coordination of N(1) to Pd enlarges the Pd—N(1)—C(1), N(1)—C(1)—C(2) and C(1)—C(2)—C(3) angles from approximately 120° to 128°, 129° and 126°, respectively, while reducing the C(1)—N(1)—N(2) angle to 111°. Presumably, these angle distortions arise from steric repulsion between the adjacent phenyl ring and the Pd coordination sphere. The chain from C(2) to C(9) in the coordinated benzalazine has a zigzag shape, nearly perpendicular to the $PdCl_2N_2$ plane. The C(1)N(1)N(2) and $PdCl_2N_2$ planes intersect at an angle of 89·5°. These steric arrangements further reduce the nonbonding interactions in the complex. The Pd—N and Pd—Cl bond distances of 2·026 (4) and 2·281 (1) Å, respectively, are comparable with the values of 2·030 (3) Å for Pd—N and 2·297 (1) Å for Pd—Cl in $Pd[(CH_3)_2C(C_3H_3N_2)_2]Cl_2$ (Minghetti, Cinnellu, Bandini, Banditelli, Demartin & Manassero, 1986).

We thank the National Science Council of the Republic of China for support of this work.

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Simple, Direct Synthesis and Structure of Hexa-μ-chloro-tetrakis-(1-methylimidazole)-μ_4-oxo-tetracopper(II)

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(*Received* 25 *July* 1988; *accepted* 6 *March* 1989)

Abstract. $[Cu_4Cl_6O(C_4H_6N_2)_4]$, $M_r = 811·32$, orthorhombic, $Pbca$, $a = 18·985\,(7)$, $b = 33·197\,(7)$, $c = 18·917\,(5)$ Å, $V = 11922\,(6)$ Å^3, $Z = 16$, $D_m = 1·80$, $D_x = 1·81$ g cm^{-3}, $\lambda(\text{Cu }K\alpha) = 1·5418$ Å, $\mu = 84·2$ cm^{-1}, $F(000) = 6432$, $T = 293$ K, $R = 0·051$ for 6860 reflections with $F_o \geq 4\sigma(F_o)$. $[Cu_4Cl_6O(1\text{-MeIm})_4]$ is readily synthesized by simply mixing concentrated methanolic solutions of copper(II) chloride hydrate and 1-methylimidazole under ambient conditions. Each of the two molecules in the asymmetric unit consists of a μ_4-O atom surrounded by a tetrahedron of Cu atoms with μ_2-Cl atoms bridging between the Cu atoms, and with 1-methylimidazole completing the distorted trigonal bipyramidal coordination around the Cu atoms. The average Cu—O bond distance is 1·902 (7) Å while the average Cu—Cl bond length is 2·417 (30) Å. Deviations of the coordination polyhedron from ideal trigonal bipyramidal symmetry in this and related compounds are also examined.

Introduction. The first example of the general class of compounds of the form $[Cu_4OX_6L_4]$ was described by Bertrand & Kelley (1966) (X = Cl and L = triphenylphosphine), see Fig. 1. It is now clear that the thermodynamic factors governing the formation of these compounds make their preparation relatively favored as evidenced by the facts that they have been encountered during the recrystallization of other products (Ainscough, Bingham, Brodie & Brown, 1984; Bertrand, 1967; Bertrand & Kelley, 1966, 1970; Davies & El-Sayed, 1983; El-Toukhy, Guang-Zuan, Davies, Gilbert, Onan & Veidis, 1984; Watt & Durney, 1974); as unexpected major products during the attempted synthesis of some other species (Harlow & Simonsen, 1977; Yampol'skaya & Ablov, 1976); as minor by-products (Kilbourn & Dunitz, 1967; Churchill, de Boer & Mendak, 1975; Carr & Harrod, 1972) and in other ways (Belford, Fenton & Truter, 1972; Davies, El-Shazly, Rupich, Churchill & Rotella, 1978; Churchill & Rotella, 1979; de Boer,

0108-2701/89/111707-07$03.00

Bright & Helle, 1972; Gill & Sterns, 1970; Harris & Sinn, 1969; Nifontova, Lavrent'ev, Ponomarev, Filipenko, Krasochka, Atovmyan & Khidekel', 1982; Ondrejovic, Macaskova & Gazo, 1972; Pickardt & Rautenburg, 1982). The scheme most used to prepare $[Cu_4OX_6L_4]$ is procedure *A*: refluxing a solvent such as methanol containing a mixture of anhydrous CuX_2 and CuO, filtering off the unreacted CuO and then adding *L* (Barnes, Inman & Hatfield, 1971). Other schemes involve refluxing a solvent containing a mixture of $CuCl_2.2H_2O$ and *L* or refluxing a solvent containing a mixture of CuX_2, *L* and either NaOH or $NaOCH_3$ (Norman, 1985).

