Volume 30
Number 23
November 13, 1991

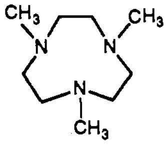
Inorganic Chemistry

Communications

Long-Range Magnetic Interactions between Manganese Centers Separated by 7 Å in $Mn^{III}Zn^{II}Mn^{III}$ and $Mn^{IV}Zn^{II}Mn^{IV}$ Complexes

The importance of magnetic coupling in multimetal proteins has stimulated much interest in exploring the ability of bridging multiatom ligands to mediate antiferromagnetic coupling in M(bridging ligand)M′ systems.[1] Both homo- and heteropolymetallic systems provide an opportunity to study experimentally and theoretically fundamental electronic processes such as electron exchange in biological metallic sites and/or their chemical models. Metal ions assembled together in such a multimetal system can exhibit drastically different magnetic properties from those of the individual ions due to electron exchange phenomenon. In addition, long-range spin exchange interactions may be intimately connected to and shed light upon mechanisms of long-range electron tunneling.

There has been much interest recently in the structure and properties of redox-active manganese complexes[2] primarily because of the involvement of manganese in photosynthetic water oxidation. In the present communication we describe two novel series of heterotrinuclear complexes with the structural units $[LMn^{III}\{\mu\text{-(dmg)}_3M^{II}\}Mn^{III}L]^{2+}$ and $[LMn^{IV}\{\mu\text{-(dmg)}_3M^{II}\}Mn^{IV}L]^{4+}$, where L = 1,4,7-trimethyl-1,4,7-triazacyclononane, dmg = dianion of dimethylglyoxime, and M^{II} = Zn, Cu, Ni, or high-spin Mn.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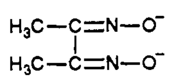
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Our continuing interest in long-range magnetic interactions[3] and the effectiveness of polyatomic bridging ligands in propagating exchange interaction[4] led us to adopt a synthetic strategy of using diamagnetic metal complexes as "spacers" for the paramagnetic centers and thus to change the distances between the interacting centers. We want to report here a moderately strong antiferromagnetic interaction between two Mn^{IV} centers, which are separated by a large distance of 7 Å. To the best of our knowledge this is the first report of such an interaction between two d^3 centers.

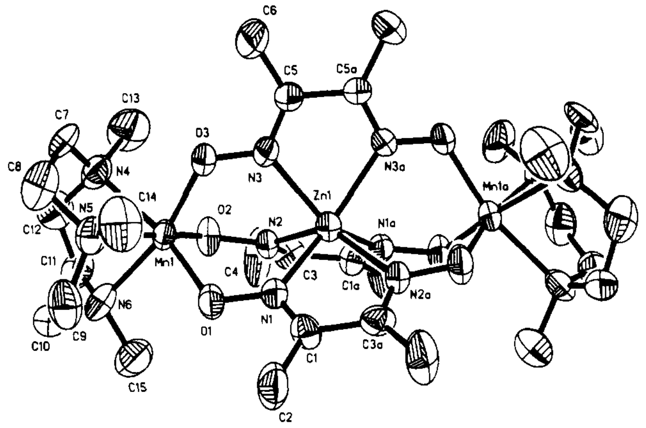

Figure 1. Structure of the cation $[L_2Mn_2(dmg)_3Zn]^{2+}$ in the crystal of **1**. Selected bond lengths (Å) and angles (deg) are as follows: Mn⋯Mn = 7.129 (2), Mn⋯Zn = 3.565 (2), Zn(1)-N(1) = 2.167 (8), Zn(1)-N(2) = 2.159 (7), Zn(1)-N(3) = 2.164 (9), Mn(1)-N(4) = 2.178 (8), Mn(1)-N(5) = 2.173 (8), Mn(1)-N(6) = 2.176 (8), Mn(1)-O(1) = 1.948 (6), Mn(1)-O(2) = 1.981 (7), Mn(1)-O(3) = 1.954 (6); Mn-Zn-Mn = 179.1 (2), N(1)-Zn(1)-N(1A) = 126.5 (3), N(1)-Zn(1)-N(2) = 87.8 (3), N(1)-Zn(1)-N(3) = 88.0 (3), O(1)-Mn(1)-O(2) = 98.0 (3), O(1)-Mn(1)-O(3) = 98.3 (3), O(1)-Mn(1)-N(4) = 168.0 (3), N(4)-Mn(1)-N(5) = 80.2 (3), N(5)-Mn(1)-N(6) = 80.6 (3), Mn(1)-O(1)-N(1) = 119.5 (6), Mn(1)-O(2)-N(2) = 117.8 (5), Mn(1)-O(3)-N(3) = 117.9 (6), Zn(1)-N(1)-O(1) = 123.7 (5), Zn(1)-N(2)-O(2) = 125.0 (6), Zn(1)-N(3)-O(3) = 124.6 (6).

