First Crystal Structure of a (μ-Oxamidato)tricopper(II)metal(II)-Type Tetranuclear Complex: Synthesis, Crystal Structure, and Magnetism of a Copper(II)manganese(II) Complex ($[Cu^{II}_3Mn^{II}(\mu\text{-}L)_3](N_3)_2 \cdot EtOH$) Incorporating a Macrocyclic Oxamide Ligand L (Macrocyclic Oxamide = 1,4,8,11-Tetraazacyclotetradecane-2,3-dione)

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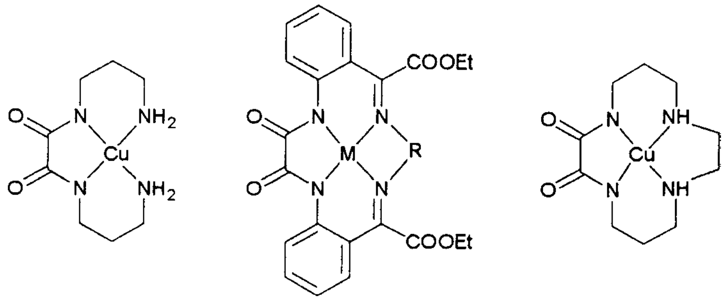
A novel oxamidato-bridged $Cu^{II}_3Mn^{II}$ tetranuclear complex incorporating a macrocyclic oxamide (macrocyclic oxamide L = 1,4,8,11-tetraazacyclotetradecane-2,3-dione) of formula $[Cu^{II}_3Mn^{II}(\mu\text{-}L)_3](N_3)_2 \cdot EtOH$ was prepared and spectroscopically, structurally, and magnetically characterized. This complex represents the first structurally characterized $[Cu^{II}_3M^{II}(\mu\text{-oxamidato})_3]$-type tetranuclear complex. The structure consists of tetranuclear units in which the central Mn^{II} atom is located on a twofold axis and linked to the each external Cu^{II} atom ion *via* the '*exo*'-*cis*-arranged O-atoms of the macrocyclic oxamidato ligands. The temperature dependence of the magnetic susceptibility for the complex was analyzed by means of the Hamiltonian $\hat{H} = -2J\hat{S}_{Mn}(\hat{S}_{Cu1} + \hat{S}_{Cu2} + \hat{S}_{Cu3})$, leading to $J = -16.3$ cm^{-1}.

Introduction. – Molecular magnetism and macrocyclic compounds are two active fields of research, encompassing chemistry, physics, biology, and material science [1][2]. At the meeting point of these two fields, polynuclear macrocyclic complexes have received considerable attention in the design of new magnetic materials and for investigating the structure and the role of the polymetallic active sites in biological systems [2–9]. A successful strategy leading to polynuclear systems is the use of metal cations to link relatively stable coordination compounds containing potential bridging units, *i.e.* 'complex ligands' [2][10–15]. A good example of a 'complex ligand' is represented by the mononuclear type of Cu^{II} complexes of *N,N'*-bis(coordinating group)-substituted oxamides [11] such as [Cu(oxpn)] (oxpn = *N,N'*-bis(3-aminopropyl)-oxamide). With these complexes as precursors, many oxamido-bridged polynuclear complexes have been prepared and studied magnetically [11–15]. Recently, this approach has been extended by using the macrocyclic analogues of the above-mentioned oxamides (*Fig. 1*) [16–19]. Noncyclic oxamides may adopt a *cis* or *trans* conformation on coordination, and this flexibility restricts the control over the type of the complex formed [11]. The macrocyclic oxamides allow the synthesis of polynuclear systems in a more controlled fashion. As far as discrete $[Cu^{II}_3Mn^{II}(\mu\text{-oxamidato})_3]$-type tetranuclear complexes is concerned, only a few examples have been reported [12][20]. Although it is well-known that the molecular topology has an important influence on



[Cu(oxpn)] [Cu(cyclam)] [CuL]

Fig. 1. *Some Cu^{II} complexes that have been used as ligands*

the magnetic properties, surprisingly, no X-ray study of the structural characterization of such complexes has been done.

With these considerations in mind and in continuation of our work on polynuclear macrocyclic complexes [16–18][21], we intend to assemble polymetallic systems by using the macrocyclic (oxamidato)copper(II) complex [CuL] as complex ligands. Our first attempts resulted in the isolation and structural characterization of a novel $Cu^{II}_3Mn^{II}$ tetranuclear complex, which we now report. Its magnetic properties are also investigated. This complex represents the first structurally characterized [$Cu^{II}_3Mn^{II}$(μ-oxamidato)$_3$-type tetranuclear complex.