The subject compound of this paper is $[Cu_4Cl_6O(1\text{-MeIm})_4]$ (Grazynska, Drozdzewski & Wojciechowski, 1979). It was first reported in 1979 and was synthesized by procedure *A*. Various features of its Raman, IR and electronic spectra have been discussed (Grazynska, Drozdzewski & Wojciechowski, 1979) as have the magnetic properties of the closely related imidazole and benzimidazole derivatives (Grazynska & Wojciechowski, 1979). We were led to a less rigorous synthesis after observing that $[Cu_4Cl_6O(1\text{-MeIm})_4]$ is obtained as a minor by-product in the preparation of [CuCl(Gly)(1-MeIm)] (Norman, 1985). In fact, simply mixing relatively concentrated methanolic solutions of $CuCl_2.2H_2O$ and 1-MeIm results in the immediate formation of the compound. Presumably equilibrium amounts of $[Cu_4Cl_6OL_4]$ ($L = H_2O$ and/or CH_3OH and/or Cl^-) are present in concentrated methanolic solutions of $CuCl_2.2H_2O$ and the addition of 1-MeIm simply results in facile substitution of *L* by 1-MeIm and precipitation of the resulting $[Cu_4Cl_6O(1\text{-MeIm})_4]$. The source of the μ_4-oxo atom in the syntheses is clearly H_2O, a conclusion consistent with the observation that addition of a stoichiometric amount of CH_3O^- substantially improves the yield. A similar conclusion was reached by Gill & Sterns (1970) with respect to the synthesis of $[Cu_4Cl_6OL_4]$ (L = 2-methylpyridine). When the mixing of the $CuCl_2.2H_2O$ solution with the 1-MeIm solution is diffusion controlled, single crystals of $[Cu_4Cl_6O(1\text{-MeIm})_4]$ result. In the diffusion experiments we performed, crystals appeared within 24 hours and continued to form for up to three weeks. It should be noted that Pickardt and Rautenberg prepared $[Cu_4Cl_6OL_4]$ (L = hexamethylenetetramine) by allowing acetone solutions of the ligand and $CuCl_2$ to mix *via* diffusion, but the details of their experiments are not given (Pickardt & Rautenburg, 1982).

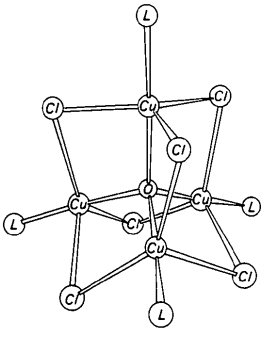

Fig. 1. General representation of $[Cu_4Cl_6OL_4]$.

After the work presented here was completed (Norman, 1985), and after most of this manuscript was written, we were made aware of the structure determination of hexachlorotetrakis(*N*-methylimidazole-*N'*)oxotetracopper(II) by Clegg, Nicholson, Collison & Garner (1988). They synthesized the compound by yet another method involving $[Cu(1\text{-MeIm})_2Cl_2]$ as a starting material and reported a crystal structure determination with the identical space group as reported here and nearly identical unit-cell parameters. However, their structure includes an acetonitrile molecule of solvation while our structure contains no solvent molecules and specifically cannot contain acetonitrile, given that none was utilized in any part of the preparation.

Experimental. *Syntheses.* To a solution of $CuCl_2.2H_2O$ (0·6822 g, 4·0 mmol) in 20 mL methanol, four mL of a 1·00 *M* solution of 1-MeIm in methanol was added in 500 μL increments over a period of two to three minutes. Upon each successive addition, the original clear green solution became increasingly opaque and yellow-brown in color as solids formed. After stirring for an additional 30 minutes, the microcrystalline yellow material was collected (0·3664 g, 45% yield based on copper).

An experimental variant of the above procedure involves diffusion and produces crystals suitable for single-crystal X-ray diffraction studies. $CuCl_2.2H_2O$ (0·8548 g, 5·0 mmol) was placed in a 10 mL beaker. This beaker was filled to approximately one half its capacity with methanol. The mixture was stirred with a glass rod to affect solution and then the 10 mL beaker was placed inside a 100 mL beaker. Then 5 mL of a 1·00 *M* solution of 1-MeIm in methanol was placed in the 100 mL beaker but *outside* of the 10 mL beaker. The small beaker was filled to capacity by gently running methanol down the sides, taking care not to overflow the beaker and to provide minimal mixing. The large beaker was also carefully filled with methanol to the level of the rim of the small beaker. At this point methanol was added dropwise at the rim of the small beaker in such a way that one half of the drop fell into the small beaker and the other half fell into the large beaker. This was continued until the approximate depth of methanol above the rim of the small beaker was 2 mm. Parafilm was placed over the rim of the large beaker, and within 24 hours, yellow-brown crystals appeared at the interface of the two solutions. After a period of three weeks (at which point the volume of crystals did not appear to increase) the product was collected (0·2409 g, 24% yield based on copper). If $NaOCH_3$ is added along with the $CuCl_2.2H_2O$ in a 1:2 ratio, the resulting yield is increased to 67% based on copper. The sample was dried *in vacuo* over P_4O_{10} for 12 hours. Analysis. Calculated for $C_{16}H_{24}N_8OCl_6Cu_4$: C, 23·69; H, 2·98; N, 13·81; Cl, 26·22; Cu, 31·33%. Found: C, 23·57; H, 2·91; N, 13·86; Cl, 25·98; Cu, 30·90%. Calculated density = 1·81, experimental density = $1{\cdot}80\ \text{g cm}^{-3}$ (flotation method using $C_2H_2Br_4$ and CCl_4).