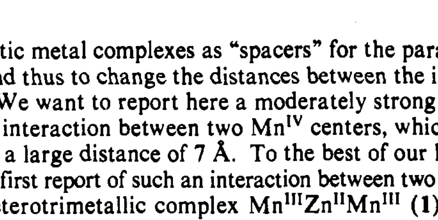

Figure 2. Cyclic voltammogram of **1** in CH_3CN at a scan rate of 0.2 V s^{-1}.

The heterotrimetallic complex $Mn^{III}Zn^{II}Mn^{III}$ (**1**) has been prepared[5] by treating a methanolic solution of the cyclic triamine with sequential additions of manganese(III) acetate dihydrate, zinc(II) acetate dihydrate, and dimethylglyoxime in the presence of triethylamine. Addition of $NaClO_4$ affords dark brown X-ray

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quality crystals. As anticipated, **1** gives rise to $Mn^{IV}Zn^{II}Mn^{IV}$ (**2**), when oxidized in acetonitrile with NO^+ as an oxidant.[5]

The structure of **1**[6] (Figure 1) clearly illustrates the trinuclear nature of the complex. A $[Zn(dmg)_3]^{4-}$ anion bridges two manganese(III) ions through its deprotonated oxime oxygens with a Mn···Zn separation of 3.565 (2) Å.

The manganese coordination geometry is distorted octahedral with three nitrogen atoms from the facially coordinated tridentate amine and three oxygen atoms from three oximate groups. The Mn–O and Mn–N distances are consistent with a high-spin d^4 configuration of the Mn(III) centers. The central ZnN_6 core is nearly trigonal prismatic. The six imine-nitrogen atoms are arranged around the Zn(II) center with a twist angle of 8.4° between the triangular faces comprising N(1)N(2)N(3) and N(1a)N(2a)N(3a) atoms. In other words the coordination polyhedron around Zn(II) is 51.6° away from octahedral symmetry.

The structure of **2** could not be determined because of the unavailability of good quality crystals; that the same structural unit is prevailing in **2** as in **1** can reasonably be assumed (loc. cit.).

Cyclic voltammetry[7] of **1** (Figure 2) shows two reversible steps at $E_1° = 0.81$ and $E_2° = 0.57$ V vs Ag/AgCl corresponding to the following electrochemical oxidation processes:

$$Mn^{IV}Zn^{II}Mn^{IV} \xrightleftharpoons{E_1°} Mn^{IV}Zn^{II}Mn^{III} \xrightleftharpoons{E_2°} Mn^{III}Zn^{II}Mn^{III}$$

Two additional quasi-reversible waves at more negative potentials, $E_3° = -0.17$ V and $E_4° = -0.45$ V vs Ag/AgCl, can be attributed to the following equilibria:

$$Mn^{III}Zn^{II}Mn^{III} \xrightleftharpoons{E_3°} Mn^{III}Zn^{II}Mn^{II} \xrightleftharpoons{E_4°} Mn^{II}Zn^{II}Mn^{II}$$

The reversible character[7] of $E_1°$ and $E_2°$ preclude any significant structural rearrangement during the redox processes; i.e., all three species have the same structure in solution and apparently can be described by the solid state structure of **1** as determined by X-ray diffraction. Identical cyclic voltammetric behavior has been observed for **2**.

