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Acta Cryst. (1984). C**40**, 756–759

Copper(I)–Olefin Complexes. Structure of 1-Chloro-2-(1-2-η-cyclohexene)-μ-[hydrotri(1-pyrazolyl)borato-N:N',N'']-dicopper(I), $C_{15}H_{20}BClCu_2N_6$

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(*Received* 9 *June* 1983; *accepted* 22 *December* 1983)

Abstract. $M_r = 457\cdot71$, triclinic, $P\bar{1}$, $a = 9\cdot951\ (3)$, $b = 11\cdot737\ (3)$, $c = 9\cdot130\ (2)$ Å, $\alpha = 100\cdot51\ (2)$, $\beta = 115\cdot80\ (2)$, $\gamma = 79\cdot15\ (2)°$, $V = 936\cdot8\ (9)$ Å^3, $Z = 2$, $D_x = 1\cdot623$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0\cdot71069$ Å (graphite monochromator), $\mu = 25\cdot078$ cm^{-1}, $F(000) = 464$, $T = 173$ K, final $R = 0\cdot026$, $R_w = 0\cdot027$ for 3582 reflections. The material was prepared from cuprous chloride and potassium hydrotri(1-pyrazolyl)borate in a dichloromethane–cyclohexene mixture. The geometry about one of the Cu^I ions, which is coordinated to two pyrazole N atoms and a cyclohexene molecule, is trigonal planar, whereas the geometry about the second Cu^I ion, which is coordinated to a pyrazole N atom and a Cl^- ion, is linear.

Introduction. Cu^I adducts with ethylene and other monoolefins have been of interest for many years (Jardine, 1975; Herberhold, 1974; Quinn & Tsai, 1969). These complexes generally lose olefin readily in the absence of excess olefin and have been only poorly characterized in most cases. Our interest in Cu^I–monoolefin coordination chemistry arises from the proposal that Cu^I ion may play a critical role in the binding of the plant hormone ethylene to its receptor site (Beyer & Blomstrom, 1980). We reported recently the synthesis, spectroscopy and structures of a series of Cu^I–monoolefin complexes that show binding of olefins, particularly ethylene, characteristic of the native systems and demonstrate that Cu^I–olefin chemistry is consistent with the proposed role of copper at the ethylene receptor site (Thompson, Harlow & Whitney, 1983). In this contribution, we present the crystallographic results on the cyclohexene complex $Cu(HBpz_3)(C_6H_{10}).CuCl$, where $HBpz_3$ is hydrotri(1-pyrazolyl)borate. This structural study was undertaken because a structure could not be assigned unambiguously to this complex on the basis of analytical and spectroscopic results alone (Thompson, Harlow & Whitney, 1983).

Experimental. Crystals grown from a dichloromethane–cyclohexene solution at 233 K as previously described (Thompson, Harlow & Whitney, 1983). Crystal $0\cdot26 \times 0\cdot27 \times 0\cdot40$ mm, encapsulated in a glass capillary under a nitrogen atmosphere. Syntex $P\bar{3}$ diffractometer, $T = 173$ K, ω-scan technique, scan width 1°, scan velocity $4\cdot0$–$10\cdot0°$ min^{-1}, ratio of total background time to scan time unity. Lattice parameters refined on the basis of 50 computer-centered reflections from diverse regions of reciprocal space. Empirical absorption correction, transmission factors $0\cdot833$–$1\cdot00$. $4° < 2\theta < 55°$ $(-12 \le h \le 12;\ 0 \le k \le 14;\ -10 \le l \le 10)$. Three standard reflections collected after every 200 reflections: no significant variation. Total number of reflections: 4299; unique data used in refinement: 3582 $[F_o^2 > 2\sigma(F_o)^2]$; number of unobserved reflections: 717. Data processed by using counting statistics and a p value of $0\cdot02$ to derive standard deviations (Corfield, Doedens & Ibers, 1967). Number of variables: 306. All crystallographic calculations performed on a Digital Equipment Corporation VAX 11/780 computer using a system of programs developed by Dr J. C. Calabrese, Central Research and Development Department, E. I. du Pont de Nemours and Company, Wilmington, Delaware. Cu atom located by direct methods. Positions of remaining non-hydrogen atoms obtained by the usual combination of structure factor and Fourier synthesis calculations

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* Contribution No. 3192.

