The Skeletal Bonding and Structure of $H_6Cu_6(PR_3)_6$ Clusters. X-Ray and Topological Studies on the $H_6Cu_6[P(p\text{-tolyl})_3]_6$ Molecule

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The structure of '[HCuP(p-tolyl)$_3$]', whose state of aggregation has been uncertain, is shown to be hexameric by single-crystal X-ray diffraction methods. Its geometry is similar to that of $H_6Cu_6(PPh_3)_6$, consisting of an octahedral core of metal atoms with a pattern of six short [average 2.54(1) Å] and six long [average 2.66(1) Å] Cu–Cu edges. There are two independent clusters in the unit cell, each situated on a center of inversion symmetry. The structural data, plus the results obtained from a modified form of Mingos' 'styx' electron counting method as applied to the (HCuL)$_6$ cluster, appear indicative of the presence of edge-briding H atoms. Crystallographic details: $H_6Cu_6[P(p\text{-tolyl})_3]_6$ crystallizes in the triclinic space group $P\bar{1}$, with a = 19.785(11) Å, b = 23.057(9) Å, c = 15.810(3) Å, α = 102.53(2)°, β = 112.39(3)°, γ = 83.96(4)°, Z = 2. Final R factor = 9.1% for 6837 reflections.

Introduction

Perhaps one of the most intriguing hydridic species reported to date is the copper cluster $H_6Cu_6(PPh_3)_6$ described by Osborn, Churchill and co-workers over a decade ago [1, 2]. Characterization of this hydride by spectroscopic means has met with only limited success. No absorption attributable to a M–H vibrational mode has been observed in the IR spectrum of this molecule, nor has a hydride resonance been found in its ^1H NMR spectrum. An X-ray structure analysis of the cluster has been performed, but unfortunately it was not possible to directly locate the H atoms in the molecule. This elusive nature of the H atoms in $H_6Cu_6(PPh_3)_6$ has resulted in two different views for the M–H bonding in this cluster hydride. Based upon the observed distortion in the Cu_6 core of the $H_6Cu_6(PPh_3)_6$ molecule, the original investigators have suggested that the H atoms are situated in bridging positions along the six edges of the two enlarged opposite triangular faces present in the Cu_6 octahedron [1, 2]. In a subsequent publication, however, it was suggested by Stucky and co-workers that the H atoms might not be involved in edge-bridging three-center Cu–H–Cu bonds at all, but rather in face-capping four-center Cu_3H bonds [3].

We had hoped to resolve this issue by carrying out a neutron diffraction analysis of the $H_6Cu_6(PPh_3)_6$ cluster, but unfortunately have been unsuccessful in growing suitably large crystals of the material for such a study (the compound tends to crystallize as thin flat plates). We have, however, found that the corresponding $P(p\text{-tolyl})_3$ complex '[HCuP(p-tolyl)$_3$]' can be crystallized in a prismatic form which seems to be more suitable. In this paper, the X-ray structure analysis of the '[HCuP(p-tolyl)$_3$]' complex is reported.

Of fundamental interest to the present study was the extent of aggregation of the '[HCuP(p-tolyl)$_3$]' molecule in the solid-state. While $H_6Cu_6(PPh_3)_6$ has been confirmed to be hexameric in the crystalline form, in the reported synthesis of '[HCuP(p-tolyl)$_3$]' by Stephens, the latter compound was referred to as being in an 'indefinite state of aggregation' [4]. The uncertainty in the nature of the molecule arises in part from the fact that in solution, this and other 1:1 copper hydride–phosphine compounds are believed to exist in the form of complex mixtures of monomers, dimers and trimers [4]. Clearly, therefore, before any neutron diffraction study of '[HCuP(p-tolyl)$_3$]' is carried out, it is necessary to first show that '[HCuP(p-tolyl)$_3$]' is also hexameric as well as structurally quite similar to $H_6Cu_6(PPh_3)_6$ in the crystalline state.

Added impetus for the structure determination of $H_6Cu_6[P(p\text{-tolyl})_3]_6$ is provided by the recent report by Goeden and Caulton that the compound is catalytically active in converting formaldehyde to methyl

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TABLE I. Crystal Data for $H_6Cu_6[P(p\text{-tolyl})_3]_6$.

Crystal Type	Triclinic
Space Group	$P\bar{1}$ (No. 2)
Unit Cell Parameters	
a, Å	19.785(11)
b, Å	23.057(9)
c, Å	15.810(3)
α, deg.	102.53(2)
β, deg.	112.39(3)
γ, deg.	83.96(4)
V, Å^3	6507(5)
Formula Units per Unit Cell, Z	2
Formula Weight, g mol^{-1}	2213.55
Calculated Density ρ(calc), g cm^{-3}	1.13
Absorption Coefficient, μ, cm^{-1} (For Mo Kα X-rays)	11.2

formate [5a]. They further reported that, in contrast to $H_6Cu_6(PPh_3)_6$, the H atoms in $H_6Cu_6[P(p\text{-tolyl})_3]_6$ are NMR-detectable (δ = 3.5 ppm), and that (under their conditions) the $H_6Cu_6L_6$ hexamers are not fragmented into smaller (monomeric and dimeric) units [5b].

