In summary, a strongly electron-deficient and sterically hindered TPP Mn–O intermediate was produced in the present *reductive* dioxygen activation system which is most probably identical with that obtained from the O-transfer reaction in TPP·Mn^{III}–PhIO system. Further studies directed to the clarification of the reductive oxygen activation mechanism and the identification of active oxidizing species are in progress.

Ordered Magnetic Bimetallic Chains: A Novel Class of One-Dimensional Compounds

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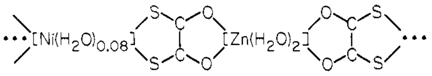
The synthesis and the study of polymetallic complexes, including one-dimensional systems, has been one of the most active fields of inorganic chemistry in the past few years.[1] Surprisingly, till now, no structurally ordered bimetallic chains of the type $(A–X–B–X–)_n$, where A and B are two different paramagnetic metal ions and X is a bridging ligand, have been described. We succeeded in synthesizing Ni(II)–Mn(II) and Cu(II)–Mn(II) compounds of this kind with dithiooxalate as a bridging ligand.

In a previous note[2] we described the crystal structure of $NiZn(S_2C_2O_2)_2(H_2O)_{2.08}$. This compound exhibits a molecular structure made of "infinite" parallel straight chains



in which Ni, Zn, and dithiooxalate groups form planar ribbons, the coordination of all Zn atoms and of a few Ni atoms being octahedrally completed with water molecules.[3]

We report here on the crystal structures and magnetic properties of the Ni(II)–Mn(II)– and Cu(II)–Mn(II)–dithiooxalato systems.[4]

Single crystals of $NiMn(S_2C_2O_2)_2(H_2O)_{7.5}$ (**1**) and $CuMn(S_2C_2O_2)_2(H_2O)_{7.5}$ (**2**) suitable for X-ray analysis were obtained by slowly cooling aqueous solutions of potassium bis(dithiooxalato)nickelate, $K_2Ni(S_2C_2O_2)_2$, or -cuprate, $K_2Cu(S_2C_2O_2)_2$, and manganese(II) sulfate. They are black (**1**) or brown (**2**), lustrous, ribbon-like crystals which are air stable but rather difficult to handle because of spontaneous shrinking and twisting upon application of the slightest mechanical stress. Both compounds crystallize in the monoclinic space group $P2_1/c$ with four formula units in cells of dimensions $a = 11.575$ (2) Å, $b = 20.654$ (6) Å, $c = 7.323$ (1) Å, and $\beta = 103.73$ (1)° for **1** and $a = 11.692$ (2) Å, $b = 20.665$ (5) Å, $c = 7.360$ (2) Å, and $\beta = 103.84$ (2)° for **2**. Intensity data were collected on an automated Enraf-Nonius CAD-4 diffractometer with use of Mo Kα radiation. The collection of intensities of compound **1** could not be completed as the crystal suddenly "died out" without any premonitory anomalies in the standard intensities. The structures were solved from Patterson and Fourier analyses and were refined by full-matrix, least-squares techniques to R indices on F_o of 0.059 for the 120 variables and 894 reflections with $I > 1.5\sigma(I)$ for compound **1** and of 0.064 for the 155 variables and 1149 reflections with $I > 2\sigma(I)$ for compound **2**.[5]

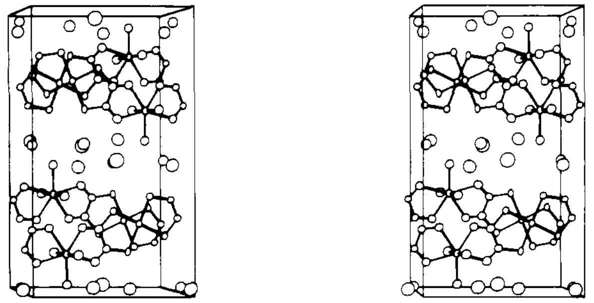


Figure 1. Stereoscopic view down the *c* axis (*b* axis vertical) of the unit cell of $Ni[Mn(H_2O)_3](S_2C_2O_2)_2·4.5H_2O$, showing the sequence of alternating layers of water molecules (single circles) and of stacked bimetallic chains. For all atoms, 50% probability thermal ellipsoids or spheres are shown.

