Pr)Cl]$_2$[Cl]$_2$, 80583-97-7; [Cu(L$_6$-Pr)(H$_2$O)(FBF$_3$)][BF$_4$], 80584-45-8; [Cu(L$_6$-Pr)Cl]$_2$[Cl]$_2$, 80593-39-1; [Co(L$_6$-Pr)(H$_2$O)(OClO$_3$)][ClO$_4$], 80584-02-7; [Cu(L$_7$-Et)(H$_2$O)(OClO$_3$)][ClO$_4$], 80584-04-9; [Cu(T$_1$)(H$_2$O)(OClO$_3$)][ClO$_4$], 80584-43-6; [Cu(T$_1$-Pr)(H$_2$O)(OClO$_3$)][ClO$_4$], 80593-67-5; Cu^{I}(L$_5$-Pr)Cl, 80583-98-8; [Cu^{I}(L$_5$-Pr)][BF$_4$], 80584-00-5; [Cu^{I}(L$_6$-Pr)][BF$_4$], 80584-06-1; L$_4$, 80583-50-2; L$_4$-Pr, 80572-94-7; L$_5$, 33007-61-3; L$_5$-Pr, 80572-95-8; L$_6$, 80572-96-9; L$_7$, 80572-97-0; L$_7$-Et, 80572-98-1; L$_7$-Pr, 80572-99-2; T$_1$, 80573-00-8; T$_2$, 80573-01-9; dinitro-3,4,5,6-tetramethylbenzene, 18801-63-3; pentamethylbenzene, 700-12-9; thiodipropionic acid, 111-17-1; phenylenediamine, 95-54-5; 2-methylpropanetricarboxylic acid, 1590-02-9.

Supplementary Material Available: Tables VI and X giving observed and calculated structure factor amplitudes (×10) and Tables V and IX giving anisotropic thermal parameters for the copper(II) and copper(I) structures, respectively (96 pages). Ordering information is given on any current masthead page.

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Preparation and Crystal Structure of Tetracopper(I) Tetrakis(6-methyl-2-oxypyridine), [Cu$_4$(mhp)$_4$]

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Sodium 6-methyl-2-oxypyridine, Na(mhp), reacts with copper(I) trifluoroacetate in ethanol to produce the tetrameric complex [Cu$_4$(mhp)$_4$], the structure of which has been determined by X-ray diffraction. Crystals are monoclinic, of space group $P2_1$, with a = 7.499 (2) Å, b = 14.572 (3) Å, c = 12.210 (3) Å, β = 107.61 (2)°, and Z = 2. The final R is 0.0297 for 2199 unique diffractometer-measured reflections. The copper atoms in the molecule form a puckered square, each edge of which is bridged by a single mhp ligand. The Cu···Cu edges range from 2.656 (1) to 2.709 (1) Å.

Introduction

The mhp anion (Hmhp = 6-methyl-2-hydroxypyridine) has been introduced in recent years as a bridging ligand for metal–metal-bonded dimers of the type [M$_2$(mhp)$_4$]. It belongs to the class of ligands which, by virtue of their electronic and steric properties, promote extremely short quadruple bonds between metal atoms of the group 6 triad (Cr, Mo, W).[2] Very short separations between pairs of metal atoms are also observed in the corresponding complexes of ruthenium,[3] rhodium,[4,5] and palladium,[6] in which the formal metal–metal bond orders are considered to be 2, 1, and 0, respectively. In all these complexes, the four bridging mhp ligands are arranged with M–N and M–O bonds each trans to their own kind, so that the overall molecular symmetry approximates closely to D_{2d}. In the case of rhodium, apart from this 2:2 ligand arrangement, a 3:1 arrangement is possible, such that the rhodium atom bonded to three mhp oxygen atoms also takes up an axial ligand approximately collinear with the Rh–Rh bond.[5,7] Mixed-ligand complexes of rhodium have also been prepared, containing both mhp and acetate bridges, the total number of bridging ligands being always 4.[5]

The mhp anion can also act as a bidentate ligand to a single metal atom[8] and, in a protonated form, as an unidentate ligand.[7]

We now report the preparation and crystal structure determination of the tetrameric copper(I) complex [Cu$_4$(mhp)$_4$], in which pairs of copper atoms are spanned by *single* mhp bridges.