0108-2701/84/050756-04$01.50

Table 1. *Final positional and 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(1)	0·62969 (2)	0·33060 (2)	0·14765 (3)	2·029 (5)
Cu(2)	0·09716 (3)	0·09734 (2)	0·05714 (3)	2·336 (5)
Cl	0·10440 (5)	−0·09564 (4)	0·16727 (6)	2·22 (1)
N(11)	0·5082 (2)	0·2094 (1)	0·0030 (2)	2·05 (3)
N(12)	0·3575 (2)	0·2198 (1)	−0·0369 (2)	1·94 (3)
N(21)	0·4659 (2)	0·4500 (1)	0·1590 (2)	2·09 (3)
N(22)	0·3233 (2)	0·4239 (1)	0·1091 (2)	1·94 (3)
N(31)	0·2713 (2)	0·1526 (1)	0·2333 (2)	2·05 (3)
N(32)	0·3336 (2)	0·2465 (1)	0·2319 (2)	1·85 (3)
C(11)	0·5361 (2)	0·1187 (2)	−0·0975 (2)	2·48 (4)
C(12)	0·4064 (2)	0·0699 (2)	−0·2000 (2)	2·76 (5)
C(13)	0·2955 (2)	0·1355 (2)	−0·1585 (2)	2·47 (4)
C(21)	0·4607 (2)	0·5655 (2)	0·2009 (2)	2·41 (4)
C(22)	0·3165 (3)	0·6147 (2)	0·1799 (3)	2·90 (5)
C(23)	0·2335 (2)	0·5225 (2)	0·1229 (3)	2·61 (5)
C(31)	0·3457 (2)	0·1194 (2)	0·3832 (2)	2·47 (4)
C(32)	0·4561 (2)	0·1904 (2)	0·4804 (2)	2·81 (5)
C(33)	0·4447 (2)	0·2694 (2)	0·3815 (2)	2·44 (4)
C(1)	0·8562 (2)	0·2854 (2)	0·2264 (2)	2·78 (5)
C(2)	0·9091 (3)	0·1784 (2)	0·3137 (3)	3·37 (6)
C(3)	0·8835 (3)	0·1978 (2)	0·4693 (3)	3·57 (6)
C(4)	0·9366 (3)	0·3111 (3)	0·5683 (3)	3·89 (6)
C(5)	0·8457 (2)	0·4155 (2)	0·4763 (3)	3·20 (5)
C(6)	0·8253 (2)	0·3946 (2)	0·2986 (3)	2·65 (5)
B	0·2819 (2)	0·2986 (2)	0·0680 (3)	2·01 (5)

Table 2. *Selected bond distances* (Å) *and bond angles* (°) *with estimated standard deviations*

Cu(1)—N(11)	1·950 (1)	N(11)—Cu(1)—N(21)	98·40 (6)
Cu(1)—N(21)	1·966 (1)	N(11)—Cu(1)—C(1)	114·85 (7)
Cu(1)—C(1)	2·039 (2)	N(21)—Cu(1)—C(6)	107·12 (7)
Cu(1)—C(6)	2·022 (2)	C(1)—Cu(1)—C(6)	39·59 (8)
Cu(2)—Cl	2·155 (1)	N(31)—Cu(2)—Cl	159·24 (4)
Cu(2)—Cl′	2·618 (1)	N(31)—Cu(2)—Cl′	98·31 (4)
Cu(2)—N(31)	1·904 (1)	Cl—Cu(2)—Cl′	102·34 (1)

and full-matrix least-squares refinement. $\sum w(|F_o| - |F_c|)^2$ minimized; $w = 1/\sigma^2(F_o)$. $(\Delta/\sigma)_{\max} = 0$ in final refinement cycle. Atomic scattering factors from Cromer & Waber (1965); anomalous-dispersion terms from *International Tables for X-ray Crystallography* (1974). After convergence of the non-hydrogen portion of the molecule in which the atoms were refined anisotropically, all H atoms were located in a Fourier difference synthesis and refined satisfactorily. Least-squares refinement converged to $R = 0{\cdot}026$, $R_w = 0{\cdot}027$. All peaks in final $\Delta\rho$ map less than 0·56 e Å^{-3}. No correction for secondary extinction.

