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(10) NMR (CDCl₃, 270 MHz) δ 1.21 (s, 3 H), 1.26 (m, 6 H), 2.63 (d, 1 H, *J* = 16 Hz), 2.89 (q, 2 H, *J* = 8 Hz), 2.98 (d, 1 H, *J* = 16 Hz), 4.15 (q, 2 H, *J* = 8 Hz); mass spectrum *m/e* (rel intensity, assigned ion) 160 (31.87 %, M⁺ − 45, OEt), 159 (10.08), 144 (100, base ion, M⁺ − 61, SEt), 143 (20.73), 116 (83.10, M⁺ − 89, COSEt), 115 (22.14). We thank Professor P. Dowd for the mass spectral data.

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Binuclear Copper(II) "Face to Face" Inclusion Complex of a Macrotricyclic Ligand

Sir:

The synthesis of macropolycyclic ligands allows the preparation of complexes containing several transition metal ions located *inside* the intramolecular cavity. The case of *binuclear "face to face"*[1] complexes where the metal ions are not bridged by a ligand and are separated by a distance of the order of 4 to 6 Å is particularly interesting: (i) there should be no direct interaction between the two metal cations, (ii) an external
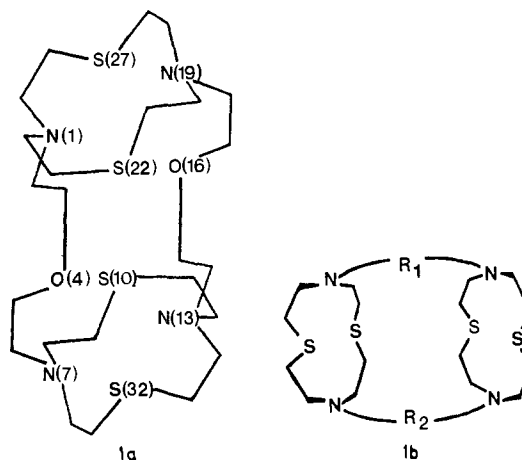
Figure 1. The ligand (L) tricyclo[17.5.5.5⁷,¹³]tetraaza-1,7,13,19-dioxa-4,16-tetrathia-10,22,27,32-tetratriacontane, $C_{24}H_{48}N_4O_2S_4$, and atomic leading.
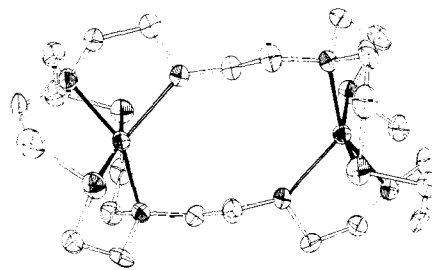
Figure 2. Structure of $[Cu_2 \subset (L)]^{4+}$ cation. All atoms are represented by 50% probability thermal ellipsoids. Selected bond distances (in Ångstroms) follow: Cu(1)–N(1), 2.020 (5); Cu(1)–N(19), 2.024 (6); Cu(1)–O(4), 2.291 (5); Cu(1)–S(22), 2.313 (1); Cu(1)–S(27), 2.323 (1); Cu(2)–N(7), 2.047 (6); Cu(2)–N(13), 2.058 (5); Cu(2)–O(16), 2.283 (4); Cu(2)–S(10), 2.306 (1); Cu(2)–S(32), 2.332 (1). Selected bond angles (in degrees) follow: N(1)–Cu(1)–S(22), 88.9 (1); N(1)–Cu(1)–S(27), 88.2 (1); N(19)–Cu(1)–S(22), 87.3 (1); N(19)–Cu(1)–S(27), 88.0 (1); O(4)–Cu(1)–N(1), 80.7 (1); O(4)–Cu(1)–N(19), 126.6 (2); O(4)–Cu(1)–S(22), 103.4 (1); O(4)–Cu(1)–S(27), 91.7 (1); N(7)–Cu(2)–S(10), 88.0 (1); N(7)–Cu(2)–S(32), 87.8 (1); N(13)–Cu(2)–S(10), 88.4 (1); N(13)–Cu(2)–S(32), 87.9 (1); O(16)–Cu(2)–N(7), 126.4 (2); O(16)–Cu(2)–N(13), 79.9 (1); O(16)–Cu(2)–S(10), 103.7 (1); O(16)–Cu(2)–S(32), 92.5 (1). The most attractive interatomic distances follow: Cu(1)⋯Cu(2), 5.621 (1); O(4)⋯O(16), 4.211 (6) Å.

