Fig. 1. Perspective view of the unit-cell contents.

Fourier map. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).* Atomic coordinates and bonding geometry are in Tables 1 and 2. Fig. 1 shows the unit cell.

Discussion. The crystal is a discrete ionic one containing an Me_4N^+ cation and an $[Mo_3(\mu_3\text{-}O)(\mu\text{-}Br)_3(\mu\text{-}O_2CH)_3Cl_3]^-$ cluster anion in each asymmetric unit.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42050 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The bond lengths and angles of the cation are in conformity with those reported in the literature. In the cluster anion three Mo atoms form an approximately equilateral triangle with an average Mo—Mo bond distance of 2·596 (1) Å. On one side of the triangular plane one μ_3-O atom binds the three Mo atoms together to form a monocapped cluster core. Each pair of Mo atoms is further bridged by a Br ligand and an HCO_2^- group. The local coordination polyhedron around each Mo atom is a distorted octahedron. The symmetry of the cluster anion as a whole is approximately C_{3v}.

The formal oxidation state for each Mo atom is $3\frac{1}{3}$, so that the metal core (Mo_3) has eight electrons to form the metal–metal bonds. As a two-center molecular orbital, the order for each Mo—Mo bond may be regarded as 4/3, which is in good agreement with the bond lengths observed (2·593, 2·596 and 2·598 Å).

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Copper(I)–Olefin Complexes. Structure of (1-2-η-Cyclohexene)-(di-2-pyridylamine)copper(I) Perchlorate, [Cu(C6H10)(C10H9N3)]ClO4*

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Abstract. $M_r = 416\cdot34$, monoclinic, $P2_1/c$, $a = 7\cdot478$ (1), $b = 25\cdot014$ (6), $c = 9\cdot530$ (1) Å, $\beta = 106\cdot23$ (1)°, $V = 1711\cdot6$ (6) Å^3, $Z = 4$, $D_x = 1\cdot615$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 14\cdot608$ cm^{-1}, $F(000) = 856$, $T = 173$ K. Final $R = 0\cdot047$ for 2946 unique observed reflections. The

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structure consists of a copper-containing cation and a well separated perchlorate anion. The geometry about the Cu^I ion, which is coordinated to two pyridine N atoms and the olefin bond of the cyclohexene molecule, is nearly a trigonal-planar arrangement. The length of the coordinated olefin C=C bond is 1·366 (6) Å.

Introduction. In this contribution, we present the crystal structure of (1-2-η-cyclohexene)(di-2-pyridylamine)-copper(I) perchlorate, $[Cu(NHpy_2)(C_6H_{10})]ClO_4$, (I). This study is part of our research effort to characterize the coordination chemistry of Cu^I–olefin complexes. This and previous work have established that these complexes show a preference for trigonal-planar geometries, although tetrahedral geometries can be prepared with the appropriate choice of ligands (Thompson, Harlow & Whitney, 1983; Thompson & Whitney, 1983, 1984a,b; Thompson & Swiatek, 1985). Coordination of noncyclic monoolefins to the Cu^I ion does not generally lead to a significant lengthening of the C—C double bond. However, the structural characterization of the Cu^I–cyclohexene complex 1-chloro-2-(1-2-η-cyclohexene)-μ-[hydrotri(1-pyrazolyl)-borato-N:N',N'']-dicopper(I) (Thompson & Whitney, 1984a) revealed a coordinated olefin bond distance [1·375 (3) Å] significantly lengthened relative to the free-molecule values [1·335 (3) and 1·34 (1) Å (Chiang & Bauer, 1969; Scharpen, Wollrab & Ames, 1968)]. This structural study was undertaken to confirm the trigonal-planar geometry about the Cu^I ion and to determine whether the lengthening of the coordinated olefin bond is characteristic of Cu^I complexes with cyclic olefins.

Experimental. Crystals grown from vapor diffusion of diethyl ether into a methanol–cyclohexene solution of (I) prepared by the literature procedure (Thompson & Swiatek, 1985); crystal 0·35 × 0·26 × 0·39 mm, encapsulated in a glass capillary under a nitrogen atmosphere; Syntex $P3$ diffractometer, graphite-monochromated Mo $K\alpha$, ω-scan technique, scan width 1°, scan speed 4·0–10·0° min^{-1}, ratio of total background time to scan time unity. Lattice parameters refined on the basis of 39 computer-centered reflections from diverse regions of reciprocal space (2θ range of 20–25°). Lorentz and polarization correction and an empirical absorption correction, transmission factors 0·908–1·00. $4 < 2\theta < 55°$ ($0 \le h \le 9$; $0 \le k \le 30$; $-12 \le l \le 12$). Four standard reflections collected after every 200 reflections: no significant variation. Total number of reflections: 4354; unique data used in refinement: 2946 $[F_o^2 > 2\sigma(F_o)^2]$; number of unobserved reflections: 1408. Data processed by using counting statistics and a p value of 0·02 to derive standard deviations (Corfield, Doedens & Ibers, 1967). Number of variables: 235. All crystallographic calculations

