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Synthesis, crystal structure and magnetic properties of the binuclear copper(II) complex of a new bis(1,4,7,10-tetraazacyclododecane) ligand

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A new binucleating macrocyclic ligand 2,6-bis(1,4,7,10-tetraazacyclododecan-10-ylmethyl)methoxy-benzene (L) and its binuclear copper(II) complex, $[Cu_2LBr_2](ClO_4)_2 \cdot 3H_2O$ (1), was prepared and the structure was determined by X-ray crystallography. Complex 1 crystallizes in monoclinic crystal system, $P2_1/n$ space group with $a = 0.8206(3)$, $b = 2.0892(8)$, $c = 2.3053(7)$ nm, $\beta = 95.83(2)°$, $V = 3.932$ nm^3, $Mr = 1017.57$, $Z = 4$, $D_c = 1.692$ g/cm^3, and $R = 0.0489$, $R_w = 0.0552$ for 6571 observed reflections with $I \geq 2\sigma(I)$. Both of the copper(II) centers are coordinated by four amine nitrogen donors of cyclen subunits and a bromide anion, and each copper(II) ion is in a square-pyramidal coordination environment. Variable temperature magnetic susceptibility studies indicate that there exists weak intramolecular antiferro-magnetic coupling ($-2J = 2.06$ cm^{-1}) between the two copper(II) centers.

Keyword Binuclear copper(II) complex, crystal structure, antiferro-magnetic coupling, binucleating macrocyclic ligand

The synthesis and complexation properties of ligands comprising linked macrocycles have attracted considerable attention in recent years.[1-5] Such ligands can form binuclear complexes and can be used in modeling studies for important biological molecules such as metalloproteins.[6] Simplified model complexes of this type may help to elucidate the factors that determine the electronic and magnetic properties in the polynuclear bio-site.

The ligands that comprise two macrocycles, such as 1,4,7-triazacyclonane, 1,5,9-triazacyclododecane, and 1,4,7,10-tetraazacyclododecane (cyclen) moieties have enabled the formation of a variety of binuclear complexes containing metal ions such as Mn(II/III), Fe(II/III), Co(II/III), Cu(II), and Zn(II).[4] These ligands tethered by various bridging groups, such as polymethylene, methylphenol and pyrazole,[1,4] provide an excellent motif to study the variations of chemical properties of binuclear complexes as changes are introduced into the ligand frameworks. The change of the bridging groups linking the binuclear metal centers might adjust the distance between metal centers in binuclear complexes and the relative properties.[2]

Macrocycles linked via polymethylene bridges and their complexes have been reported,[1,2,4] but the ligands that contain two macrocycles bridged by phenyl groups are relative rare.[7] We report herein the synthesis, crystal structure and magnetic properties of the binuclear copper (II) complex of a new bis(macrocyclic) ligand comprising two 1,4,7,10-tetraazacyclododecane (cyclen) subunits bridged by 2,6-bimethylmethoxybenzene (Chart 1).

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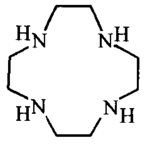
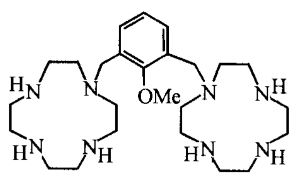
Chart 1



Cyclen



L

Experimental

Materials

Most of the reagents and solvents used were purchased at the highest commercial quality or of analytical grade, and purified prior to use when necessary. Cyclen was prepared according to the procedures reported by Richman and Atkins.[8]

Physical measurements

IR spectra were recorded on a Shimadzu FT-IR 170SX (Nicolet) spectrometer at room temperature. ^1H NMR (200 MHz) spectra were recorded on a Bruker AC-P 200 spectrometer at 25℃, with tetramethylsilane as the internal reference. Elemental analysis was performed on a P-E 200C analyzer. Electronic spectra of the complex in anhydrous methanol were recorded on a Shimadzu UV-240 spectrophotometer. Variable temperature magnetic susceptibilities were measured on a vibrating sample model CF-1 magnatometer. Diamagnetic corrections were made with Pascal's constants for all the constituent atoms, and the magnetic moments were calculated by the equation $\mu_{eff} = 2.828(\chi_M T)^{1/2}$.

