

II, in both of which the estimated standard deviations are in parentheses. The equal N—CH₃ distances are 1.464 (6) Å, and the N=CH₂ distance is 1.264 (9) Å. The H₃C—N—CH₃ bond angle is 114.1 (3)°, and the H₃C—N=CH₂ angle is 123.0 (3)°. The Ortep diagram is a simple NC₃ plane with coplanar Cl⁻, not quite equidistant from the CH₂ group and one CH₃ group. In the larger picture, each Cl⁻ is hexagonally surrounded by three NC₃ units, each of which embraces three Cl⁻ ions.

KS8. Microcrystalline KS8 was recrystallized to suitable size and shape by convective heating at 35 °C in a vertical test tube with ethanol. The data were collected and computer-processed by Kuei-Shang Huang and Raymond C. Stevens. The conditions and numerical results are listed in Tables I, III, and IV. The

Ortep projection is shown in Figure 2.

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Supplementary Material Available: Listings of anisotropic temperature factors for CDMA and for KS8 (1 page); tables of observed and calculated structure factors for CDMA and for KS8 (9 pages). Ordering information is given on any current masthead page.

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Lewis-Base Adducts of Group 11 Metal(I) Compounds. 49. Structural Characterization of Hexameric and Pentameric (Triphenylphosphine)copper(I) Hydrides

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Red and orange 1:1 adducts of copper(I) hydride with triphenylphosphine have been isolated from tetrahydrofuran as hexameric and pentameric cluster species that have been characterized crystallographically. The red hexameric species [(PPh₃)CuH]₆·0.5thf crystallizes in the monoclinic space group *P2*₁ with *a* = 14.464 (10) Å, *b* = 16.252 (9) Å, *c* = 21.487 (5) Å, β = 91.38 (3)°, *Z* = 2, and *R* = 0.052 for 5932 observed (*I* ≥ 3σ(*I*)) reflections. Cu—P distances are 2.200 (3)–2.246 (3) Å. Hydrogen atoms have been located by refinement at the centers of six triangular faces equatorial about a quasi-6 axis of the octahedral copper skeleton. A crystalline "hydrolysis" product of this compound, tentatively formulated as [(PPh₃)₆Cu₆H₄O]·thf, has also been structurally characterized, crystallizing in the orthorhombic space group *Pbca* with *a* = 40.19 (2) Å, *b* = 22.78 (2) Å, *c* = 21.72 (2) Å, *Z* = 8, and *R* = 0.071 for 5041 observed reflections in a lattice isomorphous with the previously recorded [(PPh₃)CuH]₆·dmf compound. An orange pentameric species, formulated as [(PPh₃)CuH]₅·thf, crystallizes in the monoclinic space group *P2*₁/*c* with *a* = 12.827 (6) Å, *b* = 12.952 (8) Å, *c* = 54.226 (14) Å, β = 95.96 (4)°, *Z* = 4, and *R* = 0.095 for 2393 observed reflections. The copper atoms are disposed in a distorted-trigonal-bipyramidal array with Cu_{ax}...Cu_{eq} distances ranging between 2.431 (7) and 2.582 (7) Å and Cu_{eq}...Cu_{eq} distances between 2.493 (8) and 2.608 (7) Å. The Cu—P distances range between 2.16 (1) and 2.21 (1) Å. Hydride positions were not found.

Introduction

One of the most intensively studied stoichiometric copper(I) hydride species is the 1:1 adduct with triphenylphosphine, structurally characterized as a hexameric cluster, [(PPh₃)CuH]₆, and incorporating a solvate molecule of dimethylformamide (dmf).² Hydrogen atoms were not located in this determination, and their location and the nature of their bonding has since been the subject of much conjecture and study, an X-ray study of the tri-*p*-tolylphosphine analogue casting no further light in this respect.³ During the course of the present work, hydrogen atoms have been located for the tris(dimethylamino)phosphine analogue, [P(NMe₂)₃CuH]₆, by a low-temperature study,⁴ while bridging hydrogen atoms have been located by refinement in binuclear [MeC(CH₂PPh₂)₃]CuH₂Cu[(Ph₂PCH₂)₃CMe].⁵ We have approached the problem of locating hydrogen atoms in the triphenylphosphine hexamer by seeking improvement of crystal quality through recrystallization under different conditions and from different solvent systems. From tetrahydrofuran ((CH₂)₄O = thf) we have been able to isolate crystals of a new thf-solvated phase of the hexamer that produced diffraction data of the quality and extent necessary to enable both the location and refinement of the hydrogen atoms. A structure determination undertaken on crystalline material of different habit in a similar reaction

mixture was found to be isomorphous with the previously studied dmf-solvated phase² but shown structurally to be most likely an oxo-bridged hydrolysis product. Crystalline material obtained from a further series of reactions in thf in the presence of excess reducing agent and triphenylphosphine has proved to be a novel pentameric copper cluster compound. We report the results of these structural studies here.

Experimental Section

Preparation of Compounds. [(PPh₃)CuH]₆ (1). The synthesis and general characterization of this compound are well-known,⁶ and the experiments described here constitute procedural variations with a view of maximizing crystal size and quality. Typically, copper(I) chloride (0.5 g, 0.005 mol) was stirred in 10 mL of dry thf under argon and triphenylphosphine (1.3 g, 0.005 mol) added. An initial white precipitate formed ([[(PPh₃)₃(CuCl)₂] from solid-state ³¹P NMR data). The mixture was stirred continuously while K-Selectride (5 mL of 1.0 M in thf, 0.005 mol (Aldrich)) was added, the precipitate dissolving to give a deep red solution. This was filtered, and the volume of the filtrate was reduced to ca. 50% under vacuum and then cooled to -20 °C. After several days crystals of the compound formed as large dark red hexagonal plates. One of these was mounted in a capillary and used for the structure determination.

Solid-state ³¹P NMR spectra of this compound revealed a broad, essentially featureless peak centered at -10 ppm.

[(PPh₃)₆Cu₆H₄O] (1a). A crystal of different habit, obtained on another occasion under similar recrystallization conditions, was found to be isomorphous with the previously characterized dmf-solvated structure but was subsequently characterized tentatively as a partially hydrolyzed product.

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Table I. Summary of Crystal Data for Compounds 1, 1a, and 2

	$[(\text{PPh}_3)_6\text{CuH}]_6 \cdot 0.5\text{thf}$ (solvent of 1)	$[(\text{PPh}_3)_6\text{Cu}_6\text{H}_4\text{O}] \cdot \text{thf}$ (1a)	$[(\text{PPh}_3)_5\text{CuH}]_5 \cdot \text{thf}$ (2)
formula	$\text{C}_{110}\text{H}_{100}\text{Cu}_6\text{O}_{0.5}\text{P}_6$	$\text{C}_{112}\text{H}_{102}\text{Cu}_6\text{O}_2\text{P}_6$	$\text{C}_{94}\text{H}_{88}\text{Cu}_5\text{OP}_5$
fw	1997.1	2047.1	1706.3
cryst syst	monoclinic	orthorhombic	monoclinic
space group	$P2_1$ (C_2^2 , No. 4)	$Pbca$ (D_{2h}^{15} , No. 61)	$P2_1/c$ (C_2^2 , No. 14)
$a/\text{\AA}$	14.464 (10)	40.19 (2)	12.827 (6)
$b/\text{\AA}$	16.252 (9)	22.78 (2)	12.952 (8)
$c/\text{\AA}$	21.487 (5)	21.72 (2)	54.226 (14)
β/deg	91.38 (3)		95.96 (4)
$V/\text{\AA}^3$	5049 (4)	19878 (26)	8958 (8)
$D_c/\text{g cm}^{-3}$	1.31	1.37	1.26
$\mu_{\text{Mo}}/\text{cm}^{-1}$	13.4	13.8	12.7
N_o	5932	5041	2393
R	0.052	0.071	0.095
R_w	0.048	0.058	0.098

$[(\text{PPh}_3)_5\text{CuH}]_5$ (2). $[(\text{PPh}_3)_3\text{CuCl}]$ (0.5 g, 0.0006 mol), prepared as per the literature,⁷ was dissolved in 8 mL of dry thf under argon. An excess of K-Selectride (1.0 mL of 1 M in thf, 0.0010 mol) was slowly added to give a red/orange solution. After filtration and standing of the filtrate at -20°C for 1 week, a small crop of fine orange needles (ca. 0.05 g) of the product crystallized out and were collected. On further standing at -20°C , hexagonal plates of the hexamer also crystallized out. One of the orange needles was mounted in a capillary under argon and used for the structure determination.

