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Synthesis and Magnetic Properties of New Tetranuclear Copper(II)–Nickel(II) Complexes of Macrocyclic Oxamides†

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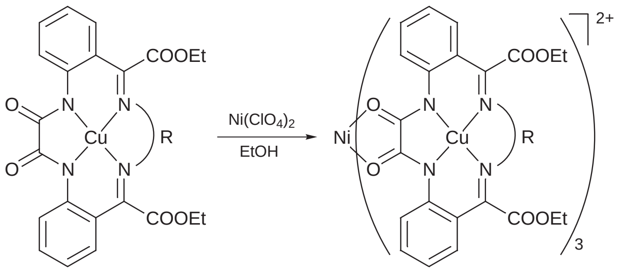
Four new oxamido-bridged $[\mathrm{Cu}^{\mathrm{II}}_3\mathrm{Ni}^{\mathrm{II}}]$ complexes of [14]N_4 and [15]N_4 macrocyclic oxamides have been prepared and characterized, and the magnetic interaction between the Cu(II) and Ni(II) ions has been investigated.

Molecular magnetism and macrocyclic compounds are two active fields of research, both involving several areas such as chemistry, physics, biology and material science.[1–3] Phenolato oxygen-bridged macrocyclic complexes, which are at the meeting point of the two fields of molecular magnetism and macrocyclic compounds, have been widely studied.[3,4] To our knowledge, however, little work has been devoted to investigating the magnetism of the polynuclear complexes of macrocyclic ligands containing multiatomic bridges such as oxamido and oximato groups. Several years ago, Christodoulou *et al.* described two such binuclear macrocyclic complexes, [Ni(α-diketo-TAD-Me$_4$)]ZnCl$_2$ and [Ni(α-diketo-TAD-Me$_4$)]Cu(NO$_3$)$_2$ [α-diketo-TAD-Me$_4$ is the dianion of 2,3-dioxo-5,6:13,14-dibenzo-7,12-dimethyl-9,10-(4′,5′-dimethylbenzo)-1,4,8,11-tetraazacyclotetradeca-7,11-diene],[5] but the diamagnetic nature of the Ni(II) ions in these complexes precluded studies of the magnetic interactions between the metal ions.



1 **2**

R	a	b	c	d
R	CH$_2$CH$_2$	CH(CH$_3$)CH$_2$	CH$_2$CH$_2$CH$_2$	C$_6$H$_4$

Scheme 1

We report here the synthesis, characterization of four novel $[\mathrm{Cu}^{\mathrm{II}}_3\mathrm{Ni}^{\mathrm{II}}]$ complexes of [14]N_4 and [15]N_4 macrocyclic oxamides. The complexes were prepared by the strategy of "complexes as ligands".[6] The mononuclear Cu(II) complexes **1** (Scheme 1) contain uncoordinated oxamido carbonyl groups, and can be used as ligands, or precursors for polynuclear complexes. Indeed, the reactions of **1** with nickel perchlorate in ethanol give tetranuclear complexes in a relatively high yield. The complexes are of formula $[(\mathrm{CuL})_3\mathrm{Ni}](\mathrm{ClO}_4)_2\cdot n\mathrm{H}_2\mathrm{O}$ ($n = 0$ for **2a–c**, $n = 1$ for **2d**). Some selected physical data for **2a-d** are given in Table 1 and, for comparison, some data for the precursors **1a–d** are also listed. The molar conductance values for the tetranuclear complexes fall in the expected range for 1:2 electrolytes.[7] The IR spectra of **2a–d** are similar. The ν(C=O) (ester) and ν(C=N) bands are observed at nearly the same frequencies as those for the corresponding Cu(II) precursor,[8,9] whereas the ν(C=O) (oxamido) bands are shifted towards lower frequencies by $\sim 80\,\mathrm{cm}^{-1}$ on tetranuclear complex formation, suggesting that the Cu(II) precursors coordinate to Ni(II) ions *via* oxamido carbonyl groups.[6] The broad intense bands at *ca.* $1100\,\mathrm{cm}^{-1}$, observed in **2a–d** and with no splitting, indicate the presence of uncoordinated perchlorate ions.[10]

With reference to the reflectance spectra of the Cu(II) precursors, the weak bands at 490–538 and 629–650 nm in the spectra of **2a–d** are tentatively attributed to the $^2B_{1g} \rightarrow {}^2E_g$ and $^2B_{1g} \rightarrow {}^2B_{2g}$ transitions of Cu(II) ions, respectively, assuming a D_{4h} site symmetry for the [CuN$_4$] chromophore.[11,12] The still weaker absorption at 750 nm, observed as a shoulder in **2a–b**, is attributable to the $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transition of the octahedral Ni(II) ion.[11] The corresponding absorption for **2c–d** may be obscured by the broad d–d transition of Cu(II) ions.

Table 1 Physical data for the complexes

Complex	$\Lambda^a/\Omega^{-1}\,\mathrm{cm}^2\,\mathrm{mol}^{-1}$	IR bands/cm^{-1} ν(C=O)^b	ν(C=O)^c	ν(C=N)	ν(ClO$_4$)	$\lambda_{\max}$/nm
2a	138	1730	1570	1620	1080	749sh, 536
1a	—	1730	1650	1615	—	550br
2b	140	1730	1575	1620	1080	750sh, 538br
1b	—	1735	1660	1620	—	547br
2c	133	1735	1585	1630	1100	629, 492sh
2c	—	1730	1655	1635	—	647, 505sh
2d	127	1725	1570	1660	1100	650br
1d	—	1720	1645	1660	—	582

[a] In 10^{-3} mol cm^{-3} DMF solutions. [b] Ester carbonyl. [c] Oxamido carbonyl.