Crystal and X-ray data. Pertinent details (beyond those presented in the *Abstract*) regarding crystal data, intensity data collection, and least-squares refinement of the structure are collected in Table 1. A yellow prismatic crystal was mounted on a glass fiber. The Laue symmetry and pattern of systematic absences ($h,k,0$ when $h = 2n + 1$; $h,0,l$ when $l = 2n + 1$; and $0,k,l$ when $k = 2n + 1$) uniquely determine the space group *Pbca*. The data were corrected for coincidence loss, Lorentz, polarization, deterioration and absorption effects. The structure was solved using a combination of direct methods and heavy-atom techniques. The eight copper positions were located using the direct methods program *RANTAN* (Jia-xing, 1981). The remaining non-H atoms were found in difference maps. H atoms were placed in their calculated positions and assigned thermal parameters according to the formula $U = [U_{11} + U_{22} + U_{33})/3] + 2{\cdot}5$ where the U_{ii}'s refer to the thermal parameters of the C atom to which a given H atom is bound. Two of the C atoms in one of the 1-MeIm rings were noted to have quite distorted thermal ellipsoids and were each replaced with two atoms at half occupancy. The disordered C atoms were assigned isotropic thermal parameters while all other non-H atoms were refined anisotropically. The function minimized by the method of least squares was $\sum w(|F_o| - |F_c|)^2$ using $1/\sigma$ weights where $\sigma(F)$ was derived using $\sigma^2(F_2) = [\text{gross counts} + (0{\cdot}035 \times \text{net counts})^2]$ and $\sigma(F) = [F^2 + \sigma(F^2)]^{1/2} - (F^2)^{1/2}$. The least-squares refinement was separated into two blocks, one for each independent molecule. This might have hidden any numerical instability caused by missing symmetry relationships between the two molecules in the asymmetric unit, so the molecules were examined to determine if they had similar packing environments. Distances from each Cu atom to neighboring molecules were calculated and indicate that each Cu atom is in a unique environment. The *XRAY76* programs (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) were used throughout the computations.

Table 1. *Crystal data and data-collection details*

Crystal size (mm)	0·17 × 0·17 × 0·67
Diffractometer type	Picker Automatic FACS-1
Radiation type	Ni filtered Cu $K\alpha$ (λ = 1·5418 Å)
No. of reflections used for constant determination	10 at 2θ = 47·2 to 47·9°
Scan type	$\omega/2\theta$
2θ range (°)	2–110
Scan rate (° min^{-1})[a]	2 in 2θ
Standard reflections	5 reflections collected every 60 minutes, correction max. 1·019
No. of unique data collected	7490 (excluding absences)
No. of reflections observed	5811
Criterion for observeds	$(F_o)^2 \geq 2\sigma(F_o)^2$
Range of absorption factors[b]	1·0–1·407
Coincidence loss[c]	$\tau = 2{\cdot}085736 \times 10^{-7}$
Reflections measured	$-h, +k, +l$
Final wR[d]	0·052
Goodness of fit[e]	1·8031
No. of contributing reflections	6860
$(\Delta/\sigma)_{\text{max}}$	0·50

(*a*) Backgrounds were collected for 10 seconds on either side of the reflection using a stationary counter, stationary-crystal technique. (*b*) Method used described in North, Phillips & Mathews (1968). (*c*) Method used described in Sletten, Sletten & Jensen (1969). (*d*) $wR = [\sum(|F_o| - |F_c|)^2/\sum w(|F_o|)^2]^{1/2}$ with $w = 1/\sigma^2(F)$. (*e*) Goodness of fit $= [\sum(|F_o| - |F_c|)^2/(N_{\text{ref}} - N_{\text{var}})]^{1/2}$. Scattering factors for Cu, Cl, C, O and N taken from Cromer & Mann (1968), scattering factor for H taken from Stewart, Davidson & Simpson (1965), anomalous-dispersion terms for Cu and Cl (both f' and f'') taken from *International Tables for X-ray Crystallography* (1962).

Discussion. Comparison of the structure reported here with that of Clegg, Nicholson, Collison & Garner (1988) (CNCG) indicates that the structures are quite similar. After correcting the y coordinate of Cu1 in their structure from 0·00172 to −0·00172, and making the necessary unit-cell transformations, comparison of 172 bond lengths and bond angles for the two structures shows only two regions where the structures differ. The bond angles around Cu1 (our atom label) (Cl12—Cu1—Cu14 and Cl13—Cu1—Cl14) differ by 1·1 and 1·4° from their counterparts in CNCG. Allowing for an underestimation of the standard deviations, these differences are significant, although it is not clear what crystal packing interactions or computational effects might be responsible for them.