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

The overall molecular structure of the complex is apparent in the drawing of the molecule (Fig. 1) and consists of weakly associated $Cu(HBpz_3)(C_6H_{10})$.CuCl units. One Cu^I ion, Cu(1), is coordinated to two pyrazole groups of the ligand $HBpz_3$ and to a cyclohexene molecule in a trigonal-planar arrangement. As shown in Fig. 2, the atoms Cu(1), C(1), C(6), N(11), and N(21) are essentially planar; the bond angles about Cu(1) sum to nearly 360°. The Cu atom is 0·142 (0) Å from the least-squares plane defined by these four atoms. The half-chair configuration of the coordinated olefin can also be seen in Fig. 2. The third pyrazole group of the ligand coordinates to a cuprous chloride moiety, which in turn is weakly associated with another cuprous chloride group from a neighboring molecule.

Selected bond distances and angles are presented in Table 2. The observed bond distances and angles for the coordinated ligand $HBpz_3$ are nearly identical to those determined in other Cu^I structures with this ligand (Mealli, Arcus, Wilkinson, Marks & Ibers, 1976; Churchill, DeBoer, Rotella, Abu Salah & Bruce, 1975;

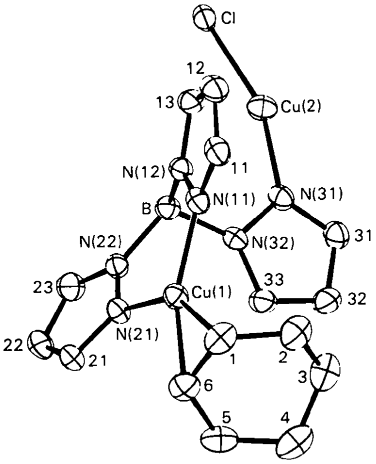

Fig. 1. View of $Cu(HBpz_3)(C_6H_{10})$.CuCl. The vibrational ellipsoids are drawn at the 50% level here and in Fig. 2. The H atoms have been omitted for clarity.

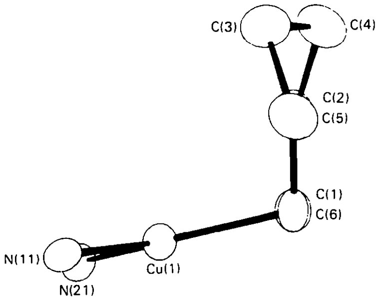

Fig. 2. Side view of Cu coordination sphere and coordinated cyclohexene.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39104 (29 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Thompson, Harlow & Whitney, 1983) and are therefore not tabulated here. There are no unusual features in the coordination sphere of either of the Cu^{I} atoms. The Cu(1)—N and Cu(1)—C contacts are consistent with those of other Cu^{I} structures, as well as those of the corresponding ethylene complex (Thompson, Harlow & Whitney, 1983; Thompson, Marks & Ibers, 1979). Also the bond angles about Cu(1) are reasonable for a trigonal-planar geometry. The C—C double-bond distance of the coordinated cyclohexene molecule [1·375 (3) Å] is approximately 0·04 Å longer than that reported for the olefinic bond of the free molecule [1·335 (3) Å (Chiang & Bauer, 1969) and 1·34 (1) Å (Scharpen, Wollrab & Ames, 1968)]. We are not aware of any other cyclohexene complex with which to compare this value. The Cu—N contact [1·904 (1) Å] for the second Cu^{I} ion in this molecule, Cu(2), is shorter than that observed in three- and four-coordinate complexes, but falls in the range observed for two-coordinate complexes (1·86–1·94 Å) and is essentially the same as that observed for $Cu(HBpz_3)(C_2H_4).CuCl$ [1·891 (2) Å] (Thompson, Harlow & Whitney, 1983). The Cu(2)—Cl contact is also typical of Cu^{I} complexes (Wells, 1975; Eller, Bradley, Hursthouse & Meek, 1977). The N(31)—Cu(2)—Cl bond angle [159·24 (4)°] is smaller than that generally observed for a linear Cu^{I} complex (171–179°). There is, however, a weakly associated cuprous chloride group from a neighboring molecule, with a Cu(2)—Cl′ distance of 2·618 (1) Å. This distance is too great to consider Cu(2) to be three-coordinate. However, interactions of this type are typical of two-coordinate Cu^{I} complexes with N ligands, which generally have present a weakly interacting atom at a rather long distance.