Experimental Section

Preparation of [Cu$_4$(mhp)$_4$]. Sodium (0.219 g, 9.5 mmol) was dissolved in ethanol (AnalaR grade). Hmhp (1.039 g, 9.5 mmol) was added, followed by copper(I) trifluoroacetate (1.682 g, 9.5 mmol in terms of the monomeric formula). A white precipitate formed almost immediately. The reaction mixture was stirred at room temperature for 1 h and then evaporated to dryness. Extraction with CH$_2$Cl$_2$ (50 mL) gave a pale yellow solution, which was reduced to a small volume by pumping. Addition of pentane afforded pale yellow flat needles, suitable for X-ray crystallographic investigation; yield 1.40 g, 86%. Anal. Calcd for C$_{24}$H$_{24}$N$_4$O$_4$Cu$_4$: Cu, 42.0; H, 3.5; N, 8.2; Cu, 37.0. Found: C, 42.0; H, 3.5; N, 7.9; Cu, 37.5. The compound is somewhat air sensitive.

Spectra. Mass spectra were recorded on an AEI MS 30 instrument using a 70-eV electron beam to produce ionization and fragmentation. ^{1}H NMR spectra (90 MHz) were recorded, for CDCl$_3$ solutions at room temperature, with a Perkin-Elmer R32 spectrometer.

Crystal Structure Determination. A crystal of dimensions 0.27 × 0.33 × 0.15 mm^3 (cut from a needle) was mounted in a glass capillary tube. All crystallographic measurements were made at room temperature, with a Stoe-Siemens AED diffractometer and graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). Unit cell dimensions were obtained from 40 automatically centered strong reflections with 20 < 2θ < 25°. The cell is monoclinic, with a = 7.499 (2) Å, b = 14.572 (3) Å, c = 12.210 (3) Å, β = 107.61 (2)°, and V = 1271.7 Å^3; Z = 2 for the formula Cu$_4$(mhp)$_4$, D_{calcd} = 1.688 g cm^{-3}, and μ = 33.5 cm^{-1}. The compound's air sensitivity and ready solubility in a range of organic solvents precluded the accurate measurement of its density.

Intensities were measured in the θ/ω scan mode by a profile-fitting procedure.[9,10] From 2532 reflections with $2\theta_{\max}$ = 50°, $h \geq 0$ and $k \geq 0$, 2199 unique data with $I > 2\sigma(I)$ were obtained after Lp and absorption corrections were applied and were used for structure solution

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Table I. Atomic Coordinates ($\times 10^4$)[a]

atom	*x*	*y*	*z*
Cu(1)	6129 (1)	5000	2775 (1)
Cu(2)	2894 (1)	4684 (1)	1155 (1)
Cu(3)	1216 (1)	5701 (1)	2388 (1)
Cu(4)	4563 (1)	6571 (1)	3096 (1)
O(1)	6720 (5)	5356 (3)	1492 (3)
C(11)	5631 (7)	5638 (4)	502 (4)
C(12)	6392 (8)	6159 (4)	−216 (5)
C(13)	5261 (9)	6466 (5)	−1243 (5)
C(14)	3367 (9)	6237 (5)	−1599 (5)
C(15)	2656 (8)	5711 (5)	−887 (4)
C(16)	665 (9)	5436 (7)	−1196 (6)
N(1)	3802 (6)	5424 (3)	173 (3)
O(2)	2131 (5)	3780 (3)	1953 (3)
C(21)	1762 (7)	3833 (4)	2920 (4)
C(22)	1822 (8)	3048 (4)	3580 (5)
C(23)	1545 (9)	3114 (5)	4647 (5)
C(24)	1196 (8)	3959 (5)	5033 (5)
C(25)	1096 (7)	4731 (4)	4378 (4)
C(26)	728 (9)	5667 (3)	4723 (6)
N(2)	1394 (5)	4653 (3)	3311 (3)
O(3)	724 (5)	6719 (3)	1477 (4)
C(31)	1830 (7)	7261 (3)	1158 (4)
C(32)	1099 (8)	7864 (4)	223 (5)
C(33)	2287 (9)	8413 (5)	−133 (5)
C(34)	4157 (9)	8400 (4)	439 (5)
C(35)	4853 (8)	7829 (4)	1374 (5)
C(36)	6884 (8)	7789 (4)	2034 (6)
N(3)	3688 (5)	7273 (3)	1734 (3)
O(4)	5467 (6)	6158 (2)	4589 (3)
C(41)	5877 (7)	5345 (4)	4968 (4)
C(42)	6142 (8)	5146 (5)	6147 (4)
C(43)	6599 (9)	4267 (5)	6535 (5)
C(44)	6766 (9)	3577 (5)	5781 (5)
C(45)	6490 (7)	3789 (4)	4667 (4)
C(46)	6609 (9)	3082 (4)	3801 (5)
N(4)	6108 (5)	4668 (3)	4258 (3)

