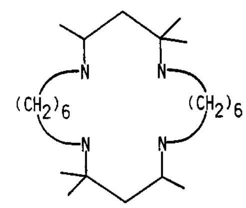
A Binuclear Copper(II) Complex with Both Metal Ions Bound within a 22-Membered Homologue of Curtis-Type Tetraaza Macrocyclic Ligands

Sir:

There is great current interest in binuclear metal complexes, particularly those of copper, in regard to metal–metal electron-exchange interactions and electron-transfer properties and as synthetic analogues for some metalloproteins.[1] Recently Nelson et al.[2] and Lippard et al.[3] reported binuclear copper(II) complexes with macrocyclic ligands that have six donor atoms. We now report the synthesis of 2,2,4,13,13,15-hexamethyl-1,5,12,16-tetraazacyclodocosane (hereafter abbreviated as Me$_6$[22]aneN$_4$) and the preparation and structure of a novel di-μ-alkoxo-bridged binuclear copper(II) complex with the meso [4*R*(*S*),15*S*(*R*)] form of Me$_6$[22]aneN$_4$, along with the electronic spectrum and magnetic properties.



Me$_6$[22]aneN$_4$

The ligand Me$_6$[22]aneN$_4$ was prepared by a method[4,5] for the synthesis of 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, Me$_6$[14]aneN$_4$, with slight modifications. Equimolar amounts of hexamethylenediamine dihydroperchlorate and hexamethylenediamine were stirred for $^1/_2$ h in absolute methanol, and to this solution was added dry acetone below −10 °C.[6] The solution was kept in a refrigerator for 2 days to yield, in 90% yield, a white precipitate of 2,2,4,13,13,15-hexamethyl-1,5,12,16-tetraazacyclodocosa-4,15-diene dihydroperchlorate, Me$_6$[22]dieneN$_4\cdot$2HClO$_4$.[7] The freshly prepared Me$_6$[22]dieneN$_4\cdot$2HClO$_4$ was reduced with NaBH$_4$ to Me$_6$[22]aneN$_4$ in a manner similar to that for hydrogenation of Me$_6$[14]dieneN$_4$[5] (yield 50%).[8] The ligand, Me$_6$[22]aneN$_4$, thus obtained was an approximately 1:1 mixture of meso [4*R*(*S*),15*S*(*R*)] and racemic [4*R*(*S*),15*R*(*S*] isomers, as evidenced by its ^{13}C NMR spectrum. The meso and racemic isomers were separated by fractional recrystallization from ethanol. The less soluble isomer was found to be the meso form. This fact is evidenced by comparison of the ^{13}C NMR spectra with that of the free ligand recovered from a Cu(II) complex containing the meso form ligand (vide infra).[9]

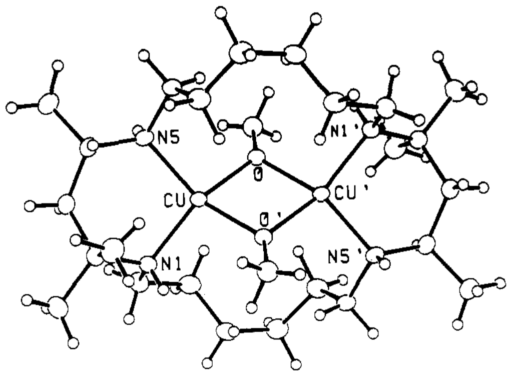


Figure 1. Perspective view of [Cu$_2$(*ms*-Me$_6$[22]aneN$_4$)(OCH$_3$)$_2$]$^{2+}$. A crystallographic center of symmetry is located at the midpoint of the line connecting two copper atoms. Bond lengths (Å): Cu–Cu′, 3.034 (1); Cu–O, 1.952 (2); Cu–O′, 1.938 (2); Cu–N(1), 2.007 (2); Cu–N(5), 2.018 (3). Bond angles (deg): Cu–O–Cu′, 102.50 (8); O–Cu–O′, 77.50 (8).