Structure Determination. Unique data sets were measured carefully at 295 K to the specified $2\theta_{\text{max}}$ limit by using a Syntex P2₁ four-circle diffractometer in conventional $2\theta/\theta$ scan mode and with monochromatic Mo K α radiation ($\lambda = 0.71069 \text{ \AA}$). N reflections were obtained, N_o with $I > 3\sigma(I)$ being considered "observed" and used in the large block least-squares refinement minimizing $\sum w\Delta^2$ after solution of the structures by direct methods and Gaussian absorption correction. Anisotropic thermal parameters were refined for non-hydrogen atoms; (x, y, z, U_{iso})_H were constrained at estimated values for the phenyl rings and solvent but where possible were located in difference maps and refined for the core hydrogen atoms. Conventional residuals on $|F|$ at convergence are quoted, R, R_w ; statistical derivative of $\sigma^2(I) = \sigma^2(I_{\text{diff}}) + 0.0005\sigma^4(I_{\text{diff}})$ was used. Neutral-atom complex scattering factors were employed,⁸ computation used the XTAL 2.2 program system⁹ implemented by S. R. Hall. Crystal data, atom coordinates, and molecular core geometries are given in Tables I–VI. Supplementary material deposited comprises crystal data tables, structure factor amplitudes, thermal and ligand hydrogen parameters, and ligand geometries.

Abnormal Features/Variations in Procedure. **thf Solvate of 1.** Solution and refinement was straightforward, with the minor exception of the partial site occupancy solvent molecule, which was constrained at 0.5 after refinement with isotropic thermal parameters. Core hydrogen atoms were clearly evident in difference maps, and all refined smoothly in x, y, z , with U_{iso} being constrained at estimated values.

2. Although the crystal was small and data were weak and limited, data collection was persevered with in recognition of the material being a new phase with an anomalous cell volume. Cu and P only were refined with anisotropic thermal parameters, C and O being isotropic. Core hydrogen atoms were neither located nor estimated. In view of the sparse distribution of reflections, profile overlap was not a serious problem despite the very long c axis, although during data measurement maximum crystal-counter distance and optimum slit settings were employed. Solvent atoms were not well localized and were constrained in the final cycles in x, y, z .

1a. Recognition of the similarity of cell dimensions and symmetry of this derivative to those previously established for the dmf solvate led to the adoption of considerable care in data measurement with the intention of refining hydrogen atom parameters. Molybdenum radiation was used to diminish absorption problems, in conjunction with the use of the counter at the limit of its arm in consequence of the long a axis; no serious problems with profile overlap were encountered, and data collection proceeded otherwise normally.

Refinement was originally initiated by using the full non-hydrogen atom parameter complement of the dmf adduct in the expectation that the molecule and its disposition would be sufficiently similar. This ex-

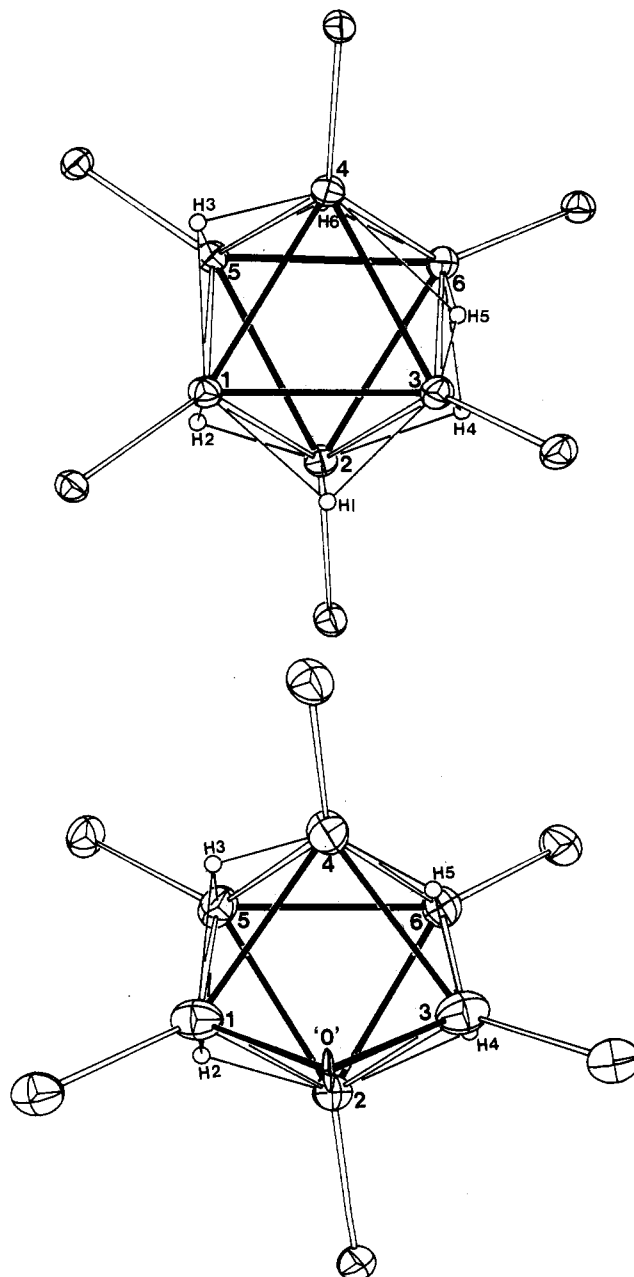


Figure 1. The molecular cores of (a, top) the thf solvate of 1 and (b, bottom) 1a projected normal to the Cu(1,3,4) face. Core labeling is shown, together with 20% thermal envelopes for the non-hydrogen atoms. Hydrogen atoms have arbitrary radii of 0.1 \AA .

pectation was not met. Reversion to phasing on the basis of the Cu_6P_6 core was more successful, leading to location of the full, fully ordered aggregate in a location similar to but not identical with that of the dmf

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Table II. Non-Hydrogen Atom Coordinates of **1** and **1a** (Core Hydrogen Atoms Included)

