were made according to Pascal constants.[20] The X-band powder ESR spectrum of copper(II) complex was recorded on a Bruker ER 420 spectrometer, operating at 110 K with a frequency modulation 100 kHz.

Crystal structure determination

Single crystals of $[Cu_3L(im)(Br)_2](ClO_4)_3\cdot H_2O$ were obtained by slow diffusion of diethyl ether vapor into an acetonitrile solution of the cryptate for a week. A summary of the parameters is given in Table 1. Diffraction data were collected on a Bruker SMART/CCDC area-detector[21] with monochromatic Mo-Kα (λ = 0.71073) radiation using Φ and ω scans. The collected data was reduced using the Bruker SHELXTL program and empirical absorption correction was made using the SHELXL-97 program.[22] The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically by full-matrix least squares. Hydrogen atoms of the ligands were placed in their calculated position with C–H = 0.93 Å. All the hydrogen atoms were assigned fixed isotropic thermal parameters (1.2× of the atoms to which they were attached) and allowed to ride on their respective parent atoms. The contribution of these hydrogen atoms was included in structure-factor calculations. All computations were carried out using the SHELXTL-PC program package.[23]

CCDC reference number 166453.

See http://www.rsc.org/suppdata/dt/b1/b109117b/ for crystallographic data in CIF or other electronic format.

Results and discussion

Synthesis and characterization

The synthesis method of L is different from usual methods since the direct reduction of the cryptand is very difficult due to its low solubility. This method is suitable for the preparation of the cryptands with low solubility.

Table 2 The assignment of ES-MS peaks of $[Cu_3L(im)(Br)_2](ClO_4)_3\cdot H_2O$ in aqueous solution

m/*z*	Assignment	Intensity (%)
630.1	$[Cu_3L(im)(Br)_2 + Br^- + (Him)]_2^{4+}\cdot H_2O$	14
601.1	$[Cu_3L(im)(Br)_2 + ClO_4^-]^{2+}$	45
591.5	$[Cu_3L(im)(Br)_2 + Br^-]^{2+}$	90
573.9	$[Cu_3L(im)(Br)_2 + H_2O + OH^-]_2^{4+}\cdot H_2O$	100
569.0	$[Cu_3L(im)(Br)_2 + H_2O + OH^-]^{2+}$	82
560.1	$[Cu_3L(im)(Br)_2 + OH^-]^{2+}$	76
516.1	$[Cu_2L(im) + ClO_4^- + 3H_2O]^{2+}$	98
495.3	$[Cu_2L(im)(Br) + ClO_4^-]^{2+}$	50
371.1	$[Cu_3L(im)(Br)_2]_2^{6+}\cdot H_2O$	52
368.1	$[Cu_3L(im)(Br)_2]^{3+}$	40
268.9	$[Cu_3L(Br) + H_2O + ClO_4^-]^{4+}$	28
221.7	$[Cu_2L + 2H_2O]^{4+}$	24
205.8	$\{[Cu_2L]_2H_2O\}^{8+}$	44
173.5	$[Cu_2L + 3H_2O + H^+]^{5+}$	25

In the IR spectrum of L, the obvious N–H stretching vibration peaks and the absence of imino stretching vibration peaks indicate that the Schiff-base ligand L^0 was completely reduced to L. In the UV–vis spectrum, the two bands at 218 and 645nm are assigned to the π–π^* transition of pyridyl and d–d transitions of copper(II) ions, respectively. In the ES-MS spectrum of L, only two peaks at *m*/*z* 705 and 344 are obseved, which are assigned to $[HL(H_2O)]^+$ and $[H_2L]^{2+}$, respectively. The simplicity of the spectrum is attributed to the thermodynamic stability and kinetic inertness of the cryptate as well as the relatively low energy of ES process. The assignments of peaks for the $[Cu_3L(im)(Br)_2]^{3+}$ ion in aqueous solution are listed in Table 2. The most intense peak of the ES-MS spectrum corresponds to the dimer species $[Cu_3L(im)(Br)_2 + H_2O + OH^-]_2^{4+}\cdot H_2O$: *m*/*z* 573.9 (100%). In addition there are prominant peaks corresponding to $[Cu_3L(im)(Br)_2 + Br^-]^{2+}$ 591.5 (90), $[Cu_3L(im)(Br)_2 + OH^- + H_2O]^{2+}$ 569.0 (82) and $[Cu_3L(im)(Br)_2]_2^{6+}\cdot H_2O$ 371.1 (50) as well as well as a weaker peak from $[Cu_3L(im)(Br)_2]^{3+}$ 368.1 (40%). All the peaks confirm the presence of the Cu_3L core in the cryptate and shows that the trinuclear species is stable in solution. The other peaks can be assigned to loss of one of the three copper ions or bromine anion and/or imdazole anion. The relatively high abundances of the dimer species indicate that these are stable under the ES-MS conditions; possibly the dimers of cryptate fragments are formed in the aqueous solution by bridging with water molecules *via* hydrogen bonds. A revised program[24] was used to calculate the isotopic distribution of peak clusters at *m*/*z* = 569.0 and 573.9 and the calculated and observed results are shown in Fig. 1.