In this paper we confirm, by a single-crystal X-ray diffraction study, the hexameric nature of $H_6Cu_6[P(p\text{-tolyl})_3]_6$ in the solid state, and present a modified topological treatment of metal hydrido clusters as applied to the present system.

Experimental

Collection and Reduction of the X-ray Data for $H_6Cu_6[P(p\text{-tolyl})_3]_6$

The synthesis of $H_6Cu_6[P(p\text{-tolyl})_3]_6$ has been reported previously [4]. Air-sensitive red prismatic crystals up to a few millimeters in length on an edge were obtained by liquid–liquid diffusion of hexane into a THF solution of the complex. A specimen of approximate dimensions 0.42 × 0.26 × 0.21 mm was chosen for the X-ray analysis, and sealed in a glass capillary under a nitrogen atmosphere. Accurate unit cell constants, and the orientation matrix used in the data collection, were derived from fifteen carefully centered reflections (20° < 2θ < 25°) on a Syntex $P2_1$ automated diffractometer employing Mo Kα radiation. The cell parameters and other relevant crystal data are presented in Table I. One hemisphere of data (+h, ±k, ±l) was collected in the ω-scan mode to a $\sin\theta/\lambda$ limit to 0.54 Å^{-1} with a variable scan speed ranging from 2.5 to 29.3°/min. During the data collection, three standard reflections [(4,8,3),

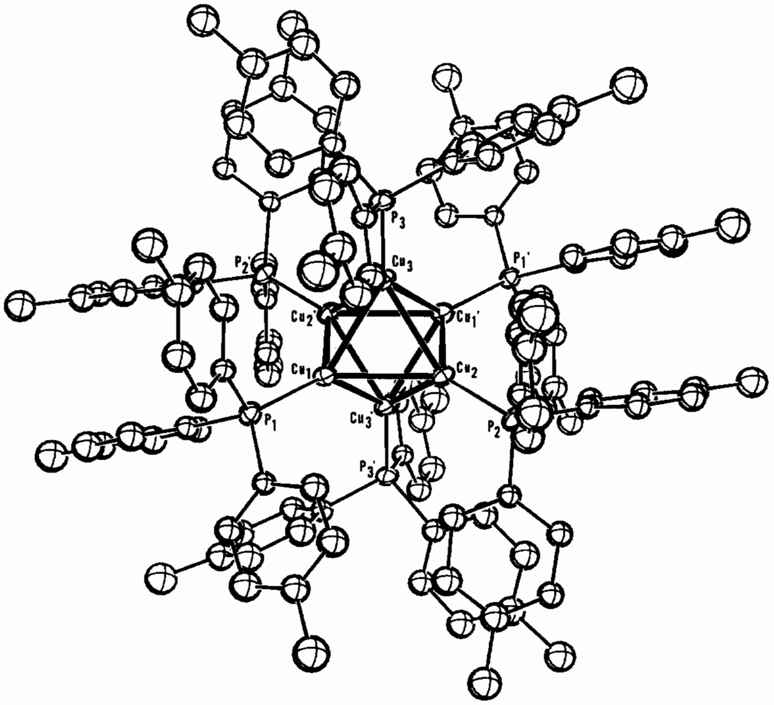


Fig. 1. A view of the $H_6Cu_6[P(p\text{-tolyl})_3]_6$ molecule (cluster *1*) approximately normal to the two larger triangular faces [*i.e.*, Cu(1,2,3); Cu(1',2',3')] of the octahedral Cu_6 core. Thermal ellipsoids in this and subsequent plots correspond to 20% probability.

TABLE II. Final Atomic Positons (Fractional Coordinates) for $H_6Cu_6[P(p\text{-}tolyl)_3]_6$.