The second area where the two structures differ is at the acetonitrile pocket in the CNCG structure. A cavity corresponding to this pocket also exists in our structure, and the disordered imidazole ligand forms one side of the cavity. Investigation of the final difference density gives no hint of solvent molecules in our structure, and there is no indication of disorder in the CNCG structure. While the CNCG unit-cell volume, 11998 Å^3, is larger than ours, 11922 Å^3, the difference (76 Å^3) is smaller than that expected for adding eight acetonitrile molecules. The net increase in the volume of the acetonitrile cavity in the CNCG structure is caused by this small increase in cell volume and the fact that the imidazole ligands forming the walls of the pocket have all moved slightly with respect to their positions in our structure.

Table 2. *Structural determinations of* $[Cu_4OX_6L_4]$ *(excluding methylimidazole structures)*

X	L	Cu[a]	X[b]	R	Reference
Cl	$OPPh_3$	1	1	0·10	Bertrand (1967); Bertrand & Kelley (1966).
Cl	$OPPh_3$	1	1	0·084	Dvorkin, Simonov, Yampol'skaya & Malinovskii (1983).
Cl	Py	4	6	0·066	Kilbourn & Dunitz (1967).
Cl	Cl	2	5 (3)	0·090	Bertrand & Kelley (1969).
Cl	2-MePy	4	6	0·082	Gill & Sterns (1970).
Cl	Cl	2	6 (4)	0·068	de Boer, Bright & Helle (1972).
Cl	Cl	2	6 (4)	0·063	Belford, Fenton & Truter (1972).
Cl	$OPEt_3$	2	2	0·036	Churchill, de Boer & Mendak (1975).
Cl	Cl	4	10 (6)	0·056	Harlow & Simonsen (1977).
Cl	3-quin	4	6	0·069	Dickinson, Helm, Baker, Black & Watson (1977).
Cl	NMP,H_2O[c]	4	6	0·0565	Davies, El-Shazly, Rupich, Churchill & Rotella (1978); Churchill & Rotella (1979).
Cl[d]	$OPPH_3$	1	1	0·054	Simonov, Dvorkin, Yampol'skaya & Zavodnik (1982).
Cl	DMF	4	6	0·062	Nifontova, Lavrent'ev, Ponomarev, Filipenko, Krasochka, Atovmyan & Khidekel' (1982).
Cl	HMT	2	4	0·064	Pickardt & Rautenburg (1982).
Cl	DENC	2	4	0·069	El-Toukhy, Guang-Zuan, Davies, Gilbert, Onan & Veidis (1984).
Br	NH_3	1	2	0·108	Bertrand & Kelley (1970).
Br	Py	4	6	0·086	Swank, Nielson & Willet (1973).

Notes: (*a*) Number of independent Cu atoms. (*b*) Number of independent Cl or Br atoms as X (number of independent Cl atoms as L). (*c*) Three L's are NMP and the fourth is H_2O. (*d*) CH_2Cl_2 solvate.

The structure of $[Cu_4Cl_6O(1\text{-MeIm})_4]$ is a typical representative of the $[Cu_4Cl_6OL_4]$ class of complexes as seen in the structure determinations cited in Table 2. In the ideal case, these complexes can be described as an O atom at the center of both a tetrahedron of Cu atoms and an octahedron of Cl atoms. These two polyhedra interpenetrate such that the apices of the tetrahedron lie just above half of the octahedral faces. If L is spherical or has threefold symmetry, then the molecular point group of the idealized complex is $\bar{4}3m$ (T_d). In the case of L = 1-MeIm, $\bar{4}3m$ symmetry is not possible. In fact there are two independent complexes in the asymmetric unit of $[Cu_4Cl_6O(1\text{-MeIm})_4]$. Consequently there are eight independent Cu atoms and twelve independent Cl atoms. The μ_4-O atoms are labelled O1 and O2 for the first and second complexes. The Cu atoms of the first complex are numbered Cu1–Cu4 and of the second, Cu5–Cu8. Cl numbering takes the form Cl*xy* where x and y are the numbers of the Cu atoms bridged by that particular Cl atom. See Fig. 2 for an explanation of the rest of the atom-numbering scheme. Table 3 lists the fractional atomic coordinates and Table 4 contains a selected list of interatomic distances and bond angles.* A stereo-representation of the complexes is shown in Fig. 3.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, additional bond distances and angles, and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52009 (38 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Fractional coordinates of the non-*H *atoms in* $[Cu_4Cl_6O(1\text{-}methylimidazole)_4]$

Coordinates $\times 10^5$ for Cu, O and Cl atoms, $\times 10^4$ for others. U_{eq} values $\times 10^3$.