Crystal structure of the trinuclear cryptate

Details of crystal data, intensity collection and refinement are listed in Table 1, while selected distances and angles are given in Table 3. The crystal structure of the cryptate cation $[Cu_3(im)(Br)_2L]^{3+}$ is shown in Fig. 2. The cryptand encapsulates three copper(II) ions which are arranged at the corners of an approximately isosceles triangle. Atom Cu(1) is coordinated in a square-pyramidal geometry with two imino nitrogen atoms N(2), N(4), one nitrogen of pyridyl N(3), one nitrogen of imidazole anion N(12) as a bridging ligand as well as one bromine anion Br(1). Besides N(13) of imidazolate, Cu(3) is also coordinated to two imino nitrogen atoms (N(9), N(11)) and one pyridyl-nitrogen N(10), leading to a square planar configuration. Cu(2) shows a similar arrangement to Cu(3) except that the imidazolate bridge is replaced by a monodentate bromine anion Br(2). The trinuclear site shows some analogy with the active site of ascorbic oxidase and other multi-copper oxidases which consist of a mononuclear type 2 and dinuclear type 3 cupric unit. In the cryptate, the average lengths of Cu–

Table 3 Selected bond distances (Å) and angles (°) for $[Cu_3L(Br)_2(im)](ClO_4)_3 \cdot H_2O$

Cu(1)–Br(1)	2.8233(5)	Cu(2)–N(8)	2.056(3)
Cu(2)–Br(2)	2.3937(5)	Cu(2)–N(7)	1.914(2)
Cu(1)–N(3)	1.921(3)	Cu(3)–N(13)	1.924(2)
Cu(1)–N(12)	1.935(3)	Cu(3)–N(9)	2.057(3)
Cu(1)–N(4)	2.076(3)	Cu(3)–N(11)	2.087(3)
Cu(1)–N(2)	2.085(3)	Cu(3)–N(10)	1.923(3)
Cu(2)–N(6)	2.053(3)	Cu(2) ··· Br(1)	2.948(5)
Cu(3)–O(7a)	2.642	Cu(3) ··· Br(2)	3.221(5)
O(1w)–N(2)	3.017	O(1w) ··· O(9a)	2.933
N(3)–Cu(1)–N(12)	171.19(10)	N(3)–Cu(1)–N(2)	82.33(11)
N(3)–Cu(1)–N(4)	82.51(11)	N(12)–Cu(1)–N(2)	96.84(11)
N(12)–Cu(1)–N(4)	96.17(11)	N(4)–Cu(1)–N(2)	160.10(11)
N(3)–Cu(1)–Br(1)	88.99(7)	N(12)–Cu(1)–Br(1)	99.82(7)
N(4)–Cu(1)–Br(1)	98.76(8)	N(2)–Cu(1)–Br(1)	93.78(7)
N(7)–Cu(2)–N(6)	81.19(11)	N(7)–Cu(2)–N(8)	82.66(10)
N(7)–Cu(2)–Br(2)	168.18(8)	N(6)–Cu(2)–N(8)	161.10(10)
N(6)–Cu(2)–Br(2)	99.64(8)	N(8)–Cu(2)–Br(2)	94.20(7)
N(10)–Cu(3)–N(13)	179.41(11)	N(10)–Cu(3)–N(9)	83.16(11)
N(10)–Cu(3)–N(11)	81.82(11)	N(13)–Cu(3)–N(9)	96.67(11)
N(13)–Cu(3)–N(11)	98.41(11)	N(9)–Cu(3)–N(11)	163.43(11)