atom	thf solvate of 1			1a		
	x	y	z	x	y	z
Cu(1) ^a	0.18180 (8)	0.00000	0.75298 (6)	0.11636 (5)	-0.01210 (7)	0.16425 (8)
Cu(2)	0.25238 (8)	0.0874 (1)	0.83576 (5)	0.08179 (4)	0.06227 (7)	0.23985 (8)
Cu(3)	0.17076 (9)	0.16945 (9)	0.75399 (7)	0.15025 (5)	0.08225 (8)	0.25068 (9)
Cu(4)	0.26913 (8)	0.0953 (1)	0.66425 (5)	0.15364 (4)	-0.03372 (7)	0.26527 (8)
Cu(5)	0.35270 (9)	0.01446 (8)	0.74552 (6)	0.09079 (4)	-0.04814 (7)	0.25937 (8)
Cu(6)	0.33892 (9)	0.18178 (8)	0.74904 (7)	0.11713 (5)	0.03329 (7)	0.33260 (7)
H(1) ^b	0.133 (5)	0.087 (6)	0.806 (4)	0.1548 (2)	0.0558 (3)	0.1541 (3)
H(2)	0.274 (6)	-0.002 (6)	0.817 (5)	0.082 (2)	0.001 (4)	0.194 (4)
H(3)	0.265 (6)	-0.000 (6)	0.680 (5)	0.126 (2)	-0.065 (4)	0.231 (4)
H(4)	0.257 (6)	0.191 (6)	0.808 (5)	0.114 (2)	0.090 (4)	0.292 (4)
H(5)	0.254 (6)	0.189 (6)	0.743 (5)	0.151 (2)	0.025 (4)	0.293 (4)
H(6)	0.372 (5)	0.095 (7)	0.722 (4)			
P(1)	0.0839 (2)	-0.1031 (2)	0.7648 (1)	0.1060 (1)	-0.0418 (2)	0.0673 (2)
P(2)	0.2478 (2)	0.0927 (2)	0.9395 (1)	0.0446 (1)	0.1339 (2)	0.2193 (2)
P(3)	0.0497 (2)	0.2524 (2)	0.7382 (2)	0.1870 (1)	0.1564 (2)	0.2529 (2)
P(4)	0.2806 (2)	0.1051 (2)	0.5609 (1)	0.1968 (1)	-0.0945 (2)	0.2706 (2)
P(5)	0.4591 (2)	-0.0800 (2)	0.7313 (1)	0.0568 (1)	-0.1238 (2)	0.2724 (2)
P(6)	0.4386 (2)	0.2863 (2)	0.7635 (1)	0.1064 (1)	0.0526 (2)	0.4313 (2)
C(111)	-0.0292 (8)	-0.0759 (7)	0.7941 (5)	0.0638 (3)	-0.0661 (6)	0.0535 (6)
C(112)	-0.0926 (8)	-0.1342 (8)	0.8130 (6)	0.0356 (4)	-0.0406 (8)	0.0795 (7)
C(113)	-0.1781 (8)	-0.113 (1)	0.8324 (6)	0.0036 (4)	-0.0534 (9)	0.069 (1)
C(114)	-0.2005 (9)	-0.027 (1)	0.8372 (7)	-0.0014 (4)	-0.1015 (7)	0.0320 (7)
C(115)	-0.1400 (8)	0.0288 (9)	0.8178 (6)	0.0247 (4)	-0.1304 (7)	0.0091 (8)
C(116)	-0.0537 (7)	0.0070 (8)	0.7958 (6)	0.0549 (4)	-0.1135 (6)	0.0167 (7)
C(121)	0.1173 (7)	-0.1802 (7)	0.8225 (5)	0.1309 (3)	-0.1038 (6)	0.0371 (6)
C(122)	0.1534 (8)	-0.1531 (8)	0.8775 (6)	0.1390 (4)	-0.1090 (7)	-0.0239 (7)
C(123)	0.169 (1)	-0.2061 (9)	0.9273 (6)	0.1545 (4)	-0.1590 (7)	-0.0440 (7)
C(124)	0.152 (1)	-0.2881 (9)	0.9206 (7)	0.1658 (4)	-0.1988 (7)	-0.0026 (8)
C(125)	0.115 (1)	-0.3174 (8)	0.8637 (7)	0.1596 (4)	-0.1944 (7)	0.0576 (7)
C(126)	0.098 (1)	-0.2649 (8)	0.8156 (6)	0.1431 (3)	-0.1449 (6)	0.0782 (7)
C(131)	0.0605 (8)	-0.1660 (7)	0.6947 (5)	0.1097 (4)	0.0142 (5)	0.0057 (7)
C(132)	0.1358 (8)	-0.2007 (9)	0.6658 (6)	0.1397 (4)	0.0455 (7)	0.0064 (9)
C(133)	0.1168 (9)	-0.2506 (9)	0.6135 (7)	0.1501 (5)	0.0926 (9)	-0.035 (1)
C(134)	0.033 (1)	-0.264 (1)	0.5891 (7)	0.1262 (5)	0.0992 (9)	-0.072 (1)
C(135)	-0.039 (1)	-0.226 (1)	0.6168 (7)	0.0949 (5)	0.0772 (7)	-0.0820 (7)
C(136)	-0.0271 (9)	-0.1776 (9)	0.6694 (7)	0.0875 (4)	0.0283 (6)	-0.0368 (8)
C(211)	0.3529 (8)	0.0584 (6)	0.9784 (5)	0.0481 (3)	0.1922 (5)	0.2756 (6)
C(212)	0.3809 (7)	0.0866 (9)	1.0391 (5)	0.0459 (4)	0.1763 (5)	0.3382 (6)
C(213)	0.4633 (9)	0.0598 (8)	1.0657 (7)	0.0494 (4)	0.2182 (6)	0.3835 (6)
C(214)	0.5211 (9)	0.0065 (8)	1.0352 (7)	0.0557 (4)	0.2761 (6)	0.3707 (7)
C(215)	0.4928 (9)	-0.0200 (8)	0.9776 (7)	0.0594 (4)	0.2913 (6)	0.3103 (7)
C(216)	0.4118 (8)	0.0049 (8)	0.9502 (6)	0.0555 (3)	0.2513 (5)	0.2637 (6)
C(221)	0.1523 (8)	0.0399 (7)	0.9772 (5)	-0.0003 (3)	0.1215 (5)	0.2130 (6)
C(222)	0.0661 (8)	0.0404 (8)	0.9479 (6)	-0.0247 (3)	0.1382 (6)	0.2548 (7)
C(223)	-0.007 (1)	0.005 (1)	0.9756 (7)	-0.0579 (4)	0.1287 (6)	0.2458 (8)
C(224)	-0.001 (1)	-0.031 (1)	1.0338 (7)	-0.0683 (3)	0.0999 (6)	0.1982 (8)
C(225)	0.087 (1)	-0.033 (1)	1.0648 (7)	-0.0452 (4)	0.0820 (6)	0.1531 (7)
C(226)	0.1643 (9)	0.0028 (9)	1.0358 (6)	-0.0119 (4)	0.0894 (6)	0.1621 (7)
C(231)	0.2361 (7)	0.1974 (6)	0.9684 (5)	0.0525 (3)	0.1718 (5)	0.1458 (5)
C(232)	0.2987 (9)	0.2542 (7)	0.9518 (5)	0.0815 (4)	0.1564 (6)	0.1176 (6)
C(233)	0.295 (1)	0.3359 (7)	0.9683 (7)	0.0903 (4)	0.1862 (7)	0.0646 (7)
C(234)	0.218 (1)	0.3603 (8)	1.0039 (7)	0.0693 (4)	0.2282 (6)	0.0403 (6)
C(235)	0.1535 (8)	0.3065 (8)	1.0196 (7)	0.0406 (4)	0.2392 (6)	0.0672 (7)
C(236)	0.1601 (8)	0.2245 (8)	1.0040 (7)	0.0320 (3)	0.2112 (5)	0.1196 (6)
C(311)	-0.0371 (7)	0.2502 (8)	0.7954 (6)	0.1683 (3)	0.2297 (5)	0.2526 (6)
C(312)	-0.0040 (8)	0.2435 (9)	0.8592 (6)	0.1445 (4)	0.2393 (6)	0.2100 (7)
C(313)	-0.0640 (8)	0.240 (1)	0.9091 (7)	0.1305 (4)	0.2940 (7)	0.2040 (8)
C(314)	-0.1574 (9)	0.246 (1)	0.8967 (7)	0.1400 (4)	0.3383 (7)	0.2427 (8)
C(315)	-0.1947 (8)	0.252 (1)	0.8361 (6)	0.1621 (4)	0.3309 (6)	0.2851 (7)
C(316)	-0.1338 (8)	0.257 (1)	0.7889 (6)	0.1787 (3)	0.2748 (6)	0.2902 (6)
C(321)	0.0680 (8)	0.3593 (8)	0.7245 (5)	0.2138 (3)	0.1583 (5)	0.3199 (6)
C(322)	0.143 (1)	0.3823 (8)	0.6878 (6)	0.2035 (4)	0.1291 (7)	0.3699 (7)
C(323)	0.159 (1)	0.4659 (9)	0.6753 (7)	0.2238 (4)	0.1324 (7)	0.4244 (7)
C(324)	0.112 (1)	0.528 (1)	0.6968 (8)	0.2536 (4)	0.1606 (8)	0.4274 (8)
C(325)	0.038 (1)	0.5073 (9)	0.7339 (7)	0.2645 (4)	0.1861 (8)	0.3747 (8)
C(326)	0.018 (1)	0.4251 (9)	0.7461 (8)	0.2448 (4)	0.1868 (7)	0.3225 (8)
C(331)	-0.0120 (7)	0.2167 (8)	0.6673 (5)	0.2160 (3)	0.1602 (6)	0.1885 (6)
C(332)	-0.0010 (9)	0.1377 (8)	0.6484 (7)	0.2320 (4)	0.1116 (7)	0.1666 (8)
C(333)	-0.0479 (8)	0.107 (1)	0.5962 (6)	0.2539 (5)	0.1116 (8)	0.1186 (7)
C(334)	-0.1024 (9)	0.156 (1)	0.5606 (7)	0.2596 (5)	0.1639 (8)	0.0901 (7)
C(335)	-0.1122 (9)	0.236 (1)	0.5771 (6)	0.2457 (4)	0.2141 (7)	0.1101 (7)
C(336)	-0.0653 (9)	0.270 (1)	0.6311 (7)	0.2234 (4)	0.2127 (6)	0.1577 (7)
C(411)	0.3892 (7)	0.0669 (6)	0.5273 (5)	0.2271 (3)	-0.0921 (6)	0.2063 (6)
C(412)	0.4672 (7)	0.0737 (8)	0.5625 (6)	0.2152 (4)	-0.0681 (7)	0.1513 (7)
C(413)	0.5499 (8)	0.0482 (9)	0.5363 (7)	0.2370 (4)	-0.0659 (8)	0.1024 (8)