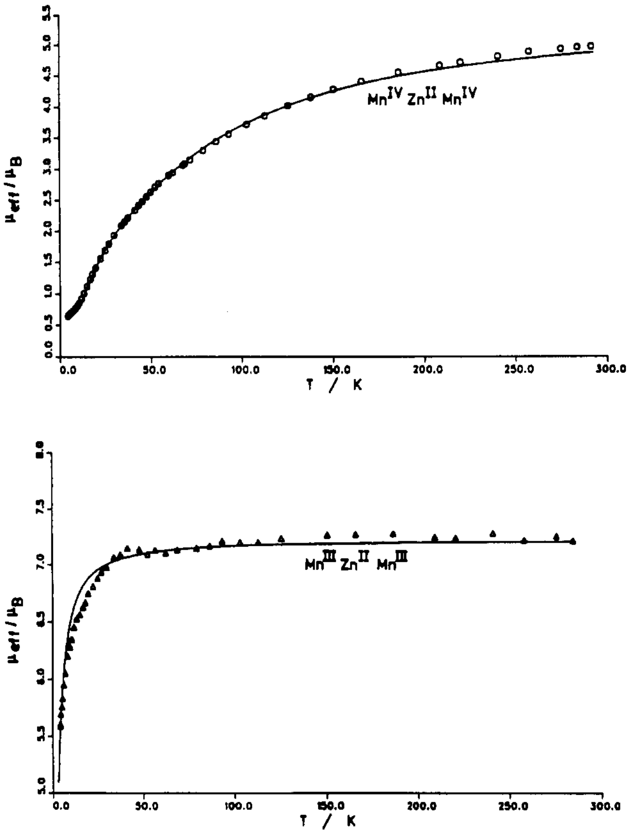

Figure 3. Plots of μ_{eff} vs T for solid **1** and **2**. The solid lines represent the best least-squares fits of the experimental data to the theoretical equation.

Figure 3 displays the μ_{eff} vs temperature data[8] for **1** and **2**. The μ_{eff} values for **1** vary slightly over the temperature range from 6.93 μ_B at 27.2 K to 7.22 μ_B at 284.5 K, which is not far away from the value $\mu_{eff} = 6.93$ μ_B, expected for two noncoupled spins of $S_1 = S_2 = 2$ with average $g = 2.00$ for an electron with no orbital angular momentum. Below 27 K the μ_{eff} begins to fall until at 4.1 K it is only 5.59 μ_B, presumably due to the sizable zero-field splitting of the orbitally nondegenerate 5_E ground state. However, this magnetic behavior may also be the result of weak antiferromagnetic interactions ($J = -0.3$ cm^{-1}) between neighboring trinuclear complexes. **1** is X-band EPR inactive even at 4 K, implying $D > 0.3$ cm^{-1}.

For **2** the magnetic moment decreases steadily with decreasing temperature and approaches the value of 0.64 μ_B at 4.1 K. This magnetic behavior is typical of antiferromagnetically coupled binuclear paramagnetic centers ($S_1 = S_2$) with a diamagnetic ground state. Appreciable spin coupling ($2J = -35.4$ cm^{-1}) is observed for **2** in which the Mn(IV) centers (d^3) are separated by a large distance of ca. 7.0 Å, which is definitely not the limit for the intramolecular spin interaction. Recently, a binuclear copper(II) complex has been described[3] where the magnetic su-

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(5) The procedure for the preparation of $[L_2Mn_2(dmg)_3Zn](ClO_4)_2$ (**1**) is as follows. Manganese(III) acetate dihydrate (0.268 g, 1 mmol) was added to a solution of 1,4,7-trimethyl-1,4,7-triazacyclononane (0.17 g, 1 mmol) in 50 mL of methanol under vigorous stirring. The resulting solution was charged with solid samples of 0.11 g (0.5 mmol) of $Zn(CH_3COO)_2 \cdot 2H_2O$, 0.116 g (1.5 mmol) of dimethylglyoxime, and 1 mL of triethylamine. The suspension was refluxed for 0.5 h under argon and then filtered in the air to get rid of any solid particles. $NaClO_4 \cdot H_2O$ (0.4 g) was added and the dark brown solution was kept at 4 °C. After 24 h dark brown crystals were collected by filtration and air-dried. Yield: 200 mg (≈20%). Anal. Calcd for $C_{30}H_{60}N_{12}O_{14}Cl_2Mn_2Zn$: C, 34.02; H, 5.71; N, 15.87; Mn, 10.38; Zn, 6.17; ClO_4, 18.78. Found: C, 34.1; H, 5.7; N, 15.7; Mn, 10.1; Zn, 6.3; ClO_4, 18.9. IR (KBr, cm^{-1}): ν(CN) 1596, ν(NO) 1185, $\nu(ClO_4)$ 1088 and 624. The procedure for the preparation of $[L_2Mn_2(dmg)_3Zn](ClO_4)_4$ (**2**) is as follows. A solution of **1** (100 mg) in CH_3CN (40 mL) under argon was stirred with 30 mg of $NOBF_4$ for 30 min. After addition of $NaClO_4$ (0.1 g) and after the reaction was allowed to stand overnight, dark brown microcrystals of **2** were collected by filtration and air dried. Yield: 90 mg (≈75%). Anal. Calcd for $C_{30}H_{60}N_{12}O_{22}Cl_4Mn_2Zn$: C, 28.64; H, 4.81; N, 13.36; Mn, 8.73; Zn, 5.20; ClO_4, 31.62. Found: C, 28.7; H, 4.9; N, 13.3; Mn, 8.9; Zn, 5.1; ClO_4, 31.4. IR (KBr, cm^{-1}): ν(CN) 1616, ν(NO) could not be observed, $\nu(ClO_4)$ 1088 and 624 (very strong). The other trimetallic complexes have been synthesized by a similar protocol, with all the complexes having satisfactory elemental analyses (C, H, N, Mn, M^{II}, and ClO_4) consistent with either the formulation $[L_2Mn^{III}_2(dmg)_3M^{II}](ClO_4)_2$ or $[L_2Mn^{IV}_2(dmg)_3M^{II}](ClO_4)_4$, where M^{II} = Zn, Cu, Ni, or Mn.