Results and Discussion. – The complex [$Cu^{II}_3Mn^{II}$(μ-L)$_3$]$(N_3)_2$ · EtOH crystallizes in the space group *C*2/*c* and has a structure that includes a cationic Cu_3Mn core, non-coordinated monovalent anions N_3^-, and solvent molecules EtOH. A perspective view of the tetranuclear cation is depicted in *Fig. 2*, and selected bond lengths and angles are listed in *Table 1*. The central Mn^{II} atom is located on a twofold axis that passes through the Cu(2) atom and the center of the C–C bond of the corresponding oxamidato group and, consequently, the molecule has a C_2 symmetry. The Mn^{II} atom is linked to each external Cu^{II} *via* the '*exo*'-*cis*-arranged O-atoms of the macrocyclic oxamidato ligand, with the Mn–Cu distances of 5.478 and 5.485 Å for Cu(1a) and Cu(2), respectively, resulting in a tetranuclear unit. Each terminal Cu^{II} atom is coordinated by four N-atoms of the macrocyclic organic ligand, with the [CuN_4] chromophore exhibiting near planarity and average Cu–N bond distances of 1.938 Å. The Cu(1a) atom is displaced from the least-squares plane by 0.0082 Å. The Cu^{II} and Mn^{II} atoms are nearly coplanar with the bridging oxamidato moiety between them, the maximum r.m.s. deviation being 0.0275 Å. Furthermore, the sum of the angles around the C- and N-atoms of the bridging oxamidato moiety is very close to 360°, implying that Cu^{II}–N–C–O is a delocalized unit as a result of the conjugation of electrons from the O-atoms and the lone pairs on the N-atoms. This is further supported by the average C–O and C–N bond lengths (1.260 and 1.287 Å, resp.), which are shorter than expected for single C–O or C–N bonds (*ca.* 1.481 and 1.462 Å, resp.) [19]. The three macrocyclic oxamidato moieties linked to the central Mn^{II} atom look like the vanes of a windmill. The packing of the molecules in two different orientations are shown in *Fig. 3*. Oriented

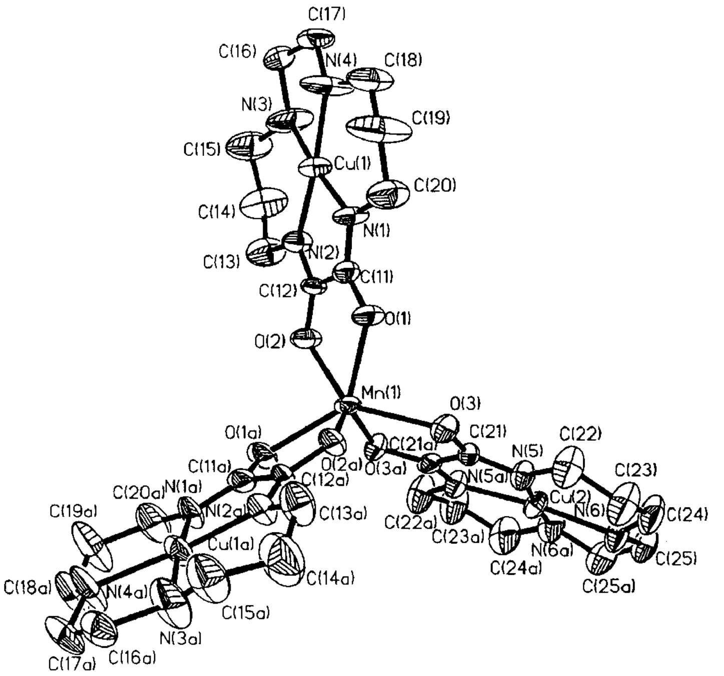


Fig. 2. *ORTEP View of the tetranuclear complex cation* $[Cu^{II}_3Mn^{II}(\mu\text{-}L)_3]^{2+}$ *with the atom numbering scheme.* L = 1,4,8,11-Tetraazacyclotetradecane-2,3-dionato(2−)-$\kappa N^1:\kappa O^2$, $\kappa N^4:\kappa O^3,\kappa N^8,\kappa N^{11}$.

along the *b* axis (*Fig. 3,a*), it can be viewed as a one-dimensional chain, while oriented along the *c* axis (*Fig. 3,b*), the chain formation may be seen as an intermolecular weak interaction between the vanes of adjacent windmills. It should be noted that there are disorder conformations within the ligands, but this disorder could not be treated successfully.