Atom	x	y	z
Cu(1)	0.0831(2)	0.4511(1)	0.5076(2)
Cu(2)	−0.0662(2)	0.4397(1)	0.4347(2)
Cu(3)	−0.0030(2)	0.5211(1)	0.3956(2)
Cu(4)	0.5269(2)	−0.0790(1)	−0.0208(2)
Cu(5)	0.5597(2)	0.0129(1)	0.1223(2)
Cu(6)	0.4244(2)	−0.0191(1)	0.0285(2)
P(1)	0.1833(3)	0.3942(3)	0.5167(4)
P(2)	−0.1451(3)	0.3656(2)	0.3603(4)
P(3)	−0.0062(4)	0.5411(3)	0.2627(4)
P(4)	0.5582(3)	−0.1744(2)	−0.0461(4)
P(5)	0.6325(4)	0.0300(3)	0.2725(4)
P(6)	0.3369(4)	−0.0451(3)	0.0670(4)
C(111)	0.2655(12)	0.4168(9)	0.6227(15)
C(112)	0.3353(15)	0.3954(11)	0.6232(18)
C(113)	0.3944(16)	0.4167(12)	0.7105(21)
C(114)	0.3804(16)	0.4542(12)	0.7804(19)
C(115)	0.3146(16)	0.4718(11)	0.7782(19)
C(116)	0.2526(13)	0.4529(10)	0.6950(17)
C(117)	0.4504(17)	0.4747(13)	0.8693(22)
C(121)	0.1743(12)	0.3163(9)	0.5157(15)
C(122)	0.1142(13)	0.2884(11)	0.4472(16)
C(123)	0.0995(14)	0.2290(12)	0.4412(18)
C(124)	0.1500(15)	0.1996(11)	0.5052(18)
C(125)	0.2096(16)	0.2259(12)	0.5768(19)
C(126)	0.2239(13)	0.2869(11)	0.5808(16)
C(127)	0.1391(17)	0.1305(14)	0.4996(21)
C(131)	0.2110(11)	0.3894(9)	0.4186(14)
C(132)	0.2027(13)	0.4435(10)	0.3849(17)
C(133)	0.2270(14)	0.4439(11)	0.3117(18)
C(134)	0.2536(14)	0.3892(12)	0.2675(19)
C(135)	0.2610(14)	0.3375(12)	0.3064(18)
C(136)	0.2400(13)	0.3344(11)	0.3821(17)
C(137)	0.2801(15)	0.3868(12)	0.1824(19)
C(211)	−0.2416(11)	0.3834(9)	0.3370(14)
C(212)	−0.2965(13)	0.3538(10)	0.2563(16)
C(213)	−0.3699(14)	0.3696(11)	0.2434(17)
C(214)	−0.3883(15)	0.4134(11)	0.3079(18)
C(215)	−0.3310(15)	0.4418(11)	0.3922(18)
C(216)	−0.2567(13)	0.4270(10)	0.4024(16)
C(217)	−0.4678(16)	0.4305(12)	0.2951(20)
C(221)	−0.1286(12)	0.3033(9)	0.4174(14)
C(222)	−0.1850(12)	0.2616(10)	0.4006(15)
C(223)	−0.1662(13)	0.2139(10)	0.4500(16)
C(224)	−0.0966(15)	0.2091(12)	0.5175(19)
C(225)	−0.0419(15)	0.2492(12)	0.5351(18)
C(226)	−0.0572(13)	0.2986(10)	0.4836(17)
C(227)	−0.0754(16)	0.1583(13)	0.5747(20)
C(231)	−0.1453(12)	0.3358(10)	0.2478(15)
C(232)	−0.1506(13)	0.3748(11)	0.1891(18)
C(233)	−0.1512(14)	0.3540(12)	0.0944(19)
C(234)	−0.1441(15)	0.2934(13)	0.0651(20)
C(235)	−0.1433(16)	0.2496(13)	0.1172(22)
C(236)	−0.1422(15)	0.2732(12)	0.2147(20)
C(237)	−0.1476(18)	0.2720(14)	−0.0399(24)
C(311)	−0.0986(12)	0.5620(10)	0.1867(16)
C(312)	−0.1366(14)	0.5277(10)	0.1046(18)
C(313)	−0.2119(16)	0.5430(13)	0.0495(20)
C(314)	−0.2412(16)	0.5922(13)	0.0851(21)
C(315)	−0.2032(17)	0.6257(13)	0.1706(21)
C(316)	−0.1306(16)	0.6100(13)	0.2266(20)
C(317)	−0.3244(19)	0.6035(14)	0.0237(23)
C(321)	0.0479(13)	0.6010(10)	0.2675(16)
C(322)	0.1154(14)	0.6070(11)	0.3416(17)
C(323)	0.1615(15)	0.6528(12)	0.3539(19)
C(324)	0.1372(16)	0.6919(12)	0.2874(20)
C(325)	0.0715(16)	0.6848(12)	0.2147(20)
C(326)	0.0254(14)	0.6384(11)	0.2054(18)
C(327)	0.1944(16)	0.7432(13)	0.3034(20)
C(331)	0.0233(12)	0.4776(9)	0.1946(15)
C(332)	0.0446(14)	0.4829(11)	0.1222(18)
C(333)	0.0711(15)	0.4284(13)	0.0725(19)
C(334)	0.0646(16)	0.3741(14)	0.0903(21)
C(335)	0.0453(15)	0.3689(12)	0.1651(20)
C(336)	0.0228(13)	0.4226(11)	0.2192(16)
C(337)	0.0925(18)	0.3186(15)	0.0436(23)
C(411)	0.5582(12)	−0.2066(10)	−0.1635(15)
C(412)	0.5541(12)	−0.2675(10)	−0.1983(16)
C(413)	0.5560(13)	−0.2894(10)	−0.2887(17)
C(414)	0.5576(13)	−0.2469(11)	−0.3405(17)
C(415)	0.5615(13)	−0.1883(11)	−0.3065(17)
C(416)	0.5611(12)	−0.1659(10)	−0.2167(16)
C(417)	0.5551(16)	−0.2696(12)	−0.4405(20)
C(421)	0.6532(12)	−0.1914(9)	0.0287(15)
C(422)	0.6705(15)	−0.1717(12)	0.1265(20)
C(423)	0.7483(18)	−0.1820(13)	0.1875(21)
C(424)	0.7980(17)	−0.2041(13)	0.1539(22)
C(425)	0.7790(16)	−0.2223(12)	0.0637(22)
C(426)	0.7067(16)	−0.2133(12)	−0.0020(19)
C(427)	0.8767(18)	−0.2099(14)	0.2251(22)
C(431)	0.5017(12)	−0.2247(9)	−0.0264(14)
C(432)	0.4275(12)	−0.2103(9)	−0.0534(14)
C(433)	0.3828(13)	−0.2481(10)	−0.0398(16)
C(434)	0.4111(14)	−0.3004(10)	−0.0037(16)
C(435)	0.4840(15)	−0.3136(11)	0.0260(18)
C(436)	0.5355(13)	−0.2759(11)	0.0162(17)
C(437)	0.3623(16)	−0.3422(13)	0.0117(20)
C(511)	0.6332(12)	0.1071(9)	0.3342(15)
C(512)	0.6406(12)	0.1229(10)	0.4300(16)
C(513)	0.6411(13)	0.1854(11)	0.4704(16)
C(514)	0.6367(12)	0.2269(10)	0.4173(16)
C(515)	0.6320(13)	0.2113(10)	0.3257(17)
C(516)	0.6293(12)	0.1503(10)	0.2795(16)
C(517)	0.6405(13)	0.2917(10)	0.4670(16)
C(521)	0.7291(12)	0.0110(10)	0.2953(16)
C(522)	0.7834(17)	0.0298(12)	0.3859(20)
C(523)	0.8618(18)	0.0124(14)	0.3919(22)
C(524)	0.8762(17)	−0.0199(12)	0.3195(22)
C(525)	0.8245(16)	−0.0366(12)	0.2348(20)
C(526)	0.7466(15)	−0.0218(11)	0.2202(17)
C(527)	0.9561(20)	−0.0298(15)	0.3438(24)
C(531)	0.6047(12)	−0.0140(9)	0.3401(14)
C(532)	0.5354(14)	0.0006(11)	0.3420(17)
C(533)	0.5091(15)	−0.0347(12)	0.3912(19)
C(534)	0.5556(16)	−0.0782(12)	0.4263(18)
C(535)	0.6204(17)	−0.0924(12)	0.4271(20)