Table 1. *Final positional and equivalent isotropic thermal parameters*

$B_{eq} = \frac{4}{3}[a^2B_{11} + b^2B_{22} + c^2B_{33} + (ab\cos\gamma)B_{12} + (ac\cos\beta)B_{13} + (bc\cos\alpha)B_{23}].$

	x	y	z	$B_{eq}(Å^2)$
Cu	0·49056 (7)	0·11297 (2)	0·21328 (5)	1·8 (1)
Cl	0·3370 (1)	0·17222 (4)	−0·4834 (1)	2·1 (1)
O(1)	0·3741 (5)	0·1881 (1)	−0·6180 (4)	3·4 (1)
O(2)	0·4941 (5)	0·1436 (2)	−0·3929 (4)	4·2 (1)
O(3)	0·1758 (5)	0·1385 (2)	−0·5153 (4)	3·9 (1)
O(4)	0·3048 (5)	0·2189 (1)	−0·4040 (4)	3·2 (1)
N(1)	0·6332 (4)	0·1659 (1)	0·1358 (3)	1·6 (1)
N(2)	0·2548 (5)	0·1211 (1)	0·0574 (4)	1·8 (1)
N(3)	0·3940 (5)	0·1761 (1)	−0·0870 (4)	1·9 (1)
C(1)	0·6567 (6)	0·0700 (2)	0·3799 (5)	2·4 (1)
C(2)	0·4814 (6)	0·0488 (2)	0·3419 (5)	2·2 (1)
C(3)	0·4331 (9)	−0·0025 (2)	0·2575 (5)	3·2 (1)
C(4)	0·5950 (16)	−0·0259 (3)	0·2157 (11)	7·3 (3)
C(51)	0·7312 (21)	0·0041 (5)	0·2011 (14)	3·7 (4)
C(52)	0·7808 (16)	−0·0113 (5)	0·2914 (18)	4·5 (4)
C(6)	0·8190 (7)	0·0430 (2)	0·3411 (6)	3·4 (2)
C(11)	0·5706 (5)	0·1879 (2)	0·0028 (4)	1·6 (1)
C(12)	0·6782 (6)	0·2229 (2)	−0·0548 (5)	2·2 (1)
C(13)	0·8551 (6)	0·2359 (2)	0·0290 (5)	2·3 (1)
C(14)	0·9218 (6)	0·2133 (2)	0·1682 (5)	2·3 (1)
C(15)	0·8085 (6)	0·1793 (2)	0·2157 (4)	1·9 (1)
C(21)	0·2427 (5)	0·1486 (2)	−0·0668 (4)	1·6 (1)
C(22)	0·0776 (6)	0·1495 (2)	−0·1824 (5)	2·3 (1)
C(23)	−0·0770 (6)	0·1228 (2)	−0·1674 (5)	2·7 (1)
C(24)	−0·0665 (6)	0·0956 (2)	−0·0381 (5)	2·7 (1)
C(25)	0·0982 (6)	0·0959 (2)	0·0678 (5)	2·3 (1)

performed as described elsewhere (Thompson & Whitney, 1984a). Cu atom located by heavy-atom Patterson method. Positions of remaining non-H atoms obtained by usual combination of structure-factor and Fourier-synthesis calculations and full-matrix least-squares refinement. $\sum w(|F_o| - |F_c|)^2$ minimized; $w = 1/\sigma(F_o)$. $(\Delta/\sigma)_{max} = 0·01$ in final refinement cycle. Atomic scattering factors from Cromer & Waber (1965); anomalous-dispersion terms from *International Tables for X-ray Crystallography* (1974). The disordered cyclohexene atom C(5) was statistically distributed between the two half-chair ring conformations and was refined as two half-atoms C(51) and C(52). A difference map indicated the presence of the attached H atoms for the disordered C atoms. All H atoms included as fixed-atom contributors with a C—H distance of 0·95 Å and $B_{iso} = 3·0$ Å^2. Least-squares refinement converged to $R = 0·047$, $wR = 0·069$. All peaks in final $\Delta\rho$ map less than 0·40 e Å^{-3}. No correction for secondary extinction.