Synthesis of ligand

2,6-Bis[1,4,7-tri(*N*-*tert*-Boc)-1,4,7,10-tetrazacyclododecan-10-ylmethyl] methoxybenzene (L-6Boc) (Boc = butoxycarbonyl) was prepared by the reaction of 3Boc-cyclen and 2,6-bis(bromomethyl)-1-methoxybenzene in the presence of excessive amount of anhydrous K_2CO_3 under reflux with the protection of Ar. The resulting crude product was purified by silica gel chromatography (CH_2Cl_2-MeOH) to afford L-6Boc as colorless amorphous solid (85% yield based on used 2,6-bromomethylmethoxybenzene). $\delta_H(D_2O)$: 1.44 and 1.46(2s, 54H, 6Boc), 2.60(t, J = 1.3 Hz, 8H, NCH_2C), 3.31—3.56(m, 24H, CH_2NBoc), 3.68(s, 3H, $PhOCH_3$), 3.80(s, 4H, NCH_2Ph), 6.99—7.43 (m, 3H, Ph).

$L\cdot 7HBr\cdot 2H_2O$ (L = 2,6-bis(1,4,7,10-tetraazacyclododecan-10-ylmethyl) methoxybenzene) was synthesized by the reaction of L-6Boc and 47% aqueous HBr in ethanol. The resulting crude powder was crystallized from EtOH-HBr aqueous solution to obtain $L\cdot 7HBr\cdot 2H_2O$ (yield: 80%). $\delta_H(D_2O)$: 2.83—3.21 (m, 32H, NCH_2); 3.74(s, 3H, $PhOCH_3$), 3.88(s, 4H, NCH_2Ph), 7.37—7.66(m, 3H, Ph). ν_{max}(KBr pellets): 3420, 2960, 2742, 1605, 1442, 1271, 1210, 1166, 1071, 1000, 969, 775, 672, 560 cm^{-1}. Anal. $C_{25}H_{59}N_8Br_7O_3$. Calcd: C, 27.8; H, 5.51; N, 10.4. Found: C, 28.1; H, 5.33; N, 9.92.

Preparation of complex

$[Cu_2LBr_2]\cdot(ClO_4)_2\cdot 3H_2O$ (**1**): $L\cdot 7HBr\cdot 2H_2O$ (104 mg, 0.1 mmol) was dissolved in redistilled H_2O (10 mL) and then neutralized by NaOH aqueous solution to pH ~ 7. To this solution, $Cu(ClO_4)_2\cdot 6H_2O$ (82 mg, 0.22 mmol) in H_2O (5 mL) was added slowly under stirring, then the solution was heated to ca. 60℃ and stirred continuously. After filtration, the filtrate was allowed to stand at room temperature. With the slow evaporation of the solvent, deep blue crystals deposited from the solution, and the single crystal suitable for X-ray analysis was obtained by recrystallization from MeOH/CH_3CN (1 : 1) mixed solvents. Anal. $C_{25}H_{54}Br_2N_8Cl_2Cu_2O_{12}$. Calcd: C, 29.5; H, 5.35; N, 11.0. Found: C, 29.8; H, 4.98; N, 10.9.

Crystallographic studies

A blue crystal (approximately 0.26 × 0.24 × 0.16 mm) of complex **1** was mounted on a glass fiber on a Siemens P4 diffractometer equipped with a graphite crystal monochromator situated in the incident beam for data collection. The determination of unit cell and data collection were performed with Mo K_α radiation (λ = 0.071073 nm). Unit cell dimensions were obtained by least-squares refinements using 20 reflections in the range of 4.84—8.29°. The intensities of reflections were measured at the $\omega / 2\theta$ scan mode in the range of $1.78° \leqslant \theta \leqslant 27°$ at room temperature, a semi-empirical absorption correction was applied (Transmax 0.391, Transmin 0.104). A total of 8585 reflections were collected, and, after systematic absence had been deleted, merging of equivalent reflections gave 6573 unique intensities of which 6571 with $I > 2\sigma(I)$ were considered to be observed and retained for refinement. The structure was solved by direct methods. Cu atoms were located from an E-map. The other non-hydrogen atoms were determined with successive difference Fourier syntheses. The final refinement was done by full matrix least-squares methods with anisotropic thermal parameters for all the non-hydrogen atoms on F^2. The hydrogen atoms were added theoretically, riding on the atoms concerned and refined with fixed thermal factors. Convergence resulted in final unweighted and weighted agreement factors of 0.0489 (R) and 0.0552 (R_w). Crystal parameters and refinement results are summarized in Tables 1.