(continued overleaf)

TABLE II. *(continued)*

Atom	x	y	z
C(536)	0.6533(14)	−0.0581(12)	0.3804(18)
C(537)	0.5239(17)	−0.1156(14)	0.4767(22)
C(611)	0.3085(13)	0.0138(10)	0.1445(17)
C(612)	0.2839(14)	0.0641(12)	0.1079(18)
C(613)	0.2608(16)	0.1160(13)	0.1650(22)
C(614)	0.2689(16)	0.1079(14)	0.2553(22)
C(615)	0.2956(16)	0.0571(14)	0.2887(21)
C(616)	0.3177(14)	0.0042(11)	0.2327(19)
C(617)	0.2397(20)	0.1691(16)	0.3169(26)
C(621)	0.2510(13)	−0.0699(10)	−0.0310(16)
C(622)	0.2596(14)	−0.1008(11)	−0.1143(19)
C(623)	0.1931(15)	−0.1190(11)	−0.1942(18)
C(624)	0.1262(15)	−0.1057(11)	−0.1864(18)
C(625)	0.1166(17)	−0.0724(13)	−0.1035(22)
C(626)	0.1803(17)	−0.0538(12)	−0.0213(20)
C(627)	0.0545(18)	−0.1235(14)	−0.2690(22)
C(631)	0.3643(14)	−0.1082(10)	0.1301(16)
C(632)	0.3105(15)	−0.1425(12)	0.1364(19)
C(633)	0.3391(18)	−0.1871(14)	0.1916(21)
C(634)	0.4070(19)	−0.2000(14)	0.2192(21)
C(635)	0.4615(15)	−0.1717(12)	0.2115(19)
C(636)	0.4375(14)	−0.1240(11)	0.1641(17)
C(637)	0.4376(22)	−0.2535(19)	0.2671(28)

TABLE III. Selected Bond Distances (Å) in $H_6Cu_6[P(p\text{-tolyl})_3]_6$.

Copper–Copper (long edges)			
Cu(1)–Cu(2)	2.749(4)	Cu(4)–Cu(5)	2.668(4)
Cu(1)–Cu(3)	2.647(4)	Cu(4)–Cu(6)	2.602(4)
Cu(2)–Cu(3)	2.656(4)	Cu(5)–Cu(6)	2.614(4)
Copper–Copper (short edges)			
Cu(1)–Cu(2′)	2.517(4)	Cu(4)–Cu(5′)	2.500(4)
Cu(1)–Cu(3′)	2.544(4)	Cu(4)–Cu(6′)	2.594(4)
Cu(2)–Cu(3′)	2.510(4)	Cu(5)–Cu(6′)	2.557(4)
Copper···Copper (trans)			
Cu(1)···Cu(1′)	3.744(4)	Cu(4)···Cu(4′)	3.674(4)
Cu(2)···Cu(2′)	3.711(4)	Cu(5)···Cu(5′)	3.638(4)
Cu(3)···Cu(3′)	3.597(4)	Cu(6)···Cu(6′)	3.674(4)
Copper–Phosphorus			
Cu(1)–P(1)	2.234(7)	Cu(4)–P(4)	2.216(7)
Cu(2)–P(2)	2.242(7)	Cu(5)–P(5)	2.230(7)
Cu(3)–P(3)	2.222(7)	Cu(6)–P(6)	2.214(8)
Phosphorus–Carbon			
P(1)–C(111)	1.86(2)	P(4)–C(411)	1.84(2)
P(1)–C(121)	1.82(2)	P(4)–C(421)	1.85(2)
P(1)–C(131)	1.81(2)	P(4)–C(431)	1.84(3)
P(2)–C(211)	1.82(3)	P(5)–C(511)	1.83(2)
P(2)–C(221)	1.80(2)	P(5)–C(521)	1.83(3)
P(2)–C(231)	1.76(2)	P(5)–C(531)	1.87(3)
P(3)–C(311)	1.85(2)	P(6)–C(611)	1.82(2)
P(3)–C(321)	1.81(3)	P(6)–C(621)	1.85(2)
P(3)–C(331)	1.81(2)	P(6)–C(631)	1.86(2)