	x	y	z	U_{eq}*
Complex (1)				
Cu1	96819 (6)	21310 (3)	56861 (6)	47·8
Cu2	104773 (6)	27838 (3)	48204 (6)	49·0
Cu3	98088 (7)	20499 (3)	40561 (6)	52·1
Cu4	88311 (6)	26970 (3)	47294 (7)	52·9
Cl12	106334 (13)	26026 (7)	60283 (12)	71
Cl13	99265 (13)	15416 (6)	49788 (11)	55
Cl14	84785 (12)	23128 (7)	57654 (13)	68
Cl23	107880 (13)	24724 (7)	37325 (12)	67
Cl24	95343 (11)	32954 (6)	47015 (11)	55
Cl34	86629 (13)	22764 (7)	36806 (12)	69
O1	97034 (25)	24187 (13)	48242 (23)	37
N11	9691 (4)	1868 (2)	6592 (3)	51
C11	9779 (5)	1489 (3)	6729 (4)	54
N12	9731 (4)	1414 (2)	7426 (4)	74
C12	9567 (6)	2058 (3)	7223 (5)	76
C13	9606 (6)	1778 (4)	7749 (5)	82
C14	9826 (7)	1023 (3)	7785 (5)	101
N21	11253 (4)	3164 (2)	4775 (4)	56
C21	11785 (5)	3225 (3)	5188 (5)	66
N22	12225 (4)	3505 (2)	4940 (4)	66
C22	11375 (6)	3420 (3)	4204 (5)	82
C23	11966 (6)	3628 (3)	4313 (6)	81
C24	12894 (6)	3638 (3)	5265 (6)	96
N31	9950 (5)	1669 (2)	3312 (4)	65
C31	10326 (6)	1713 (3)	2742 (6)	81
N32	10343 (5)	1378 (3)	2337 (5)	87
C32	9706 (9)	1284 (3)	3284 (6)	131
C33	9955 (9)	1103 (3)	2689 (6)	126
C34	10707 (7)	1328 (4)	1651 (6)	121
N41	7949 (4)	2993 (2)	4700 (4)	71
C41	7827 (5)	3370 (3)	4636 (5)	64
N42	7172 (4)	3464 (2)	4777 (5)	69
C421	7342 (11)	2827 (6)	4555 (12)	80
C422	7316 (12)	2842 (7)	5092 (12)	85
C431	6828 (12)	3109 (7)	4697 (12)	80
C432	6877 (14)	3148 (8)	5165 (14)	94
C44	6828 (6)	3857 (3)	4805 (7)	106
Complex (2)				
Cu5	74905 (6)	2962 (3)	21726 (6)	36·4
Cu6	60894 (6)	−1527 (3)	18516 (6)	33·0
Cu7	73257 (6)	−6127 (3)	25433 (6)	34·1
Cu8	65234 (6)	436 (3)	34030 (6)	35·9
Cl56	67045 (15)	3680 (8)	11968 (13)	39
Cl57	83796 (11)	−2341 (7)	23176 (11)	19
Cl58	72689 (12)	6188 (6)	33055 (11)	30
Cl67	65898 (12)	−7952 (7)	15578 (12)	24
Cl68	53755 (10)	569 (6)	28434 (10)	19
Cl78	68744 (12)	−6191 (6)	37599 (11)	25
O2	68568 (24)	−1061 (13)	24973 (24)	14
N51	8108 (4)	721 (2)	1841 (4)	23
C51	8108 (6)	1102 (3)	2052 (5)	32
N52	8508 (5)	1335 (2)	1634 (4)	37
C52	8512 (7)	727 (3)	1242 (6)	48
C53	8752 (7)	1099 (3)	1127 (6)	50
C54	8632 (8)	1769 (3)	1725 (7)	76
N61	5282 (3)	−218 (2)	1237 (3)	20
C61	4681 (4)	−22 (3)	1284 (4)	15
N62	4245 (3)	−129 (2)	755 (4)	17
C62	5217 (5)	−463 (3)	643 (4)	21
C63	4574 (5)	−410 (3)	355 (4)	24
C64	3526 (5)	24 (3)	644 (5)	18
N71	7757 (4)	−1137 (2)	2610 (4)	18
C71	7453 (5)	−1484 (3)	2489 (5)	21
N72	7872 (4)	−1798 (2)	2637 (4)	23
C72	8393 (5)	−1235 (3)	2862 (6)	24
C73	8468 (6)	−1642 (3)	2870 (7)	22
C74	7690 (5)	−2234 (3)	2535 (6)	32
N81	6194 (4)	208 (2)	4325 (3)	21
C81	5581 (5)	360 (2)	4474 (4)	31
N82	5503 (4)	456 (2)	5156 (3)	30
C82	6551 (5)	191 (3)	4947 (5)	27
C83	6126 (6)	354 (3)	5458 (5)	38
C84	4897 (6)	635 (3)	5500 (5)	39

* $U_{eq} = \frac{1}{3}\sum_i U_{ii}$.

Table 4. *Selected bond distances, non-bonding distances* (Å) *and angles* (°) *for* [Cu_4Cl_6O(1-*methylimidazole*)$_4$]

