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Crystal Structure and Molecular Configuration of a Tetranuclear Copper(II) Complex Active as a Catalyst in the Oxidative Coupling of Phenols by Dioxygen: $Cu_4OCl_6(nmp)_3(OH_2\cdots nmp)$ (nmp = *N*-Methyl-2-pyrrolidinone)

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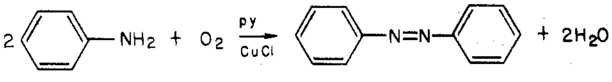
The species $Cu_4OCl_6(nmp)_3(OH_2\cdots nmp)$, an active catalyst for the oxidative coupling of phenols by dioxygen, has been studied by means of a single-crystal X-ray structural analysis. The complex crystallizes in the centrosymmetric monoclinic space group $P2_1/n$ with $a = 9.062$ (2) Å, $b = 22.051$ (5) Å, $c = 17.278$ (3) Å, $\beta = 96.65$ (1)°, $V = 3429.4$ (11) Å^3, ρ(obsd) = 1.733 (5) g cm^{-3}, and ρ(obsd) = 1.738 g cm^{-3} for formula weight 879.43 and $Z = 4$. Diffraction data were collected on a Syntex $P2_1$ diffractometer using graphite-monochromatized Mo Kα radiation. The structure was solved via direct methods (using MULTAN) and refined via least-squares methods to $R_F = 5.65\%$ and $R_{wF} = 4.69\%$ for those 3203 independent reflections with $4.5 < 2\theta < 40.0°$. The complex has a central μ_4-oxide ion [O(50)] surrounded tetrahedrally by four copper atoms [Cu–O(50)(av) = 1.896 ± 0.005 Å; Cu···Cu(av) = 3.095 ± 0.025 Å]; the six chloride ligands are each in a μ_2-bridging mode and bridge each of the Cu···Cu vectors. The Cu_4OCl_6 core of the molecule has approximate T_d symmetry. Three of the copper atoms are linked to nmp ligands [Cu(2)–O(20) = 1.913 (5) Å, Cu(3)–O(30) = 1.919 (5) Å, Cu(4)–O(40) = 1.923 (5) Å] while the fourth copper atom is linked to an aquo ligand [Cu(1)–OH_2 = 1.936 (6) Å]. The aquo ligand is additionally involved in hydrogen bonding to an otherwise free nmp molecule in the crystal lattice.

Introduction

The utility of copper(I) chloride as a catalyst in the oxidative coupling of terminal acetylenes by dioxygen (eq 1) in pyridine

$$2RC{\equiv}CH + {}^1/_2O_2 \xrightarrow[\text{CuCl}]{\text{py/MeOH}} RC{\equiv}C{-}C{\equiv}CR + H_2O \qquad (1)$$

(py) has been known for some time.[1-3] Copper(I) chloride is also an active catalyst for the coupling of aromatic amines[4-6] (eq 2) and phenols[7] (eq 3).



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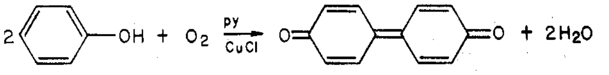


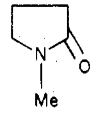
(3)

Davies and co-workers[8-10] have examined the reaction of copper(I) chloride with oxygen in pyridine, with a view toward determining the stoichiometry for the formation of the initiator of the above catalytic processes. The important overall stoichiometry appears to be[9] that shown in eq 4. (All pyridine

$$2CuCl + {}^1/_2O_2 \xrightarrow{\text{py}} \text{“}CuCl_2\text{”} + \text{“}CuO\text{”} \qquad (4)$$

ligands are omitted in this equation.) The "$CuCl_2$" component has been identified specifically as py_2CuCl_2,[8,9] but the precise nature of the "CuO" component is unknown, although a copper peroxide moiety is believed to be present.[8] Attempts to crystallize "CuO" from the separated initiator solution yields insoluble, catalytically inactive, copper(II) oxide.

Recently, Davies and co-workers[10,11] have studied the use of the amide *N*-methyl-2-pyrrolidinone (nmp), **1**, in place of pyridine. The reaction of copper(I) chloride with dioxygen in **1** yields a brown, catalytically active solution, which resists all attempts at separation and is believed to contain a single copper-containing product (i.e., the "$CuCl_2$" and "CuO" moieties of eq 4 appear now to be combined into a single species).[10] Spectroscopic, cryoscopic, and other physical measurements of this product strongly suggest the formula $(nmp)_3Cu_4Cl_4O_2$. Again, attempts to crystallize this material from nmp have been unsuccessful. However, addition of 1,2-dimethoxyethane (DME) to an nmp solution of this product yields an unstable, amorphous, yellow-green solid; if this solid is washed with DME and allowed to stand under DME in a loosely closed container, orange-brown crystals of a *catalytically active* (relative to eq 3) complex are obtained.[10,11] The present paper describes the identification of this material, by X-ray diffraction, as the polynuclear species $Cu_4OCl_6(nmp)_3(OH_2\cdots nmp)$. This molecule is closely related to the known species $Cu_4OCl_6L_4$ (**2**),[12] having the "basic



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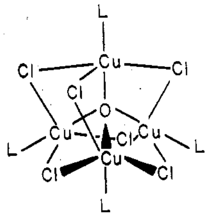

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Table I. Experimental Data for the X-ray Diffraction Study of $Cu_4OCl_6(nmp)_3(OH_2\cdots nmp)$

(A) Crystal Data

crystal system: monoclinic
space group: $P2_1/n$[a]
unit cell parameters[b]
$a = 9.062$ (2) Å
$b = 22.051$ (5) Å
$c = 17.278$ (3) Å
$\beta = 96.65$ (1)°
$V = 3429.4$ (11) Å^3
temp, 22.1 (5) °C
$Z = 4$
mol wt 897.43
ρ(obsd)[c] = 1.733 (5) g cm^{-3}
ρ(calcd) = 1.738 g cm^{-3}

(B) Intensity Data

radiation: Mo Kα ($\bar{\lambda}$ 0.710 73 Å)
monochromator: highly oriented graphite
reflections measd: $+h,+k,\pm l$
max 2θ measd: 40.0°
min 2θ measd: 4.5°
scan type: coupled θ(crystal)–2θ(counter)
scan speed: 4.0°/min
scan range: symmetrical, from $[2\theta(K\alpha_1) - 0.9]°$ to $[2\theta(K\alpha_2) + 0.9]°$
bkgd measurement: stationary crystal/stationary counter at beginning and end of scan, each for half of the time taken for the scan
standard reflections: 3, measd every 47 reflections (percent variances from the mean: 3.62% for 105, 3.14% for 410, and 4.54% for 0,10,2)
data set information: 3827 reflections collected, of which 131 were systematic absences and 231 were standard reflections (equivalent reflections were averaged,[d] yielding 3203 symmetry–independent reflections)

(C) Data Treatment Parameters

"ignorance factor": $p = 0.04$, applied to $\sigma(F^2)$ as $[\{\sigma(F^2)\}^2 + \{pF^2\}^2]^{1/2}$
absorption coeff:[e] $\mu = 2.972$ mm^{-1}