(3,3,0), (−2,2,4)] were monitored at 50-reflection intervals, and showed no significant changes in their intensities. An analysis of the intensity values of an axial reflection ($\chi = 90°$) *versus* spindle angle ϕ revealed only an 8% variation in intensities. Consequently, the diffraction data were corrected for Lorentz-polarization effects, but not for absorption. Data reduction resulted in a total of 6837 reflections for which F^2 was greater than $3\sigma(F^2)$.

Structure Solution and Refinement of $H_6Cu_6[P(p\text{-tolyl})_3]_6$

The structure analysis was carried out in the triclinic space group $P\bar{1}$ (No. 2). Direct methods (using the program MULTAN [6]) revealed the positions of the six crystallographically-independent copper atoms, while the remaining non-hydrogen atoms were located in subsequent difference-Fourier maps [7]. The structural model obtained was then refined for several cycles with all atoms having isotropic temperature factors. This was then followed by least-squares refinement in which the copper and phosphorus atoms were assigned anisotropic temperature factors, while the carbon atoms were maintained as isotropic. The structure converged to give final agreement factors of R = 0.091 and R_w = 0.113 [8]. Attempts to locate the hydride hydrogen atoms at this stage from a series of difference-Fourier syntheses based on low-angle data (containing 75, 50, and 25% of the reflections) were unsuccessful. No attempt was made to locate the hydrogen atoms of the aromatic rings in the difference maps, nor were their idealized calculated positions included in the least-squares analyses. The largest residual peak in the final difference map was 1.1 eÅ^{-3}. The final atomic coordinates are presented in Table II and selected distances in Table III.

Results and Discussion

The Molecular Structure of $H_6Cu_6[P(p\text{-tolyl})_3]_6$

The 1:1 copper hydride-P(p-tolyl)$_3$ complex '[HCuP(p-tolyl)$_3$]' has been found to exist in the form of two crystallographically-independent hexanuclear $H_6Cu_6[P(p\text{-tolyl})_3]_6$ clusters (*1* and *2*) in the

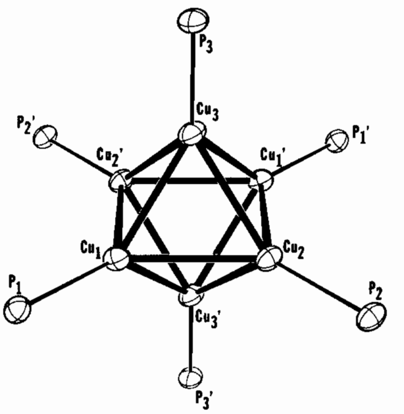


Fig. 2. A view of the Cu_6P_6 core of the $H_6Cu_6[P(p\text{-}tolyl)_3]_6$ molecule (cluster *1*).

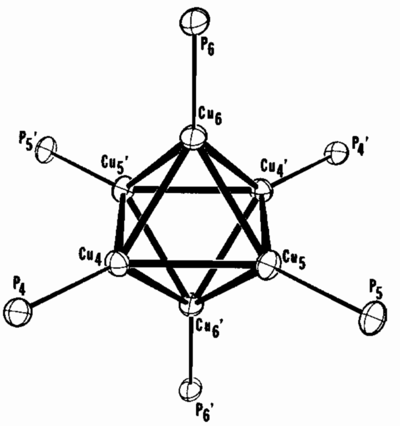


Fig. 4. A view of the Cu_6P_6 core of the $H_6Cu_6[P(p\text{-}tolyl)_3]_6$ molecule (cluster *2*).

solid-state. The two clusters, and their Cu_6P_6 cores, are illustrated in Figs. 1–4.