substrate should be able to interact by *inclusion* simultaneously with the two metal ions. Such compounds may be able to act as *catalysts*, as dioxygen or dinitrogen *carriers*, and as attractive *models* for some metalloproteins.[2,3]

Ligand (L) shown in Figure 1a is tetraaza-1,7,13,19-dioxa-4,16-tetrathia-10,22,27,32-tricyclo-[17.5.5.5⁷,¹³]tetratriacontane, $C_{24}H_{48}N_4O_2S_4$.[4] It contains two twelve-membered macrocyclic subunits with four hetero donor atoms, N_2S_2. The two subunits are joined together by two lateral five-membered chains, each carrying an ether group.

Addition of copper(II) perchlorate to a chloroform solution of L gives a violet solution for a 2:1 ratio of metal to ligand.[4] Crystals of $[Cu^{II}{}_2 \subset (C_{24}H_{48}N_4O_2S_4)](ClO_4)_4(H_2O)$ **1** obtained by slow evaporation produce, when redissolved in nitromethane, intense absorptions near 400 and 600 nm (380 nm ($\epsilon \simeq 4000$ M⁻¹ cm⁻¹) and 550 nm ($\epsilon = 1200$ M⁻¹ cm⁻¹)). The very strong absorption near 400 nm can be assigned to $\pi(s)$ → Cu charge transfer. The band at 550 nm could be assigned also to a charge-transfer transition ($\sigma(s)$ → Cu); however, in view of the somewhat distorted geometry around the copper(II) cations (see below) and the presence of two thioethers in the ligand donor set, this transition could also arise from a ligand field absorption of enhanced intensity.[5-7]

1 crystallizes in the monoclinic space group $P2_1/n$ (an alternate setting of $P2_1/c$) with $a = 15.736$ (4), $b = 27.491$ (7),

$c = 9.493$ (3) Å; $\beta = 100.50$ (2)°; $\rho_o = 1.79$ (2), $\rho_c = 1.802$ g cm^{-3} with $Z = 4$. A total of 6546 independent nonzero reflections were measured on a Philips PW1100 diffractometer and 4874 reflections with $I > 3\sigma(I)$ were used in subsequent structure solution and least-squares refinement. Final block-diagonal matrix least-squares refinements with anisotropic thermal parameters for all nonhydrogen atoms converged to $R_F = 0.062$ and $R_{wF} = 0.091$.

The structure of **1** consists of discrete complex cations $[Cu^{II}_2 \subset (L)]^{4+}$ (Figure 2), perchlorate anions, and water molecules.

The two copper(II) ions are located *inside*[8] the molecular cavity of the macrotricyclic ligand (L). Each cation is bound to two nitrogens, two sulfurs, and one oxygen atom. The data (distances, angles, and dihedral angles) show that the complex cation has a virtual center of symmetry, a feature which implies an *identical role* for the two copper(II) cations. Their coordination polyhedron is a somewhat distorted tetragonal pyramid in which the metal ion lies ~0.34 Å *out* of the basal N$_2$S$_2$ plane[9,10] toward the axial oxygen atom. The four Cu–N and four Cu–S bond distances range from 2.020 (5) to 2.058 (5) and 2.306 (1) to 2.332 (1) Å, respectively. The values of the Cu(1)–O(4) and Cu(2)–O(16) bond lengths are 2.291 (5) and 2.283 (4) Å. The Cu(1)···Cu(2) separation of 5.621 (1) and the O(4)···O(16) distance of 4.211 (6) Å indicate that (i) there is little if any direct interaction between the two copper centers, as shown also by the EPR spectral data[4] ($g_\perp = 2.045\ g_\| = 2.132$ and $A_\| = 8$ mK); (ii) there is a *large cavity* between the two copper cations which should allow *insertion* of a diatomic substrate. There is no evidence that such a process occurs; however, when adding KO$_2$ to $[Cu^{II}_2 \subset (L)]^{4+}$ or dioxygen to $[Cu^I_2 \subset (L)]^{2+}$, similar electronic spectra are obtained.[4] Among the possible binding modes of O$_2^{n-}$ ($n = 1, 2$) to two metal centers[11] (μ-dioxygen bridging), the transplanar C_{2h} and nonplanar C_2 modes fit particularly well for the complex cation present in **1** since these modes necessarily impose a Cu···Cu distance varying between 4.0 and 5.2 Å owing to the Cu–O–O and dihedral Cu–O–O–Cu angles. In $[Cu^{II}_2 \subset (L)]^{4+}$ the N$_2$S$_2$ planes are almost parallel, the angle between their normals being 1.34°; this feature should lead to a value near 180° for the Cu–O–O–Cu torsion angle. The planar cis C_{2v} bonding mode of O$_2$ as proposed for hemocyanin[11a] probably necessitates the synthesis of a dissymetric ligand with $R_1 \neq R_2$ (Figure 1b).

