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$[Cu(C_{13}H_{30}P_2O_6)_2][Cu_2Cl_6]$: an Unusual Chloro-bridged Linear Polymer

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Abstract

The crystal and molecular structure of $[Cu(MBP)_2][Cu_2Cl_6]$, where MBP = tetraisopropyl methylenebisphosphonate $[(C_3H_7O)_2P(O)CH_2P(O)(OC_3H_7)_2]$, has been determined at room temperature. The compound belongs to the triclinic system, space group $P\bar{1}$, $a = 10.799(1)$, $b = 11.129(1)$, $c = 11.509(1)$ Å, $\alpha = 99.56(1)$, $\beta = 115.24(1)$, $\gamma = 94.69(1)°$, $R = 0.028$ for 3979 unique observed reflections. The structure is comprised of essentially linear chains of alternating $Cu(MBP)_2^{2+}$ cations and $Cu_2Cl_6^{2-}$ anions which are linked together by singly-bridging Cl atoms of the anion. Two such bridges result in a tetragonal geometry about the Cu(II) in the centrosymmetric cation, with the Cl bridges forming elongated bonds to the axial positions of the cation. The $Cu_2Cl_6^{2-}$ anions are centrosymmetric with the two Cu centers in the dimer linked together by a double Cl bridge. The geometry of the Cu in the anion is pseudotetrahedral (dihedral angle = 44.34(2)°). The magnetic properties and the visible-near IR spectrum are discussed with respect to the observed structure.

Introduction

Examples of compounds containing the $Cu_2Cl_6^{2-}$ unit are numerous [1, 2]. Whether this dimeric unit exists as a discrete ion or as a bridged unit forming a portion of a larger structure is a function of the cation, and is particularly influenced by the cation size. In the presence of large cations such as $[(C_6H_5)_4X]^+$, where X = P, As or Sb, the $Cu_2Cl_6^{2-}$ is found as well isolated, discrete ions [3–5]. However, with small cations such as K^+ or NH_4^+, bridging interactions occur between the copper dimers, resulting in extended structures in which the Cu centers are six-coordinate [6]. Cations of intermediate size also contain bridged dimer units, but with copper having a coordination number of five [1]. The geometry of the $Cu_2Cl_6^{2-}$ unit varies from square planar with small cations to pseudotetrahedral in compounds in which it is found as a discrete anion [1, 7].

The compounds have interesting magnetic properties due to electronic interactions between the copper centers. Either antiferromagnetic or ferromagnetic behavior is observed, depending on the bond angles within the dimer and whether or not it forms extended structures [1, 2]. Only two structural determinations have been reported for compounds which contain both complex Cu^{2+} cations as well as the $Cu_2Cl_6^{2-}$ anion. One compound, $[CuL_3][Cu_2Cl_6]\cdot C_3H_6O$, where L is the diphosphine dioxide, $Ph_2P(O)CH_2P(O)Ph_2$, has discrete dimeric anions which are not able to interact with the coordinatively saturated Cu(II) cation [8]. A second compound [9], $[Cu(TMSO)_4][Cu_2Cl_6]$, where TMSO is tetramethylenesulfoxide, is composed of chains of alternating cations and dimeric anions with single chloride bridges linking the ions. These are the only two examples of bridging copper dimers in which the coordination number of the copper in the dimeric anion remains at four. We have prepared the compound $[Cu(MBP)_2][Cu_2Cl_6]$, where MBP = tetraisopropyl methylenebisphosphonate, $[(C_3H_7O)_2P(O)CH_2P(O)(OC_3H_7)_2]$, which is analogous to the TMSO compound, and report its crystal structure and its spectral and magnetic properties.

Experimental

Synthesis

$[Cu(MBP)_2][Cu_2Cl_6]$ was prepared according to the literature [10] (originally reported as $8CuCl_2\cdot 5MBP$). Yellow–brown crystals suitable for X-ray analysis were formed from 2-propanol solution upon refrigeration for two days. They exhibit a yellow–green pleochroism. The compound was obtained under conditions of excess of MBP (mole ratio of $CuCl_2$:MBP = 1:3). The same compound is obtained

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0020-1693/90/$3.50

by reacting stoichiometric amounts of reactants. The appearance, infrared spectrum and decomposition temperature matched that of the literature preparation [10].