[a] $P2_1/n$ is a nonstandard setting of the centric, monoclinic space group $P2_1/c[C_{2h}{}^5$; No. 14] and has the equivalent positions $\pm(x, y, z)$ and $\pm(^1/_2 - x, {}^1/_2 + y, {}^1/_2 - z)$. [b] Determined by a least-squares fit of the setting angles of the unresolved Mo K$\bar{\alpha}$ peaks of 24 reflections with $2\theta = 17.3$–29.4°. [c] Measured by neutral buoyancy in 1-bromobutane/1,2-dibromoethane solution. [d] The agreement between the averaged, symmetry-equivalent reflections was $R(I) = 3.6\%$. [e] Nine reflections at various 2θ values were measured at 10° intervals of ψ (the azimuthal angle, corresponding to rotation of the crystal about its diffraction vector for that reflection) from $\psi = 0$ to 350°. The reflections and their 2θ values and ratios of maximum to minimum intensities, respectively, are as follows: 10$\bar{3}$, 7.99, 1.309; 105, 13.20, 1.258; 006, 14.27, 1.272; 037, 17.57, 1.274; 109, 22.47, 1.304; 1,5,10, 26.56, 1.258; 4,2,$\overline{11}$, 30.58, 1.269; 4,6,$\overline{11}$, 32.40, 1.263; 2,1,$\overline{15}$, 38.47, 1.346. These reflections were used to correct the intensity data empirically for absorption; for details of the absorption correction, see M. R. Churchill and F. J. Hollander, *Inorg. Chem.*, 16, 2493 (1977).

beryllium acetate" core of T_d symmetry. It is important to note, however, that the related species $Cu_4OCl_6(nmp)_4$ (**2**, L = nmp) is found to be catalytically inactive.[11]

Experimental Section

Collection and Correction of X-ray Diffraction Data. A crystalline sample of $Cu_4OCl_6(nmp)_3(OH_2\cdots nmp)$ was provided by Professor Geoffrey Davies of Northeastern University, Boston, Mass. The large (ca. 1 mm × 1 mm × 1 mm) brown crystals showed macroscopic C_{2h} point group symmetry; the crystal chosen for the X-ray structural analysis was cleaved from the corner of one of the large crystals, its shape approximating that of a rectangular solid of dimensions 0.35 mm × 0.30 mm × 0.20 mm. The crystal was jammed into a 0.3-mm diameter glass capillary, which was flushed with argon, flame-sealed, fixed into an aluminum pin with beeswax, and set in a eucentric goniometer head.

Preliminary precession and cone-axis photographs gave approximate unit cell parameters, indicated that the crystal was indeed monoclinic with C_{2h} ($2/m$) Laue symmetry, and revealed the systematic absences $0k0$ for $k = 2n + 1$ and $h0l$ for $h + l = 2n + 1$, which are consistent with the centrosymmetric space group $P2_1/n$ (see footnote *a* of Table I).

Table II. Data for the Structural Solution via MULTAN

(A) Statistical Distribution of Normalized Structure Factor Amplitudes

function	obsd	theoretical[a] centric	theoretical[a] acentric
$\langle\lvert E\rvert\rangle$	0.804	0.798	0.886
$\langle\lvert E\rvert^2\rangle$	1.000[b]	1.000	1.000
$\langle\lvert E^2 - 1\rvert\rangle$	0.966	0.968	0.736
$\lvert E > 1.0$, %	32.66	31.73	36.79
$\lvert E > 2.0$, %	4.78	4.55	1.89
$\lvert E > 3.0$, %	0.16	0.27	0.01

(B) MULTAN Data

reflections input: 269 with $\lvert E\rvert > 1.75$
Σ_2 relationships found: 3022
minimum "triple-product" value: 5.35

Σ_1 Reflections

hkl	$\lvert E\rvert$	phase angle	probability
040	1.89	180°	0.99
4,0,10	2.50	0°	0.98

Origin Fixing Reflections

hkl	$\lvert E\rvert$	phase angle	parity class
274	2.49	0°	eoe
295	2.75	0°	eoo
543	3.19	0°	oeo

Structure Solution Parameters: "Phasing" Reflections[c]

hkl	$\lvert E\rvert$	selected phase angle
24$\bar{6}$	2.49	0°
41$\bar{7}$	3.25	0°
51$\bar{6}$	3.17	180°

"absolute figure of merit": 1.260
"residual": 12.09
"combined figure of merit": 3.000

[a] I. L. Karle, K. S. Dragonette, and S. A. Brenner, *Acta Crystallogr*, 19, 713 (1965). [b] Fixed by an adjustable scale factor. [c] "Phasing" reflections are those reflections with large $\lvert E\rvert$ values and large phase reliability indices (α_h), which are allowed to take on variable phase angles, 0° and 180° in this case.

The crystal was now transferred to a Syntex $P2_1$ four-circle automated diffractometer controlled by a Data General NOVA 1200 computer and disk storage system.[13] After accurate centering in a monochromated Mo Kα X-ray beam, the crystal's relative orientation and accurate unit cell parameters were determined, and intensity data were collected as described previously.[14] The primary data set was now corrected for the effects of absorption, averaged (where appropriate), and corrected for Lorentz and polarization effects on our NOVA 1200 in-house computer (vide supra) using a locally modified version of the Syntex XTL conversational crystallographic program package.[15] Specifics of data collection and correction are listed in Table I.

Solution and Refinement of the Structure. All calculations were done on a CDC 6600/CYBER 173 computer at the State University of New York at Buffalo. Programs used in the structural analysis were as follows: MULTAN (phase determination from $\lvert E\rvert$ values via the tangent formula) by G. Germain, P. Main, and M. M. Woolfson; JIMDAP (a modified version of A. Zalkin's FORDAP for Fourier synthesis) by J. A. Ibers and co-workers; LSHF (structure factor calculations and full-matrix least-squares refinement), STAN1 (distances, angles, and esd's), and PLOD (least-squares planes, esd's, and dihedral angles) by B. G. DeBoer; ORTEP-II (thermal ellipsoid plotting routine) by C. K. Johnson.

Analytical scattering factors[16a] for all neutral nonhydrogen atoms and the hydrogen atomic scattering factors of Stewart et al.[17], converted to analytical form,[18] were used; the real and imaginary coefficients of anomalous dispersion[16b] were included for all nonhydrogen atoms.

Table III. Positional and Isotropic Thermal Parameters and Esd's[a,c]