The major objective of this study was to assign a structure to the Cu^{I}–cyclohexene complex. Elemental analyses suggested the formulation $Cu(HBpz_3)(C_6H_{10}).CuCl$. However, room-temperature NMR data indicated three equivalent pyrazole rings; hence, arrangement of two Cu^{I} atoms, the ligand $HBpz_3$, cyclohexene, and a Cl^- ion could not be assigned unambiguously. The overall structure shown in Fig. 1 is the same as that for the ethylene analog $Cu(HBpz_3)(C_2H_4).CuCl$ described previously (Thompson, Harlow & Whitney, 1983). These two structures and the analytical and spectroscopic data for $Cu(HBpz_3)$(propylene).CuCl and the CuF analogs of these three olefin complexes suggest that the trigonal-planar geometry, which is well established for Cu^{I} complexes (Eller, Bradley, Hursthouse & Meek, 1977), is the dominant structural type for Cu^{I}–monoolefin complexes. Tetrahedral complexes can be obtained with ligands that constrain the metal ion to non-planar interactions. This structural chemistry is similar to the olefin chemistry of the d^{10} metal ions Ni^0 and Pt^0. There are a large number of structurally characterized Ni^0 and Pt^0 olefin complexes that are trigonal planar; however, tetrahedral complexes can be obtained with the proper choice of ligands (Ittel & Ibers, 1976).

Although the Cu^{I} ethylene and cyclohexene complexes have the same overall structure, the interaction between metal ion and olefin is clearly different in these two cases. A common feature of the few structurally characterized Cu^{I}–monoolefin complexes reported previously is a relatively unperturbed double bond. The similarity in bond length between free and coordinated olefin suggests that σ bonding is the dominant interaction between metal ion and olefin; π back-bonding from metal to olefin is thus not of great importance. However, unlike the previously reported Cu^{I}–monoolefin complexes (Pasquali, Floriani, Gaetani-Manfredotti & Chiesi-Villa, 1979; Thompson, Harlow & Whitney, 1983), the observed C—C bond distance for the coordinated cyclohexene molecule [1·375 (3) Å] is clearly lengthened relative to the free-molecule values of 1·335 (3) and 1·34 (1) Å found by electron diffraction and microwave techniques, respectively. A major difference between the compound reported here and the three other structurally characterized monoolefin complexes is the type of olefin. A cyclic olefin complex is described here, whereas ethylene and 1-hexene complexes have been characterized previously. It has been suggested that relief of strain is the most important factor in the bonding of cyclic olefins to transition metals (Hartley, 1969, 1972, 1973); a lengthened olefin bond may be a manifestation of this bonding interaction. Characterization of other Cu^{I}–cyclohexene complexes is in progress to determine if a lengthening of the double bond is typical of these complexes.

The technical assistance of Ms R. M. Swiatek and Mr L. Lardear is gratefully acknowledged. Helpful discussions with Drs S. D. Ittel and D. L. Thorn are greatly appreciated.