IR and Electronic Spectra. The IR spectrum of the $[Cu^{II}_3Mn^{II}(\mu\text{-}L)_3](N_3)_2$ complex shows two strong bands at *ca.* 1600 and *ca.* 1440 cm^{-1}, attributed to the $\tilde{\nu}$(N−C−O) stretching bands, which are characteristic of the bridging oxamidato moiety [12]. The appearance of a strong and sharp band at *ca.* 2050 cm^{-1} indicates the presence of free N_3^- anions [22].

The electronic absorption spectra of the complex in MeCN below 500 nm are dominated by intense bands due to intraligand and charge-transfer transitions in the $[Cu^{II}L]$chromophore [21]. A relatively stronger band centered at 510 nm (ε = 123 M^{-1} cm^{-1}) is observed and can be attributed to the d-d transitions of Cu^{II} in an environment close to square planar, due to the Cu^{II} chromophore [12]. The coordination environment of Mn^{II} in the complex is a distorted octahedron. Thus, according to ligand-field theory and assuming O_h symmetry, the ground-state of Mn^{II} is $^6A_{1g}$. Because d-d transitions of Mn^{II} ($^6A_{1g} \rightarrow {}^4T_{1g}$(G), $^4T_{2g}$(G), $^4A_{1g}\ldots$) are spin-forbidden, no characteristic band of Mn^{II} is found in the spectrum of the complex [23].

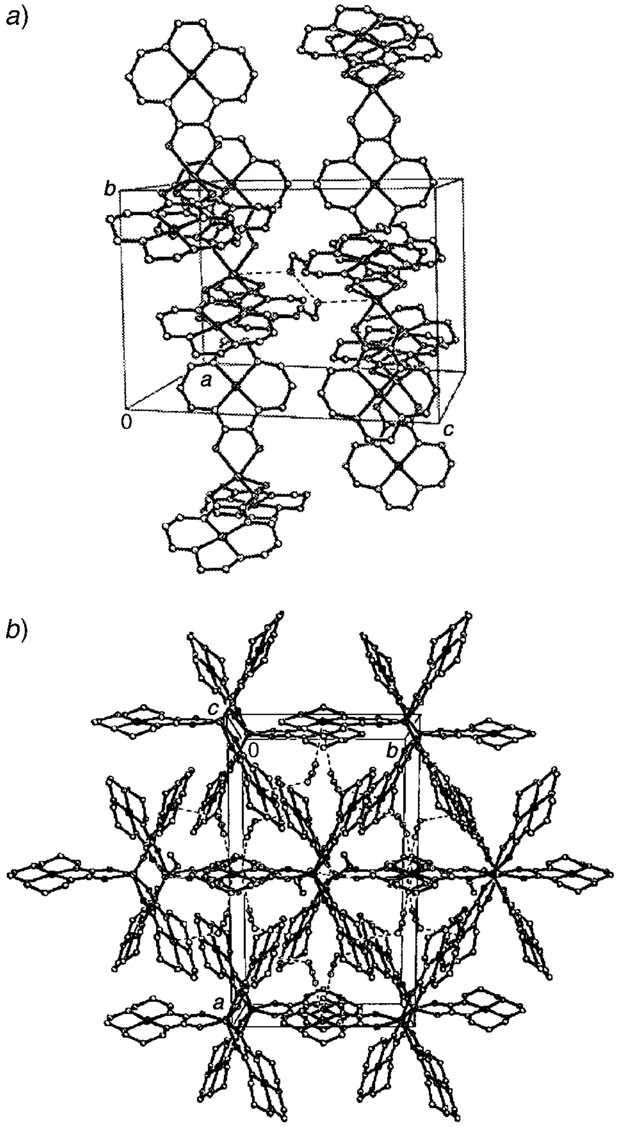


Fig. 3. *Packing diagrams of the complex* $[Cu^{II}_3Mn^{II}(\mu\text{-}L)_3](N_3)_2 \cdot EtOH$ *in two orientations:* a) *orientation along the* b *axis and* b) *orientation along the* c *axis*

ESR Spectra. The polycrystalline X-band ESR spectrum at room temperature exhibits a broad signal centered at $g = 2.02$, indicating a magnetic exchange interaction between the metal ions [24]. Acocording to *Kambe*'s approach [25], the coupling between a $S = 5/2$ spin (Mn^{II}) and three $S = 1/2$ spins (Cu^{II}) gives rise to eight spin states. On the basis of the *Boltzmann* distribution and the parameters obtained from magnetic studies (*vide infra*), all the coupled spin states are significantly populated at

Table 1. *Selected Bond Lengths* [Å] *and Angles* [°] *for the Complex* $[Cu^{II}_3Mn^{II}(\mu\text{-}L)_3](N_3)_2 \cdot EtOH$