To dry methanol solutions of the meso form ligand and of 2 equiv of Cu(ClO$_4$)$_2\cdot$6H$_2$O was added 2,2-dimethoxypropane (10% in volume), and each solution was refluxed for $^1/_2$ h to remove water. When the two solutions were mixed at room temperature, immediate complexation occurred, yielding a blue-green precipitate. Recrystallization from hot methanol gave polyhedral crystals, elemental analysis of which was consistent with [Cu$_2$(Me$_6$[22]aneN$_4$)(OCH$_3$)$_2$](ClO$_4$)$_2$.[10]

The crystal structure has been determined by single-crystal X-ray analysis. Crystal data: Cu$_2$Cl$_2$O$_{10}$N$_4$C$_{26}$H$_{58}$; M_r = 784.8; a = 16.734 (3), b = 8.549 (1), c = 13.103 (2) Å; β = 111.05 (1)°; V = 1749.4 (5) Å^3; Z = 2; D_c = 1.49, D_m = 1.50 g cm^{-3}; space group $P2_1/a$. The structure was solved by Patterson and Fourier methods and refined to R = 0.037 for 3806 observed reflections.[11] A perspective drawing of the complex is shown in Figure 1, along with selected distances and angles.

The macrocyclic ligand in this complex is the meso isomer, and the six-membered chelate rings take chair forms. Of particular interest is the fact that two alkoxo-bridged copper ions are bound within the tetraaza macrocycle. The copper ions are tetracoordinated with two N atoms of the macrocycle and two O atoms of the alkoxo groups, the dihedral angle between the NCuN and OCuO planes being 36.6°. Two copper ions and four N atoms of the macrocycle are coplanar within 0.001 Å. The Cu···Cu separation is 3.034 (1) Å, and

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(1) See, for example: (a) Malmstrom, B. G. *Adv. Chem. Ser.* **1977**, *No. 162*, 173. (b) Tweedle, M. F.; Wilson, L. J.; Garcia-Iniguez, L.; Babcock, G. T.; Palmer, G. *J. Biol. Chem.* **1978**, *253*, 8065.

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(6) The same reaction at room temperature did not give the desired product but yielded brown tarry materials. Similar condensation reactions of penta-, octa-, or dodecamethylenediamine hydroperchlorate with dry acetone at low temperature (below −10 °C) proceeded successfully to give white precipitates of the 20-, 26-, and 34-membered homologues, Me$_6$[20]dieneN$_4\cdot$2HClO$_4$, Me$_6$[26]dieneN$_4\cdot$2HClO$_4$, and Me$_6$[34]dieneN$_4\cdot$2HClO$_4$. Reductions of these dienes with NaBH$_4$ (see text) yielded the corresponding tetraazacycloalkanes, Me$_6$[20]aneN$_4$, Me$_6$[26]aneN$_4$, and Me$_6$[34]aneN$_4$. The cyclic nature of these compounds was evidenced by the ^{13}C NMR spectra and an X-ray analysis of *ms*-(Me$_6$[20]aneN$_4$)$\cdot$4HClO$_4\cdot$6H$_2$O. Details will be reported elsewhere.

(7) This material is unstable as is the 18-membered homologue Me$_6$[18]dieneN$_4$ (Martin, J. W. L.; Timmons, J. H.; Martell, A. E.; Willis, C. J. *Inorg. Chem.* **1980**, *19*, 2328) and deteriorates to brown tar within 1 day at room temperature even in vacuo. IR (Nujol mull, cm^{-1}): ν(NH) 3130, ν(C=N) 1660. ^{1}H NMR (CD$_3$CN, 100 MHz, 0 °C, δ): 1.33 (s, 2, –C(CH$_3$)$_2$–), 1.89 (s, 1, N=C(CH$_3$)–). Me$_6$[22]dieneN$_4$ decomposes rapidly in CD$_3$CN at room temperature.

(8) Anal. Calcd for Me$_6$[22]aneN$_4$, C$_{24}$H$_{52}$N$_4$: C, 72.67; H, 13.21; N, 14.12. Found: C, 72.14; H, 13.68; N, 13.91.