Table II (Continued)

atom	thf solvate of 1			1a		
	x	y	z	x	y	z
C(414)	0.5538 (9)	0.017 (1)	0.4795 (7)	0.2681 (4)	-0.0848 (8)	0.1054 (7)
C(415)	0.475 (1)	0.0082 (9)	0.4451 (6)	0.2797 (4)	-0.1081 (7)	0.1590 (7)
C(416)	0.3884 (9)	0.0322 (9)	0.4680 (6)	0.2591 (4)	-0.1140 (6)	0.2079 (7)
C(421)	0.1881 (7)	0.0532 (7)	0.5166 (5)	0.1839 (3)	-0.1700 (6)	0.2727 (7)
C(422)	0.1555 (8)	0.0822 (9)	0.4577 (5)	0.1604 (4)	-0.1855 (6)	0.3157 (8)
C(423)	0.086 (1)	0.0401 (8)	0.4276 (6)	0.1480 (4)	-0.2423 (8)	0.3179 (8)
C(424)	0.048 (1)	-0.0294 (9)	0.4522 (7)	0.1580 (4)	-0.2830 (6)	0.276 (1)
C(425)	0.080 (1)	-0.0589 (9)	0.5078 (7)	0.1804 (4)	-0.2692 (6)	0.2315 (9)
C(426)	0.1478 (9)	-0.0185 (8)	0.5403 (6)	0.1931 (4)	-0.2123 (6)	0.2294 (7)
C(431)	0.2722 (8)	0.2107 (7)	0.5313 (5)	0.2234 (3)	-0.0907 (6)	0.3384 (6)
C(432)	0.1956 (8)	0.2558 (7)	0.5465 (6)	0.2283 (3)	-0.0365 (7)	0.3665 (7)
C(433)	0.1847 (9)	0.3354 (9)	0.5262 (6)	0.2478 (4)	-0.0317 (8)	0.4182 (8)
C(434)	0.255 (1)	0.3695 (7)	0.4890 (6)	0.2608 (4)	-0.0814 (8)	0.4397 (8)
C(435)	0.3311 (9)	0.3258 (8)	0.4748 (7)	0.2604 (4)	-0.1345 (8)	0.4213 (7)
C(436)	0.3412 (9)	0.2446 (8)	0.4953 (6)	0.2391 (4)	-0.1400 (7)	0.3657 (7)
C(511)	0.5736 (7)	-0.0434 (8)	0.7085 (5)	0.0580 (3)	-0.1794 (5)	0.2102 (6)
C(512)	0.5931 (7)	0.0404 (8)	0.7150 (6)	0.0313 (4)	-0.1957 (6)	0.1765 (6)
C(513)	0.6739 (8)	0.075 (1)	0.7000 (7)	0.0350 (4)	-0.2366 (7)	0.1292 (7)
C(514)	0.7387 (9)	0.033 (1)	0.6785 (8)	0.0642 (4)	-0.2639 (6)	0.1194 (6)
C(515)	0.7280 (8)	-0.055 (1)	0.6696 (6)	0.0906 (4)	-0.2476 (6)	0.1531 (7)
C(516)	0.6421 (9)	-0.090 (1)	0.6841 (6)	0.0881 (4)	-0.2050 (6)	0.1996 (7)
C(521)	0.4834 (8)	-0.1429 (7)	0.8014 (5)	0.0134 (3)	-0.1046 (5)	0.2835 (6)
C(522)	0.4059 (8)	-0.1773 (8)	0.8308 (6)	-0.0086 (3)	-0.1345 (5)	0.3203 (7)
C(523)	0.4169 (8)	-0.2256 (9)	0.8829 (6)	-0.0413 (4)	-0.1148 (6)	0.3284 (7)
C(524)	0.5050 (9)	-0.2330 (8)	0.9095 (6)	-0.0519 (4)	-0.0665 (7)	0.2975 (7)
C(525)	0.5787 (9)	-0.201 (1)	0.8821 (7)	-0.0300 (4)	-0.0373 (7)	0.2608 (9)
C(526)	0.5692 (8)	-0.1542 (8)	0.8273 (6)	0.0014 (3)	-0.0567 (7)	0.2536 (8)
C(531)	0.4315 (8)	-0.1557 (7)	0.6714 (5)	0.0651 (3)	-0.1678 (5)	0.3413 (6)
C(532)	0.458 (1)	-0.2387 (8)	0.6742 (7)	0.0782 (3)	-0.1417 (5)	0.3935 (6)
C(533)	0.435 (1)	-0.2914 (9)	0.6264 (7)	0.0831 (4)	-0.1720 (6)	0.4453 (6)
C(534)	0.393 (1)	-0.2638 (9)	0.5737 (7)	0.0773 (4)	-0.2296 (5)	0.4474 (7)
C(535)	0.367 (1)	-0.1837 (8)	0.5709 (6)	0.0636 (3)	-0.2606 (6)	0.3978 (7)
C(536)	0.3885 (9)	-0.1311 (8)	0.6172 (6)	0.0580 (3)	-0.2279 (5)	0.3452 (6)
C(611)	0.5255 (7)	0.2994 (7)	0.7039 (5)	0.1248 (3)	0.1188 (6)	0.4633 (6)
C(612)	0.6165 (8)	0.326 (1)	0.7142 (6)	0.1390 (4)	0.1226 (7)	0.5237 (6)
C(613)	0.6761 (8)	0.336 (1)	0.6668 (7)	0.1558 (4)	0.1734 (7)	0.5413 (8)
C(614)	0.647 (1)	0.317 (1)	0.6076 (7)	0.1561 (5)	0.2205 (6)	0.5054 (8)
C(615)	0.561 (1)	0.292 (1)	0.5971 (7)	0.1432 (4)	0.2195 (6)	0.4471 (8)
C(616)	0.4992 (9)	0.2826 (9)	0.6422 (5)	0.1271 (4)	0.1680 (6)	0.4267 (7)
C(621)	0.5066 (7)	0.2678 (7)	0.8351 (5)	0.1208 (3)	-0.0040 (5)	0.4869 (6)
C(622)	0.5228 (8)	0.1874 (8)	0.8534 (6)	0.1033 (4)	-0.0205 (6)	0.5396 (6)
C(623)	0.5704 (9)	0.1971 (9)	0.9059 (7)	0.1146 (5)	-0.0661 (8)	0.5764 (7)
C(624)	0.6054 (9)	0.228 (1)	0.9433 (6)	0.1436 (5)	-0.0907 (8)	0.5645 (8)
C(625)	0.5939 (8)	0.309 (1)	0.9280 (6)	0.1605 (5)	-0.0775 (8)	0.5112 (8)
C(626)	0.5426 (8)	0.3306 (8)	0.8711 (6)	0.1475 (4)	-0.0338 (7)	0.4706 (6)
C(631)	0.3943 (7)	0.3902 (7)	0.7764 (5)	0.0615 (3)	0.0601 (5)	0.4480 (6)
C(632)	0.3174 (8)	0.3979 (8)	0.8108 (6)	0.0501 (4)	0.0980 (6)	0.4943 (7)
C(633)	0.2814 (9)	0.4765 (9)	0.8243 (7)	0.053 (4)	0.1047 (6)	0.5016 (8)
C(634)	0.320 (1)	0.5461 (8)	0.8027 (7)	-0.0058 (4)	0.0752 (6)	0.4680 (8)
C(635)	0.400 (1)	0.5389 (8)	0.7700 (8)	0.0064 (4)	0.0380 (7)	0.4214 (8)
C(636)	0.436 (1)	0.4618 (9)	0.7538 (7)	0.0396 (3)	0.0297 (6)	0.4133 (7)
O(1)	0.2143	0.1276	0.2100	0.3542 (5)	0.0112 (9)	0.250 (2)
C(2)	0.2848	0.0678	0.2146	0.3455 (7)	0.0602 (9)	0.289 (2)
C(3)	0.3325	0.1110	0.2609	0.3240 (7)	0.016 (1)	0.318 (1)
C(4)	0.2831	0.1455	0.2848	0.3020 (5)	0.041 (1)	0.274 (1)
C(5)	0.2245	0.1599	0.2668	0.3244 (7)	0.035 (1)	0.225 (1)