Mn(1)–O(1)	2.158(6)	Cu(1)–N(3)	1.960(10)
Mn(1)–O(2)	2.212(6)	Cu(1)–N(4)	1.970(10)
Mn(1)–O(3)	2.170(6)	Cu(2)–N(6)	1.955(10)
Cu(1)–N(2)	1.916(8)	Cu(2)–N(5)	1.944(7)
Cu(1)–N(1)	1.904(9)	O(1)–C(11)	1.262(10)
		O(2)–C(12)	1.246(10)
O(1)–Mn(1)–O(1)[a])	131.0(3)	N(2)–Cu(1)–N(1)	82.9(4)
O(1)–Mn(1)–O(3)	88.7(2)	N(2)–Cu(1)–N(3)	97.2(4)
O(1)–Mn(1)–O(3)[a])	133.3(2)	N(2)–Cu(1)–N(4)	175.0(5)
O(3)–Mn(1)–O(3)[a])	73.9(4)	N(1)–Cu(1)–N(3)	176.1(5)
O(1)–Mn(1)–O(2)	74.0(2)	N(1)–Cu(1)–N(4)	98.7(5)
O(3)–Mn(1)–O(2)	131.3(2)	N(3)–Cu(1)–N(4)	81.6(5)
O(1)–Mn(1)–O(2)[a])	88.5(2)	N(6)–Cu(2)–N(6)[a])	83.6(7)
O(3)–Mn(1)–O(2)[a])	85.5(2)	N(6)–Cu(2)–N(5)[a])	174.2(4)
O(2)–Mn(1)–O(2)[a])	137.3(3)	N(6)–Cu(2)–N(5)	96.8(4)
		N(5)–Cu(2)–N(5)[a])	83.4(5)

[a]) Symmetry transformation: $-x+1, y, -z+1/2$.

room temperature, and all make their contributions to the ESR absorption, thus resulting in a broad signal.

Magnetic Properties. The magnetic susceptibility was measured in the temperature range 80–300 K on a *LDJ-9600* vibrating-sample magnetometer in an applied magnetic field of 5000 G. The room temperature value for $\chi_M T$ (4.84 cm^3 mol^{-1} K, where χ_M is the molar magnetic susceptibility) is lower than that expected for a Mn^{II} and three isolated Cu^{II} atoms ($\chi_M T = 5.49$ cm^3 mol^{-1} K). Upon cooling to 80 K, the $\chi_M T$ value steadily decreases, suggesting that an antiferromagnetic interaction between the Cu^{II} and Mn^{II} atoms is operative.

The magnetic analysis was initially carried out by means of the theoretical expression of the magnetic susceptibility deduced from the spin Hamiltonian $\hat{H} = -2J\hat{S}_{Mn}(\hat{S}_{Cu1} + \hat{S}_{Cu2} + \hat{S}_{Cu3})$. The theoretical expression is given by *Eqn. 1*, where J is the exchange integral between the Cu^{II} and Mn^{II} atoms, N_α is the temperature-independent paramagnetism ($450 \cdot 10^{-6}$ cm^3 mol^{-1}), and the other symbols have their usual meanings. The best fitting for the experimental data gives $J = -16.3$ cm^{-1}, $g = 2.13$. The agreement factor $R = \Sigma(\chi_{obs} - \chi_{calc})^2/\Sigma\chi^2_{obs}$ is $5.5 \cdot 10^{-4}$.

$$\chi_M = \frac{Ng^2\beta^2}{KT}\left(\frac{A}{B}\right) + N_\alpha \qquad (1)$$

$$A = 2 + 10\exp(4J/kT) + 20\exp(7J/kT) + 28\exp(10J/kT) + 56\exp(13J/kT) + 60\exp(18J/kT)$$

$$B = 3 + 5\exp(4J/kT) + 10\exp(7J/kT) + 7\exp(10J/kT) + 14\exp(13J/kT) + 9\exp(18J/kT)$$

According to *Kahn* [2], the antiferromagnetic interaction between Cu^{II} and Mn^{II} arises from the non-zero overlap between the magnetic orbitals centered at the two metal ions and delocalized towards ligands. A main factor influencing the magnitude of the interaction is the overlap between the molecular orbitals of the bridging groups and the singly-occupied d orbitals of the metal [12]. The $|J|$ value for the present complex is larger than that for $[Cu_3Mn(ss\text{-}oxpn)_3](ClO_4)_3 \cdot 2H_2O$ ($J = -13.3$ cm^{-1}) [12]. The difference may be tentatively attributed to the difference in the planarity of the $[CuN_4]$ chromophores in the two complexes. The better the planarity is, the larger the overlap between the singly-occupied d orbitals of the Cu^{II} atoms and the bridging orbitals is, and the stronger the interaction between the Cu^{II} and Mn^{II} atoms is. It is very likely that the conjugating systems in the macrocyclic complex reported here favors a better planarity, thus results in a stronger interaction.