Crystallographic Data Collection and Structure Determination

X-ray intensity data collection was performed on an Enraf-Nonius CAD4 automatic diffractometer using Mo Kα radiation (λ = 0.71073 Å). Calculations were carried out on a VAX 11/750 computer using the SDP/VAX structure solution package [11]. The structure was solved using conventional Patterson and Fourier techniques and refined by full-matrix least-squares to $R = 0.028$. Additional crystallographic parameters and data are given in Table 1. Final atomic coordinates for non-hydrogen atoms are reported in Table 2. Bond distances and angles are listed in Table 3.

Results and Discussion

The structure of $[Cu(MBP)_2][Cu_2Cl_6]$ consists of non-interacting chains of alternating $Cu(MBP)_2^{2+}$ cations and $Cu_2Cl_6^{2-}$ anions (Fig. 1). Both cation and anion are centrosymmetric, Cu(1) lying on a crystallographic center.

In the cation (Fig. 2) Cu(1) is bonded to two bidentate methylene bisphosphonate ligands such that the CuO_4 unit is essentially square planar. The coordination sphere is completed by chlorine atoms from the $[Cu_2Cl_6]^{2-}$ anion, leading to a coordination number of six and a tetragonally-distorted octahedral environment. At 2.865 Å, the axial Cu–Cl bonds are typical for the elongated bonds in tetragonal Cu(II) [1, 12] and are 0.56 Å longer than the longest bond observed in the anion. The equatorial Cu–O bonds are short (1.934(2), 1.953(2) Å) and the difference of 0.019 Å between the two bond lengths is significant. A similar distortion from ideal tetragonal symmetry was observed in the $[Cu(TMSO)_4]^{2+}$ cation [9], but the difference between the long and short Cu–O bonds was less (0.010 Å). The distortion thus cannot be attributed to a chelate strain effect of the MBP ligand since it is also observed for the monodentate TMSO ligand. However, the O(1)–Cu(1)–O(4) bond angle, the chelate bite angle, is 92.64(7)°, while for the TMSO-containing cation the corresponding angle is very nearly 90°. Although there are two sets of Cu–O bond distances, the P(1)–O(1) and P(2)–O(4) distances are equal to within experimental uncertainty.

It is interesting that in the compound of Yatsimirskii *et al.* [8] three tetraphenylmethylenediphosphine dioxide ligands form a distorted octahedral geometry about the Cu in the cation, whereas with the very similar ligand MBP only two ligands

TABLE 1. Crystallographic parameters and data for $[Cu(MBP)_2][Cu_2Cl_6]$

Empirical formula	$C_{26}H_{60}Cu_3Cl_6O_{12}P_4$
Formula weight	1091.99
Crystal class	triclinic
Space group	$P\bar{1}$
Lattice constants	
a (Å)	10.799(1)
b (Å)	11.129(1)
c (Å)	11.509(1)
α (°)	99.56(1)
β (°)	115.24(1)
γ (°)	94.69(1)
V (Å^3)	1215.5
Z	1
D_{calc} (g cm^{-3})	1.49
Crystal dimensions (mm)	0.25 × 0.35 × 0.30
Temperature (°C)	21 ± 1
Absorption coefficient, (cm^{-1})	18.1
Total no. reflections	5062
No. unique reflections	4770
2θ maximum (°)	52.0
Minimization function	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
Parameters refined	232
R: unweighted	0.028
weighted	0.044

TABLE 2. Positional parameters for $[Cu(MBP)_2][Cu_2Cl_6]$ [a]