(6) Crystal data: $[C_{30}H_{60}N_{12}O_6Mn_2Zn](ClO_4)_2$, monoclinic, $C2/c$, a = 32.567 (5) Å, b = 9.032 (1) Å, c = 16.747 (2) Å, β = 108.46 (1)°, V = 4672.6 Å^3, Z = 4, D_c = 1.505 g cm^{-3}, λ(Mo Kα) = 0.71073 Å, μ = 1.21 mm^{-1}, $F(000)$ = 2200, T = 293 (1) K, R = 0.0797, R_w = 0.0653 for 2241 unique observed intensities ($F > 4\sigma(F)$), brown-red crystal, size 0.10 × 0.19 × 0.30 mm, Nicolet R3m/V diffractometer. The structure was solved by Patterson and Fourier methods (SHELXTL-PLUS) and full-matrix least-squares refinement based on F and 276 parameters, with all but H atoms refined anisotropically, H atoms fixed in idealized positions with U_{iso} = 0.08 Å^2, and empirical absorption correction via ψ scans.

(7) CV parameters: solvent CH_3CN, 0.1 M $(TBA)PF_6$, platinum-button working electrode, scan rates 20–500 mV s^{-1}, 298 K, potential range +2.0 to −1.7 V. That two reversible transfers of one electron per center occur is evident from the adherence to the following criteria: (i) the $E_1°$ and $E_2°$ values are independent of scan rates; (ii) the difference in peak potential values ΔE_p ($= E_{pa} - E_{pc}$) is constant and equal to 75 and 65 mV for the first ($E_1°$) and the second ($E_2°$) waves, respectively; (iii) the ratio of the peak currents due to cathodic (i_{pc}) and anodic (i_{pa}) sweeps is close to unity (1.04 ± 0.02 for the $E_1°$ wave and 1.02 ± 0.02 for the $E_2°$ wave) at different scan rates; (iv) the current function $i_p v^{-1/2}$ is substantially constant.

(8) Magnetic susceptibilities of powdered samples were recorded on a Faraday-type magnetometer using a sensitive Cahn R6 electrobalance in the temperature range 4.1–284.5 K. The applied magnetic field was ≈0.58 T. Experimental susceptibility data were corrected for the underlying magnetism. Corrections for diamagnetism were estimated as -508×10^{-6} cm^3 mol^{-1} for **1** and -571×10^{-6} cm^3 mol^{-1} for **2**. The susceptibility data were fitted by means of least-squares methods to the formula for the paramagnetic susceptibility which results from the isotropic spin Hamiltonian $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$ with $S_1 = S_2 = 2$ for **1** and $S_1 = S_2 = {}^3/_2$ for **2**. The best fit parameters are $J = -0.3$ cm^{-1} and g = 2.09 for **1** and $J = -17.7$ cm^{-1} and $g = 2.03$ for **2**.

perexchange mechanism is operative through the bridging terephthalato dianion between two copper centers separated by a distance of 11.25 Å. Of the two possible superexchange pathways, σ- and π-exchanges, the π-pathway appears to provide the dominant antiferromagnetic interaction in **2** (t_{2g}^3-configurated Mn(IV) centers).

The results described in the present paper show that tris(dimethylglyoximato)metalate(II) dianions are capable of coordinating as a bridging ligand to give rise to various kinds of trinuclear complexes. These materials are ideally suited for the study of intramolecular magnetic-exchange interactions.

Acknowledgment. This work is supported by the DFG. P.C. is thankful to Prof. K. Wieghardt for his help and interest. Our thanks are also due to Dr. E. Bill and Prof. A. Trautwein (Lübeck, Germany) for obtaining the EPR spectra.