Discussion. The final positional parameters for non-H atoms appear in Table 1.*

The overall molecular structure of the complex, apparent in Fig. 1, consists of a $[Cu(NHpy_2)(C_6H_{10})]$ cation and a well separated perchlorate anion and is the same as that of the ethylene, propylene, and acetylene analogs (Thompson & Whitney, 1984b). The Cu^I ion is coordinated to two pyridyl N atoms of the $NHpy_2$ ligand and to a cyclohexene molecule in a trigonal-planar arrangement. The bond angles about the Cu atom sum to nearly $360°$. The Cu atom is $0·137$ (8) Å from the plane defined by C(1), C(2), N(1), and N(2). The dihedral angle between the planes defined by Cu, C(1), and C(2) and Cu, N(1), and N(2) is $10·1$ (1)°.

Selected bond distances and angles are presented in Table 2. The observed bond distances and angles for the $NHpy_2$ ligand are nearly identical to those determined in other Cu^I structures and are therefore not tabulated here (Thompson & Whitney, 1984b). There are no unusual features in the coordination sphere of the Cu^I atom. The Cu—N and Cu—C contacts are similar to those of the corresponding ethylene complex and are consistent with other Cu^I structures (Thompson et al., 1983; Thompson & Whitney, 1984b; Jardine, 1975). The bond angles about the Cu^I ion are reasonable for a trigonal-planar geometry. In Fig. 1, the disorder about C(5) of the cyclohexene ring is indicated.

The C=C bond distance of the coordinated olefinic bond [$1·366$ (6) Å] is significantly longer than the free olefin values cited above and is essentially the same as that observed for the Cu^I-cyclohexene complex with the ligand hydrotri(1-pyrazolyl)borate (Thompson & Whitney, 1984a). The copper inner coordination sphere is the same in both cases. The IR and ^1H NMR spectra for these two complexes as well as of a series of complexes with bidentate nitrogen-donating ligands (Thompson & Swiatek, 1985) are all similar. These results and others (Jardine, 1975; Ganis, Lepore & Paiaro, 1969) suggest that coordination of cyclic olefins
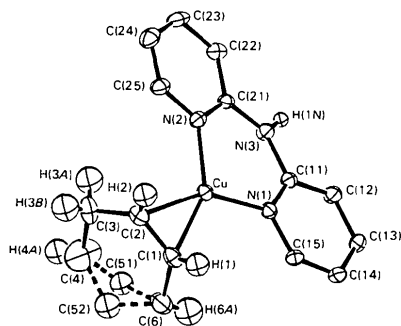
to the Cu^I ion in general leads to significant lengthening of the olefin bond. This effect on bond length is not observed with noncyclic olefins (Thompson et al., 1983; Thompson & Whitney, 1984b) and may be a manifestation of relief of strain, an important factor in the bonding of cyclic olefins to transition metals (Hartley, 1969, 1972, 1973).

Table 2. *Selected bond distances* (Å) *and bond angles* (°) *with e.s.d.'s*

Cu—N(1)	1·969 (3)	C(1)—C(2)	1·366 (6)
Cu—N(2)	1·973 (3)	C(1)—C(6)	1·522 (7)
Cu—C(1)	2·029 (4)	C(2)—C(3)	1·504 (7)
Cu—C(2)	2·032 (4)	C(3)—C(4)	1·496 (10)
Cl—O(1)	1·441 (3)	C(4)—C(51)	1·303 (15)
Cl—O(2)	1·438 (3)	C(4)—C(52)	1·423 (14)
Cl—O(3)	1·434 (3)	C(6)—C(51)	1·634 (14)
Cl—O(4)	1·448 (3)	C(6)—C(52)	1·440 (13)
N(1)—Cu—N(2)	96·4 (1)	C(2)—C(1)—C(6)	122·4 (4)
N(1)—Cu—C(1)	111·8 (2)	C(1)—C(2)—C(3)	122·8 (4)
N(2)—Cu—C(2)	111·2 (2)	C(2)—C(3)—C(4)	112·7 (6)
C(1)—Cu—C(2)	39·3 (2)	C(3)—C(4)—C(51)	121·3 (8)
O(1)—Cl—O(2)	110·1 (2)	C(3)—C(4)—C(52)	120·9 (7)
O(1)—Cl—O(3)	109·5 (2)	C(4)—C(51)—C(6)	113·8 (9)
O(1)—Cl—O(4)	110·1 (2)	C(4)—C(52)—C(6)	119·0 (9)
O(2)—Cl—O(3)	109·4 (3)	C(51)—C(6)—C(1)	107·3 (6)
O(2)—Cl—O(4)	108·4 (2)	C(52)—C(6)—C(1)	113·5 (6)
O(3)—Cl—O(4)	109·4 (2)		

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Fig. 1. View of the $[Cu(NHpy_2)(C_6H_{10})]$ cation. The vibrational ellipsoids are drawn at the 50% level. H atoms on the pyridine rings have been omitted. The disorder about C(5) of the cyclohexene ring is shown.