The shift of the d–d absorption of the [CuN$_4$] and [CuN$_2$O$_2$] chromophores, which occurs when mononuclear

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Cu(II) precursors coordinate to another metal ion to form polynuclear complexes, has been related to changes in the strength of the ligand field around Cu(II) ions and in the planarity of the [CuN_4] and [CuN_2O_2] chromophores.[12,13] The blue-shifts of the d–d (Cu) bands for **2a–c** suggest increased ligand fields and enhanced planarity of the [CuN_4] chromophores on tetranuclear complex formation. However, a red shift is observed for **2d**, suggesting a weakened ligand field. The difference between **2d** and the other three complexes may be owing to the following reasons: the π conjugation system in the precursor **1d**, formed from *o*-phenylenediamine, is more extended than those in the other three precursors. The more extended π conjugation may result in nearly strict coplanarity of the [CuN_4] chromophores in **1d**. The planar [CuN_4] chromophores may undergo some distortion upon coordination to Ni(II) ions, so as to lead to a decrease in the ligand field around the Cu(II) ions. The most direct and forceful evidence for the above argument may come from X-ray crystallographic studies. Unfortunately, all our efforts to obtain single crystals were unsuccessful.

The temperature dependence of magnetic susceptibility (χ_M) for **2a** was measured in the 2–300 K temperature range and is shown as χ_M *versus* T and $\chi_M T$ *versus* T plots in Fig. 1. The experimental value of $\chi_M T$ at room temperature is *ca.* 1.68 cm^3 mol^{-1} K, less than the spin-only value (2.12 cm^3 mol^{-1} K) expected for an uncoupled [Cu_3Ni] unit. The $\chi_M T$ value decreases continuously upon cooling and reaches a plateau in the 30–6.2 K temperature range with $\chi_M T = 0.40-0.42$ cm^3 mol^{-1} K, as expected for a spin-doublet state. The above features are indicative of an antiferromagnetic interaction between the copper and nickel ions. $\chi_M T$ decreases rapidly upon cooling further to 2 K. The magnetic analysis was carried out by using the theoretical expression of the magnetic susceptibility deduced from the Heisenberg spin Hamiltonian:

$$\hat{H} = -2J\hat{S}_{\mathrm{Ni}} \cdot (\hat{S}_{\mathrm{Cu1}} + \hat{S}_{\mathrm{Cu2}} + \hat{S}_{\mathrm{Cu3}})$$

and the molecular field approximation:[14]

$$\chi'_M = \chi_M/[1 - 2zJ'\chi_M/Ng^2\beta^2]$$

where J is the exchange integral between Cu(II) and Ni(II) ions, zJ' denotes the intermolecular exchange integral, and the other symbols have their usual meanings. The fit of the experimental data gives $J = -53.7\ \mathrm{cm}^{-1}$, $g = 2.19$, $zJ' = -2.64\ \mathrm{cm}^{-1}$ and $F = 1.1 \times 10^{-4}$, where F is the agreement factor defined as $F = \sum(\chi_{\mathrm{obsd}} - \chi'_{\mathrm{calc}})^2 \sum \chi_{\mathrm{obsd}}$. These values suggest that both the intramolecular and intermolecular magnetic interactions are antiferromagnetic.

Experimental

General Procedure for the Preparation of the Complexes.—Complexes **1** were prepared as described elsewhere.[8,9] A solution of $Ni(ClO_4)_2 \cdot 6H_2O$ (1.50 mmol) in ethanol (10 cm^3) was added to the suspension of **1** (4.50 mmol) in ethanol (10 cm^3). The mixture was stirred under reflux for 5 h, and then filtered. The precipitate thus obtained was washed successively with ethanol and diethyl ether, recrystallized from ethanol/acetone. **2a** (82%), brown (Found: C, 46.9; H, 3.6; N, 8.9. $C_{72}H_{66}N_{12}O_{26}Cl_2Cu_3Mn$ requires C, 47.11; H, 3.62; N, 9.16%). **2b** (68%), red–brown (Found: C, 47.9; H, 3.6; N, 9.2. $C_{75}H_{72}N_{12}O_{26}Cl_2Cu_3Mn$ requires C, 47.98; H, 3.86; N, 8.95%). **2c** (80%), green (Found: C, 47.5; H, 3.7; N, 8.7. $C_{75}H_{72}N_{12}O_{26}Cl_2Cu_3Mn$ requires C. 47.98; H, 3.86; N, 8.95%). **2d** (86%), yellow–brown (Found: C, 50.1; H, 3.4; N. 8.0. $C_{84}H_{68}N_{12}O_{27}Cl_2Cu_3Mn$ requires C, 50.50; H, 3.43; N, 8.41%).

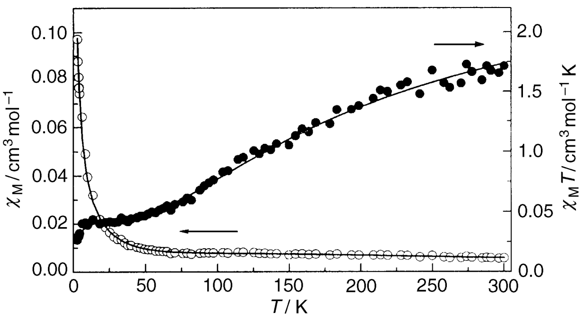

Fig. 1 χ_M *versus T* and $\chi_M T$ *versus T* plots for **2a**.

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