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Highly Reduced Organometallics. 3.[1]
Tetrasodium Tetracarbonylmetalates(4−) of Chromium, Molybdenum, and Tungsten, Na$_4$M(CO)$_4$

Sir:

Highly reduced organometallics which have properties consistent with those expected for noncluster binary carbonyl trianions, i.e., V(CO)$_5^{3-}$,[2] M(CO)$_4^{3-}$ (M = Mn and Re),[3] and M′(CO)$_3^{3-}$ (M′ = Co, Rh, and Ir),[1] have been recently prepared by reduction of carbonylmetalate monoanions, M(CO)$_x^{1-}$, in liquid ammonia and/or hexamethylphosphoramide (HMPA). We now report on the syntheses and properties of more highly reduced species, tetrasodium tetracarbonylmetalates(4−) of chromium, molybdenum, and tungsten. These are the first examples of noncluster binary metal carbonyl tetraanions[4] and the only compounds presently containing molybdenum and tungsten in a formal −4 oxidation state.[5] A new synthetic approach, which may be of general importance as a route to other families of "superreduced" organometallics, has been used in this synthesis of Na$_4$M(CO)$_4$: *the reduction of substituted organometallics*.

Reduction of a noncluster metal complex containing both good and poor π-acceptor ligands often causes preferential loss of weaker or non-π acceptors.[6] Trivial examples where this generalization holds include the reduction of metal carbonyl halides.[7] More interesting and less well-understood examples involve reduction of phosphine or cyclopentadienyl substituted metal carbonyls.[8] We find that reduction of diamine substituted group 6 carbonyls, i.e., (TMEDA)M(CO)$_4$,[9] by sodium in liquid ammonia[10] provides essentially quantitative yields of analytically pure Na$_4$M(CO)$_4$ (**1**)[11] according to the equation

$$(TMEDA)M(CO)_4 + 4Na \rightarrow Na_4M(CO)_4 + TMEDA$$
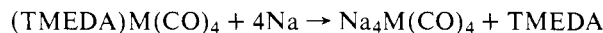
The presence of the readily displaceable TMEDA ligand, which is not attacked by sodium in liquid ammonia, and the preformed M(CO)$_4$ unit appear to be of crucial importance in this synthesis.[12,13]

Infrared spectra of **1** (Figure 1) show bands at exceedingly low energies for terminal carbonyl groups. These values are almost 200 cm^{-1} lower than those reported for Na$_3$M′(CO)$_4$ (M′ = Mn and Re)[3] which suggests that these insoluble "tetraanions" are most reasonably formulated as [M(CONa)$_4$]$_x$ where extensive and strong sodium ion–carbonyl oxygen interactions may be responsible for the very low ν(CO) values.[14,15] Differences in the spectra of Na$_4$W(CO)$_4$ and other Na$_4$M(CO)$_4$ shown in Figure 1 are not understood; however, they do not appear to be due to carbonyl containing impurities which form on partial oxidation of Na$_4$M(CO)$_4$. Other preparations of Na$_4$Mo(CO)$_4$ have provided infrared spectra nearly identical with those of Na$_4$W(CO)$_4$.

Treatment of slurries of **1** in tetrahydrofuran (THF) with 2 equiv of Ph$_3$SnCl results in an immediate reaction and formation of new anions which, on the basis of infrared data,