[a] Estimated standard deviations in the last place of figures are given in parentheses.

and refinement. Absorption corrections were of an empirical type, based on the measurement of sets of equivalent reflections at a series of azimuthal (ψ) angles. The discrepancy index for the azimuthal scan data was reduced from 0.055 to 0.018 by the derived corrections. Transmission factors for the complete data set ranged from 0.345 to 0.477.

Systematic absences ($0k0$ for k odd only) are consistent with space groups $P2_1$ and $P2_1/m$. The former was indicated by intensity distribution statistics and confirmed by successful structure refinement. The four Cu atoms were located by automatic direct methods and the remaining atoms by subsequent difference syntheses.

Refinement with anisotropic thermal parameters for all non-H atoms, and with the y coordinate of Cu(1) fixed at 0.5 to establish the origin, was by a cascade least-squares method, the quantity $\sum w\Delta^2$ being minimized [$\Delta = |F_o| - |F_c|$; $w^{-1} = (\sigma(F_o))^2 + 0.0005F_o^2$, which produced a satisfactory analysis of variance]. Hydrogen atoms were included in the refinement, with constraints on geometry (all C–H = 0.96 Å; H–C–H = 109.5° for methyl groups; aromatic H on external bisector of C–C–C angle) and with isotropic thermal parameters fixed at 1.3 (aromatic) or 1.5 (methyl) times the equivalent isotropic value[11] for the corresponding C atom.

The final value of $R = 0.0297$, with $R_g = 0.0367$ [$R = \sum|\Delta|/\sum|F_o|$; $R_g = (\sum w\Delta^2/\sum wF_o^2)^{1/2}$]. All parameter shifts in the final cycles were less than the corresponding parameter esd values (the largest shifts were for methyl group orientations). A final difference synthesis contained no features outside the range ±0.3 e Å^{-3}. The rms deviation of a reflection on an absolute scale of $|F_o|$ [$=(\sum w\Delta^2/\sum w)^{1/2}$] was 0.68 electron and showed no systematic trends with indices, sin θ, or $|F_o|$; no correction for secondary extinction was necessary.

Refinement of the inverse structure resulted in significantly higher R (0.0340) and R_g (0.0427). Scattering factors, including contributions for anomalous dispersion, were taken from ref 12.

Table II. Bond Lengths (Å) and Angles (Deg)

Cu(1)–Cu(2)	2.666 (1)	Cu(2)–Cu(3)	2.681 (1)
Cu(3)–Cu(4)	2.709 (1)	Cu(4)–Cu(1)	2.656 (1)
Cu(1)–O(1)	1.828 (4)	Cu(2)–O(2)	1.830 (4)
Cu(3)–O(3)	1.823 (4)	Cu(4)–O(4)	1.843 (4)
Cu(1)–N(4)	1.878 (4)	Cu(2)–N(1)	1.887 (5)
Cu(3)–N(2)	1.879 (5)	Cu(4)–N(3)	1.892 (4)
Cu(4)–Cu(1)–Cu(2)	85.1 (1)	Cu(1)–Cu(2)–Cu(3)	88.0 (1)
Cu(2)–Cu(3)–Cu(4)	83.8 (1)	Cu(3)–Cu(4)–Cu(1)	87.6 (1)
Cu(4)–Cu(1)–O(1)	96.6 (1)	Cu(2)–Cu(1)–O(1)	79.3 (1)
Cu(1)–Cu(2)–O(2)	95.2 (1)	Cu(3)–Cu(2)–O(2)	79.9 (1)
Cu(2)–Cu(3)–O(3)	98.6 (2)	Cu(4)–Cu(3)–O(3)	79.1 (1)
Cu(3)–Cu(4)–O(4)	101.0 (1)	Cu(1)–Cu(4)–O(4)	79.5 (1)
Cu(4)–Cu(1)–N(4)	87.0 (1)	Cu(2)–Cu(1)–N(4)	113.5 (1)
Cu(1)–Cu(2)–N(1)	87.2 (1)	Cu(3)–Cu(2)–N(1)	111.3 (1)
Cu(2)–Cu(3)–N(2)	85.8 (1)	Cu(4)–Cu(3)–N(2)	107.3 (1)
Cu(3)–Cu(4)–N(3)	86.0 (1)	Cu(1)–Cu(4)–N(3)	112.8 (1)
O(1)–Cu(1)–N(4)	167.0 (2)	O(2)–Cu(2)–N(1)	168.7 (2)
O(3)–Cu(3)–N(2)	172.6 (2)	O(4)–Cu(4)–N(3)	166.3 (2)