Each $H_6Cu_6[P(p\text{-}tolyl)_3]_6$ cluster possesses crystallographic inversion symmetry ($C_i \equiv \bar{1}$), with a central core consisting of a distorted octahedron of copper atoms. Each copper atom in turn is bonded to a single $P(p\text{-}tolyl)_3$ ligand. The distortion observed is similar to that reported earlier for $H_6Cu_6(PPh_3)_6$, and is characterized by two opposite triangular faces being significantly larger than the remaining six faces in these polyhedral structures [1, 2]. The 'long' Cu–Cu distances within these larger faces range from 2.647(4) to 2.749(4) Å with a mean of 2.68(3) Å for *1*, and 2.602(4) to 2.668(4) Å with a mean of 2.63(2) Å for *2*. The 'short' Cu–Cu distances observed for the smaller faces of the octahedra vary from 2.510(4) to 2.544(4) Å with a mean of 2.52(1) Å for *1*, and 2.500(4) to 2.594(4) Å with a mean of 2.55(3) Å for *2*. Averaging over the two independent $H_6Cu_6[P(p\text{-}tolyl)_3]_6$ clusters, we obtain the mean

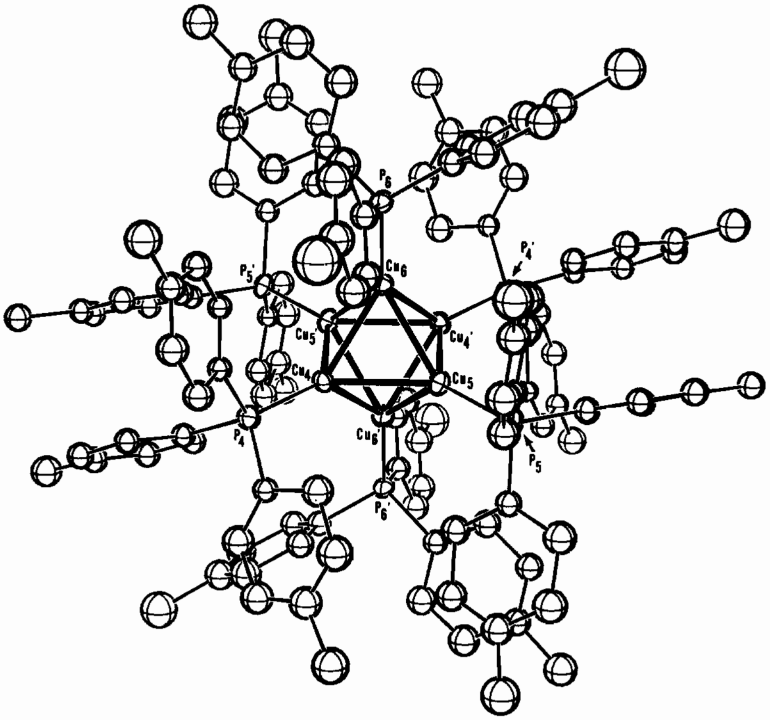


Fig. 3. The $H_6Cu_6[P(p\text{-}tolyl)_3]_6$ molecule (cluster *2*) approximately normal to the two larger triangular faces of the Cu_6 octahedron.

values of 2.54(1) and 2.66(1) Å for 'short' and 'long' Cu–Cu distances, respectively. These distances are essentially identical with the corresponding mean values of 2.542(44) and 2.655(17) Å found earlier in $H_6Cu_6(PPh_3)_6$ [1, 2]. For comparison, the Cu–Cu distance in elemental copper is 2.556 Å [9].

In spite of the similarities in the Cu_6 core structures of $H_6Cu_6[P(p\text{-tolyl})_3]_6$ and $H_6Cu_6(PPh_3)_6$, however, it is noted that the peripheral shell of coordinated ligands in these molecules exhibits a number of subtle changes upon substituting P(p-tolyl)$_3$ for PPh_3. In $H_6Cu_6[P(p\text{-tolyl})_3]_6$ one finds more extensive ring stacking (Figs. 1 and 3), and a more symmetrical positioning of the phosphorus atoms of the P(p-tolyl)$_3$ ligands. Thus, for *1* and *2*, we find that the P–Cu···Cu(trans) angles range only from 176.3(2) to 179.5(2)° [*versus* 168.3(3) to 177.3(3)° for $H_6Cu_6(PPh_3)_6$], while the P–Cu–Cu(cis) angles vary from 131.8(2) to 139.4(2)° [*versus* 123.5(3) to 145.4(3)° for $H_6Cu_6(PPh_3)_6$]. These numbers may be compared with the ideal values of 180 and 135° for P–Cu···Cu(trans) and P–Cu–Cu(cis) angles, respectively. Interestingly, the packing of the p-tolyl groups in $H_6Cu_6[P(p\text{-tolyl})_3]_6$ also differs from that found in $Au_6[P(p\text{-tolyl})_3]_6^{2+}$ [10], and is presumably the result of the substantial reduction in size of the central core structure of the molecule in going from Au_6 to Cu_6 [mean Au···Au(trans) = 4.27(1) Å; mean Cu···Cu (trans) = 3.67(2) Å].