atom	x	y	z	B_{iso},[b] Å^2	atom	x	y	z	B_{iso},[b] Å^2
Cu(1)	0.52969 (9)	0.37497 (4)	0.27118 (5)	3.57	H(1)	0.360 (9)	0.290 (4)	0.294 (5)	7.6 (28)
Cu(2)	0.66111 (10)	0.50051 (4)	0.24224 (5)	3.33	H(10)	0.333 (6)	0.333 (3)	0.244 (3)	2.0 (24)
Cu(3)	0.79830 (10)	0.38685 (4)	0.17618 (5)	3.62	H(2A)	0.1584	0.2309	0.1856	6.7
Cu(4)	0.83446 (10)	0.41000 (4)	0.35655 (5)	3.53	H(2E)	0.3042	0.2345	0.1465	6.7
Cl(12)	0.40968 (21)	0.47212 (8)	0.25729 (12)	4.31	H(3A)	0.2139	0.1578	0.0744	10.5
Cl(13)	0.58567 (22)	0.31786 (9)	0.15952 (12)	4.74	H(3E)	0.1010	0.1423	0.1327	10.5
Cl(14)	0.65259 (22)	0.34513 (10)	0.39618 (12)	5.10	H(4A)	0.2469	0.0670	0.1703	8.0
Cl(23)	0.74457 (27)	0.48355 (10)	0.11734 (12)	5.62	H(4E)	0.3787	0.0972	0.1347	8.0
Cl(24)	0.83817 (24)	0.51644 (9)	0.35530 (12)	4.72	H(5A)	0.4524	0.0530	0.2824	8.0
Cl(34)	1.00597 (20)	0.36116 (9)	0.27160 (12)	4.46	H(5B)	0.5417	0.1115	0.3065	8.0
O(50)	0.7082 (5)	0.4177 (2)	0.2612 (2)	2.8	H(5C)	0.4008	0.0956	0.3457	8.0
O(10)	0.3492 (7)	0.3335 (3)	0.2903 (4)	6.3	H(22A)	0.3642	0.5753	0.1384	6.6
O(1)	0.3663 (7)	0.2175 (2)	0.3046 (3)	5.8	H(22E)	0.4842	0.5646	0.0825	6.6
N(1)	0.3552 (7)	0.1284 (3)	0.2393 (4)	5.3	H(23A)	0.4101	0.6468	0.0181	8.0
C(1)	0.3267 (8)	0.1861 (3)	0.2462 (5)	4.1	H(23E)	0.2880	0.6568	0.0730	8.0
C(2)	0.2436 (10)	0.2090 (4)	0.1740 (5)	5.9	H(24A)	0.4126	0.7308	0.1281	7.2
C(3)	0.2015 (14)	0.1526 (5)	0.1280 (7)	10.2	H(24E)	0.5331	0.7216	0.0720	7.2
C(4)	0.2992 (11)	0.1040 (4)	0.1652 (6)	7.2	H(25A)	0.6714	0.7519	0.2054	8.2
C(5)	0.4451 (11)	0.0941 (4)	0.2984 (6)	8.0	H(25B)	0.6593	0.7060	0.2726	8.2
O(20)	0.6317 (6)	0.5860 (2)	0.2296 (3)	4.9	H(25C)	0.7761	0.6959	0.2147	8.2
N(21)	0.5730 (7)	0.6745 (3)	0.1700 (4)	4.8	H(32A)	1.0467	0.4608	0.0741	6.5
C(21)	0.5586 (8)	0.6158 (3)	0.1774 (4)	3.6	H(32E)	1.1197	0.4289	0.1492	6.5
C(22)	0.4440 (9)	0.5934 (4)	0.1154 (5)	5.4	H(33A)	1.3230	0.4172	0.0983	8.4
C(23)	0.3913 (11)	0.6505 (4)	0.0709 (5)	7.0	H(33E)	1.2572	0.4570	0.0285	8.4
C(24)	0.4771 (10)	0.7022 (4)	0.1082 (5)	6.1	H(34A)	1.3066	0.3383	0.0219	7.6
C(25)	0.6788 (11)	0.7103 (4)	0.2199 (6)	7.6	H(34E)	1.2247	0.3768	−0.0451	7.6
O(30)	0.8944 (6)	0.3530 (2)	0.0928 (3)	4.7	H(35A)	1.0997	0.2666	−0.0422	7.5
N(31)	1.0871 (7)	0.3393 (3)	0.0239 (4)	4.8	H(35B)	0.9380	0.2875	−0.0355	7.5
C(31)	1.0168 (9)	0.3702 (3)	0.0725 (4)	3.8	H(35C)	1.0281	0.2542	0.0338	7.5
C(32)	1.1014 (9)	0.4262 (4)	0.0939 (5)	5.8	H(42A)	1.1400	0.4938	0.4429	6.2
C(33)	1.2418 (11)	0.4220 (5)	0.0587 (5)	7.4	H(42E)	1.1789	0.4511	0.3767	6.2
C(34)	1.2269 (9)	0.3658 (5)	0.0083 (5)	6.9	H(43A)	1.4049	0.4472	0.4314	8.2
C(35)	1.0340 (11)	0.2821 (4)	−0.0078 (5)	7.0	H(43E)	1.3624	0.4851	0.5014	8.2
O(40)	0.9623 (6)	0.3938 (3)	0.4510 (3)	5.2	H(44A)	1.3736	0.4034	0.5723	7.9
N(41)	1.1892 (7)	0.3720 (3)	0.5104 (4)	5.1	H(44E)	1.4066	0.3649	0.5010	7.9
C(41)	1.0964 (9)	0.4056 (3)	0.4641 (4)	4.0	H(45A)	1.2289	0.3024	0.5834	8.5
C(42)	1.1814 (9)	0.4556 (4)	0.4316 (5)	5.4	H(45B)	1.0774	0.3342	0.5887	8.5
C(43)	1.3376 (9)	0.4505 (5)	0.4696 (6)	7.2	H(45C)	1.0967	0.2911	0.5194	8.5
C(44)	1.3414 (10)	0.3940 (5)	0.5193 (5)	7.3					
C(45)	1.1447 (12)	0.3203 (4)	0.5541 (5)	7.9					

[a] Esd's, shown in parentheses, have been right adjusted to the last digit of the preceding number. These are derived from the inverse of the final least-squares matrix. [b] "Equivalent isotropic" thermal parameters are given here; for full anisotropic thermal parameters, see Table IV. [c] The positions and isotropic thermal parameters of H(1) and H(10) were refined; all other hydrogen atoms were allowed to refine as their attached carbons and were assigned isotropic thermal parameters of approximately 1.0 + the "equivalent" B_{iso} of their attached carbons (see text).

The function minimized in the least-squares process was $\sum w(|F_o| - |F_c|)^2$, where $w = [\sigma(F_o)]^{-2}$. Discrepancy indices and the estimated standard deviation of an observation of unit weight or "goodness-of-fit" (GOF) are defined in eq 5–7, where NO is the number of reflections and NV is the number of parameters refined.

$$R_F = \left[\frac{\sum ||F_o| - |F_c||}{\sum |F_o|}\right] \times 100\ (\%) \tag{5}$$

$$R_{wF} = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\sum w|F_o|^2}\right]^{1/2} \times 100\ (\%) \tag{6}$$

$$\mathrm{GOF} = \left[\frac{\sum w(|F_o| - |F_c|)^2}{(\mathrm{NO} - \mathrm{NV})}\right]^{1/2} \tag{7}$$

The structure was solved by the tangent formula as developed in MULTAN.[19] The calculation of normalized structure factor amplitudes, $|E|$, and the application of MULTAN to the solution of X-ray structures in our research group have been described previously;[20] the statistical distribution of $|E|$'s and MULTAN data specific to the solution of this structure are collected in Table II. The solution given therein was used to phase an "E map" from which were determined the positions of the four copper atoms (arranged at the apices of a tetrahedron) and six chlorine atoms (bridging each edge of this tetrahedron) in the molecule. Refinement of a Wilson plot scale factor and positional and isotropic thermal parameters of these ten heavy atoms led to R_F

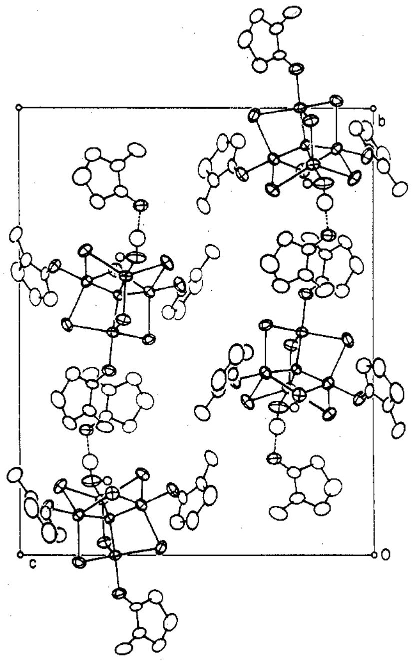

Figure 1. Packing of $Cu_4OCl_6(nmp)_3(OH_2\cdots nmp)$ molecules into the unit cell, projected on (100). (ORTEP-II diagram, 30% probability ellipsoids.)