Conclusions. – A novel oxamidato-bridged tetranuclear $Cu^{II}_3Mn^{II}$ complex incorporating a bridging macrocyclic oxamidato ligand was synthesized and characterized by X-ray-analysis and IR, ESR, and electronic spectra. This complex represents the first structurally characterized $[Cu^{II}_3M^{II}(\mu\text{-oxamidato})_3]$-type tetranuclear complex. The structure consists of tetranuclear units in which the central Mn^{II} atom is located on a twofold axis and linked to each of the external Cu^{II} atom *via* the '*exo*'-*cis*-arranged O-atoms of the macrocyclic oxamidato ligand. The temperature dependence of the magnetic susceptibility for the complex was analyzed by means of the Hamiltonian $\hat{H} = -2J\hat{S}_{Mn}(\hat{S}_{Cu1} + \hat{S}_{Cu2} + \hat{S}_{Cu3})$, leading to $J = -16.3$ cm^{-1}.

Experimental Part

General. All chemicals were of A.R. grade and used as received. The mononuclear precursor (1,4,8,11-tetraazacyclotetradecane-2,3-dionato(2−)-$\kappa N^1,\kappa N^4,\kappa N^8,\kappa N^{11}$)copper ([CuL]) was prepared as described elsewhere [19]. Electronic spectrum: *Shimadzu UV-2401-PC* spectrophotometer; in MeCN. X-Band ESR spectrum: *Bruker ER-200-D-SRC* spectrometer. IR Spectra: *Shimadzu IR-408* spectrometer; KBr pellets; only main bands; in cm^{-1}. Variable-temperature magnetic susceptibilities: *LDJ 9600* vibrating-sample magnetometer;

Table 2. *Summary of Crystal Data for the Complex* $[Cu^{II}_3Mn^{II}(\mu\text{-}L)_3](N_3)_2 \cdot EtOH$

Formula	$C_{32}H_{60}Cu_3MnN_{18}O_7$
M_r	1054.54
Crystal system	Monoclinic
Space group	$C2/c$
a [Å]	21.418(4)
b [Å]	12.252(2)
c [Å]	18.021(4)
α [°]	90
β [°]	105.62(3)
γ [°]	90
V [Å^3]	4554.3(15)
Z	4
μ(MoK_α) [cm^{-1}]	17.17
T/K	293(2)
Reflections measured	3987
Unique reflections	3856
R(int)	0.0349
R_1, wR_2 ($I > 2\sigma(I)$)	0.0622, 0.1594
R_1, wR_2 (all data)	0.2087, 0.1981

diamagnetic corrections were made with *Pascal*'s constants for all the constituent atoms [26]. Elemental analyses (C, H, N): *Perkin-Elmer 240* analyser.

*Tricoppertris[*μ*-(1,4,8,11-tetraazacyclotetradecane-2,3-dionato(2−)-*$\kappa N^1{:}\kappa O^2,\kappa N^4{:}\kappa O^3,\kappa N^8,\kappa N^{11}$*)]manganese(2+) Azide Ethanol (1:2:1* ($[Cu_3Mn(\mu\text{-}L_3](N_3)_2 \cdot C_2H_5OH$). A soln. of [CuL] (3 equiv.) and $Mn(ClO_4)_3 \cdot 6\,H_2O$ (1 equiv.) in H_2O/EtOH 1:1 afforded the desired crystals upon slow evaporation of the solvent in the presence of excess NaN_3 at r.t. over a period of several days. IR (KBr): 3400*w* (br.), 3100*m*, 2050 (sh), 1600*s*, 1440*m*, 1310*m*, 1160*m*, 1090*w*, 1070*w*, 980*w*, 940*w*, 880*w*, 790*m*. Anal. calc. for $C_{32}H_{60}Cu_3MnN_{18}O_7$: C 36.44, H 5.75, N 23.91; found: C 36.20, H 5.40, N 24.12.

Crystallography. Intensity data for the single crystal of the complex were collected on an *Enraf-Nonius CAD4*. The structures were solved by direct methods and subsequent *Fourier* difference techniques, and refined anisotropically by full-matrix least-squares on F^2 [27]. Crystal data and structure refinements are summarized in *Table 2*. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publication no CCDC-167327. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk).

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