^a For **1**, $\nu(\text{Cu}(1))$ defines the origin. ^b In **1a**, for H(1) read O(1).

solvate. The same coordinate setting and atom labeling was employed. When a $2\sigma(J)$ "observed" criterion for data was used, stable and meaningful anisotropic thermal parameter refinement was achieved for all non-hydrogen atoms, including those of a solvent molecule, seemingly with full site occupancy (on the basis of refinement of this parameter for a few cycles; ultimately reset to unity) and fully ordered, albeit in association with high-amplitude thermal envelopes. At this stage it had become evident that the source of the initial inability to refine the structure by using the dmf solvate parameters was more profound than a simple exchange of solvent moieties in the lattice. The interatomic distances in the Cu_6 core differed significantly and nontrivially from those of the dmf solvate and had a pronounced asymmetry. Examination of a difference map for core hydrogen atoms showed the presence of a substantial artifact on one of the edges of the Cu_6 aggregate. Given the mode of synthesis, our initial reaction was that this artifact was most likely chlorine; stable refinement was achieved with anisotropic thermal motion and a site occupancy converging to ca. 0.66. This model was

ultimately rejected, however, as being improbable on a number of grounds. First, if 0.66 of the molecules contain chlorine and a highly distorted molecular core, then 0.34 do not. These latter molecules should have a core geometry conforming to that of the dmf solvate. In such a situation, substantial disorder would be expected to be observed among the copper atoms, particularly those nearest the chlorine. However, copper and phosphorus atom parameter refinement was well-behaved, with no abnormally large or anisotropic thermal envelopes. Second, the crystal used for data collection was subjected to an electron microprobe analysis and no trace of chlorine found. Subsequent attempts to synthesize chloride-containing species all failed.

A second possibility was that the artifact was oxygen, in the present environment most likely bound as a bridging oxo group. Stable refinement as a fully populated oxygen atom was achieved. However, the thermal ellipsoid was of low amplitude and highly anisotropic (Figure 1b). Release of the constraint on the population gave a site occupancy of 1.18 with a more credible ellipsoid, while substitution of a fluorine