Table IV. Anisotropic Thermal Parameters and Esd's[a,b]

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	$\langle U\rangle$[c]
Cu(1)	2.43 (4)	3.04 (4)	5.26 (6)	−0.01 (3)	0.55 (4)	0.18 (4)	0.174, 0.196, 0.258
Cu(2)	3.41 (5)	2.67 (4)	3.84 (5)	0.17 (3)	0.13 (4)	0.20 (3)	0.181, 0.206, 0.226
Cu(3)	3.30 (5)	3.86 (5)	3.83 (5)	0.11 (4)	0.91 (4)	−0.65 (4)	0.185, 0.214, 0.239
Cu(4)	3.09 (5)	3.88 (5)	3.48 (5)	−0.26 (4)	−0.17 (4)	0.72 (4)	0.185, 0.200, 0.244
Cl(12)	2.97 (9)	3.60 (10)	6.50 (12)	0.91 (8)	1.11 (8)	0.63 (8)	0.171, 0.223, 0.291
Cl(13)	4.15 (11)	4.61 (10)	5.45 (12)	−0.88 (8)	0.45 (9)	−1.70 (9)	0.193, 0.238, 0.294
Cl(14)	4.12 (11)	6.23 (12)	4.99 (11)	−1.02 (9)	0.72 (9)	2.40 (10)	0.179, 0.238, 0.324
Cl(23)	7.67 (14)	5.53 (12)	4.04 (11)	2.35 (10)	2.33 (10)	1.69 (9)	0.191, 0.229, 0.353
Cl(24)	5.71 (12)	3.40 (9)	4.60 (11)	0.11 (8)	−1.36 (9)	−0.65 (8)	0.191, 0.218, 0.308
Cl(34)	2.56 (9)	5.41 (11)	5.38 (11)	1.08 (8)	0.33 (8)	0.06 (9)	0.167, 0.262, 0.271
O(50)	2.5 (2)	2.8 (2)	3.0 (2)	0.0 (2)	0.3 (2)	0.4 (2)	0.18, 0.18, 0.20
O(10)	3.8 (3)	3.9 (4)	11.6 (8)	−0.1 (3)	1.7 (4)	0.7 (4)	0.21, 0.22, 0.38
O(1)	7.5 (4)	3.7 (3)	5.9 (4)	0.2 (3)	−0.1 (3)	−0.2 (3)	0.22, 0.27, 0.32
N(1)	5.1 (4)	4.0 (4)	6.6 (5)	0.1 (3)	0.3 (4)	−0.8 (4)	0.22, 0.25, 0.30
C(1)	3.4 (4)	3.5 (5)	5.4 (6)	−0.6 (4)	0.8 (4)	0.4 (4)	0.19, 0.23, 0.26
C(2)	5.8 (5)	5.7 (5)	5.9 (5)	0.7 (4)	−1.0 (4)	1.0 (4)	0.22, 0.28, 0.31
C(3)	11.9 (10)	9.1 (8)	8.5 (8)	−1.1 (8)	−3.8 (7)	−1.5 (7)	0.25, 0.35, 0.45
C(4)	8.3 (7)	5.3 (6)	8.3 (7)	−2.5 (5)	2.9 (6)	−1.2 (5)	0.22, 0.29, 0.38
C(5)	8.2 (7)	5.9 (6)	10.0 (8)	1.9 (5)	1.6 (6)	2.2 (6)	0.24, 0.32, 0.38
O(20)	5.7 (3)	3.2 (3)	5.5 (3)	0.5 (2)	−0.6 (3)	0.6 (2)	0.19, 0.25, 0.30
N(21)	5.6 (4)	3.4 (4)	5.1 (4)	0.8 (3)	−0.2 (3)	1.0 (3)	0.18, 0.26, 0.28
C(21)	4.6 (5)	2.1 (4)	4.4 (5)	0.3 (3)	1.0 (4)	0.5 (3)	0.16, 0.22, 0.25
C(22)	4.5 (5)	5.5 (5)	6.1 (5)	1.7 (4)	−0.2 (4)	−0.2 (4)	0.20, 0.27, 0.30
C(23)	6.3 (6)	8.9 (7)	5.8 (6)	2.8 (6)	0.5 (5)	2.2 (5)	0.22, 0.28, 0.38
C(24)	7.7 (6)	5.2 (5)	5.5 (5)	2.6 (5)	1.4 (5)	2.2 (5)	0.19, 0.27, 0.35
C(25)	9.7 (7)	3.9 (5)	9.0 (7)	0.5 (5)	−0.2 (6)	1.5 (5)	0.21, 0.33, 0.37
O(30)	4.3 (3)	5.4 (3)	4.5 (3)	−0.5 (3)	1.4 (2)	−1.8 (2)	0.19, 0.23, 0.30
N(31)	5.0 (4)	5.9 (4)	3.5 (4)	1.4 (4)	0.5 (3)	−0.7 (3)	0.20, 0.23, 0.30
C(31)	4.1 (5)	5.2 (5)	2.2 (4)	0.7 (4)	0.9 (4)	−0.4 (3)	0.15, 0.22, 0.26
C(32)	4.5 (5)	6.6 (6)	6.5 (5)	−0.4 (4)	2.0 (4)	−0.4 (4)	0.21, 0.28, 0.31
C(33)	8.3 (7)	9.8 (8)	4.2 (5)	−1.9 (6)	1.5 (5)	0.3 (5)	0.22, 0.30, 0.38
C(34)	3.6 (5)	11.7 (8)	5.9 (6)	1.3 (5)	2.1 (4)	1.4 (6)	0.18, 0.27, 0.39
C(35)	9.0 (7)	7.2 (6)	5.0 (5)	2.3 (5)	1.2 (5)	−1.9 (5)	0.20, 0.30, 0.37
O(40)	4.2 (3)	7.2 (4)	4.0 (3)	−1.4 (3)	−0.8 (2)	1.7 (2)	0.19, 0.22, 0.33
N(41)	4.5 (4)	6.1 (4)	4.5 (4)	1.4 (4)	−0.6 (3)	−0.5 (3)	0.21, 0.24, 0.31
C(41)	4.0 (5)	5.2 (5)	2.6 (4)	0.2 (4)	−0.9 (4)	−0.5 (4)	0.16, 0.24, 0.26
C(42)	4.6 (5)	6.3 (5)	5.4 (5)	−0.6 (4)	0.7 (4)	−0.1 (4)	0.24, 0.26, 0.29
C(43)	3.6 (5)	12.0 (8)	6.1 (6)	−1.4 (5)	0.1 (4)	−1.0 (6)	0.20, 0.28, 0.39
C(44)	4.4 (6)	11.9 (9)	5.5 (6)	2.4 (5)	−0.1 (4)	−1.8 (6)	0.22, 0.25, 0.41
C(45)	10.4 (8)	6.4 (6)	6.4 (6)	1.9 (6)	−1.1 (5)	2.1 (5)	0.21, 0.33, 0.38

[a] See footnote *a* of Table III. [b] These have units of Å^2 and they enter the calculated structure factor equation in the form $\exp[-0.25(a^{*2}h^2B_{11} + b^{*2}k^2B_{22} + c^{*2}l^2B_{33} + 2a^*b^*hkB_{12} + 2a^*c^*hlB_{13} + 2b^*c^*klB_{23})]$. [c] These values are the root-mean-square amplitudes of vibration (in Å) of the atom along the three principal axes (minor, median, and major, respectively) of its vibrational ellipsoid. For relative orientations, see the figures.

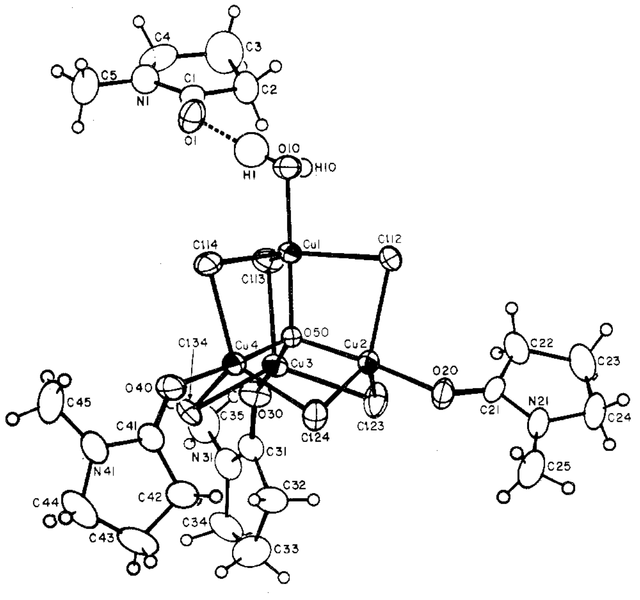

Figure 2. Labeling of atoms within the $Cu_4OCl_6(nmp)_3(OH_2\cdots nmp)$ molecule.