A Modified 'Styx' Formulism for Metal Hydrido Clusters [11]

The X-ray results just presented suggest that a future neutron diffraction study of the $H_6Cu_6[P(p\text{-tolyl})_3]_6$ molecule may indeed be appropriate. However, until such a study has been completed, the M–H bonding in both $H_6Cu_6[P(p\text{-tolyl})_3]_6$ and the related $H_6Cu_6(PPh_3)_6$ cluster remains to be answered. A topological study of the present system was therefore undertaken in an attempt to qualitatively predict the positions of the H atoms in these molecules. In particular, we note that in recent years, Mingos and co-workers have succeeded in developing a localized bond treatment for metal hydrido clusters which successfully predicts the known face-bridging structure of $H_4Re_4(CO)_{12}$ on the one hand, and the edge-bridging structure of $H_4Ru_4(CO)_{12}$ on the other [14, 15]. We have now extended this localized bond approach, primarily by the inclusion of an orbital parameter, to facilitate a similar treatment of $H_6Cu_6L_6$ system; the goal being to distinguish between the face-bridging structure suggested by Stucky *et al.*, [3] and the edge-bridging structure proposed by Osborn, Churchill *et al.* [1, 2].

A description of the method is perhaps useful at this point, prior to a discussion of the results obtained. In analogy to Lipscomb's styx notation [16], Mingos *et al.* have suggested that the skeletal bonding of metal hydrido clusters may be roughly approximated as the sum of the following localized two-electron bond types:

s = number of M–H–M 3c–2e bonds
t = number of M_3 3c–2e bonds
y = number of M–M 2c–2e bonds
x = number of $(\mu_3\text{-H})M_3$ 4c–2e bonds

For metal clusters of the general formula $[M(CO)_3]_pH_q^z$, it has been shown that the values of the styx parameters may be obtained from the eqns. of balance

$$x = q - s \qquad (1)$$

$$t = (3\text{-}n)p + z - q - x \qquad (2)$$

$$2y = np - z - q - 2t \qquad (3)$$

where n is the number of electrons available for skeletal bonding from each metal atom. The variable n is defined, in turn, by

$$n = v - 6 \qquad (4)$$

where v is the total number of metal valence electrons. The three criteria employed in the derivation of equations *1–3* are (1) the conservation of hydrogen AO's, (2) the conservation of metal AO's available for skeletal bonding, and (3) the conservation of skeletal electrons.

We point out here that the skeletal electron-counting procedure used above (eqn. *4*) is in fact a special case of the counting scheme [17, 18]

$$n = v + \ell - 12 \qquad (5)$$

where ℓ is the total number of electrons supplied by the ligands to each metal atom. Moreover, equation *5* can also be further parameterized to give

$$n = v + \ell + 2u - m \qquad (6)$$

where u corresponds to the number of AO's donated by each metal atom to skeletal bonding, and m is the number of electrons needed to fill all of the accessible metal valence orbitals (usually 18). Lastly, we note that the term (3 – n)p in eqn. *2* arises from the assumption that each $M(CO)_3$ fragment contributes three orbitals for skeletal bonding. Thus, equation *2* may be rewritten in the general form

$$t = (u - n)p + z - q - x \qquad (7)$$

Substituting equation *6* into equations *3* and *7*, followed by a re-expression of the x and 2t terms in the latter two equations as functions of s, the equations of balance for the clusters $(ML_a)_pH_q^z$ (in which the ligands L are terminally bound) can be reformulated as

$$x = q - s \tag{1}$$

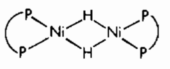
$$t = (m - v - \ell - u)p + z - 2q + s \tag{8}$$

$$2y = (v + \ell - m)3p + 4up - 3z + 3q - 2s \tag{9}$$

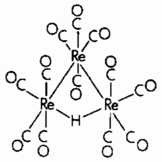
It should be pointed out that this set of modified styx equations is itself only a special case of a more general group of equations yet to be developed. Nevertheless, in their present form, these equations of balance are capable of rationalizing the known structures of a fairly broad range of metal hydrido clusters. Extension of the method to handle similar clusters (*e.g.*, metal alkyls and aryls), as well as non-hydride-containing clusters, is also possible but will not be covered here. Instead, we turn now to the application of these equations of balance to the copper hydrido clusters $H_6Cu_6L_6$.

The Skeletal Bonding and Structure of $H_6Cu_6L_6$ Clusters: A Modified 'Styx' Approach

The manipulation of the topological equations *1, 8,* and *9,* and the kinds of structural information obtainable for a given metal hydrido cluster is perhaps best illustrated with an example. For this purpose, we present next a treatment of the simple molecule $\{Ni[Cy_2P(CH_2)_3PCy_2]\}_2H_2$ (Cy = cyclohexyl) (*I*) [19]. For this particular $(ML_a)_pH_q^z$ compound, we assign the descriptive parameters p = 2, q = 2, z = 0, v = 10, ℓ = 4, and m = 18. Substituting these values into equations *1, 8,* and *9,* we obtain.



