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Synthesis and crystal structure of a new oxamidato-bridged trinuclear Cu_2^{II} Mn^{II} complex containing a macrocyclic ligand

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SYNTHESIS AND CRYSTAL STRUCTURE OF A NEW OXAMIDATO-BRIDGED TRINUCLEAR $\text{Cu}^{\text{II}}_2 \text{Mn}^{\text{II}}$ COMPLEX CONTAINING A MACROCYCLIC LIGAND

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A new oxamidato-bridged trinuclear complex $[(\text{CuL})_2\text{Mn}](\text{ClO}_4)_2$ ($\text{H}_2\text{L} = 2,3\text{-dioxo-}5,6,14,15\text{-dibenzo-}1,4,8,12\text{-tetraazacyclo-pentadeca-}7,3\text{-dien}$) was prepared and its structure determined. The complex is monoclinic, space group $\text{P}2_1/n$, with $a = 10.625(3)$, $b = 11.602(3)$, $c = 16.020(5)$ Å, $\beta = 91.031(5)^\circ$, $Z = 2$; it was refined to $R1 = 0.0555$. In the solid state, the structure consists of centrosymmetric $[(\text{CuL})_2\text{Mn}]^{2+}$ cations separated by perchlorate anions; the central manganese atom is four coordinated with square planar geometry.

Keywords: Macrocyclic ligands; Trinuclear complexes; Crystal structure

INTRODUCTION

Polymetallic complexes with extended bridged structures are of current interest due to their novel magnetic properties [1]. Recently, studies in this area have been extended by using macrocyclic analogues of oxamides [2–5]. Non-cyclic oxamides may adopt a *cis* or *trans* conformation on coordination, and this flexibility restricts control over type of complex formed [6]. Macrocyclic oxamides allow the synthesis of polynuclear systems in a more controlled fashion. With these considerations in mind and in continuation of our work on polynuclear complexes [2–4,7–9], we have turned to polymetallic systems assembled by using a macrocyclic copper(II) oxamide as a complex ligand. We describe here the synthesis and characterization of a new complex $[(\text{CuL})_2\text{Mn}](\text{ClO}_4)_2$ ($\text{H}_2\text{L} = 2,3\text{-dioxo-}5,6,14,15\text{-dibenzo-}1,4,8,12\text{-tetraazacyclo-pentadeca-}7,3\text{-dien}$).

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EXPERIMENTAL

Starting Materials

All starting reagents were of A.R. grade and used as purchased. The complex CuL ($H_2L = 2,3\text{-dioxo-}5,6,14,15\text{-dibenzo-}1,4,8,12\text{-tetraazacyclopentadeca-}7,3\text{-dien}$) was prepared as described elsewhere [10].

$[(CuL)_2Mn](ClO_4)_2$

Single crystals of the title complex were grown from a methanol solution by a slow diffusion method using an H-shape tube. CuL (0.3 mmol) was added to one arm and $Mn(ClO_4)_2 \cdot 6H_2O$ (0.15 mmol) to the other; the tube was filled with methanol. Deep green crystals, suitable for X-ray determination, formed after two weeks. *Anal.* found (%): C, 43.41; H, 3.18; N, 10.80. Calc. for $C_{38}H_{32}N_8O_{12}Cl_2Cu_2Mn$: C, 43.64; H, 3.06; N, 10.71.

Physical Measurements

Elemental analyses were performed on a Perkin-Elmer 240 instrument. Infrared spectra were recorded on a Shimadzu IR-408 spectrophotometer in the range $4000\text{--}600\text{ cm}^{-1}$ using KBr pellets.

X-ray Crystallography

A crystal of the complex was mounted on a BRUKER SMART 1000 CCD diffractometer equipped with graphite-monochromatized $MoK\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$). Cell parameters were determined by a least-squares procedure. A total of 7995 independent reflections was collected, of which 3459 were considered as observed [$I > 2\sigma(I)$] and used for the structure determination. A SADABS absorption correction was applied. The structure was solved by direct methods (SHELXL-97 and SHELXS-97) [11] and refined by full-matrix least-squares methods on F^2 . Crystallographic data are listed in Table I. Final atomic coordinates for non-hydrogen atoms and equivalent thermal parameters are listed in Table II.