Table III. Non-Hydrogen Atom Coordinates and Thermal Parameters for **2**

atom	x	y	z	$10^3 U_{11}$ Å ²	atom	x	y	z	$10^3 U_{11}$ Å ²
Cu(1)	0.8298 (4)	0.7447 (4)	0.15838 (9)	*	C(324)	0.522 (3)	0.525 (4)	0.2134 (8)	129 (20)
Cu(2)	0.7005 (4)	0.8274 (4)	0.09025 (9)	*	C(325)	0.592 (3)	0.504 (4)	0.1965 (8)	113 (18)
Cu(3)	0.6614 (4)	0.7534 (5)	0.13246 (9)	*	C(326)	0.581 (3)	0.551 (3)	0.1735 (7)	98 (17)
Cu(4)	0.8382 (4)	0.7171 (4)	0.11428 (9)	*	C(331)	0.403 (3)	0.782 (3)	0.1374 (6)	70 (14)
Cu(5)	0.7918 (4)	0.8957 (4)	0.1317 (1)	*	C(332)	0.303 (3)	0.759 (3)	0.1296 (6)	77 (14)
P(1)	0.8896 (9)	0.7067 (9)	0.1960 (2)	*	C(333)	0.228 (3)	0.828 (4)	0.1312 (8)	116 (18)
P(2)	0.6228 (9)	0.891 (1)	0.0553 (2)	*	C(334)	0.252 (3)	0.926 (3)	0.1392 (7)	98 (17)
P(3)	0.5094 (8)	0.6906 (9)	0.1385 (2)	*	C(335)	0.347 (3)	0.956 (4)	0.1460 (8)	114 (18)
P(4)	0.9465 (8)	0.6065 (9)	0.1007 (2)	*	C(336)	0.424 (3)	0.877 (3)	0.1479 (7)	96 (16)
P(5)	0.8516 (9)	1.0524 (9)	0.1327 (2)	*	C(411)	0.886 (3)	0.514 (3)	0.0815 (7)	98 (17)
C(111)	0.879 (2)	0.569 (3)	0.2054 (5)	41 (12)	C(412)	0.919 (3)	0.464 (4)	0.0615 (8)	129 (20)
C(112)	0.844 (3)	0.534 (3)	0.2283 (7)	88 (16)	C(413)	0.872 (4)	0.380 (5)	0.047 (1)	193 (26)
C(113)	0.846 (3)	0.432 (3)	0.2342 (7)	89 (16)	C(414)	0.776 (4)	0.358 (4)	0.0520 (9)	152 (22)
C(114)	0.881 (3)	0.366 (3)	0.2172 (7)	81 (15)	C(415)	0.734 (4)	0.394 (4)	0.0721 (9)	169 (24)
C(115)	0.905 (3)	0.391 (4)	0.1951 (8)	128 (19)	C(416)	0.795 (4)	0.479 (4)	0.0888 (9)	143 (21)
C(116)	0.905 (3)	0.491 (3)	0.1877 (7)	86 (16)	C(421)	1.039 (3)	0.660 (3)	0.0809 (6)	71 (14)
C(121)	1.033 (3)	0.729 (3)	0.2046 (6)	57 (12)	C(422)	1.002 (3)	0.741 (4)	0.0658 (8)	128 (19)
C(122)	1.077 (3)	0.811 (3)	0.1936 (6)	69 (14)	C(423)	1.082 (3)	0.785 (4)	0.0493 (8)	128 (19)
C(123)	1.176 (3)	0.832 (3)	0.1983 (7)	99 (17)	C(424)	1.176 (4)	0.744 (4)	0.0491 (8)	149 (21)
C(124)	1.236 (3)	0.773 (3)	0.2163 (6)	74 (14)	C(425)	1.205 (3)	0.676 (4)	0.0639 (8)	117 (18)
C(125)	1.192 (3)	0.693 (3)	0.2288 (7)	87 (16)	C(426)	1.141 (3)	0.624 (4)	0.0804 (7)	111 (18)
C(126)	1.087 (3)	0.669 (3)	0.2230 (7)	85 (15)	C(431)	1.036 (3)	0.540 (3)	0.1240 (6)	60 (13)
C(131)	0.834 (3)	0.780 (3)	0.2224 (6)	70 (14)	C(432)	1.056 (3)	0.440 (3)	0.1218 (8)	114 (18)
C(132)	0.717 (3)	0.782 (3)	0.2186 (7)	94 (16)	C(433)	1.120 (4)	0.394 (4)	0.1412 (9)	166 (23)
C(133)	0.661 (3)	0.832 (4)	0.2360 (8)	119 (19)	C(434)	1.164 (3)	0.451 (3)	0.1604 (7)	77 (15)
C(134)	0.726 (3)	0.870 (3)	0.2549 (7)	94 (16)	C(435)	1.152 (3)	0.556 (3)	0.1607 (7)	77 (15)
C(135)	0.830 (3)	0.877 (4)	0.2591 (8)	109 (18)	C(436)	1.078 (2)	0.597 (3)	0.1436 (6)	49 (12)
C(136)	0.883 (3)	0.825 (3)	0.2428 (7)	93 (16)	C(511)	0.939 (3)	1.081 (3)	0.1116 (7)	83 (15)
C(211)	0.528 (3)	0.993 (3)	0.0591 (6)	63 (14)	C(512)	1.013 (3)	1.011 (3)	0.1018 (7)	84 (16)
C(212)	0.454 (3)	0.975 (3)	0.0759 (7)	84 (15)	C(513)	1.079 (4)	1.039 (4)	0.0834 (8)	126 (19)
C(213)	0.379 (3)	1.050 (4)	0.0801 (8)	121 (19)	C(514)	1.090 (4)	1.130 (4)	0.0747 (9)	165 (24)
C(214)	0.381 (3)	1.138 (3)	0.0680 (7)	106 (17)	C(515)	1.028 (4)	1.193 (4)	0.0803 (8)	132 (20)
C(215)	0.449 (3)	1.154 (3)	0.0523 (7)	93 (16)	C(516)	0.952 (3)	1.175 (4)	0.0969 (7)	103 (17)
C(216)	0.525 (3)	1.087 (3)	0.0460 (6)	69 (14)	C(521)	0.936 (3)	1.081 (3)	0.1620 (6)	63 (13)
C(221)	0.544 (3)	0.800 (3)	0.0359 (7)	76 (15)	C(522)	0.904 (3)	1.054 (4)	0.1838 (8)	120 (19)
C(222)	0.593 (3)	0.703 (4)	0.0365 (8)	135 (20)	C(523)	0.959 (3)	1.072 (4)	0.2066 (8)	129 (20)
C(223)	0.540 (4)	0.637 (4)	0.0198 (9)	156 (23)	C(524)	1.051 (4)	1.121 (4)	0.2070 (9)	169 (24)
C(224)	0.446 (4)	0.655 (4)	0.0078 (8)	138 (21)	C(525)	1.083 (4)	1.143 (4)	0.1877 (9)	159 (23)
C(225)	0.396 (3)	0.748 (3)	0.0075 (7)	93 (15)	C(526)	1.030 (3)	1.128 (4)	0.1634 (7)	106 (17)
C(226)	0.452 (3)	0.817 (3)	0.0231 (7)	97 (17)	C(531)	0.758 (2)	1.161 (3)	0.1331 (6)	49 (12)
C(231)	0.708 (3)	0.949 (3)	0.0360 (6)	53 (13)	C(532)	0.785 (3)	1.255 (3)	0.1412 (6)	83 (15)
C(232)	0.692 (3)	0.944 (3)	0.0104 (7)	93 (16)	C(533)	0.714 (4)	1.341 (4)	0.1430 (9)	153 (22)
C(233)	0.766 (3)	1.000 (3)	-0.0064 (7)	103 (17)	C(534)	0.616 (4)	1.314 (4)	0.1314 (8)	134 (20)
C(234)	0.846 (3)	1.039 (4)	0.0073 (8)	123 (19)	C(535)	0.584 (3)	1.224 (4)	0.1220 (8)	126 (19)
C(235)	0.864 (4)	1.051 (4)	0.0314 (8)	143 (21)	C(536)	0.655 (3)	1.146 (3)	0.1204 (7)	105 (17)
C(236)	0.795 (3)	1.006 (3)	0.0450 (7)	97 (17)	O(11)	0.175	0.322	0.030	133 (25)
C(311)	0.458 (3)	0.590 (3)	0.1170 (6)	69 (14)	C(12)	0.214	0.406	0.031	80 (30)
C(312)	0.388 (3)	0.513 (3)	0.1228 (7)	93 (16)	C(13)	0.156	0.440	0.015	138 (42)
C(313)	0.356 (4)	0.438 (4)	0.1042 (8)	130 (20)	C(14)	0.116	0.363	0.000	160 (46)
C(314)	0.395 (3)	0.452 (4)	0.0832 (8)	118 (19)	C(15)	0.160	0.294	0.005	203 (56)
C(315)	0.459 (4)	0.523 (5)	0.076 (1)	185 (26)	O(21)	0.457	0.139	0.218	224 (38)
C(316)	0.492 (3)	0.587 (4)	0.0949 (8)	132 (20)	C(22)	0.522	0.073	0.214	221 (60)
C(321)	0.507 (3)	0.626 (3)	0.1662 (6)	57 (13)	C(23)	0.590	0.120	0.200	189 (52)
C(322)	0.437 (3)	0.636 (3)	0.1845 (7)	84 (15)	C(24)	0.549	0.180	0.186	179 (50)
C(323)	0.448 (4)	0.586 (4)	0.2066 (9)	174 (25)	C(25)	0.439	0.200	0.197	202 (56)

* Asterisk indicates anisotropic thermal parameters were used in refinement.

form factor for oxygen gave a similar result with unit population. However, it seemed unlikely that fluorine could be present in the sample as no fluorine compounds were used in the synthesis. Moreover, with oxygen, the four requisite hydrogen atoms required were readily located in difference maps and refined in x , y , z as for the solvate of **1**. No substantial evidence for a fifth hydrogen was evident from a difference map computed after convergence with only the seventh largest residue as a feature near the Cu₆ core; this did not refine satisfactorily. The present description is therefore in terms of the oxo bridge, presumably a minor product consequent on hydrolysis and/or oxidation, and associated core hydrogens.

Discussion

Hexameric thf Hemisolvate of 1. Although, in respect to hydrogen atom location, the noncentrosymmetric space group reduces the limits of resolution of the structural data, the results that have been obtained are generally reasonable and self-consistent. The complex is a new phase of [(PPh₃)CuH]₆, solvated with thf rather than dmf as found previously,² and the atoms are numbered

similarly. Comparison of similar types of core-edge distances reveal surprising variations. The edges of the upper and lower "trans" faces, defined by their longer Cu...Cu distances (and absences of hydrogen atoms (see below), are nearly 0.1 Å longer in the thf vs the dmf solvate, while those forming the equatorial belt are appreciably shorter, indicative of a pronounced "squashing" of the octahedron in the thf vs the dmf solvate. The distances between the centroids (C(0)) of the upper and lower trans faces are 1.90₈ and 2.03₀ Å, respectively.