Atom	x	y	z	B (Å^2)[b]
Cu1	0.500	0.500	0.500	2.819(8)
Cu2	0.17145(3)	0.55368(3)	0.08207(3)	3.338(6)
Cl1	0.33916(6)	0.47492(6)	0.22217(6)	4.43(2)
Cl2	0.29737(7)	0.72312(6)	0.09094(7)	4.91(2)
Cl3	0.03104(6)	0.36783(6)	−0.03723(7)	5.03(2)
P1	0.52230(6)	0.21475(5)	0.45364(5)	2.80(1)
P2	0.29901(6)	0.28818(5)	0.52396(5)	2.92(1)
O1	0.5647(2)	0.3469(1)	0.4596(1)	3.21(3)
O2	0.4194(2)	0.1371(2)	0.3148(1)	3.71(4)
O3	0.6486(2)	0.1453(1)	0.4997(2)	3.47(4)
O4	0.3448(1)	0.4131(1)	0.5121(2)	3.21(3)
O5	0.2557(2)	0.2892(2)	0.6364(2)	3.90(4)
O6	0.1688(2)	0.2124(2)	0.4018(2)	4.21(4)
C1	0.4342(2)	0.1967(2)	0.5518(2)	2.97(5)
C2	0.4291(3)	0.1492(3)	0.1926(2)	5.31(7)
C3	0.2918(4)	0.0881(4)	0.0825(3)	7.9(1)
C4	0.5417(5)	0.1017(7)	0.1846(4)	15.4(2)
C5	0.7854(3)	0.2043(2)	0.6100(3)	4.28(6)
C6	0.8711(4)	0.2616(4)	0.5539(4)	9.0(1)
C7	0.8440(4)	0.1063(3)	0.6797(3)	6.5(1)
C8	0.3418(3)	0.3634(3)	0.7708(2)	4.54(6)
C9	0.3294(4)	0.2870(4)	0.8625(3)	7.6(1)
C10	0.2911(4)	0.4841(3)	0.7825(4)	7.6(1)
C11	0.0857(3)	0.2562(2)	0.2821(3)	4.31(6)
C12	−0.0120(4)	0.1441(3)	0.1846(4)	7.7(1)
C13	0.0153(4)	0.3577(3)	0.3101(4)	7.6(1)

[a] Numbers in parentheses are e.s.d.s. [b] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter.

TABLE 3. Structural data for $[Cu(MBP)_2][Cu_2Cl_6]$ [a]

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Bond distances (Å)					
Cu1	Cl1	2.8647(6)	P2	O6	1.546(1)
Cu1	O1	1.953(2)	P2	C1	1.795(2)
Cu1	O4	1.934(2)	O2	C2	1.480(4)
Cu2	Cu2′	3.3570(4)	O3	C5	1.479(2)
Cu2	Cl1	2.2107(7)	O5	C8	1.471(3)
Cu2	Cl2	2.1939(8)	O6	C11	1.477(3)
Cu2	Cl3	2.2870(6)	C2	C3	1.487(4)
Cu2	Cl3′	2.3047(8)	C2	C4	1.397(7)
P1	O1	1.486(2)	C5	C6	1.494(6)
P1	O2	1.551(1)	C5	C7	1.485(4)
P1	O3	1.560(2)	C8	C9	1.501(6)
P1	C1	1.784(3)	C8	C10	1.499(5)
P2	O4	1.484(2)	C11	C12	1.496(4)
P2	O5	1.551(2)	C11	C13	1.479(5)

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
Bond angles (°)							
Cl1	Cu1	Cl1′	180.(0)	O4	P2	O6	114.76(9)
Cl1	Cu1	O1	87.90(4)	O4	P2	C1	110.7(1)
Cl1	Cu1	O1′	92.10(4)	O5	P2	O6	102.6(1)
Cl1	Cu1	O4	91.32(4)	O5	P2	C1	107.6(1)
Cl1	Cu1	O4′	88.68(4)	O6	P2	C1	106.49(9)
O1	Cu1	O1′	180.(0)	Cu1	O1	P1	134.5(1)
O1	Cu1	O4	92.64(7)	P1	O2	C2	123.7(2)
O1	Cu1	O4′	87.36(7)	P1	O3	C5	122.3(1)
O4	Cu1	O4′	180.(0)	Cu1	O4	P2	138.3(1)
Cl1	Cu2	Cl2	98.44(3)	P2	O5	C8	122.4(2)
Cl1	Cu2	Cl3	95.59(3)	P2	O6	C11	125.9(1)
Cl1	Cu2	Cl3′	146.56(3)	P1	C1	P2	113.0(1)
Cl2	Cu2	Cl3	149.23(3)	O2	C2	C3	105.7(3)
Cl2	Cu2	Cl3′	96.79(3)	O2	C2	C4	112.4(3)
Cl3	Cu2	Cl3′	86.04(2)	C3	C2	C4	114.1(3)
Cu1	Cl1	Cu2	140.22(3)	O3	C5	C6	108.0(2)
Cu2	Cl3	Cu2′	93.96(3)	O3	C5	C7	106.6(2)
O1	P1	O2	115.11(9)	C6	C5	C7	114.6(3)
O1	P1	O3	112.21(9)	O5	C8	C9	106.4(2)
O1	P1	C1	112.1(1)	O5	C8	C10	108.1(2)
O2	P1	O3	104.81(9)	C9	C8	C10	113.9(3)
O2	P1	C1	103.9(1)	O6	C11	C12	105.5(2)
O3	P1	C1	108.0(1)	O6	C11	C13	111.8(3)
O4	P2	O5	114.0(1)	C12	C11	C13	113.7(3)