	$n = 1$	$n = 2$	$n = 3$	$n = 4$
O(*n*)–C(*n*1)	1.304 (5)	1.294 (7)	1.288 (7)	1.276 (6)
C(*n*1)–C(*n*2)	1.405 (8)	1.392 (8)	1.413 (7)	1.422 (7)
C(*n*1)–N(*n*)	1.344 (6)	1.346 (7)	1.357 (6)	1.359 (7)
C(*n*2)–C(*n*3)	1.359 (7)	1.383 (10)	1.363 (10)	1.372 (10)
C(*n*3)–C(*n*4)	1.394 (9)	1.372 (10)	1.364 (8)	1.394 (10)
C(*n*4)–C(*n*5)	1.381 (10)	1.368 (9)	1.381 (8)	1.348 (9)
C(*n*5)–C(*n*6)	1.481 (9)	1.478 (9)	1.493 (7)	1.498 (9)
C(*n*5)–N(*n*)	1.384 (6)	1.392 (7)	1.360 (7)	1.373 (7)
Cu(*n*)–O(*n*)–C(*n*1)	129.6 (4)	129.1 (4)	130.8 (3)	129.7 (3)
O(*n*)–C(*n*1)–C(*n*2)	119.4 (4)	120.1 (5)	119.8 (5)	120.1 (5)
O(*n*)–C(*n*1)–N(*n*)	120.0 (5)	120.0 (5)	120.3 (4)	120.4 (4)
C(*n*2)–C(*n*1)–N(*n*)	120.6 (4)	119.9 (5)	119.8 (5)	119.5 (5)
C(*n*1)–C(*n*2)–C(*n*3)	119.7 (5)	120.1 (6)	119.5 (5)	118.9 (6)
C(*n*2)–C(*n*3)–C(*n*4)	120.1 (6)	118.9 (6)	119.9 (6)	120.5 (6)
C(*n*3)–C(*n*4)–C(*n*5)	119.2 (5)	121.3 (6)	120.3 (6)	118.9 (6)
C(*n*4)–C(*n*5)–C(*n*6)	122.8 (5)	125.0 (6)	122.6 (6)	122.1 (5)
C(*n*4)–C(*n*5)–N(*n*)	120.5 (5)	119.0 (6)	120.5 (5)	122.2 (5)
C(*n*6)–C(*n*5)–N(*n*)	116.7 (6)	116.0 (5)	116.9 (5)	115.8 (5)
Cu(*n*′)–N(*n*)–C(*n*1)	118.3 (3)	119.6 (4)	118.5 (4)	117.9 (3)
Cu(*n*′)–N(*n*)–C(*n*5)	121.7 (4)	119.6 (4)	121.4 (3)	122.0 (4)
C(*n*1)–N(*n*)–C(*n*5)	119.9 (5)	120.8 (5)	120.0 (4)	119.8 (4)

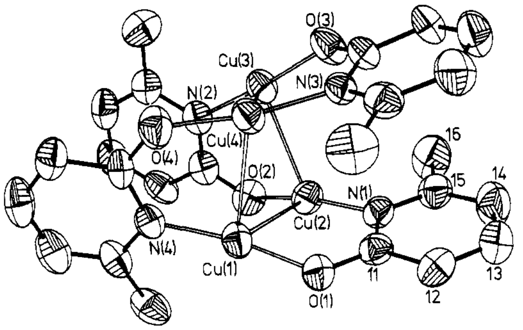

Figure 1. Molecular structure of $[Cu_4(mhp)_4]$, with thermal motion depicted as 50% probability ellipsoids.