(9) For *ms*-Me$_6$[22]aneN$_4$: mp 127 °C; IR (Nujol mull) ν(NH) 3250 cm^{-1}. For *rac*-Me$_6$[22]aneN$_4$: mp 75–76 °C; IR (Nujol mull) ν(NH) 3245 cm^{-1}. ^{13}C{^{1}H} NMR spectra of the meso and racemic ligands each consist of 12 line signals, carbon atoms being pairwise equivalent in each isomer. ^{13}C NMR (CDCl$_3$, 25 MHz, δ): *ms*-Me$_6$[22]aneN$_4$, 21.6, 25.7, 28.5, 28.6, 29.1, 31.0, 31.4, 42.2, 48.0, 48.7, 51.5, 52.8; *rac*-Me$_6$[22]aneN$_4$, 21.6, 26.2, 28.3, 28.4, 29.1, 31.0, 31.3, 42.1, 47.8, 48.2, 51.7, 52.9.

(10) Anal. Calcd for [Cu$_2$(Me$_6$[22]aneN$_4$)(OCH$_3$)$_2$](ClO$_4$)$_2$, Cu$_2$Cl$_2$C$_{26}$H$_{58}$N$_4$O$_{10}$: C, 39.79; H, 7.45; N, 7.14. Found: C, 39.18; H, 7.74; N, 6.91. Reaction of Cu(ClO$_4$)$_2\cdot$6H$_2$O with the ligand mixture in the meso and racemic forms yielded only [Cu$_2$(*ms*-Me$_6$[22]aneN$_4$)(OCH$_3$)$_2$](ClO$_4$). This was evidenced by IR spectra of the complexes and ^{13}C NMR spectra of the free ligand recovered from the Cu(II) complexes.

(11) A Rigaku AFC-5 diffractometer was used, Mo Kα, $|F| > 3\sigma(F)$. The procedures used for data collection as well as methods used in the solution and refinement of the structure were standard and have been described previously (Ito, T.; Toriumi, K.; Ito, H. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1096).

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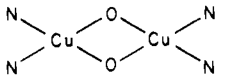
the angle Cu–O–Cu is 102.50 (8)°. These values suggest the possibility that a relatively strong antiferromagnetic interaction operates between the Cu(II) ions.[12] In fact, the magnetic moments were 0.87 μ_B at 299 K and 0.19 μ_B at 81 K.[13] No ESR signal was observed in DMF solution at liquid nitrogen temperature.

A DMF solution of the complex shows three electronic absorption bands at 13.7 × 10^3 (ϵ = 340), 16.6 × 10^3 (ϵ = 320), and 25.4 × 10^3 cm^{-1} (ϵ = 2200). The spectrum was essentially the same as a solid-state absorption spectrum in Nujol mull, indicating that the coordination geometry remains unchanged in solution. Two bands at lower energy are assigned to d–d transitions. It has been reported that binuclear copper(II) complexes having the



chromophore show a characteristic band at (24–29) × 10^3 cm^{-1} associated with a pπ(O) → $d_{x^2-y^2}$(Cu) transition.[14] This binuclear band corresponds to the absorption at 25.4 × 10^3 cm^{-1}.

Further characterization and study on the related chemistry are in progress.

Acknowledgment. The authors thank Professors S. Kida and H. Okawa for magnetic susceptibility measurements.

Registry No. Me_6[22]dieneN_4·2$HClO_4$, 86012-79-5; *meso*-Me_6-[22]aneN_4, 86012-80-8; *rac*-Me_6[22]aneN_4, 86087-12-9; [Cu_2-(Me_6[22]aneN_4)(OCH_3)$_2$](ClO_4)$_2$, 85995-18-2; Me_6[20]dieneN_4·2$HClO_4$, 85995-23-9; Me_6[26]dieneN_4·2$HClO_4$, 85995-25-1; Me_6-[34]dieneN_4·2$HClO_4$, 85995-27-3; Me_6[20]aneN_4, 85995-28-4; Me_6[26]aneN_4, 85995-29-5; Me_6[34]aneN_4, 86012-81-9; hexamethylenediamine dihydroperchlorate, 41195-09-9; hexamethylenediamine, 124-09-4; acetone, 67-64-1; pentamethylenediamine hydroperchlorate, 85995-19-3; octamethylenediamine hydroperchlorate, 85995-20-6; dodecamethylenediamine hydroperchlorate, 85995-21-7.