TABLE I Crystallographic data for the complex

Formula	$C_{38}H_{32}N_8O_{12}Cl_2Cu_2Mn$
fw	1045.64
Crystal dimensions (mm)	$0.30 \times 0.25 \times 0.15$ mm
Temperature (K)	293(2)
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	10.652(3)
b (Å)	11.602(3)
c (Å)	16.020(5)
β (°)	91.031(5)
Z	2
D_c ($g\text{ cm}^{-3}$)	1.754
λ (MoK α) (Å)	0.71073
$F(000)$	1058
R_1	0.0555
wR_2	0.1402

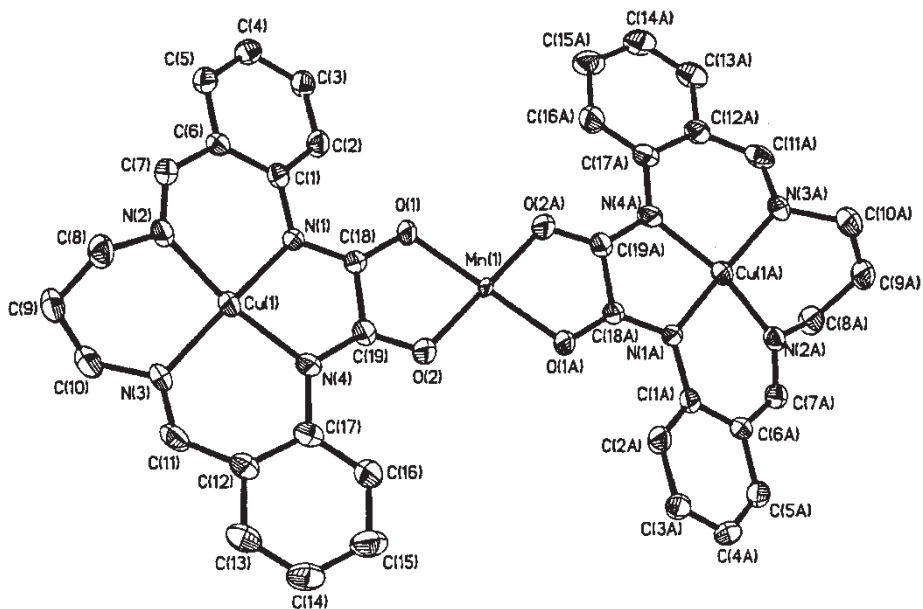
TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for non-hydrogen atoms of $[(\text{CuL})_2\text{Mn}](\text{ClO}_4)_2$

Atom	x/a	Y/b	z/c	U_{eq}
Cu(1)	6155(1)	9102(1)	1843(1)	44(1)
Mn(1)	10000	10000	0	37(1)
O(1)	8307(4)	9338(4)	-138(2)	51(1)
O(2)	9505(4)	10170(4)	1162(3)	61(1)
N(1)	6611(4)	8878(4)	677(3)	37(1)
N(2)	4376(5)	9160(4)	1570(3)	44(1)
N(3)	5836(5)	8946(5)	3029(3)	50(1)
N(4)	7882(5)	9628(5)	2019(3)	43(1)
C(1)	5810(6)	8488(5)	16(3)	39(1)
C(2)	6261(7)	8042(6)	-732(4)	49(2)
C(3)	5458(7)	7690(6)	-136(4)	52(2)
C(4)	4187(7)	7766(6)	-1269(4)	50(2)
C(5)	3714(7)	8162(6)	-539(4)	49(2)
C(6)	4501(6)	8512(5)	128(3)	40(1)
C(7)	3878(6)	8921(6)	870(4)	45(2)
C(8)	3535(8)	9594(8)	2229(5)	59(2)
C(9)	3499(8)	8811(10)	2974(5)	75(3)
C(10)	4724(9)	8259(10)	3259(6)	76(3)
C(11)	6524(7)	9393(7)	3599(4)	58(2)
C(12)	7714(7)	9972(6)	3516(4)	51(2)
C(13)	8235(9)	10408(7)	4275(5)	63(2)
C(14)	9422(8)	10846(6)	4321(5)	65(2)
C(15)	10156(9)	10854(7)	3613(5)	75(2)
C(16)	9653(8)	10445(7)	2861(5)	66(2)
C(17)	8429(7)	10026(5)	2791(4)	47(2)
C(18)	7750(5)	9243(5)	544(3)	41(2)
C(19)	8458(6)	9711(6)	1311(4)	45(2)
Cl(1)	9353(2)	2849(2)	9048(1)	65(1)
O(3)	9219(5)	2031(5)	9221(3)	81(2)
O(4)	10464(7)	2710(7)	8625(6)	154(3)
O(5)	9212(11)	3960(7)	9347(5)	181(5)
O(6)	8419(9)	2669(10)	8451(5)	184(5)