Observed and calculated structure factors, anisotropic thermal parameters, and hydrogen atom parameters are available as supplementary material. Atomic coordinates, bond lengths and angles, and equations of least-squares planes are given in the Tables I–III.

Results and Discussion

Description of Structure. The four copper atoms in the tetrameric molecule are arranged approximately in a square, which is subject to a considerable puckering or "butterfly" distortion, the angles of folding about the two diagonals being 137.6 and 138.8° (see Figure 1 and Table III); these angles would be 180° for a planar arrangement. The mean distance between adjacent copper atoms is 2.678 Å, while the two

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Table III. Least-Squares Planes, in the Form $ax + by + cz = d$ (Crystal Coordinates)

plane	atoms	a, Å	b, Å	c, Å	d, Å	rms dev, Å
1	Cu(1),Cu(2),Cu(3)	2.2407	11.9368	−6.8015	5.4542	0
2	Cu(2),Cu(3),Cu(4)	0.6190	−9.3570	8.5648	−3.2144	0
3	Cu(3),Cu(4),Cu(1)	−1.4754	−3.8625	11.7122	0.4150	0
4	Cu(4),Cu(1),Cu(2)	4.4057	6.4461	−10.0561	3.1325	0
5	C,N,O of ligand 1	−2.6180	12.1404	6.2819	5.6831	0.0087
6	C,N,O of ligand 2	6.6474	2.0737	1.8513	2.5269	0.0198
7	C,N,O of ligand 3	−2.5364	10.3948	8.3926	8.0594	0.0141
8	C,N,O of ligand 4	7.1778	3.0051	−1.1708	5.2486	0.0179

planes	dihedral angle, deg	planes	dihedral angle, deg
1-3	137.6	2-4	138.8

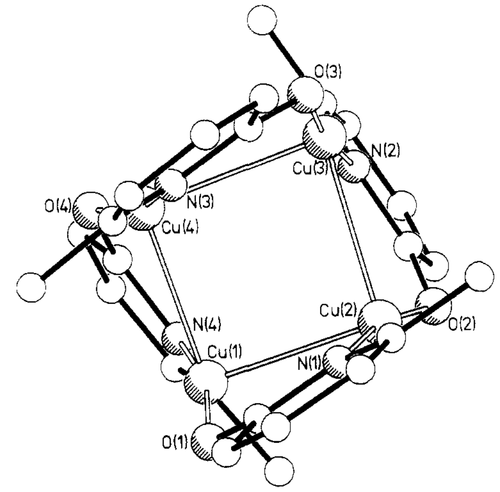

Figure 2. Parallel projection (without perspective), showing the twisting of the ligands away from the Cu···Cu edges.

diagonals measure 3.598 (1) and 3.713 (1) Å.

Each edge of the puckered square is bridged by one mhp ligand, so that each copper atom is coordinated by one oxygen and one nitrogen atom of different ligands. The ligands lie alternately above and below the Cu_4 mean plane, producing almost linear O–Cu–N arrangements (see Table II). The planes of the ligands (Table III) are not parallel to the Cu···Cu lines that they bridge, however, but are twisted away from them, in such a way that the ligand–ligand separations across the Cu_4 ring are rather greater than the Cu···Cu edges (Figure 2). Clearly this twist reduces steric interactions between the mhp ligands while maintaining Cu–ligand bonding. A very similar arrangement of four metal atoms with bridging ligands has been found in two crystalline modifications of $Pt_4(OAc)_8$, which has four additional ligands in an equatorial belt.[13] The deviation of the four metal atoms from their mean plane is greater in $[Cu_4(mhp)_4]$ (rms deviation = 0.349 Å) than in $[Pt_4(OAc)_8]$ (rms deviation = 0.108 and 0.116 Å for the two forms).