= 25.7%. A difference Fourier synthesis showed an oxygen atom (O(50)) in the center of the copper tetrahedron, three nmp groups, each oxygen bound to a copper atom, an oxygen atom (O(10)) bound to the fourth copper atom, and an nmp group, whose carbonyl oxygen (O(1)) was approximately 2.6 Å from O(10). Two full-matrix least-squares cycles of isotropic refinement for the 40 nonhydrogen atoms yielded $R_F = 11.3\%$, $R_{wF} = 10.7\%$, and GOF = 2.804. We now desired to refine all of these nonhydrogen atoms anisotropically, but due to (artificially imposed) computer storage limitations, all of the 361 resulting parameters could not be refined in a single full-matrix cycle. This problem was circumvented via an "alternate-cycle" block refinement—refinement of the positional and anisotropic thermal parameters of the Cu_4OCl_6 core, O(10), and the O(1)→C(5) nmp ring in one cycle (172 parameters) and refinement of parameters of the other three nmp groups in another cycle (190 parameters); the scale factor was refined in each cycle. Continued refinement in this manner led to $R_F = 6.7\%$, $R_{wF} = 6.0\%$, and GOF = 1.629.

A difference Fourier synthesis now yielded the positions of the two hydrogen atoms of the O(10) water molecule, one of which, H(1), was along the O(10)→O(1) vector, approximately 1.8 Å from O(1); this indicates strongly that the O(1)→C(5) nmp ring is hydrogen bonded to the rest of the molecule through H(1); no other hydrogen atoms were clearly discernible from this map. Therefore, the positions of the remaining hydrogen atoms were calculated, assuming an idealized sp^3 geometry about the carbon atoms in question and d(C–H) = 0.95 Å;[21] the methyl hydrogens were placed in a staggered conformation relative to the N→ring C bonds. Isotropic thermal parameters for these calculated hydrogens were fixed throughout the rest of the refinement at values assigned by $B_H = [1.0 + B_{C,iso}]$ Å^2. Subsequent refinement was carried out by including and refining positional and isotropic thermal parameters for H(1) and H(10) in

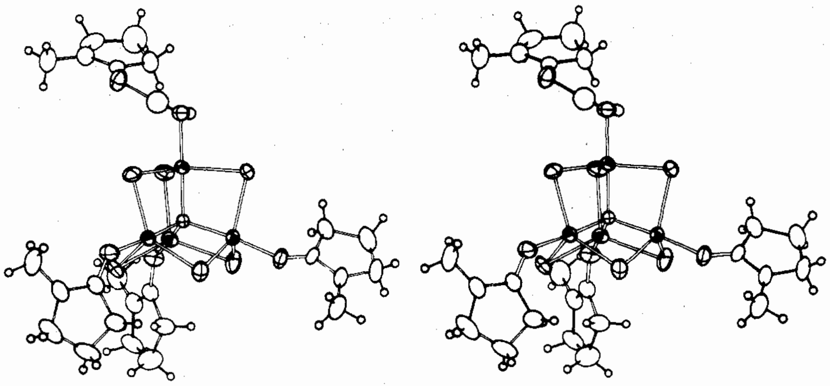

Figure 3. Stereoscopic view of the $Cu_4OCl_6(nmp)_3(OH_2\cdots nmp)$ molecule.

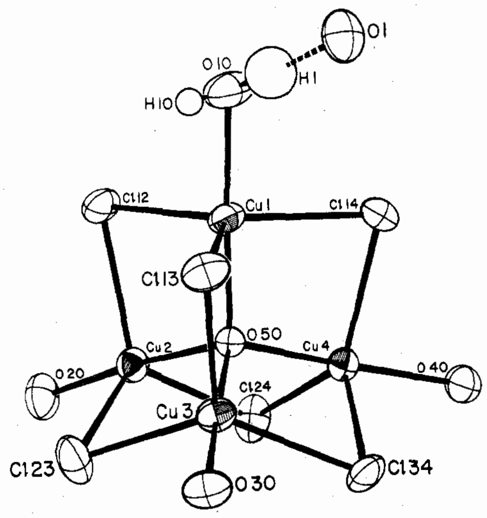

Figure 4. The $Cu_4OCl_6(O)_3(OH_2\cdots O)$ core of the $Cu_4OCl_6(nmp)_3(OH_2\cdots nmp)$ molecule.

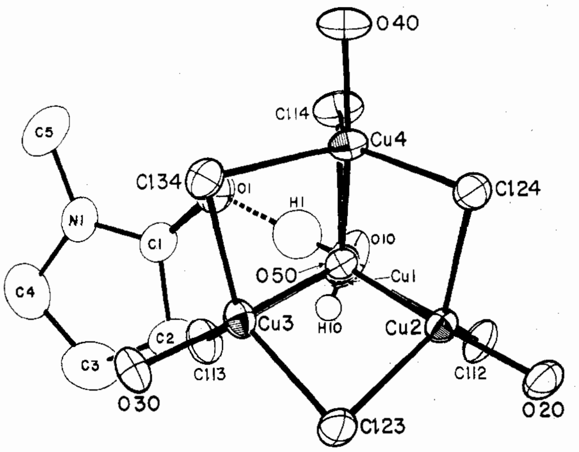

Figure 5. A portion of the $Cu_4OCl_6(nmp)_3(OH_2\cdots nmp)$ structure, viewed down the O(50)–Cu(1)–O(10) axis and showing the geometry of the hydrogen-bonded Cu(1)–$OH_2\cdots$nmp system.

Table V. Interatomic Distances (Å) and Esd's[a]