Table 1 Crystal data for complex **1**

Chem. formula	$C_{25}H_{54}Br_2N_8Cl_2Cu_2O_{12}$
F_w	1017.57
Crystal system	monoclinic
Space group	$P2_1/n$
a (nm)	0.8206(3)
b (nm)	2.0892(8)
c (nm)	2.3053(7)
β (°)	95.83(2)
V (nm^3)	3.932
Z	4
D_c (g/cm^3)	1.692
λ (nm)	0.071073
μ (mm^{-1})	3.311
Max-min transmission (%)	0.391 and 0.104
T (K)	293(2)
Max. 2θ	54
No. of unique data	6573
No of observed data [$I \geqslant 2\sigma(I)$]	6571
Parameters refined	451
R	0.0489
R_w	0.0552
GOF(S)	1.015
Max residual peak and hole (e/nm^3)	592 and −530

Results and discussion

Preparation of copper(II) complex

The preparation of $[Cu_2(L)Br_2](ClO_4)_2 \cdot 3H_2O$ (**1**) was achieved by reacting $L \cdot 7HBr \cdot 2H_2O$ with $Cu(ClO_4)_2 \cdot 6H_2O$ in aqueous solution at pH ~ 7. The result of elemental analysis for complex **1** is well consistent with its composition. The IR spectrum of **1** shows absorption bands from the benzene ring skeletal vibrations in 1400—1500 cm^{-1} range, the vibrational absorption band for methoxy group at 1620 cm^{-1} and for perchlorate at 1090 and 624 cm^{-1}. The complex gave a d-d absorption peak at 592 nm in methanol, which is typical for the five-coordinated copper(II) complexes with square-pyramidal or distorted square-pyramidal geometry for (d_{xy}, $d_{yz} \rightarrow d_{x^2-y^2}$) transition.[1]

Description of the crystal structure

The molecular structure of the title compound consists of discrete $[Cu_2LBr_2]^{2+}$ cations and ClO_4^- counter anions and three uncoordinated H_2O molecules. The ORTEP structure with the atom-numbering scheme of the cation is presented in Fig. 1. We can see that in the binuclear complex cation, the 2,6-dimethyl-methoxybenzene group bridges the two cyclen subunits equally, and the two copper(II) centers sit equivalently above relevant basal planes of the donor nitrogens of each cyclen subunit. The coordination sphere surrounding each central copper(II) atom is essentially square-pyramidal geometry, and close to C_{4v} symmetry (the geometric parameter $\tau = 0.04$ and 0.053).[9] The axial position is occupied by one bromide ion, and the four donor nitrogens of cyclen form the basal plane. The Cu(1) and Cu(2) atoms are 0.05715 nm and 0.05430 nm above the relative least-square planes. This is because the cavity of the cyclen macrocycle is a little tight for copper(II) ion and copper(II) can not completely fill into the cavity. The dihedral angle between the least-square planes formed by N(1)-N(2)-N(3)-N(4) and N(5)-N(6)-N(7)-N(8) is 155°, and this implies that the two planes are nearly in parallel position. The dihedral angles between the phenyl ring plane and the two N_4 planes are 29.2° and 163.9°, respectively. We have expected the methoxy group will take part in the coordination to at least one copper(II) center, but in fact, it has not taken part in the coordination to both copper(II) centers. This might be due to the low coordination ability of methoxy group and steric hindrance between the two macrocycles. But the existence of this group should have affected the relative position of the two macrocycles and will further block the formation of other bridge between the two metal centers so that the two metal centers could keep independent from each other. This may offer a good model system for the study of two nearly independent metal centers in one complex. We can further expect that if the methyl group could be removed from the methoxy group, the coordination mode of the binucleating ligand will become quite different. Further studies are under way in our laboratory.