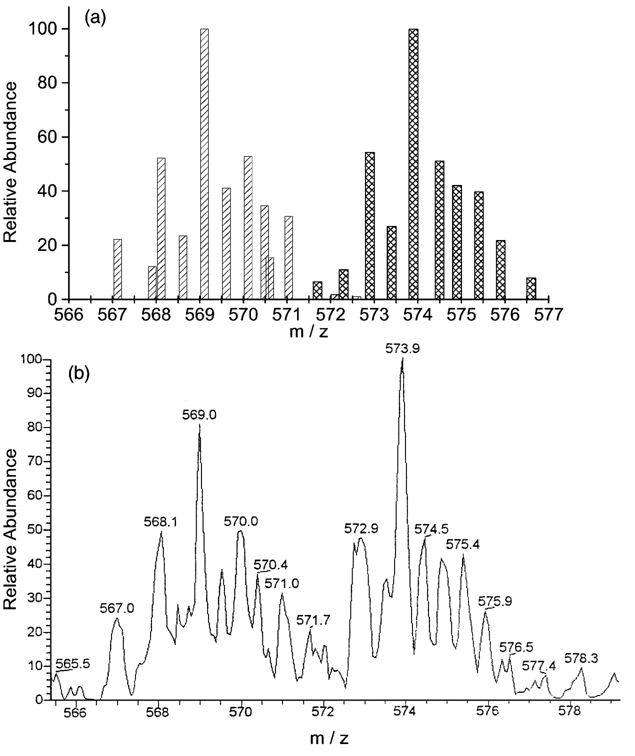

Fig. 1 The isotopic distribution of peak clusters at *m*/*z* 569.0 and 573.9: (a) calculated, (b) experimental.

N(imino), Cu–N(py) and Cu–N(imidazolate) are 2.069, 1.930 and 1.920 Å, respectively, which can be considered as normal covalent bonds. The Cu(1)–Br(1) bond distance is 2.823 Å implying only a weak interaction. The Cu(2)–Br(2) bond length of 2.394 Å is within the range of values (2.37–2.43 Å) reported by previous authors. The Cu(2) ··· Br(1) and Cu(3) ··· Br(2) separations are 2.948 and 3.221 Å, respectively, being slightly longer than that of Cu(1)–Br(1) (2.823 Å). The Cu(1)–Br(1)–Cu(2) angle is 138.8°.

Although in the cryptate the copper–copper separations of 5.388 (Cu(1) ··· Cu(2)), 5.365 (Cu(1) ··· Cu(3)) and 5.778 Å (Cu(2) ··· Cu(3)) are larger than those of 3.4, 3.9 and 4.0 Å observed in a trinuclear cupric unit of ascorbic oxidase, the information from this new trinuclear cryptate is useful to understand various properties of multicopper oxidases. The separation Cu(3) ··· O(7a), namely the distance between one copper in a trinuclear copper(II) molecule and one oxygen atom of perchlorate anion in another molecule, is 2.642 Å, indicating an interaction between two cryptate molecules *via* ClO_4^-. Two hydrogen atoms of a water molecule link an imine nitrogen N(2) and one oxygen atom (O(9a)) of a perchlorate anion, respectively, forming two intermolecular hydrogen bonds; the separations O(1w) ··· N(2) and O(1w) ··· O(9a) are 3.017 and 2.933 Å, respectively. The intermolecular hydrogen bonds and the weak interaction between two molecules of cryptate *via* ClO_4^- results in the formation of a dimer of the cryptate as revealed in the ES-MS spectrum.

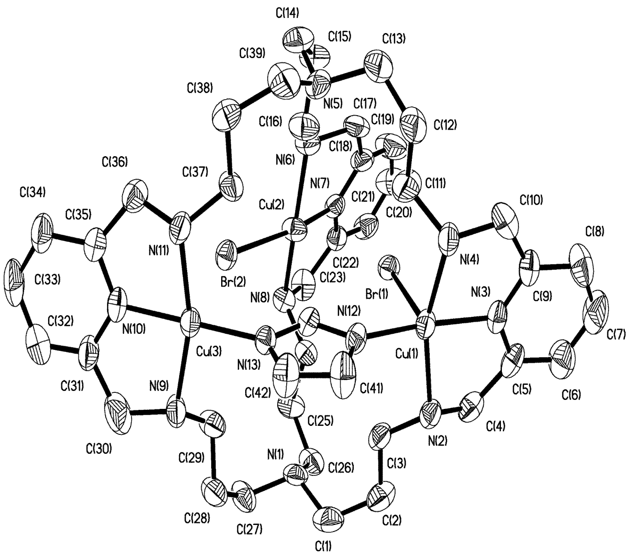

Fig. 2 Crystal structure of $[Cu_3L(im)(Br)_2]^{3+}$; hydrogen atoms and counter ions have been omitted for clarity.