RESULTS AND DISCUSSION

Crystal Structure

Single-crystal X-ray analysis reveals that the complex $[(\text{CuL})_2\text{Mn}](\text{ClO}_4)_2$ includes a cationic $\text{Cu}_2\text{Mn}^{\text{II}}$ core and non-coordinated ClO_4^- ions. A perspective view of the trinuclear cation is depicted in Fig. 1 and selected bondlengths and angles are listed in Table III. The cation has a centre of symmetry at the manganese atom. The central Mn^{II} atom and external Cu^{II} atoms are bridged by macrocyclic oxoamide groups. Each copper is coordinated by four nitrogen atoms of the macrocyclic organic ligand, with the $[\text{CuN}_4]$ chromophore exhibiting near planarity. Cu1 is displaced from the least-squares plane by 0.0458 \AA , and deviations of the four donor atoms (N1, N2, N3, N4) from the plane are -0.2835 , 0.2916 , -0.2564 and 0.3024 \AA , respectively. The central manganese atom sits in a planar site involving four oxygen atoms of two oxamidato groups. Copper and manganese atoms are nearly coplanar with the bridging oxamidato moiety, the maximum deviation being 0.0496 \AA , with a Mn–Cu distance of 5.197 \AA .

FIGURE 1 Perspective view of the $[(\text{CuL})_2\text{Mn}]^{2+}$ cation with atom labelling scheme.TABLE III Selected bondlengths (Å) and angles ($^\circ$) for the complex

Cu(1)–N(2)	1.938(5)	N(2)–Cu(1)–N(3)	92.1(2)
Cu(1)–N(3)	1.945(5)	N(2)–Cu(1)–N(4)	159.4(2)
Cu(1)–N(4)	1.954(5)	N(3)–Cu(1)–N(4)	94.0(2)
Cu(1)–N(1)	1.957(4)	N(2)–Cu(1)–N(1)	92.74(19)
Mn(1)–O(2)	1.954(4)	N(3)–Cu(1)–N(1)	166.3(2)
Mn(1)–O(2)#1	1.954(4)	N(4)–Cu(1)–N(1)	85.98(19)
Mn(1)–O(1)#1	1.969(4)	O(2)–Mn(1)–O(2)#1	180.000(1)
Mn(1)–O(1)	1.969(4)	O(2)–Mn(1)–O(1)#1	96.67(17)
		O(2)#1–Mn(1)–O(1)#1	83.33(17)
		O(2)–Mn(1)–O(1)	83.33(17)
		O(2)#1–Mn(1)–O(1)	96.67(17)
		O(1)#1–Mn(1)–O(1)	180.0(2)

Spectroscopic Properties

The infrared spectrum shows bands characteristic of bridging oxamide [4] at ca 1640 cm^{-1} ($\nu\text{C}=\text{O}$, imido group), and at ca 1600 , 1570 , 1550 cm^{-1} ($\nu\text{C}=\text{N}$, imido group). A broad band at ca 1100 cm^{-1} is attributed to perchlorate; the lack of splitting is consistent with non-coordination.

Acknowledgments

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Supplementary Material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 200944. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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