I



II

$$x = 2 - s \tag{10}$$

$$t = (4 + s) - 2u \tag{11}$$

$$y = (-9 - s) + 4u \tag{12}$$

Note that the numerical values of the structural parameters s, t, y and x (or styx numbers) can be obtained from these last three equations once the value(s) of u is known, and upon recognizing that the total number of M-H-M bonds (s) may not exceed the total number of H ligands (q) in the molecule, *i.e.*, 0 ⩽ s ⩽ q. By applying the latter condition first, and compiling the results obtained in a tabular form as shown below, the allowed value(s) of u becomes readily obvious upon inspection since meaningful solutions correspond only to non-negative values of t and y. Thus, for the nickel dimer $\{Ni[Cy_2P(CH_2)_3PCy_2]\}_2H_2$, only u = 3 is allowed, giving the styx numbers (2, 0, 1, 0). Hence, from such a topological treatment, it is suggested that each nickel atom donates three AO's to skeletal bonding, and that these in turn are allocated to two M–H–M bonds (s = 2) and an additional M–M bond (y = 1), consistent with the known structure of the molecule [19].

s	t = (4 + s) − 2u	y = (−9 − s) + 4u	x = 2 − s
0	4 − 2u	−9 + 4u	2
1	5 − 2u	−10 + 4u	1
2	6 − 2u	−11 + 4u	0

Another good example is the trinuclear dianion $[Re(CO)_4]_3H^{2-}$ (*II*) [20, 21]. In this case, the styx approach must now elicit the correct structure from a choice of two bonding modes, edge *vs.* face-bridging. For $[(ReL_4)_3H]^{2-}$ we have p = 3, q = 1, z = −2, v = 7, ℓ = 8, m = 18; which when substituted into equations *1, 8, 9* yields (x = 1 − s), (t = 5 − 3u + s) and (y = 6u − 9 − s). From these equations one can readily show that only u = 2 yields a valid solution (1, 0, 2, 0), consistent with the observation that the H atom in the molecule occupies an edge-bridging (s = 1) position rather than the alternate face-capping possibility. The choice of u = 2 is also consistent with the fact that each ReL_4 unit uses two orbitals to complete an octahedral coordination geometry.

Focussing now on the system of primary interest here, *i.e.*, $H_6Cu_6L_6$ or $(CuL)_6H_6$, we note that the descriptive parameters are p = 6, q = 6, z = 0, ℓ = 2, and m = 18. Through a similar treatment, equations *1, 8,* and *9* now give

s	t = (18 + s) − 6u	y = (−36 − s) + 12u	x = 6 − x
0	18 − 6u	−36 + 12u	6
1	19 − 6u	−37 + 12u	5
2	20 − 6u	−38 + 12u	4
3	21 − 6u	−39 + 12u	3
4	22 − 6u	−40 + 12u	2
5	23 − 6u	−41 + 12u	1
6	24 − 6u	−42 + 12u	0

Upon inspection, however, it becomes rapidly obvious that in this case there is more than one allowable value for u, and more than one acceptable solution for the styx numbers. When u = 3, the styx numbers (0,0,0,6) are obtained, while u = 4 gives the alternative solution (6,0,6,0). The first of these suggests that the $H_6Cu_6L_6$ cluster is likely to contain face-bridging H atoms, while the second solution favors the alternative edge-bridging geometry.

Another difference is that, in the (6,0,6,0) structure, six pairs of electrons formally correspond to six M–M bonds in the cluster (y = 6), while in the (0,0, 0,6) structure these electrons are presumably localized on the Cu atoms as six non-bonding pairs. Apparently, in their present form, the topological equations are not yet able to single out one unique solution. It is satisfying to note, however, that the (0,0,0,6) solution is fully consistent with the face-bridging structure proposed by Stucky and co-workers [3], while the (6,0,6,0) solution is in agreement with the edge-bridging structure suggested by Osborn, Churchill and co-workers [1, 2].

At this point, it is perhaps of some significance to recall that the octahedral M_6 core is not unique to the $H_6Cu_6L_6$ cluster, but has been previously observed in a variety of molecules such as $Mo_6Cl_8^{4+}$ and $Nb_6Cl_{12}^{2+}$ [22, 23], as well as in other group Ib clusters, *e.g.*, $Au_6[P(p\text{-tolyl})_3]_6^{2+}$ and $Cu_{6-n}M_n(2\text{-}Me_2NC_6H_4)_4X_2$ (M = Cu, Ag, Au; X = Cl, Br, I) [10, 24–26]. Interestingly, the skeletal bonding in the latter molecules can all be best rationalized in terms of a contribution of four AO's from each metal atom [27]. Hence, assuming that the bonding in the $H_6Cu_6L_6$ cluster is no exception, we are inclined to favor the styx solution (6,0,6,0) corresponding to the value of u = 4.

Conclusion

To summarize, a modified styx approach has been applied to the cluster $H_6Cu_6L_6$ in an attempt to predict the positions of the H atoms in the molecule. Two solutions were obtained, (0,0,0,6) and (6,0,6,0), consistent with structures containing face-bridging and edge-bridging H atoms, respectively. We presently favor the latter of these due to the known tendency of group Ib metal atoms in octahedral clusters to donate four AO's (u = 4) to skeletal bonding. To verify these results, we hope to carry out sometime in the future a neutron diffraction analysis of the $H_6Cu_6[P(p\text{-tolyl})_3]_6$ cluster. As there existed a level of uncertainty as to the degree of aggregation in the latter molecule [4], the appropriateness of such a study had to be initially considered somewhat in doubt. However, a single-crystal X-ray analysis has now been completed, and has established beyond question the hexameric nature of the $H_6Cu_6[P(p\text{-tolyl})_3]_6$ molecule.

Acknowledgements

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