(A) Copper–Copper Contacts			
Cu(1)···Cu(2)	3.0772 (13)	Cu(2)···Cu(3)	3.0755 (13)
Cu(1)···Cu(3)	3.1005 (13)	Cu(2)···Cu(4)	3.1037 (13)
Cu(1)···Cu(4)	3.0752 (13)	Cu(3)···Cu(4)	3.1374 (14)
	mean: 3.095 ± 0.024 Å[b]		
(B) Bond Distances within the Cu_4OCl_6 Core			
Cu(1)–Cl(12)	2.4020 (20)	Cu(2)–Cl(12)	2.4059 (21)
Cu(1)–Cl(13)	2.4066 (22)	Cu(3)–Cl(13)	2.4457 (21)
Cu(1)–Cl(14)	2.4044 (23)	Cu(4)–Cl(14)	2.3437 (21)
Cu(2)–Cl(23)	2.3973 (22)	Cu(3)–Cl(23)	2.3881 (22)
Cu(2)–Cl(24)	2.4059 (21)	Cu(4)–Cl(24)	2.3474 (21)
Cu(3)–Cl(34)	2.4213 (21)	Cu(4)–Cl(34)	2.5016 (21)
	mean: 2.406 ± 0.041 Å[b]		
Cu(1)–O(50)	1.897 (4)	Cu(3)–O(50)	1.889 (4)
Cu(2)–O(50)	1.895 (4)	Cu(4)–O(50)	1.902 (4)
	mean: 1.896 ± 0.005 Å[b]		
(C) Copper–Oxygen and Hydrogen–Oxygen Distances			
Cu(1)–O(10)	1.936 (6)	Cu(2)–O(20)	1.913 (5)
		Cu(3)–O(30)	1.919 (5)
		Cu(4)–O(40)	1.923 (5)
		mean: 1.918 ± 0.005 Å[b]	
O(10)–H(1)	0.95 (8)	O(1)···H(1)	1.62 (8)
O(10)–H(10)	0.81 (5)		
(D) Carbon–Oxygen and Carbon–Nitrogen Distances			
C(1)–O(1)	1.242 (8)	C(31)–O(30)	1.259 (8)
C(21)–O(20)	1.242 (8)	C(41)–O(40)	1.238 (8)
	mean: 1.245 ± 0.009 Å[b]		
C(1)–N(1)	1.308 (9)	C(31)–N(31)	1.304 (8)
C(21)–N(21)	1.310 (8)	C(41)–N(41)	1.318 (9)
	mean: 1.310 ± 0.006 Å[b]		
C(4)–N(1)	1.428 (10)	C(5)–N(1)	1.444 (10)
C(24)–N(21)	1.432 (9)	C(25)–N(21)	1.447 (10)
C(34)–N(31)	1.449 (10)	C(35)–N(31)	1.435 (10)
C(44)–N(41)	1.453 (11)	C(45)–N(41)	1.451 (10)
	mean: 1.442 ± 0.009 Å[b]		
(E) Carbon–Carbon Distances			
C(1)–C(2)	1.469 (10)	C(31)–C(32)	1.478 (11)
C(2)–C(3)	1.501 (12)	C(32)–C(33)	1.475 (11)
C(3)–C(4)	1.488 (13)	C(33)–C(34)	1.512 (12)
C(21)–C(22)	1.488 (10)	C(41)–C(42)	1.491 (10)
C(22)–C(23)	1.523 (11)	C(42)–C(43)	1.495 (11)
C(23)–C(24)	1.483 (12)	C(43)–C(44)	1.510 (13)
	mean: 1.493 ± 0.016 Å[b]		

[a] See footnote *a* of Table III. [b] The errors associated with the mean values were calculated from $\sigma = [[\Sigma(\bar{X} - X_i)^2]/(N-1)]^{1/2}$, where $\bar{X}$ is the mean, X_i is the value of the *i*th observation, and *N* is the number of observations.

the first of the alternate cycles and coupling the shifts of the positional parameters of the calculated hydrogens to those of their attached carbon atoms.

The effect of secondary extinction was accounted for by the refinement of a secondary extinction parameter, *c*, in each of the subsequent alternate cycles. This parameter enters the equation for the corrected structure factor (F_c^{cor}) in the form[22,23] $F_c^{cor} = F_c^{uncor.}(1 + c(F_c^{uncor})^2)^{-1/4}$.

Refinement was now continued to convergence, the final values of the discrepancy indices being $R_F = 5.65\%$ and $R_{wF} = 4.69\%$ with GOF = 1.279 for 3203 independent reflections and 370 variable parameters; the data-to-parameter ratio was 8.66:1. The final value of the secondary extinction parameter (*c*) was 1.24 (27) × 10^{-5} e^{-2}.

Table VI. Intramolecular Angles (deg) and Esd's[a]

(A) Angles about Copper Atoms			
Cl(12)-Cu(1)-Cl(13)	121.44 (8)	Cl(13)-Cu(3)-Cl(23)	112.72 (9)
Cl(12)-Cu(1)-Cl(14)	119.42 (9)	Cl(13)-Cu(3)-Cl(34)	118.32 (8)
Cl(13)-Cu(1)-Cl(14)	117.27 (9)	Cl(23)-Cu(3)-Cl(34)	127.08 (9)
Cl(12)-Cu(2)-Cl(23)	117.26 (9)	Cl(14)-Cu(4)-Cl(24)	128.63 (9)
Cl(12)-Cu(2)-Cl(24)	120.08 (8)	Cl(14)-Cu(4)-Cl(34)	114.48 (9)
Cl(23)-Cu(2)-Cl(24)	120.23 (9)	Cl(24)-Cu(4)-Cl(34)	114.49 (8)
	mean: 119.3 ± 4.8° [b]		
O(10)-Cu(1)-Cl(12)	93.27 (19)	O(30)-Cu(3)-Cl(13)	95.14 (16)
O(10)-Cu(1)-Cl(13)	98.64 (21)	O(30)-Cu(3)-Cl(23)	96.65 (17)
O(10)-Cu(1)-Cl(14)	91.70 (22)	O(30)-Cu(3)-Cl(34)	92.03 (17)
O(20)-Cu(2)-Cl(12)	98.50 (17)	O(40)-Cu(4)-Cl(14)	90.77 (16)
O(20)-Cu(2)-Cl(23)	96.04 (17)	O(40)-Cu(4)-Cl(24)	100.72 (18)
O(20)-Cu(2)-Cl(24)	91.13 (16)	O(40)-Cu(4)-Cl(34)	93.65 (18)
	mean: 94.9 ± 3.3° [b]		
O(50)-Cu(1)-Cl(12)	85.91 (13)	O(50)-Cu(3)-Cl(13)	84.83 (14)
O(50)-Cu(1)-Cl(13)	85.77 (14)	O(50)-Cu(3)-Cl(23)	85.65 (14)
O(50)-Cu(1)-Cl(14)	84.63 (14)	O(50)-Cu(3)-Cl(34)	85.80 (14)
O(50)-Cu(2)-Cl(12)	85.85 (13)	O(50)-Cu(4)-Cl(14)	86.25 (14)
O(50)-Cu(2)-Cl(23)	85.26 (14)	O(50)-Cu(4)-Cl(24)	84.86 (14)
O(50)-Cu(2)-Cl(24)	83.37 (14)	O(50)-Cu(4)-Cl(34)	83.28 (13)
	mean: 85.1 ± 1.0° [b]		
O(50)-Cu(1)-O(10)	175.23 (26)	O(50)-Cu(3)-O(30)	177.51 (22)
O(50)-Cu(2)-O(20)	174.23 (21)	O(50)-Cu(4)-O(40)	174.38 (22)
	mean: 175.3 ± 1.5° [b]		
(B) Copper-Oxygen-Copper Angles			
Cu(1)-O(50)-Cu(2)	108.51 (20)	Cu(2)-O(50)-Cu(3)	108.76 (20)
Cu(1)-O(50)-Cu(3)	109.97 (21)	Cu(2)-O(50)-Cu(4)	109.69 (21)
Cu(1)-O(50)-Cu(4)	108.12 (20)	Cu(3)-O(50)-Cu(4)	111.74 (21)
	mean: 109.5 ± 1.3° [b]		
(C) Copper-Chlorine-Copper Angles			
Cu(1)-Cl(12)-Cu(2)	79.59 (6)	Cu(2)-Cl(23)-Cu(3)	79.98 (7)
Cu(1)-Cl(13)-Cu(3)	79.43 (6)	Cu(2)-Cl(24)-Cu(4)	81.52 (7)
Cu(1)-Cl(14)-Cu(4)	80.72 (7)	Cu(3)-Cl(34)-Cu(4)	79.16 (6)
	mean: 80.1 ± 0.9° [b]		
(D) Angles about Oxygen and Hydrogen of Coordinated Water			
Cu(1)-O(10)-H(10)	84 (4)	Cu(1)-O(10)-H(1)	114 (5)
H(1)-O(10)-H(10)	93 (6)	O(10)-H(1)···O(1)	176 (5)
(E) Angles about nmp Oxygens			
C(1)-O(1)···H(1)	117 (3)	C(21)-O(20)-Cu(2)	131.2 (5)
		C(31)-O(30)-Cu(3)	125.6 (5)
		C(41)-O(40)-Cu(4)	126.7 (5)
		mean: 127.8 ± 3.0° [b]	
(F) Angles within nmp Rings			
O(1)-C(1)-N(1)	125.0 (8)	O(1)-C(1)-C(2)	124.8 (7)
	mean: 124.9 ± 0.1° [b]		
O(20)-C(21)-N(21)	122.8 (7)	O(20)-C(21)-C(22)	128.1 (6)
O(30)-C(31)-N(31)	122.2 (7)	O(30)-C(31)-C(32)	129.0 (7)
O(40)-C(41)-N(41)	122.4 (8)	O(40)-C(41)-C(42)	128.7 (7)
mean: 122.5 ± 0.3° [b]		mean: 128.6 ± 0.5° [b]	
N(1)-C(1)-C(2)	110.2 (7)	N(31)-C(31)-C(32)	108.6 (7)
N(21)-C(21)-C(22)	109.0 (7)	N(41)-C(41)-C(42)	108.8 (7)
	mean: 109.2 ± 0.7° [b]		
C(5)-N(1)-C(1)	123.2 (8)	C(5)-N(1)-C(4)	123.4 (8)
C(25)-N(21)-C(21)	123.2 (7)	C(25)-N(21)-C(24)	121.0 (7)
C(35)-N(31)-C(31)	122.5 (7)	C(35)-N(31)-C(34)	123.0 (7)
C(45)-N(41)-C(41)	124.1 (8)	C(45)-N(41)-C(44)	121.6 (7)
	mean: 122.8 ± 1.0° [b]		
C(1)-N(1)-C(4)	113.2 (7)	C(31)-N(31)-C(34)	114.3 (7)
C(21)-N(21)-C(24)	115.8 (7)	C(41)-N(41)-C(44)	114.0 (8)
	mean: 114.3 ± 1.1° [b]		
C(1)-C(2)-C(3)	103.9 (7)	C(31)-C(32)-C(33)	107.0 (7)
C(2)-C(3)-C(4)	105.4 (8)	C(32)-C(33)-C(34)	105.4 (8)
C(3)-C(4)-N(1)	104.4 (8)	C(33)-C(34)-N(31)	104.2 (7)
C(21)-C(22)-C(23)	103.9 (7)	C(41)-C(42)-C(43)	106.4 (7)
C(22)-C(23)-C(24)	107.4 (7)	C(42)-C(43)-C(44)	105.7 (7)
C(23)-C(24)-N(21)	103.8 (6)	C(43)-C(44)-N(41)	104.8 (7)
	mean: 105.2 ± 1.2° [b]		