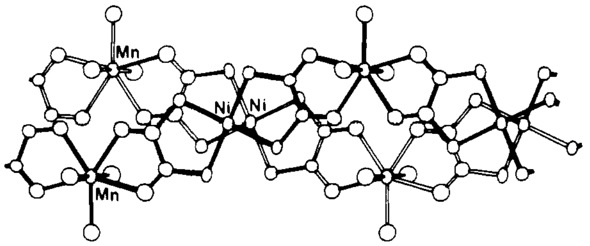


Figure 2. View of two successive chains of $\{Ni(S_2C_2O_2)[Mn(H_2O)_3](O_2C_2S_2)\}_\infty$ along a glide plane *c* represented by the dotted line.

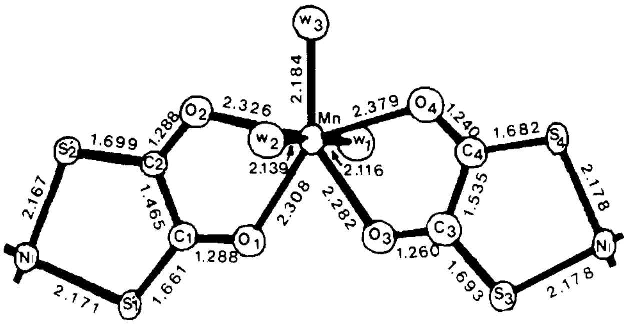


Figure 3. View of the chain repeat unit $Ni(S_2C_2O_2)[Mn(H_2O)_3](O_2C_2S_2)Ni$.

The two compounds are isostructural. Figures 1–3, illustrating their structures, are from the Ni derivative. The structures consist of "infinite"-chain molecules $···A(S_2C_2O_2)[Mn(H_2O)_3](O_2C_2S_2)···$ (A = Ni, Cu) criss-crossing glide planes *c* and stacked along these planes. Each layer of stacked chains is separated from the next one by intervening water molecules (Figure 1). Figure 2 illustrates the way two neighboring chains are related within a layer. A repeat unit $\{Ni(S_2C_2O_2)[Mn(H_2O)_3](O_2C_2S_2)\}$ is represented in Figure 3. The nickel (copper) atoms lie quite in the glide plane ($y = 0.2514$ (1) and 0.2518 (2), respectively); they are planarily coordinated to two dithiooxalate groups through their sulfur atoms. The Ni–S bond lengths (2.171 (5), 2.167 (5), 2.178 (5), 2.178 (5) Å) are about 0.1 Å shorter than the Cu–S ones (2.269 (6), 2.272 (7), 2.288 (6), 2.267 (6) Å). Angles around Ni and Cu are, respectively, S(1)–Ni–S(2) = 92.2 (2)°, S(1)–Ni–S(3) = 179.2 (6)°, S(1)–Ni–S(4) = 87.8 (2)°, S(2)–Ni–S(3) = 87.6 (2)°,

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(2) Maury, F.; Gleizes, A.; Galy, J. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1980**, *291*, 49–52.

(3) We have previously shown that the planar anion $Ni(S_2C_2O_2)_2^{2-}$ gives rise to one-dimensional stackings with alkali and alkaline earth ions as countercations: Gleizes, A.; Clery, F.; Bruniquel, M. F.; Cassoux, P. *Inorg. Chim. Acta* **1979**, *37*, 19–26. Maury, F.; Gleizes, A. *Ibid.* **1980**, *41*, 185–194. Gleizes, A.; Maury, F.; Cassoux, P.; Galy, J. *Z. Kristallogr.* **1981**, *155*, 293–305.

(4) We also synthesized palladium(II) manganese(II) and platinum(II) manganese(II) dithiooxalates. Their X-ray powder patterns look quite similar. The X-ray single-crystal structure of the Pt derivative was found to be identical with those of the Ni and Cu derivatives presented here.

(5) Listings of atomic positional and thermal parameters are available as supplementary material. See paragraph at the end of paper regarding supplementary material.