Copper(I) forms a wide range of polynuclear complexes, with two to eight copper atoms and a rich variety of structural types, as well as polymeric species.[14] For tetrameric complexes, a highly symmetrical arrangement is the Cu_4 tetrahedron, which is observed in several determined structures, including those with a Cu_4X_4 "cubane-like" core.[15] Less symmetrical geometries found for species with single-atom bridges are the so-called "step" or "chair" arrangement[16] and the cyclooctatetraene-like tub.[17] In a few cases, virtually perfect Cu_4 squares have been reported.[18] In these complexes, the copper atoms are linked by single-atom bridges, which also lie in the Cu_4 plane, so that there are no steric repulsions between ligands. With three-atom bridges, Cu_4 squares are not found as such, but are distorted. The usual distortion is to a planar parallelogram, with one diagonal not much longer than the average edge.[19] The bridging ligands are arranged alternately above and below the Cu_4 plane, but the parallelogram arrangement reduces steric interactions between the pairs of ligands on the same side. The same effect is observed in the gold(I) complex $[Au_4(S_2CMe)_4]$.[20] Complexes with three-atom bridges, however, sometimes occur as dimers, even though the ligands are very similar to those found for parallelogram tetramers. Thus, for example, the complex with the 1,3-diphenyltriazeno ligand is a dimer, $[Cu_2(PhNNNPh)_2]$,[21] but the 1,3-dimethyltriazeno ligand produces a tetramer, $[Cu_4(MeNNNMe)_4]$.[19] Copper(I) benzoate is a tetramer, $[Cu_4(O_2CPh)_4]$,[19b] as is the trifluoroacetate, which also contains weakly coordinated benzene, $[Cu_4(O_2CCF_3)_4(C_6H_6)_2]$;[19a] the acetate, on the other hand, is a dimer, in which the $Cu_2(OAc)_2$ units are further linked together to form polymeric chains.[22]

The only other butterfly distortion observed for a Cu_4 square occurs in $[Cu_4(MeC_6H_3CH_2NH_2)_4]$.[23] Here the situation is more complex, however, as the bridging ligands are of the single-atom type (carbon bridges), which might be expected to produce a planar arrangement, as in $[Cu_4(O\text{-}t\text{-}Bu)_4]$ and $[Cu_4(CH_2SiMe_3)_4]$,[18] but are also coordinated to copper through their nitrogen atoms, thus increasing the copper coordination number and changing the coordination geometry.

In oligomeric copper(I) complexes, a wide range of copper–copper separations is observed.[14] In most cases, a particularly strong Cu–Cu bond is not considered to be present.[15-19] Dimers and tetramers have been investigated by means of extended Hückel calculations on model compounds, and the conclusion has been drawn[14] that there is probably "a soft attractive Cu(I)–Cu(I) interaction, overlaid on top of the ligand set requirements". The observed Cu···Cu distances in $[Cu_4(mhp)_4]$ would appear to be in accord with this, being not particularly short in comparison with those in other oligomeric complexes. The wide range covered by the four

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shortest $Cu\cdots Cu$ distances in $[Cu_4(mhp)_4]$ also suggests a weak bond at most, with significant accommodation to crystal packing forces.

We note that in $[Cu_4(mhp)_4]$ the mhp ligand does not produce a notably short metal–metal separation. This is in contrast to the $[M_2(mhp)_4]$ complexes, in which the separations are among the very shortest observed for each metal.[2a,3–6] Clearly, a single mhp bridge is much less effective in this respect than a set of four.

Spectra. The ^1H NMR spectrum of $[Cu_4(mhp)_4]$ is consistent with equivalence of all the mhp groups, for a solution in $CDCl_3$ at room temperature. A single peak is observed at a τ value of 7.43; this is assigned[24] to the four equivalent methyl groups, and the peak area is scaled to be equal to 12 atoms. There is an overlapping pair of doublets, centered at τ 3.91, with a total area corresponding to eight hydrogen atoms, and this is attributed to the hydrogen atoms attached to C-3 and C-5 atoms split by coupling to the hydrogen attached to C-4. The latter atom is considered to give rise to the doublet of doublets centered at τ 3.02, with a total area corresponding to four hydrogen atoms.