[a] See footnote *a* of Table III. [b] See footnote *b* of Table V.

Table VII. Least-Squares Planes and Esd's[a]

atom[b]	dev,[c] Å	atom[b]	dev,[c] Å
Plane I: $0.8585X + 0.5024Y - 0.1025Z = 7.524$			
Cl(12)*	0.000 (2)	Cu(1)	−0.191 (1)
Cl(13)*	−0.000 (2)	O(10)	−2.122 (6)
Cl(14)*	−0.000 (2)	O(50)	1.706 (4)
Plane II: $-0.1863X + 0.9701Y - 0.1553Z = 8.819$			
Cl(12)*	−0.000 (2)	Cu(2)	0.217 (1)
Cl(23)*	0.000 (2)	O(20)	2.125 (5)
Cl(24)*	−0.000 (2)	O(50)	−1.677 (4)
Plane III: $-0.5138X + 0.3680Y + 0.7750Z = 2.138$			
Cl(13)*	0.000 (2)	Cu(3)	−0.192 (1)
Cl(23)*	−0.000 (2)	O(30)	−2.109 (5)
Cl(34)*	−0.000 (2)	O(50)	1.697 (4)
Plane IV: $0.5311X - 0.0915Y + 0.8423Z = 7.751$			
Cl(14)*	−0.000 (2)	Cu(4)	0.214 (1)
Cl(24)*	−0.000 (2)	O(40)	2.127 (5)
Cl(34)*	0.000 (2)	O(50)	−1.687 (4)
Plane V: $0.0253X + 0.1659Y + 0.9858Z = 6.105$			
Cu(1)*	−0.038 (1)	O(50)*	−0.009 (4)
Cu(2)*	−0.037 (1)	O(10)	0.092 (6)
Cl(12)*	0.056 (2)	O(20)	0.056 (5)
Cl(34)*	0.028 (2)		
Plane VI: $0.4437X - 0.6582Y + 0.6082Z = -0.7265$			
Cu(1)*	0.004 (1)	O(50)*	0.006 (4)
Cu(3)*	0.004 (1)	O(10)	0.063 (6)
Cl(13)*	−0.008 (2)	O(30)	0.086 (5)
Cl(24)*	−0.006 (2)		
Plane VII: $-0.4546X + 0.8078Y + 0.3753Z = 6.440$			
Cu(1)*	0.050 (1)	O(50)*	0.004 (4)
Cu(4)*	0.046 (1)	O(10)	0.195 (6)
Cl(14)*	−0.069 (2)	O(40)	−0.075 (5)
Cl(23)*	−0.032 (2)		
Plane VIII: $0.8586X + 0.2731Y + 0.4338Z = 9.484$			
Cu(2)*	0.062 (1)	O(50)*	0.038 (4)
Cu(3)*	0.066 (1)	O(20)	0.276 (5)
Cl(14)*	−0.059 (2)	O(30)	0.133 (5)
Cl(23)*	−0.107 (2)		
Plane IX: $0.8473X + 0.0504Y - 0.5287Z = 3.091$			
Cu(2)*	−0.066 (1)	O(50)*	−0.002 (4)
Cu(4)*	−0.067 (1)	O(20)	−0.061 (5)
Cu(13)*	0.042 (2)	O(40)	−0.121 (5)
Cu(24)*	0.093 (2)		
Plane X: $0.4136X + 0.8990Y - 0.1437Z = 10.064$			
Cu(3)*	0.017 (1)	O(50)*	0.011 (4)
Cu(4)*	0.017 (1)	O(30)	−0.020 (5)
Cl(12)*	−0.016 (2)	O(40)	−0.136 (5)
Cl(34)*	−0.028 (2)		
Plane XI: $0.9953X + 0.0382Y - 0.0884Z = 2.429$			
O(10)*	−0.017 (6)	O(1)*	−0.010 (6)
H(10)*	−0.00 (5)	C(1)	−0.189 (8)
H(1)*	0.03 (8)		

Selected Dihedral Angles

plane to plane		angle, deg	plane to plane		angle, deg
I	II	69.91	VI	VII	120.34
I	III	70.39	VI	VIII	117.72
I	IV	71.11	VI	X	119.71
II	III	70.59	VII	IX	122.88
II	IV	71.43	VII	X	118.97
III	IV	69.75	IX	X	118.15
V	VI	120.10	XI	I	28.02
V	VII	119.51	XI	V	93.19
V	VIII	119.65	XI	VI	68.73
V	IX	119.43	XI	VII	62.95

[a] Equations of planes are expressed in orthonormal (Å) coordinates (X, Y, Z) which are related to the fractional coordinates (x, y, z) by the transformation

$$\begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = \begin{pmatrix} a & 0 & c\cos\beta \\ 0 & b & 0 \\ 0 & 0 & c\sin\beta \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

[b] Those atoms marked with an asterisk were given unit weight in the corresponding plane; those unmarked were given zero weight. [c] See footnote *a* of Table III.

The function $\sum w(|F_o| - |F_c|)^2$ showed no appreciable dependence upon either $(\sin\theta)/\lambda$ or $|F_o|$ thereby indicating a correctly chosen weighting scheme. A final difference map showed as its greatest features three peaks (each 0.48 e Å^{-3} in height) at −0.500, 0.214, 0.432; −0.379, 0.117, 0.029; and −0.082, 0.265, 0.000; the correctness and completeness of the structure is thus confirmed.