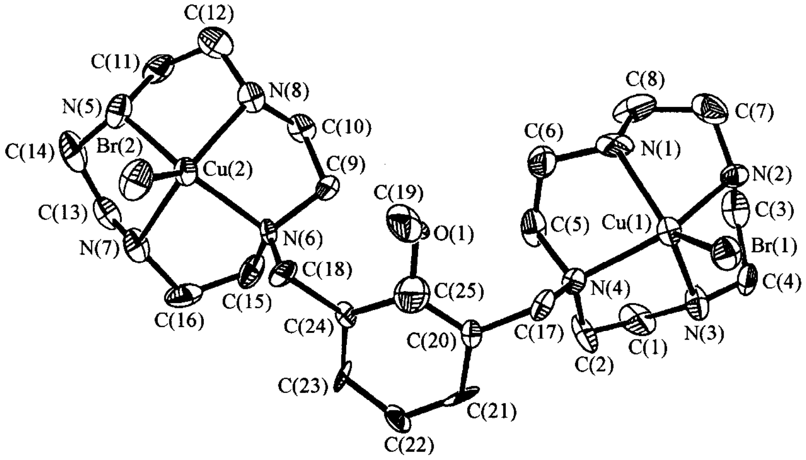


Fig. 1 ORTEP structure of $Cu_2LbR_2^{2+}$ showing the atom-numbering scheme with 30% probability.

Table 2 Atomic coordinates (× 10^4) of non-hydrogen atoms of complex **1**

Atom	*x*	*y*	*z*	*U* (eq)	Atom	*x*	*y*	*z*	*U* (eq)
Cu(1)	-10559(3)	6380(1)	-229(1)	36(1)	Cu(2)	-13487(3)	10231(1)	-2363(1)	34(1)
Br(1)	-8514(2)	5775(1)	-763(1)	44(1)	Br(2)	-11762(3)	10120(1)	-3218(1)	58(1)
N(1)	-12507(18)	6553(7)	-812(5)	50(4)	N(2)	-12048(5)	5728(6)	102(5)	35(4)
N(3)	-9563(6)	6496(6)	590(5)	48(4)	N(4)	-9916(6)	7352(6)	-338(5)	28(4)
N(5)	-15421(6)	10743(7)	-2728(6)	44(4)	N(6)	-12228(6)	9819(6)	-1653(5)	33(4)
N(7)	-12615(8)	11073(6)	-2022(6)	46(4)	N(8)	-15078(5)	9512(6)	-2324(6)	34(4)
O	-10560(12)	8245(5)	-1703(5)	33(3)	C(1)	-9868(5)	7162(9)	731(7)	64(6)
C(2)	-9245(3)	7562(8)	264(7)	57(6)	C(3)	-12136(5)	5932(8)	719(6)	51(6)
C(4)	-10359(5)	6045(8)	973(7)	56(6)	C(5)	-11612(5)	7603(8)	-503(8)	51(6)
C(6)	-12497(4)	7227(9)	-989(8)	58(6)	C(7)	-13631(4)	5724(9)	-247(7)	68(7)
C(8)	-13998(6)	6380(5)	-511(8)	71(7)	C(9)	-13253(7)	9262(8)	-1475(7)	44(5)
C(10)	-14979(9)	9376(8)	-1692(7)	41(5)	C(11)	-16868(10)	10446(9)	-2511(7)	52(6)
C(12)	-16693(12)	9720(9)	-2583(8)	55(6)	C(13)	-14112(12)	11470(8)	-1982(8)	53(6)
C(14)	-15151(13)	11415(8)	-2571(8)	60(6)	C(15)	-12168(13)	10337(8)	-1194(7)	53(6)
C(16)	-11671(12)	10947(9)	-1458(7)	58(6)	C(17)	-8804(12)	7528(7)	-782(6)	38(5)
C(18)	-10551(9)	9601(8)	-1783(7)	38(5)	C(19)	-9789(12)	8095(8)	-2223(7)	58(6)
C(20)	-8562(12)	8237(7)	-849(7)	27(4)	C(21)	-7559(10)	8610(10)	-448(7)	50(6)
C(22)	-7468(12)	9267(8)	-492(7)	46(5)	C(23)	-8523(10)	9577(8)	-905(7)	36(5)
C(24)	-9558(10)	9252(8)	-1323(6)	26(4)	C(25)	-9529(12)	8576(1)	-1284(7)	85(4)
Cl(1)	-3339(7)	8762(2)	565(2)	49(1)	Cl(2)	-125(9)	7472(4)	2548(3)	76(2)
O(1)	-4224(13)	8178(6)	485(6)	88(5)	O(2)	-4310(12)	9238(7)	766(7)	120(6)
O(3)	-2883(12)	8981(8)	55(8)	89(11)	O(4)	-2166(14)	8662(8)	994(10)	97(11)
O(5)	-1036(13)	7824(11)	2150(8)	81(10)	O(6)	-645(12)	7392(13)	3051(7)	118(13)
O(7)	1291(12)	7725(13)	2598(10)	134(14)	O(8)	-63(14)	6910(10)	2300(11)	135(24)
OW1	6080(16)	7243(6)	1383(5)	85(5)	OW2	-3819(17)	13722(7)	-1066(6)	114(6)