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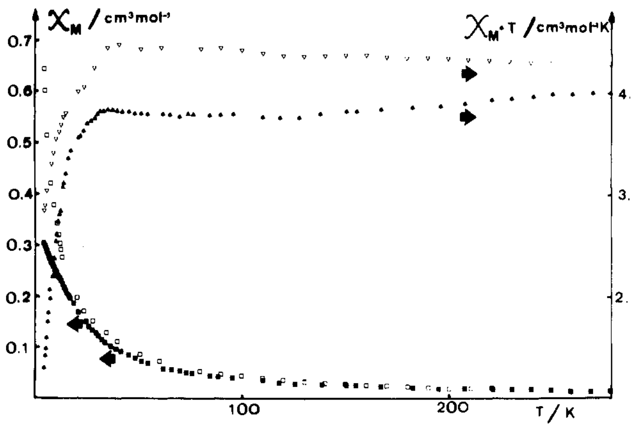

Figure 4. Temperature dependence of the magnetic susceptibility, χ_m, and of the product $\chi_m T$ for the compounds $\{NiMn(S_2C_2O_2)_2(H_2O)_{7.5}\}_\infty$, (Ni(II)-Mn(II)), and $\{CuMn(S_2C_2O_2)_2(H_2O)_{7.5}\}_\infty$, (Cu(II)-Mn(II)). The molar weight chosen is the weight of the above dimeric entities. Diamagnetic corrections were evaluated at 280×10^{-6} and 270×10^{-6} cm^3 mol^{-1}, respectively. Ni(II)-Mn(II): χ_m (□), $\chi_m T$ (▽); Cu(II)-Mn(II): χ_m (■), $\chi_m T$ (▲).

S(2)-Ni-S(4) = 178.5 (3)°, and S(3)-Ni-S(4) = 92.5 (2)° and S(1)-Cu-S(2) = 91.9 (2)°, S(1)-Cu-S(3) = 178.0 (3)°, S(1)-Cu-S(4) = 89.1 (2)°, S(2)-Cu-S(3) = 87.7 (2)°, S(2)-Cu-S(4) = 177.5 (3)°, and S(3)-Cu-S(4) = 91.5 (2)°. The manganese atoms stand back from each side of the glide planes (y = 0.3512 (1) in both compounds) and are heptacoordinated to oxygen atoms located at the vertices of a nearly regular pentagonal bipyramid: four oxygen atoms from two dithiooxalate groups and one from water molecule w(3) are equatorial (69.0 (4)° $\le$ O_{eq}-Mn-O_{eq} $\le$ 75.9 (4)° in **1** and 69.0 (5)° $\le$ O_{eq}-Mn-O_{eq} $\le$ 75.7 (5)° in **2**; $\sum$(O_{eq}-Mn-O_{eq}) = 360.5 (20)° in both compounds); the axial positions are occupied by water molecules w(1) and w(2) (O_{ax}-Mn-O_{ax} = 178.0 (4)° in **1** and 178.4 (5)° in **2**; 86.1 (4)° $\le$ O_{ax}-Mn-O_{eq} $\le$ 94.2 (4)° in **1** and 86.1 (5)° $\le$ O_{ax}-Mn-O_{eq} $\le$ 95.0 (5)° in **2**. The Mn-O bond lengths and the interatomic distances in the dithiooxalate groups do not differ significantly in either compound (Figure 3). Within a chain, the atoms of the dithiooxalate groups, water molecules w(3), and nickel (copper) and manganese are almost coplanar with a mean plane approximately parallel to ($10\bar{2}$). Within a layer of chains, the planar groups NiS_4 or CuS_4 form stacks in which each of them is staggered with respect to the next one and is nearly perpendicular to the stacking direction [001]. The Ni-Ni and Cu-Cu separations are equal to 3.662 (1) and 3.681 (1) Å, respectively. The closest S-S separations between two successive chains range from 3.913 (7) to 3.981 (6) Å in **1** and from 3.917 (9) to 3.951 (9) Å in **2** and are therefore markedly larger than twice the sulfur van der Waals radius (1.85 Å). On the other hand, weak interchain hydrogen bonds involving water molecules w(1), w(2), and w(3) and oxygen atoms O(3), O(1), and O(2) are highly probable: O_w-O = 2.77 (2), 2.81 (2), and 2.78 Å in **1** and 2.77 (2), 2.87 (2), and 2.75 (2) Å in **2**; however, this point cannot be discussed further since the hydrogen atoms were not located. The shortest contacts between a layer of chains and a layer of water molecules involve only water molecules: 2.76 (2) Å $\le$ O_w-O_w $\le$ 2.81 (2) Å in **1** and 2.71 (2) Å $\le$ O_w-O_w $\le$ 2.86 (2) Å in **2**. Within a layer of water molecules the shortest O-O distances range from 2.65 (2) to 2.86 (2) Å in **1** and from 2.58 (2) to 2.84 (2) Å in **2**.