Supplementary Material Available: Listings of atomic coordinates and isotropic thermal parameters (Table SI), bond lengths and angles (Tables SII and SIII), anisotropic thermal parameters (Table SIV), and hydrogen atom parameters (Table SV) (9 pages); a listing of observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

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Received May 15, 1991

Synthesis and Characterization of (β-Diketonato)copper(I) Alkyne Complexes: Structural Characterization of (Hexafluoroacetylacetonato)(diphenylacetylene)copper(I)

The synthesis of copper compounds for the chemical vapor deposition (CVD) of copper is receiving much research attention. Among the requirements of copper compounds for this purpose are high volatility, to achieve high deposition rates, and the presence of a facile decomposition mechanism, to facilitate deposition of pure copper films.[1] In the past it has proven difficult to satisfy all these requirements simultaneously. Copper(II) bis(β-diketonates) exhibit high vapor pressures,[2] but their thermal decomposition results in formation of pure films only at a substrate temperature of 350 °C.[3] At higher temperatures significant carbon and oxygen contamination has been observed, while, below this temperature, no deposition is observed. On the other hand, copper(I) compounds such as copper(I) *tert*-butoxide[4] and cyclopentadienylcopper(I) Lewis base compounds[5-7] have lower volatility but have led to the deposition of purer copper films over a lower and wider temperature range. More recently the deposition of copper films from copper(I) β-diketonate compounds, (β-diketonate)CuL$_n$, where L = PMe$_3$, vinyltrimethylsilane, and 1,5-cyclooctadiene (1,5-COD) and n = 1, have been described.[1,8-13] These species exhibit interesting structural chemistry. The monophosphine adducts such as (β-diketonate)Cu(PMe$_3$) are monomeric with an approximately trigonal-planar copper(I) coordination environment,[11] while (β-diketonate)Cu(1,5-COD) has been described as "3 + 1" coordinate with an asymmetrically bound 1,5-COD ligand.[12] Their volatility is close to that of the copper(II) bis(β-diketonate) compounds, and a thermally induced disproportionation mechanism (eq 1) has resulted in the deposition

$$2(\beta\text{-diketonate})\mathrm{Cu^IL}_n \rightarrow \mathrm{Cu}^0 + \mathrm{Cu^{II}}(\beta\text{-diketonate})_2 + 2n\mathrm{L} \qquad (1)$$

of pure copper films.[1,8-13] In addition, selective deposition of copper from these species onto various substrates has been observed as a function of the nature of the substrate, the deposition temperature, and the nature of the β-diketonate ligand.[1,9] At present, there is no fundamental understanding of the factors which affect selective deposition of copper from such precursors, although a number of studies have addressed the reactions of β-diketones with metal surfaces.[14] The first step in such a study is to device a series of compounds in which the steric and electronic demands of both the β-diketonate and Lewis base ligands can be subtly varied in a systematic fashion and which deposit pure copper via thermally induced disproportionation. Here we report the synthesis spectroscopic and structural characterization of a new series of compounds, (β-diketonato)copper(I) alkyne, which are volatile, monomeric, and capable of systematic substitution and undergo thermally induced disproportionation reactions to produce pure copper films.

The (β-diketonato)copper(I) alkyne complexes, where alkyne = bis(trimethylsilyl)acetylene (BTMSA), diphenylacetylene (DPA), and 2-butyne and where β-diketonate = hexafluoroacetylacetonate (hfac), were prepared by the addition of Na(β-diketonate) to a mixture of CuCl and the corresponding alkyne in diethyl ether solution according to the reaction shown in eq 2.[15] Similar methods have been used to prepare cyclo-

$$\mathrm{CuCl} + \text{excess alkyne} + \mathrm{Na(hfac)} \rightarrow \mathrm{(hfac)Cu(alkyne)} + \mathrm{NaCl} \qquad (2)$$

pentadienylcopper(I) alkyne complexes, and dimeric (alkyne)-copper(I) chloride complexes have previously been isolated.[16] The

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(15) A typical experimental procedure is presented here together with spectroscopic and analytical data for three representative compounds. A solution containing an excess (about 1.5 equiv) of alkyne in 50 mL of Et$_2$O was transferred to a cold (0° C) slurry solution of CuCl in 50 mL of Et$_2$O, and the solution mixture was stirred for 30 min to make the alkyne adduct of CuCl. Addition of a solution of Na(β-diketonate) (1.2 equiv) in Et$_2$O into the reaction flask resulted in immediate formation of a yellow solution, which was continuously stirred for 5 h. Removal of volatile species in vacuo gave a pale yellow solid. The pure product (β-diketonate)Cu(alkyne) was obtained by extraction and recrystallization with pentane in approximately 30–60% yield depending on the alkyne. The yields and properties are summarized as follows: (hfac)Cu(2-butyne), 33% yield, pale yellow solid, sublimed at room temperature; (hfac)Cu(BTMSA), 62% yield, yellow solid, sublimed at room temperature; (hfac)Cu(DPA), 35% yield, pale yellow solid, sublimes >70 °C. Spectroscopic characterization data are available as supplementary material.