Complex (1)			
Cu1—O1	1·890 (5)	Cu3—Cl34	2·409 (3)
Cu2—O1	1·905 (5)	Cu4—Cl14	2·432 (3)
Cu3—O1	1·911 (5)	Cu4—Cl24	2·394 (2)
Cu4—O1	1·905 (5)	Cu4—Cl34	2·447 (3)
Cu1—N11	1·924 (7)	Cu1—Cu2	3·108 (2)
Cu2—N21	1·942 (7)	Cu1—Cu3	3·105 (2)
Cu3—N31	1·912 (7)	Cu1—Cu4	3·068 (2)
Cu4—N41	1·943 (7)	Cu2—Cu3	3·104 (2)
Cu1—Cl12	2·477 (3)	Cu2—Cu4	3·143 (2)
Cu1—Cl13	2·415 (2)	Cu3—Cu4	3·112 (2)
Cu1—Cl14	2·368 (3)	O1—Cl12	2·946 (5)
Cu2—Cl12	2·381 (3)	O1—Cl13	2·957 (5)
Cu2—Cl23	2·377 (3)	O1—Cl14	2·950 (5)
Cu2—Cl24	2·478 (2)	O1—Cl23	2·922 (5)
Cu3—Cl13	2·438 (2)	O1—Cl24	2·937 (5)
Cu3—Cl23	2·408 (3)	O1—Cl34	2·967 (5)
O1—Cu1—N11	176·3 (2)	N21—Cu2—Cl23	93·2 (2)
O1—Cu2—N21	177·4 (2)	N21—Cu2—Cl24	95·6 (2)
O1—Cu3—N31	177·3 (3)	N31—Cu3—Cl13	93·3 (2)
O1—Cu4—N41	176·0 (3)	N31—Cu3—Cl23	95·2 (3)
O1—Cu1—Cl12	83·7 (2)	N31—Cu3—Cl34	96·6 (3)
O1—Cu1—Cl13	85·8 (1)	N41—Cu4—Cl14	92·9 (2)
O1—Cu1—Cl14	86·9 (2)	N41—Cu4—Cl24	93·5 (2)
O1—Cu2—Cl12	86·1 (1)	N41—Cu4—Cl34	98.8 (2)
O1—Cu2—Cl23	85·3 (2)	Cl12—Cu1—Cl13	121·1 (1)
O1—Cu2—Cl24	83·1 (2)	Cl12—Cu1—Cl14	121·7 (1)
O1—Cu3—Cl13	84·8 (1)	Cl13—Cu1—Cl14	115·3 (1)
O1—Cu3—Cl23	84·3 (2)	Cl12—Cu2—Cl23	133·6 (1)
O1—Cu3—Cl34	86·0 (2)	Cl12—Cu2—Cl24	110·5 (1)
O1—Cu4—Cl14	84·8 (1)	Cl23—Cu2—Cl24	113·5 (1)
O1—Cu4—Cl24	85·4 (1)	Cl13—Cu3—Cl23	121·0 (1)
O1—Cu4—Cl34	85·0 (1)	Cl13—Cu3—Cl34	120·7 (1)
N11—Cu1—Cl12	92·8 (2)	Cl23—Cu3—Cl34	116·1 (1)
N11—Cu1—Cl13	97·1 (2)	Cl14—Cu4—Cl24	127·3 (1)
N11—Cu1—Cl14	93·9 (2)	Cl14—Cu4—Cl34	108·6 (1)
N21—Cu2—Cl12	96·5 (2)	Cl24—Cu4—Cl34	121·9 (1)
Complex (2)			
Cu5—O2	1·900 (5)	Cu7—Cl78	2·456 (3)
Cu6—O2	1·908 (5)	Cu8—Cl58	2·384 (2)
Cu7—O2	1·905 (5)	Cu8—Cl68	2·423 (2)
Cu8—O2	1·893 (5)	Cu8—Cl78	2·396 (2)
Cu5—N51	1·938 (7)	Cu5—Cu6	3·109 (2)
Cu6—N61	1·937 (6)	Cu5—Cu7	3·113 (2)
Cu7—N71	1·928 (7)	Cu5—Cu8	3·081 (2)
Cu8—N81	1·931 (7)	Cu6—Cu7	3·091 (2)
Cu5—Cl56	2·386 (3)	Cu6—Cu8	3·117 (2)
Cu5—Cl57	2·454 (3)	Cu7—Cu8	3·116 (2)
Cu5—Cl58	2·432 (2)	O2—Cl56	2·935 (5)
Cu6—Cl56	2·426 (3)	O2—Cl57	2·942 (5)
Cu6—Cl67	2·400 (3)	O2—Cl58	2·956 (5)
Cu6—Cl68	2·417 (2)	O2—Cl67	2·941 (5)
Cu7—Cl57	2·401 (3)	O2—Cl68	2·938 (5)
Cu7—Cl67	2·407 (3)	O2—Cl78	2·934 (5)
O2—Cu5—N51	177·8 (3)	N61—Cu6—Cl67	94·3 (2)
O2—Cu6—N61	176·7 (2)	N61—Cu6—Cl68	93·1 (2)
O2—Cu7—N71	177·0 (3)	N71—Cu7—Cl57	97·5 (2)
O2—Cu8—N81	178·7 (2)	N71—Cu7—Cl67	94.0 (2)
O2—Cu5—Cl56	85·7 (2)	N71—Cu7—Cl78	94·5 (2)
O2—Cu5—Cl57	84·0 (2)	N81—Cu8—Cl58	92·1 (2)
O2—Cu5—Cl58	85·1 (2)	N81—Cu8—Cl68	95·6 (2)
O2—Cu6—Cl56	84·3 (2)	N81—Cu8—Cl78	95·5 (2)
O2—Cu6—Cl67	85·3 (1)	Cl56—Cu5—Cl57	126·0 (1)
O2—Cu6—Cl68	84·7 (2)	Cl56—Cu5—Cl58	122·0 (1)
O2—Cu7—Cl57	85·4 (2)	Cl57—Cu5—Cl58	109·7 (1)
O2—Cu7—Cl67	85·2 (2)	Cl56—Cu6—Cl67	108·9 (1)
O2—Cu7—Cl78	83·5 (2)	Cl56—Cu6—Cl68	117·5 (1)
O2—Cu8—Cl58	86·7 (1)	Cl67—Cu6—Cl68	131·1 (1)
O2—Cu8—Cl68	84·8 (2)	Cl57—Cu7—Cl67	118·5 (1)
O2—Cu8—Cl78	85·5 (1)	Cl57—Cu7—Cl78	117·5 (1)
N51—Cu5—Cl56	93·1 (2)	Cl67—Cu7—Cl78	121·4 (1)
N51—Cu5—Cl57	98·2 (2)	Cl58—Cu8—Cl68	119·0 (1)
N51—Cu5—Cl58	94·0 (2)	Cl58—Cu8—Cl78	126·3 (1)
N61—Cu6—Cl56	98·9 (2)	Cl68—Cu8—Cl78	113·0 (1)