The susceptibility vs. temperature curves of the Ni(II)-Mn(II) and Cu(II)-Mn(II) systems are shown in Figure 4. The magnetic behavior of Ni(II)-Mn(II) follows the Curie law expected for isolated Mn(II) ions down to 35 K ($\chi_m T$ = 4.3-4.5 cm^3 mol^{-1} K), in agreement with the planar surrounding of diamagnetic nickel(II) ions by sulfur. The decrease of $\chi_m T$ below 35 K could be due to the effects of a weak antiferromagnetic interaction or zero-field splitting of Mn(II) in heptacoordinated symmetry.

The magnetic behavior of Cu(II)-Mn(II) is more peculiar. The curves χ_m and $\chi_m T$ seem to look like those of Ni(II)-Mn(II) but the values are quite different: at 300 K, $\chi_m T$ is smaller (4.0 cm^3 mol^{-1} K) than expected for isolated Cu(II) and Mn(II) ions and even smaller than the value found for the Ni(II)-Mn(II) system. $\chi_m T$ very sharply decreases upon cooling from 300 to 30 K and then sharply decreases below 30 K to $\chi_m T$ = 1.3 cm^3 mol^{-1} K. These values and this behavior suggest that Cu(II) and Mn(II) are antiferromagnetically coupled. A complete interpretation of these magnetic data in terms of magnitude of interaction is not yet feasible. Indeed, the theoretical expression for the magnetic susceptibility of a chain of alternating $^1/_2$-$^5/_2$ spins has never been derived. Nevertheless, if the interaction between nearest neighbor Cu(II) and Mn(II) atoms is antiferromagnetic, the ground state of the chain is nonmagnetic and $\chi_m T$ should decrease continuously down to zero upon cooling to very low temperatures. This behavior contrasts with what is expected for an A-B heterobinuclear complex with $S_A = {}^1/_2$ and $S_B = {}^5/_2$. In this latter case, when the temperature is low enough for the $S = 3$ state to be totally depopulated, $\chi_m T$ is constant and equal to $2N\beta^2 g^2/k$ (i.e., 3.0 cm^3 mol^{-1} K if $g = 2$).

This preliminary work demonstrates the feasibility of preparing structurally ordered magnetic bimetallic chains, in spite of the kinetic and entropic hindrances. Our groups are now engaged in further studies along similar lines.

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Supplementary Material Available: Listings of atomic positional and thermal parameters for $NiMn(S_2C_2O_2)_2(H_2O)_{7.5}$ and $CuMn(S_2C_2O_2)_2(H_2O)_{7.5}$ (2 pages). Ordering information is given on any current masthead page.

Synthesis of Macrocyclic Peptide Thiolactones as Models of the Metastable Binding Sites of α_2-Macroglobulin and Complement Protein C3b

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A macrocyclic thiolactone ring is common to the metastable binding sites of two serum proteins, the protease inhibitor α_2-macroglobulin[1,2] and the complement component C3b.[3] As shown in structure **1**, the macrocycle is believed to be a derivative of 1-thia-5,8,11-triazacyclopentadecane having a novel thiolester bond between the cysteine thiol group and the side-chain carboxyl group of the second glutamic acid residue of Cys-Gly-Glu-Glu. The 15-membered ring contains three amide bonds, one thioester bond, and three chiral centers (3*R*, 9*S*, 12*S*; Cys and both Glu residues in the L configuration). This paper describes the synthesis and characterization of three macrocyclic peptide thiolactones (**1b,d,f**) as initial models of these metastable binding sites.

Proteolytic cleavage of complement protein C3 into C3a anaphylatoxin and the activated protein C3b exposes both the COOH-terminal inflammatory site[4] of C3a and the internal

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