The mass spectrum of $[Cu_4(mhp)_4]$ contains as its highest intensity feature a peak at an m/e value of 342; this is the lowest m/e feature in a set of adjacent peaks that extend to 347. The m/e values of these peaks and their relative intensities correspond very closely to those expected for the $Cu_2(mhp)_2^+$ ion. A reasonably intense set of peaks is observed between m/e values of 234 and 239, with an intensity profile expected for $Cu_2(mhp)^+$; a less intense set of four peaks is observed between m/e 171 and 174, and these values, together with their intensity profile, are consistent with the formation of $Cu(mhp)^+$. Peaks are also observed at higher (>300) m/e values, consistent with the formation of $Cu_4(mhp)_3^+$, $Cu_4(mhp)_2^+$, and $Cu_4(mhp)^+$ ions; they have, however, very low intensity, compared with the peaks corresponding to $Cu_2(mhp)_2^+$. Therefore, in one sense, the mass spectrum of $[Cu_4(mhp)_4]$ differs from those of $[M_2(mhp)_4]$ (M = Cr, Mo, W;[2a,24] Ru, Rh[24]), since all of the latter molecules show clear evidence for the production of the corresponding molecular ion. In another sense, however, $[Cu_4(mhp)_4]$ resembles these other mhp complexes in that its mass spectrum is dominated by ions that contain two metal atoms. As discussed for $[Pd_2(mhp)_4]$,[6] the fragmentation of $[Cu_4(mhp)_4]$ is consistent with a very weak net bonding attraction between the metal atoms (vide supra); a rearrangement of the bridging mhp groups is presumed to occur upon the dissociation of the Cu_4 tetramer to the Cu_2 dimer, with the latter involving two mhp groups bridging the two metal atoms.

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Supplementary Material Available: Tables of observed and calculated structure factors, anisotropic thermal parameters, and hydrogen atom parameters (15 pages). Ordering information is given on any current masthead page.

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X-ray Crystal Structure of a Tetrabridged Ferrocenophane Trimer: 6,9,12-Trioxo[3.3.3](1,1′)[4](2,2′)[4](3,3′)[4](4,4′)[4](5,5′)ferrocenophane[1,2]

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The structure of the tetrabridged ferrocenophane trimer **3**, synthesized by treatment of $[4_4]$ferrocenophanepropionic acid (**2**) with polyphosphate ester, has been determined by the X-ray crystallographic method. The compound is the first intermolecular [3.3.3](1,1′)ferrocenophane composed of three cage-type ferrocene moieties. It was crystallized from $CDCl_3$ as $(C_{29}H_{36}OFe)_3\cdot 2CDCl_3$ in space group $P2_1nb$ with four molecules per unit cell of dimensions $a = 23.30$ (2) Å, $b = 21.69$ (2) Å, $c = 14.94$ (1) Å, $D_m = 1.399$ g cm^{-3}, $D_x = 1.416$ g cm^{-3}, $R = 0.083$, and $R_w = 0.0091$. The molecule of **3** is characterized by a macrocyclic structure with a pseudo-D_3 symmetry having a screw conformation of the tetramethylene bridges. For the methylene carbon atoms, no unusual anisotropy of the thermal vibration was found even though it was commonly observed in bridged ferrocene molecules previously determined.

Introduction

Previously, we reported synthesis of tetrabridged ferrocenophanes and their molecular structures by X-ray crystallographic analysis.[6,7] As a step to synthesize pentabridged ferrocenophane ("superferrocenophane"[8]), a novel cage compound containing an iron atom in the center of the molecule, $[4_4]$ferrocenophanepropionic acid (**2**) was synthesized via several steps from tetrabridged ferrocenophane **1**. However, an attempt at the formation of the last bridge by cyclization of propionic acid (**2**) resulted in the production of a ferrocenophane trimer (**3**) as the major product besides certain other intramolecular cyclization product.[10] The interesting macrocyclic trimer **3** is the first example of [3.3.3](1,1′)ferrocenophane consisting of both inter- and intramolecular

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(1) Organometallic Compounds. 33. For part 32, see ref 4.

(2) The nomenclature of ferrocenophanes in the present paper is according to that presented by Vögtle and Neumann.[5] The numbering of the atoms is shown in Figure 1.

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(8) The pentabridged ferrocenophane may be named "superferrocenophane" as a ferrocene analogue of Boekelheide's "superphane".[9]

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(10) The synthesis of propionic acid (**2**) will be published elsewhere together with the result on the structure of the intramolecular cyclization product, whose X-ray crystallographic analysis is in progress.

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