Less comprehensive structural detail is available on the P(*p*-tolyl)₃ and P(NMe₂)₃ adducts for comparison; the former in addition has the drawback of disorder. For the P(*p*-tolyl)₃ adduct, ⟨Cu...Cu⟩ distances are (long edges) 2.68 (3) and (short edges) 2.63 (2) Å; C(0)...C(0') distances are 1.99₂ and 2.05 Å, so that the long distances span a range 2.65₅-2.80₄ Å, with the present thf solvate being intermediate, while the short distances span a range of 2.47₈-2.54₂ Å, with the P(NMe₂)₃ adduct being intermediate.

Table IV. $P_6Cu_6H_6$ Core Distances (Å) for **1** and **1a**

	1		1a
	thf solvate	dmf solvate ²	
Edges of the "trans" Faces			
Cu(1)-Cu(3)	2.759 (2)	2.667 (5)	3.162 (3)
Cu(3)-Cu(4)	2.707 (2)	2.650 (5)	2.664 (3)
Cu(4)-Cu(1)	2.783 (2)	2.637 (2)	2.701 (3)
Cu(2)-Cu(5)	2.721 (2)	2.674 (5)	2.576 (3)
Cu(5)-Cu(6)	2.728 (2)	2.667 (5)	2.663 (3)
Cu(6)-Cu(2)	2.739 (2)	2.632 (6)	2.552 (3)
av	2.740	2.655	2.720
Edges of the "Equatorial" Belt			
Cu(1)-Cu(2)	2.477 (2)	2.592 (5)	2.738 (3)
Cu(2)-Cu(3)	2.482 (2)	2.595 (5)	2.799 (3)
Cu(3)-Cu(6)	2.445 (2)	2.530 (6)	2.486 (3)
Cu(6)-Cu(4)	2.495 (2)	2.545 (5)	2.573 (3)
Cu(4)-Cu(5)	2.477 (2)	2.498 (5)	2.550 (3)
Cu(5)-Cu(1)	2.492 (2)	2.494 (6)	2.449 (3)
av	2.478	2.542	2.600
Cu(1)-P(1)	2.213 (3)	2.241 (9)	2.251 (5)
Cu(2)-P(2)	2.233 (3)	2.244 (8)	2.257 (4)
Cu(3)-P(3)	2.229 (4)	2.262 (8)	2.245 (5)
Cu(4)-P(4)	2.236 (3)	2.221 (8)	2.224 (5)
Cu(5)-P(5)	2.200 (3)	2.217 (7)	2.218 (4)
Cu(6)-P(6)	2.246 (3)	2.252 (9)	2.230 (4)
av	2.226	2.240	2.238
Hydride Distances			
	1		1a^c
H(1)-Cu(1,2,3)	1.95 (10), 1.82 (8), 1.84 (10)		
H(2)-Cu(1,2,5)	1.90 (9), 1.54 (10), 1.96 (9)	1.55 (9), 1.71 (9), 1.85 (9)	
H(3)-Cu(1,4,5)	2.00 (10), 1.59 (10), 1.88 (9)	1.92 (9), 1.50 (9), 1.60 (8)	
H(4)-Cu(2,3,6)	1.79 (10), 1.73 (9), 1.77 (10)	1.83 (9), 1.74 (9), 1.56 (9)	
H(5)-Cu(3,4,6)	1.28 (9), 2.29 (10), 1.23 (9)	1.59 (9), 1.47 (9), 1.64 (9)	
H(6)-Cu(4,5,6)	1.91 (8), 1.43 (10), 1.61 (10)		

^cIn **1a**, "O"-Cu(1,3) = 2.198 (7), 2.191 (7) Å.

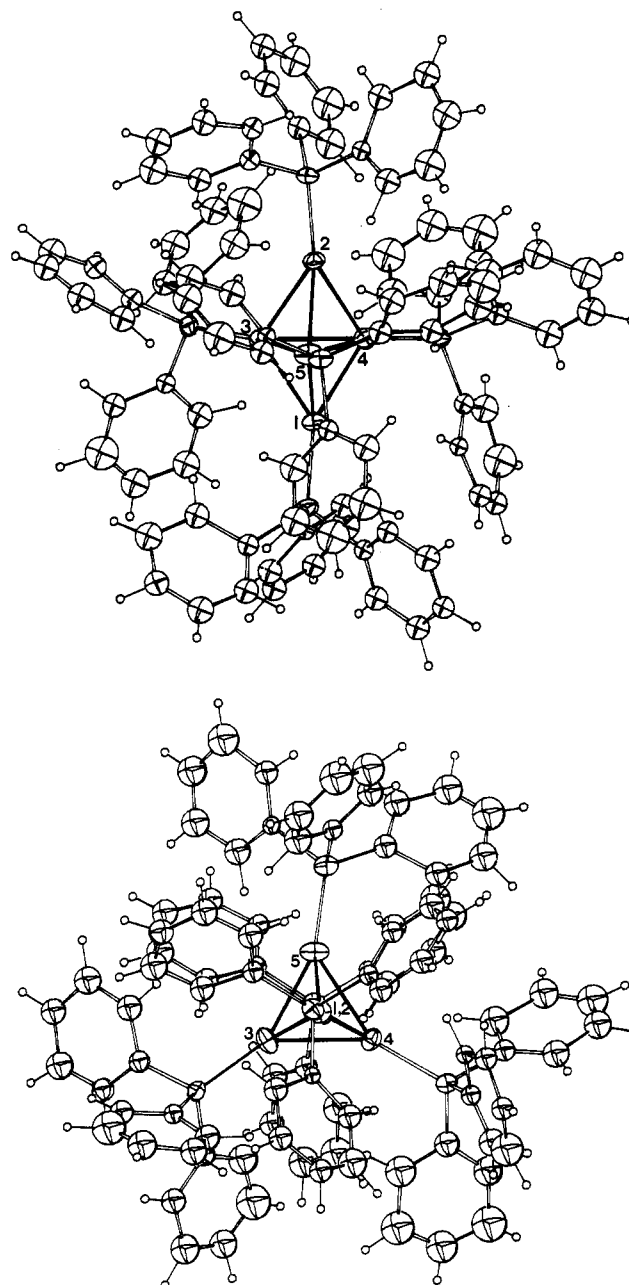
Table V. P(m)-Cu(m)-Cu(n) Hexamer Angles (deg)

m	n	1		1a
		thf solvate	dmf solvate	
1	3	135.9 (1)	145.4 (3)	147.1 (1)
	4	143.4 (1)	140.6 (3)	143.8 (1)
	2	127.3 (1)	127.5 (3)	130.8 (1)
2	5	135.8 (1)	123.5 (3)	127.7 (2)
	5	139.2 (1)	145.3 (3)	146.2 (1)
	6	133.1 (1)	135.8 (3)	135.4 (1)
3	1	135.8 (1)	134.1 (3)	131.6 (1)
	3	131.4 (1)	126.4 (2)	123.4 (1)
	4	130.4 (1)	144.6 (3)	143.9 (2)
4	1	125.8 (1)	133.2 (2)	135.2 (1)
	2	142.3 (1)	135.9 (2)	140.5 (1)
	6	136.2 (1)	125.9 (3)	132.4 (2)
5	1	140.0 (1)	129.5 (3)	126.0 (1)
	3	136.8 (1)	136.3 (3)	131.6 (1)
	5	133.7 (1)	132.0 (3)	134.1 (1)
6	1	130.3 (1)	140.7 (3)	141.7 (1)
	2	142.2 (1)	133.9 (2)	133.9 (1)
	6	138.7 (1)	133.9 (3)	135.2 (1)
1	1	129.9 (1)	135.8 (3)	128.8 (1)
	4	127.1 (1)	134.6 (3)	134.8 (1)
	2	129.2 (1)	126.8 (3)	126.9 (1)
5	1	135.3 (1)	128.0 (3)	129.4 (1)
	3	133.8 (1)	141.4 (3)	134.7 (1)
	4	140.8 (1)	140.4 (3)	140.6 (1)