Supplementary Material Available: Tables of atomic coordinates of non-hydrogen atoms and bond lengths and angles and a stereoview of the molecular structure (3 pages). Ordering information is given on any current masthead page.

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[13] Temperature dependence of the magnetic susceptibility failed to obey perfectly the Bleaney–Bowers equation on the basis of a binuclear structure. But the value of 2*J* was estimated to be ~−600 to −700 cm^{-1}.

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Division of Applied Molecular Science
Institute for Molecular Science
Okazaki National Research Institutes
Okazaki 444, Japan

Masahiro Yamashita
Haruko Ito
Tasuku Ito*

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Localized Ion States in the Valence Photoelectron Spectra of Mixed-Metal Carbonyl Sulfide Clusters

Sir:

Advances in the field of cluster chemistry in the past decade have been substantial, and numerous reviews have appeared discussing their unique chemical and structural properties.[1] These compounds are of additional interest because of the possible similarities between chemisorption on transition-metal surfaces and the chemistry of transition-metal clusters.[2] Two important catalytic aspects of the interaction between metals and sulfur are the effectiveness of sulfur as a catalyst poison and the importance of metal sulfides for hydrodesulfurization.[3] In our previous work we have found that the combination of photoelectron (PE) spectroscopy has proven useful in elucidating the electronic structure of cluster systems.[4]

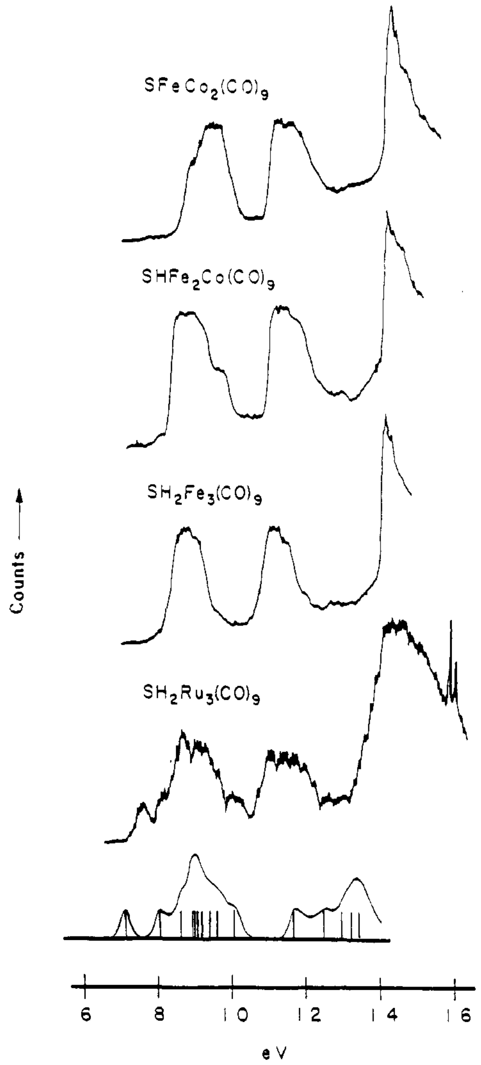

Figure 1. Partial photoelectron spectra for $SFeCo_2(CO)_9$, $SHFe_2$-$Co(CO)_9$, $SH_2Fe_3(CO)_9$, and $SH_2Ru_3(CO)_9$. The theoretical spectrum of $SH_2Fe_3(CO)_9$ derived from Fenske–Hall molecular orbital calculations is shown under the experimental PE spectra.

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