As can be seen by examining Table 5, the cores of the two complexes are nearly regular Cu_4O tetrahedra, and the average values of the Cu—O distances and Cu—O—Cu angles of the two cores are indistinguishable from those of the complexes cited in Table 2.

The coordination polyhedron around the Cu ions is a distorted trigonal bipyramid. One rather small distortion is found in the N—Cu—O angles which are slightly below 180°; they range in value from 176° to 178·7° (Table 4) and have a mean value of 177·2 (9)°. A somewhat more conspicuous deviation is to be found in the relative placement of the three Cl atoms with respect to the Cu—O axis. This deviation can be expressed in terms of the O—Cu—Cl angles (which in the ideal case are 90°) or in terms of the displacement of the Cu atom from the plane defined by the three Cl atoms bonded to it (in the ideal case the displacement is zero). In the two complexes reported here, the mean value found for the angle is 85·1 (9)° and that for the displacements is 0·21 (1) Å toward the N atom (Table 6). As can be seen in Table 6, the distortion observed for the two complexes is the same as that found for the similar complexes cited in Table 2.

A simple ideal model can be constructed which gives some insight into these distortions. The model contains Cu atoms with trigonal bipyramidal coordination and with the average Cu—O and Cu—N bond distances observed in complexes (1) and (2). The four Cu atoms are positioned at the corners of a regular tetrahedron centered on an O atom with the Cu—O distance being 1·902 Å (Table 5). N atoms representing the imidazole ligating atoms are placed on an extension of the Cu—O lines at a distance of

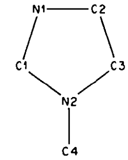

Fig. 2. The C and N atoms of 1-MeIm are numbered in the convention C*wzd* and N*wz* where *w* is the number of the Cu atom to which the 1-MeIm is bonded and *z* is the number shown in the figure. The disordered C atoms in the ligand bound to Cu4 are denoted by the *d* in the atom names. H atoms have the same numbers as the C atoms to which they are bound except for H*w*5 and H*w*6 which are the second and third H atoms of the methyl group.

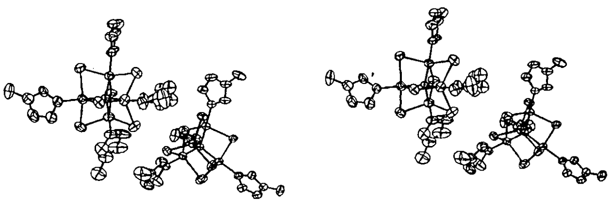

Fig. 3. Stereoscopic view of the two independent molecules of [Cu_4Cl_6O(1-MeIm)$_4$]. See text for atom-numbering scheme.

Table 5. *The* OCu_4-*tetrahedra geometry* (Å *and* °)

	Low	High	Mean*	*n*†
Cu—O				
Complex (1)	1·890 (4)	1·910 (4)	1·902 (9)	4
Complex (2)	1·893 (5)	1·908 (5)	1·902 (7)	4
Both complexes			1·902 (7)	4
Literature‡	1·869 (8)	1·939 (7)	1·908 (15)	30
Cu—O—Cu				
Complex (1)	107·9 (2)	111·2 (2)	109·5 (11)	6
Complex (2)	108·3 (2)	110·3 (2)	109·5 (8)	6
Both complexes			109·5 (9)	12
Literature‡	106·3 (8)	115·8 (8)	109·4 (15)	52

* Standard deviation calculated from distribution of values.

† Number of values used to compute mean.

‡ Computed from data found in the references cited in Table 2.