Table VI. Pentamer Core Distances (Å)

atoms	dist
Cu(1)-Cu(3,4,5)	2.455 (7), 2.431 (7), 2.451 (8)
Cu(2)-Cu(3,4,5)	2.578 (7), 2.526 (7), 2.582 (7)
Cu(3)-Cu(4,5)	2.608 (7), 2.493 (8)
Cu(4)-Cu(5)	2.592 (8)
Cu(1)···Cu(2)	4.034 (7)
Cu(n)-P(n) (n = 1-5)	2.16 (1), 2.21 (1), 2.17 (1), 2.18 (1), 2.17 (1)

As for the $[(PPh_3)CuH]_6$ ·dmf cluster, the hydride ligands triply bridge the six triangular Cu_3 faces, flanking the hexamer, the average Cu-H distance being 1.75 Å. The hydride anions adopt

Figure 2. Two views of a molecule of **2**.

an approximately octahedral architecture with the average H···H distance along the edges of 2.9 Å. The formation of an octahedral rather than a tetrahedral cluster as found for chloride, bromide, and iodide complexes is consistent with a smaller radius for the hydride anion. Cu-P distances range from 2.200 (3) to 2.246 (3) Å (average value 2.226 Å). These distances are quite characteristic of the $[(PPh_3)Cu]$ molecular fragment found in a wide range of compounds.¹⁰ Each of the PPh_3 ligands adopt the minimum energy "head to tail" arrangement of phenyl groups normally found in comfortably packed PPh_3 complexes.

The differences between these systems and those observed in the presumed hydrolysis/solvolytic artifact, **1a**, are even more pronounced. Of the six equatorial hydrides of **1**, four are well defined in **1a**. H(1), expected on face Cu(1,2,3), is not evident and instead is replaced by the oxygen atom on edge Cu(1)-Cu(2), this edge being greatly elongated, so that it is by far the longest in any of the Cu_6 cores (3.162 (3) Å), while Cu(2)-Cu(1,3) distances are also lengthened but to a lesser extent. The unique nature of the system makes it difficult to speculate as to expect-

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tations concerning the length of Cu(1)-Cu(3) and associated Cu-O distances. A hydrogen atom also appears to be lacking on the face trans to Cu(1,2,3), namely Cu(4,5,6), although there is no corresponding effect on the associated Cu-Cu, P geometries. (Among the equatorial distances in the study of the dmf solvate, Cu(2)-Cu(1,3) distances were noted as unusually long; it seems unlikely that this was the result of any partial decomposition in that core since there was no corresponding lengthening of Cu(1)-Cu(3).)

Pentameric thf Solvate. 1:1 copper(I) hydride:monodentate ligand adducts have thus far only been structurally characterized as hexamers;²⁻⁴ with oligodentate ligands, dimeric⁵ and octameric species⁴ have been structurally authenticated, μ_3 -bridging hydrogen atoms being located in the former. In this context, the isolation of the present pentamer was unexpected. The five copper atoms are disposed in a trigonal-bipyramidal array (Figure 2). This array is distorted from ideal trigonal-bipyramidal symmetry in two ways: first, one pyramid shows $\text{Cu}_{\text{ax}}\cdots\text{Cu}_{\text{eq}}$ bond lengths ca. 0.1 Å longer than the other, and second, the equatorial copper atoms form an isosceles rather than an equilateral triangle ($\text{Cu}_{\text{eq}}\cdots\text{Cu}_{\text{eq}} = 2.608$ (7), 2.592 (8), and 2.492 (8) Å). The $\text{Cu}_{\text{ax}}\cdots\text{Cu}_{\text{ax}}$ distance is 4.034 (8) Å. Comparison of this cluster with pentameric clusters in the anions $[\text{Cu}_5(\mu_2\text{-S}^t\text{Bu})_6]^{-11}$ and $[\text{Cu}_5\text{Ph}_6]^{-12}$ shows important differences in the geometries. In these latter compounds, the pentanuclear skeleton has been described as a "squashed" trigonal bipyramid. For example, in $[\text{Li}(\text{thf})_4][\text{Cu}_5\text{Ph}_6]^{-12}$ the $\text{Cu}_{\text{ax}}\cdots\text{Cu}_{\text{ax}}$ distance is 3.269 (4) Å while the $\text{Cu}_{\text{eq}}\cdots\text{Cu}_{\text{eq}}$ distances are 3.165 (4) Å. The $\langle\text{Cu}_{\text{ax}}\cdots\text{Cu}_{\text{eq}}\rangle$

distance of 2.452 (4) Å, the atoms here being bridged by Ph ligands, is similar to the value found for **2**.

The five triphenylphosphine ligands form single Cu-P bonds to each of the copper atoms with distances ranging between 2.16 (1) and 2.21 (1) Å. These distances are shorter than those found in the regular hexamer, and in the general context of $(\text{PPh}_3)\text{-Cu}$ compounds, shorter distances have been found only for $(\text{PPh}_3)\text{-Cu}(\eta\text{-C}_5\text{H}_5)^{13}$.

The question of location of the hydride anions in this complex is of considerable interest; the answer to which is not, as yet, available from the structural data. The evidence from the hexamer structure suggests that facial center locations are likely to be preferred. In the present array, differentiation of one of the six faces might be expected to result in the face devoid of hydrogen atoms having significantly longer edges; no face in the present structure presents itself as an obvious candidate in this respect. A further possibility is that the cluster may be the $[(\text{PPh}_3)_5\text{Cu}_5\text{H}_6]^-$ anion. While this is consistent with the relatively symmetrical disposition of the copper atoms in the cluster, we have not, as yet, been able to provide supporting evidence, such as the presence of a counterion.

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Supplementary Material Available: Thermal parameters (Tables SUP 1-SUP 3), ligand hydrogen parameters (Table SUP 4), ligand non-hydrogen geometries (Tables SUP 5-SUP 7), and crystal data (Table SUP 8) (18 pages); tables of structure factor amplitudes (63 pages). Ordering information is given on any current masthead page.

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Kinetics and Mechanism of Hydrogen Peroxide Reactions of Diperoxo(amine)chromium(IV) Complexes: Evidence for Formation of an Oxodiperoxo(amine)chromium(VI) Intermediate

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The kinetics of the reactions of hydrogen peroxide with two chromium(IV)-diperoxo complexes $\text{Cr}(\text{O}_2)_2(\text{en})(\text{H}_2\text{O})$ and $\text{Cr}(\text{O}_2)_2(\text{dien})$ have been investigated in aqueous acidic media at 30 °C, $I = 1.00$ (NaClO_4). Two kinetic stages were observed. The first stage corresponded to the formation of a blue diperoxo intermediate of the form $\text{Cr}(\text{O})(\text{O}_2)_2\text{L}$ where $\text{L} = \text{en}$ or dien and water ligands (if any) are omitted. A mechanism involving the entry of free peroxide ligand into the coordination sphere of the metal ion prior to a redox process involving the conversion of Cr(IV) to Cr(VI) has been favored on the basis of kinetic results.

Introduction

Peroxo complexes of transition-metal ions have attracted much attention,^{1,2} and comparisons of the reactivity of peroxo derivatives of d^0 transition-metal ions with that of free hydrogen peroxide have been made.³⁻⁶ However, little is known of the reactivity of diperoxo derivatives of d^2 ions like chromium(IV). Among the few well-characterized complexes of chromium(IV), the derivatives

diperoxo(amine)chromium(IV), $\text{Cr}(\text{O}_2)_2(\text{en})(\text{H}_2\text{O})$ (**1**), and diperoxo(diethylenetriamine)chromium(IV), $\text{Cr}(\text{O}_2)_2(\text{dien})$ (**2**), have many unusual and interesting features.⁷⁻¹⁰ These complexes have formed useful intermediates in the synthesis of chromium(III) amine complexes.⁷⁻⁹ The mechanistic studies, on these complexes, however, have been limited.^{10,11}

Since complexes **1** and **2** contain both Cr(IV) and O_2^{2-} ligands, which are capable of reduction as well as oxidation, the redox

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