Magnetic properties

The temperature (T) dependence of $\chi_m T$ (product of molar susceptibility and temperature) in the range of 2–300 K is shown in Fig. 3. As the temperature is lowered, the experimental magnetic moment decreased from 3.15 μ_B at 300.04 K to 1.69 μ_B at 2.04 K. The μ_{eff} value (1.69 μ_B) of the trinuclear copper(II) species at 2.04 K indicates that an antiferromagnetic interaction exists among the copper(II) ions, with the overall spin of the trinuclear unit close to 1/2. The experimental data in Fig. 3 also shows that $\chi_m T$ is still decreasing even at 2.04 K and it is possible that a weak interaction exists between Cu(1) and Cu(2) through Br(1). Based on a linear trinuclear model, the susceptibility data could be fitted well by eqn. (1)[4]

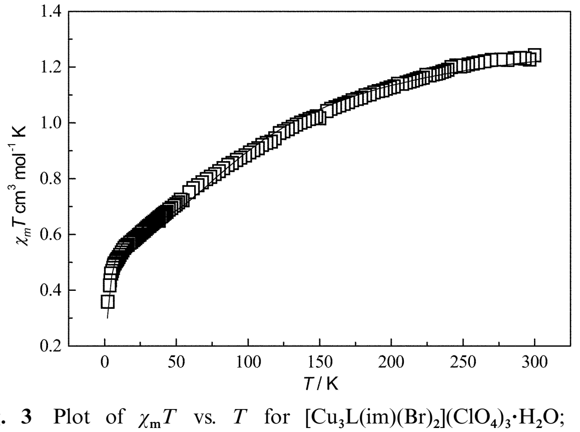

Fig. 3 Plot of $\chi_m T$ vs. T for $[Cu_3L(im)(Br)_2](ClO_4)_3 \cdot H_2O$; (□) experimental data, (—) the fitting curve.

$$
\begin{gathered}
\chi_\mathrm{m} = \frac{Ng^2\beta^2}{4kT}\frac{X}{Y} + N_\alpha \\
X = 10 + \exp[(-J_{13} - J_{12} + (J_{13}^{\ 2} - J_{12}J_{13} + J_{12}^{\ 2})^{1/2})/kT] + \\
\exp[(-J_{13} - J_{12} - (J_{13}^{\ 2} - J_{12}J_{13} + J_{12}^{\ 2})^{1/2}/kT)] \\
Y = 2 + \exp[(-J_{13} - J_{12} + (J_{13}^{\ 2} - J_{12}J_{13} + J_{12}^{\ 2})^{1/2})/kT] + \\
\exp[(-J_{13} - J_{12} - (J_{13}^{\ 2} - J_{12}J_{13} + J_{12}^{\ 2})^{1/2}/kT)]
\end{gathered} \quad (1)
$$

with the usual meanings for the symbols. N_α was set at 180×10^{-6} cm^3 mol^{-1} for the trinuclear moiety. Upon fitting the $\chi_\mathrm{m}T$–T data, the parameters $g = 2.16$, $J_{13} = -22.5$ cm^{-1} and $J_{12} = -3.12$ cm^{-1} with an agreement factor $R = 4.8 \times 10^{-4}$ were obtained. The values of J_{12} and J_{13} imply that the antiferromagnetic coupling between Cu(1) and Cu(2) is weaker than that between Cu(1) and Cu(3) by bridging of imidazolate.

The X-band powder ESR spectrum of the copper(II) complex at 110 K gave $g_\perp = 2.017$, $g_\parallel = 2.320$ and $g = 2.13$ ($g = [(2 + g_\perp^{\ 2} + g_\parallel^{\ 2})/3]^{1/2}$. This g value is in good agreement with that obtained above by the magnetic property investigations.

Acknowledgements

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