Table 6. *The* $CuCl_3ON$-*polyhedra geometry* (Å *and* °)

	Low	High	Mean*	*n*
Cu displacement†				
This work	0·180	0·225	0·207 (14)	8
Literature‡	0·180	0·312	0·222 (26)	35
Cu—Cl				
This work	2·368 (3)	2·478 (2)	2·417 (30)	24
Literature‡	2·310 (8)	2.679 (8)	2·412 (61)	102
O—Cu—Cl				
This work	83·1 (2)	86·9 (2)	85·1 (9)	24
Literature‡	76·9 (6)	90·8 (6)	84·8 (19)	104
Cl—Cu—Cl				
This work	108·93 (10)	133·2 (9)	119·3 (67)	24
Literature‡	95·9 (4)	155·0 (4)	119·2 (97)	109
Cu—Cl—Cu				
This work	76·70 (8)	80·89 (8)	79·7 (10)	12
Literature‡	76·7 (3)	82·8 (1)	80·4 (11)	53
Cu—N				
This work	1·912 (7)	1·943 (7)	1·932 (10)	
N—Cu—Cl				
This work	92·1 (2)	98.9 (2)	95·0 (20)	

* Standard deviation calculated from distribution of values.

† Displacement of the Cu from the plane defined by the three Cl atoms to which it is bonded.

‡ Computed from the data found in the references cited in Table 2.

1·932 Å from the Cu (Table 6), and the Cl atoms are located on the intersection of lines originating at the Cu atoms and perpendicular to the Cu—O bonds. A slice through the center of this model is shown in Fig. 4(*a*). This slice is the plane containing two Cu atoms, two N atoms, one Cl atom and the O atom. The Cu—Cl distance arising in this model is 2·690 Å, a value significantly longer than that observed in complexes (1) and (2) (2·412 Å). In order to achieve the 2·412 Å distance and to symmetrically bridge two Cu atoms, each Cl atom must 'move' toward the O atom on the line bisecting the Cu—O—Cu angle. In addition to achieving the desired 2·412 Å Cu—Cl distance, this movement results in the O—Cu—Cl angle becoming 85° and, of course, places the Cu atom outside the plane described by the three Cl atoms to which it is bound. In addition both the Cl—O and the Cl—N separations are shortened as seen in Fig. 4 where the ideal and average cases are compared. The conclusion which follows is that the equilibrium positions of the Cl atoms in these clusters clearly involve a balancing of at least two forces: namely the increasingly favorable bonding interactions resulting from Cu—Cl bonds being shorter than those in the model and the increasingly unfavorable non-bonding interactions between Cl and O and between Cl and N arising from separations shorter than those in the model.

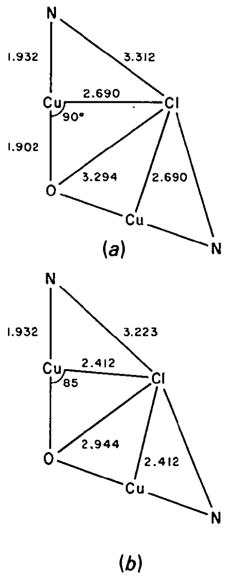

Fig. 4. Slices of (*a*) ideal and (*b*) average models for $[Cu_4Cl_6O(1\text{-}MeIm)_4]$.

Further analysis can be made in the manner of Kilbourn & Dunitz (1967) who examined distortions of the Cl atoms from the average case represented in Fig. 3. We conclude that intermolecular repulsive contacts are the most likely reason for this further distortion of Cl atoms in $[Cu_4Cl_6O(1\text{-}MeIm)_4]$.

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Structure of Undecacarbonyl[tris(pentafluorophenyl)phosphine]-*triangulo*-triosmium, a Substituted Osmium Cluster Containing a Fluorinated Triphenylphosphine Ligand

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(*Received* 19 *October* 1988; *accepted* 20 *March* 1989)

Abstract. $[Os_3(CO)_{11}\{P(C_6F_5)_3\}]$, $M_r = 1410{\cdot}87$, monoclinic, $P2_1/n$, $a = 19{\cdot}058\,(1)$, $b = 9{\cdot}109\,(1)$, $c = 20{\cdot}424\,(2)$ Å, $\beta = 105{\cdot}53\,(1)°$, $V = 3416\,(1)$ Å^3, $Z = 4$, $D_m = 2{\cdot}74\,(2)$, $D_x = 2{\cdot}743$ g cm^{-3}, μ(Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å) = $113{\cdot}3$ cm^{-1}, $F(000) = 2560$, $T = 297\,(1)$ K, $R_F = 0{\cdot}022$ for 3529 reflections. The Os atoms form an approximate isosceles triangle. Each Os atom exhibits a distorted octahedral coordination geometry. The carbonyl groups are all terminal and the bulky phosphine ligand is coordinated equatorially.

Introduction. Axial, equatorial and bridging (Churchill & Wasserman, 1982; Ditzel, Gomez-Sal, Johnson, Lewis & Raithby, 1987) substitution of carbonyl groups in $Os_3(CO)_{12}$ clusters is known. Substitution is likely to occur at an equatorial site if the ligand is a bulky two-electron donor such as $P(OCH_3)_3$ (Benfield, Johnson, Raithby & Sheldrick, 1978) or $P^t\mathrm{Bu}_2(NH_2)$ (Ehrenreich, Herberhold, Suss-Fink, Klein & Thewalt, 1983). On the other hand, small, non-π-acceptor ligands such as H (Churchill & DeBoer, 1977) or CH_3CN (Dawson, Johnson,

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