Table 3 Selected bond distances (10^{-1} nm) and angles (°) for complex **1**

Bond distance (10^{-1} nm)			
Cu(1)—N(3)	1.996(12)	Cu(2)—N(8)	1.998(12)
Cu(1)—N(1)	2.014(13)	Cu(2)—N(5)	2.024(13)
Cu(1)—N(2)	2.030(12)	Cu(2)—N(7)	2.027(12)
Cu(1)—N(4)	2.120(12)	Cu(2)—N(6)	2.037(12)
Cu(1)—Br(1)	2.520(3)	Cu(2)—Br(2) 2.551(3)	
Bond angle (°)			
N(3)-Cu(1)-N(1)	146.2(6)	N(8)-Cu(2)-N(5)	85.9(6)
N(3)-Cu(1)-N(2)	86.0(5)	N(8)-Cu(2)-N(7)	147.2(5)
N(1)-Cu(1)-N(2)	84.5(6)	N(5)-Cu(2)-N(7)	86.29(6)
N(3)-Cu(1)-N(4)	85.0(5)	N(8)-Cu(2)-N(6)	85.8(5)
N(1)-Cu(1)-N(4)	86.5(5)	N(5)-Cu(2)-N(6)	150.4(5)
N(2)-Cu(1)-N(4)	148.6(5)	N(7)-Cu(2)-N(6)	85.7(5)
N(3)-Cu(1)-Br(1)	107.1(4)	N(8)-Cu(2)-Br(2)	112.5(4)
N(1)-Cu(1)-Br(1)	106.6(4)	N(5)-Cu(2)-Br(2)	101.6(4)
N(2)-Cu(1)-Br(1)	107.7(4)	N(7)-Cu(2)-Br(2)	100.2(4)
N(4)-Cu(1)-Br(1)	103.7(3)	N(6)-Cu(2)-Br(2)	107.8(4)

In complex **1**, the Cu—N distances are in the range of 0.1996(1)—0.2120(1) nm, being normal Cu—N_{amine} coordination bond.[10] The two Cu—Br bond distances are 0.2523 and 0.2551 nm, respectively, and can be considered as common axial Cu—Br length.[9] The intramolecular Cu—Cu distance is 0.9609 nm, being longer than that of the dicopper(II) complexes of the bimacrocyclic ligand linked by a bridging carboxyl group,[10] and corresponding to that of the bimacrocyclic dicopper complex linked by a polymethylene group.[2] This makes the two copper(II) centers remain nearly independent to each other so that only very weak spin coupling between them has been observed (this will be discussed later in this paper). This also suggests that changing the bridging groups linking the two macrocycle subunits can adjust the distance between the two metal centers in the relative binuclear complexes, and so that to adjust the relative properties and functions of the relative complexes. This is very important for the design of functional complexes.

Fig. 2 shows a perspective view of the molecular stacking of complex **1** in the unit cell. It shows an interesting stacking pattern. The OW1···O1 (0.2837 nm) and OW2···N3 (0.2915 nm) distances suggest that there exists hydrogen bonding between H_2O and perchlorate, and the amine groups. Therefore, H_2O molecules link uncoordinated perchlorate ions and the amine group in the macrocycle of the ligand through hydrogen bonding and this will stabilize the crystal structure.