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The Structure of μ_3-Thio-μ_3-tris(disulfido)chlorato-*cyclo*-tris[(diethyl dioxodithiophosphato-*S*,*S*′)molybdenum](3*Mo*–*Mo*), $C_{12}H_{30}ClMo_3O_6P_3S_{13}$

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(*Received* 24 *December* 1982; *accepted* 5 *December* 1983)

Abstract. $M_r = 1103\cdot34$, triclinic, $P\bar{1}$, $a = 11\cdot570$ (2), $b = 13\cdot093$ (1), $c = 14\cdot399$ (2) Å, $\alpha = 102\cdot62$ (1), $\beta = 102\cdot15$ (1), $\gamma = 111\cdot87$ (1)°, $V = 1870$ (1) Å^3, $Z = 2$, $D_x = 1\cdot960$ g cm^{-3}, graphite-monochromatized Mo $K\alpha$, $\lambda = 0\cdot71073$ Å, $\mu = 18\cdot935$ cm^{-1}, $F(000) = 1092$, $T = 295$ K, final $R = 0\cdot055$ for 4113 reflections. In the thio-capped trinuclear Mo cluster, some of the skeleton atoms are in a distorted pseudocubane configuration with three S atoms capped by a Cl atom. The S—Cl bonding is covalent.

Introduction. In the course of studying the behavior of middle-valence Mo atoms in an EtOH–HCl medium, a series of stable trinuclear Mo clusters was synthesized and investigated by X-ray crystallography, including $(C_5H_7S_2)_3[Mo_3(\mu_3\text{-}S)_2(\mu\text{-}Cl)_3Cl_6]$ and $(C_5H_7S_2)_3[Mo_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3Cl_7]$ (Huang Jinling, Shang Maoyu, Huang Jianquan & Lu Jiaxi, 1982; Huang Jinling, Shang Maoyu, Liu Shixiong & Lu Jiaxi, 1982). It seemed interesting to pursue further study on this kind of compound in connection with its chemical behavior, such as ligand replacement reactions. In this respect, we were able to obtain a new trinuclear cluster with the $[S_2P(OEt)_2]^-$ radical as its terminal ligand.

Experimental. Straw-yellow long parallelepipeds, produced by K_2MoOCl_5 and P_2S_5 in EtOH saturated with HCl gas; $0\cdot15 \times 0\cdot19 \times 0\cdot37$ mm. Enraf–Nonius CAD-4 diffractometer, 25 reflections for measuring lattice parameters, $2 \leq 2\theta \leq 46°$, h 0–12, k −12–12, l −14–14; 5193 data, all unique, 4113 with $I \geq 3\sigma(I)$; Enraf–Nonius crystallographic computing package (Frenz, 1980), PDP 11/70 computer. Lp correction, absorption ignored; heavy-atom method, anisotropic full-matrix refinement on F, H not determined; final $R = 0\cdot055$, $R_w = 0\cdot061$, $w = 1$; atomic scattering factors from *International Tables for X-ray Crystallography* (1974).*

Discussion. Table 1 gives the atomic coordinates and Table 2 the interatomic distances and angles. Figs. 1 and 2 show the structure and the packing of the cluster, respectively.

In the cluster three Mo atoms form an equilateral-triangle configuration with an average Mo—Mo bond length of $2\cdot725$ (3) Å. One μ_3-S atom [S(1)] binds the three Mo atoms together to form a monocapped cluster core. Each pair of Mo atoms is bridged further by an S_2^{2-} ligand in such a manner that one of the S atoms [S(3), S(5), S(7)] lies basically on the plane formed by the three Mo atoms and the other [S(2), S(4), S(6)] is situated on the side opposite to the μ_3-S atom. The cluster unit $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3]$ has been reported in several cases, *e.g.* $(NH_4)_2[Mo_3S_{13}]$ (Müller, Pohl, Dartmann, Cohen, Bennet & Kirchner, 1979), $Mo_3S_7Cl_4$ (Marcoll, Rabenau, Mootz & Wunderlich, 1974) and $\{Mo_3S_7[S_2P(Et)_2]_3\}$ $[S_2P(Et)_2]$ (Keck, Kuchen, Mathow, Meyer, Mootz & Wunderlich, 1981). Nevertheless, the title structure differs sharply from these because of the presence of an additional Cl atom bridging the three out-of-plane S atoms, with an average

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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 39088 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0108-2701/84/050759-03$01.50