Final positional and isotropic thermal parameters are collected in Table III, and final anisotropic thermal parameters are given in Table IV.

Discussion

Interatomic distances and their esd's are listed in Table V, while interatomic angles (with esd's) are given in Table VI. Least-squares planes (and atomic deviations therefrom) are collected in Table VII. The crystal is composed of units of $Cu_4OCl_6(nmp)_3(OH_2\cdots nmp)$ which are mutually separated by normal van der Waals distances; the packing of these molecular species in the unit cell is illustrated in Figure 1. The scheme used for labeling atoms is indicated in Figure 2 and a stereoscopic view of the molecular structure appears as Figure 3.

The molecule consists of a tetrahedral arrangement of copper(II) atoms which enclose a μ_4-oxide ion and which are bridged by six μ_2-chloride ligands lying above the six edges of the tetrahedron. The Cu_4OCl_6 core has approximate, but not exact, T_d symmetry. The central μ_4-oxide ion, O(50), is linked symmetrically to all four copper atoms, the individual bond lengths ranging from 1.889 (4) to 1.902 (4) Å and averaging 1.896 ± 0.005 Å.[24] Distances within the tetrahedral array of copper atoms are Cu(1)···Cu(4) = 3.0752 (13) Å, Cu(2)···Cu(3) = 3.0755 (13) Å, Cu(1)···Cu(2) = 3.0772 (13) Å, Cu(1)···Cu(3) = 3.1005 (13) Å, Cu(2)···Cu(4) = 3.1037 (13) Å, and Cu(3)···Cu(4) = 3.1374 (14) Å; the average of these six independent measurements is 3.095 ± 0.024 Å. The chloride ligands occupy μ_2-bridging positions over the edges of the Cu_4 tetrahedron. The bridges are close to symmetrical, with Cu–Cl distances ranging from 2.3437 (21) to 2.5016 (21) Å; the greatest asymmetry occurs for the system Cu(3)–Cl(34)–Cu(4) in which Cu(3)–Cl(34) = 2.4213 (21) Å and Cu(4)–Cl(34) = 2.5016 (21) Å [Δ = 0.0803 (29) Å]. Angles at the bridging chlorine atoms are all acute, with individual values ranging from 79.16 (6) to 81.52 (7)° and averaging 80.1 ± 0.9°.

Three of the copper atoms are linked directly to the oxygen atoms of nmp ligands, the individual copper–oxygen distances being Cu(2)–O(20) = 1.913 (5) Å, Cu(3)–O(30) = 1.919 (5) Å, and Cu(4)–O(40) = 1.923 (5) Å (average = 1.918 ± 0.005 Å). Angles at the oxygen atoms of nmp ligands show some variations, with values of C(21)–O(20)–Cu(2) = 131.2 (5)°, C(31)–O(30)–Cu(3) = 125.6 (5)°, and C(41)–O(40)–Cu(4) = 126.7 (5)°.

The present structure differs from all previously reported $Cu_4OCl_6L_4$ structures in that the four copper atoms are not linked to equivalent ligands. The fourth copper atom in the present structure is bonded to a water molecule (or "aquo ligand") which is further hydrogen bonded to an otherwise free nmp molecule in the crystal lattice. The Cu–OH_2 linkage, Cu(1)–O(10), is 1.936 (6) Å in length, i.e., slightly longer than the Cu–O(nmp) bond lengths. The hydrogen atoms of the aquo ligand were located and refined in the course of the crystal structure analysis. Resulting dimensions are as follows: O(10)–H(10) = 0.81 (5) Å, O(10)–H(1) = 0.95 (8) Å, Cu(1)–O(10)–H(10) = 84 (4)°, Cu(1)–O(10)–H(1) = 114 (5)°, and H(10)–Cu(1)–H(1) = 93 (6)°. This aquo ligand is hydrogen bonded to the oxygen atom of an nmp molecule; dimensions within the O(10)–H(1)···O(1) system are O(10)–H(1) = 0.95 (8) Å, H(1)···O(1) = 1.62 (8) Å, and O(10)–H(1)···O(1) = 176 (5)°. Figures 4 and 5 show views of the hydrogen bonding.

The fact that the present $Cu_4OCl_6(nmp)_3(OH_2\cdots nmp)$ molecule is a catalyst for the oxidative coupling of phenols (eq

3), whereas the symmetrical species $Cu_4OCl_6(nmp)_4$ is catalytically *inactive*, clearly suggests that Cu(1) of the present structure is actively involved in the catalytic cycle. Further work is, however, required before the detailed steps of the mechanism are elucidated. Such steps might involve replacement of the aquo ligand by dioxygen or deprotonation of the aquo ligand. Also, the precise molecular geometry of the species "$(nmp)_3Cu_4Cl_4O_2$" has still to be ascertained.

Each of the copper(II) atoms is in a (slightly distorted) trigonal-bipyramidal coordination geometry, with chloride ligands in the three equatorial sites and oxygen atoms bonded at the axial sites. The distortions of the $CuCl_3O_2$ moieties from D_{3h} symmetry are clearly indicated by planes I–IV of Table VII. In each case the central Cu(II) ion is displaced outward (i.e., away from O(50)) from the plane defined by the three equatorial chloride ligands.

Finally, we note that all distances and angles within the nmp ligands are in the expected ranges.

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Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

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Notes

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Nickel(0) Complexes with the Hybrid Bidentate Ligand 1-(Thioethyl)-2-(diphenylphosphino)ethane. Synthesis and Catalytic Properties of the Related Nickel Hydride Derivative

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The chemistry of the zerovalent complexes of nickel with phosphite and phosphine ligands (L) has been extensively studied in recent years in view of their relevance in homogeneous catalysis. It has been recognized that the reactivity of the NiL_4 complexes is particularly influenced by their tendency to give coordinatively unsaturated NiL_3 and NiL_2 species in solution.[1-3] Also, in the case of the hydrido derivative $[NiHL_4]^+$, which can be easily obtained by protonation of the corresponding nickel(0) complex,[4-8] the reactivity appears strictly dependent on the possibility of dissociating one ligand to give a free coordination site at the nickel atom.[2,9-11]

Since the nature of donor atoms can have a profound influence on the ease with which the ligands undergo dissociation, we have attempted to prepare $Ni(L-L')_2$ and $[NiH(L-L')_2]^+$ complexes with hybrid bidentate ligands (L–L′) containing both phosphorus and sulfur donor atoms. It seemed likely, in fact, that these complexes could become coordinatively unsaturated in solution since the sulfur end of the chelate would easily be displaced from the metal atom. In particular, we have chosen ligands of the type $(C_6H_5)_2PCH_2CH_2SR$ (R = CH_3, C_2H_5, C_6H_5) since previous investigations on their coordinating properties have shown that in their complexes of nickel(II) the dissociation of the thioether group can occur quite readily.

This paper reports the synthesis and chemistry of some nickel(0) derivatives with the ligand 1-(thioethyl)-2-(diphenylphosphino)ethane ($(C_6H_5)_2PCH_2CH_2SC_2H_5$, abbreviated P-SEt). Moreover we describe the preparation of the nickel hydride $[NiH(P\text{-}SEt)_2]^+$ and its catalytic behavior in olefin isomerization reactions.

Experimental Section

All operations involving air-sensitive complexes were performed under argon. Melting points were determined in evacuated, sealed capillaries and were uncorrected. Tetrahydrofuran was distilled from $LiAlH_4$. Other solvents were dried in the usual manner. All solvents were purged with argon. Infrared spectra were recorded on a Perkin-Elmer 457 grating spectrometer and GLC's on a Hewlett-Packard 5750 gas chromatograph. ^1H NMR spectra were taken using a Bruker 90-MHz instrument. Elemental analyses were performed

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