Magnetic properties

The temperature dependence of susceptibility value and magnetic moment for complex **1** is shown in Fig. 3. The dominant features of the data are that magnetic susceptibility values increase upon cooling. The solid curve in Fig. 3 is the best fit of the experimental data according to the modified Bleaney-Bowers equation[12] for the spin-exchange coupled copper(II) dimers:

$$\chi_M = 4g^2\beta^2[3 + \exp(-2J / KT)]^{-1}/(KT) + N_\alpha \qquad (1)$$

Eq. (1) results from a consideration of the eigenvalues of $H = -2JS_1S_2$, of the Heisenberg exchange Hamiltonion for the two interacting $S = 1/2$ centers. The χ_M value represents the susceptibility per binuclear unit, and $2J$ is the exchange coupling constant. N_α is the temperature independent paramagnetism, 120×10^{-6} egs/mol. Other symbols have their usual meanings. A least-squares fit to the experimental data has been carried out, and the best fit line is shown in Fig. 3, where $g = 2.10$, $2J = -2.06$ cm^{-1}, and the agreement factor F is defined as $\sum[(\chi_M)_{obs} - (\chi_M)_{calcd}]^2/\sum(\chi_M)_{obs} = 1.22 \times 10^{-3}$. The results indicate that there exists a very weak intramolecular antiferromagnetic interaction within each molecule. This may be due to the fact that the intramolecular Cu(1)—Cu(2) distance of 0.9609 nm in complex **1** is rather large, and the two copper(II) centers are not linked directly by other bridges.

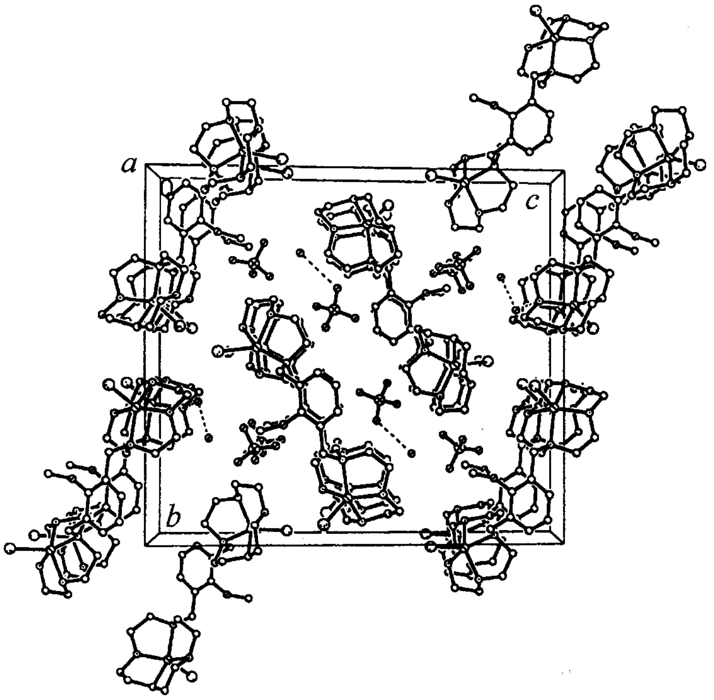


Fig. 2 Perspective view of the molecular stacking in the unit cell of **1**.

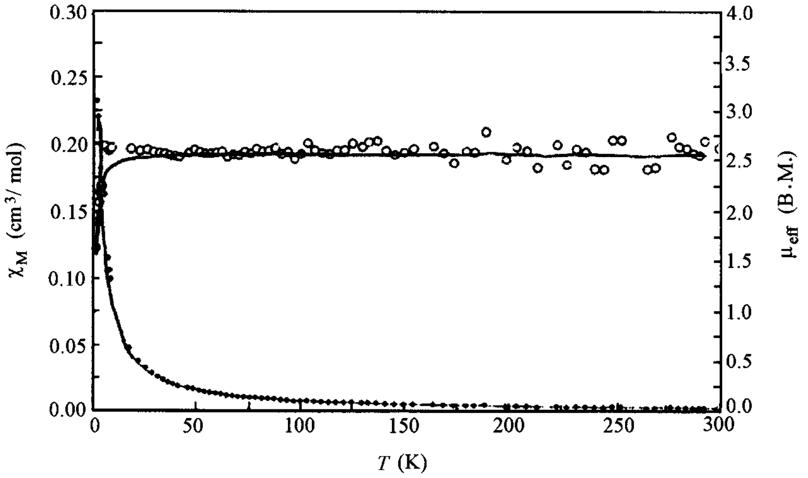


Fig. 3 Temperature dependence of χ_M and μ_{eff} of the solid sample of **1**.

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