[a] Numbers in parentheses are e.s.d.s in the least significant digits.

coordinate to the cationic Cu inspite of the synthesis being done with a Cu:ligand mole ratio of 1:3. It is tempting to ascribe the ligands' coordination ability to the difference in their Lewis basicity, but it may simply be a function of the solvents used in the preparation of the complexes and the relative ability of a Cl in the dimeric unit to bridge to the cationic Cu in the different solvents. Yatsimirskii *et al.* recrystallized their compound from acetone and found that it contained one mole of solvated acetone [8]. $[Cu(MBP)_2][Cu_2Cl_6]$ was synthesized in 2-propanol. A series of copper(II) halide (Br or Cl) complexes has been reported in which the compound obtained is highly dependent upon the solvent [9]. $[Cu(TMSO)_4][Cu_2Cl_6]$ can be prepared from methanol or ethanol, but not from other common alcohols [9]. Thus, it appears that there is delicate balance between the ligand, the strength of the Cu–Cl(bridge) bond and the solvent.

The geometry of Cu(2) in the centrosymmetric $[Cu_2Cl_6]^{2-}$ anion is pseudotetrahedral; the two Cu centers are bonded together by a double chloride

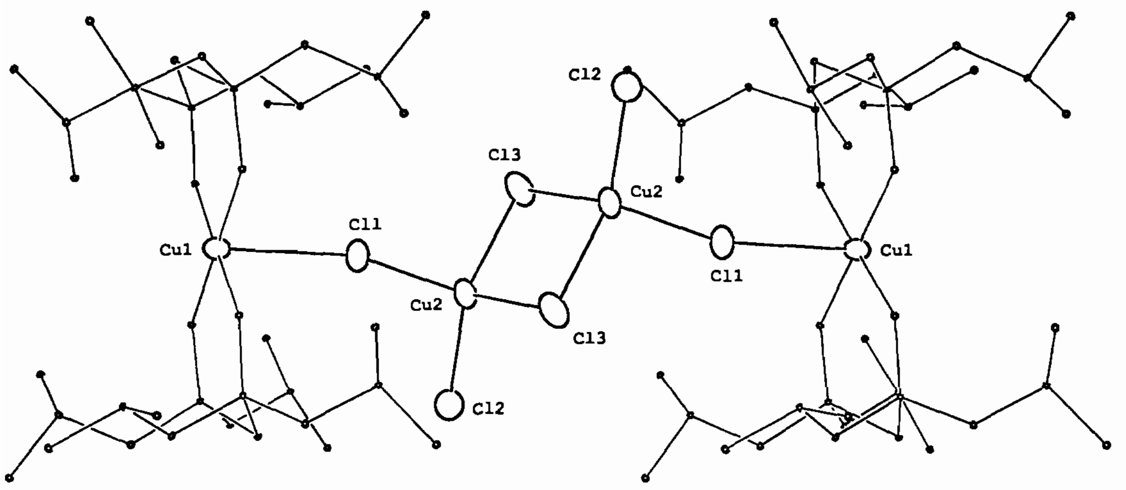

Fig. 1. Chain of alternating $Cu(MBP)_2^{2+}$ and $Cu_2Cl_6^{2-}$ ions. Each Cu(1) in the cation has an additional bond to a Cl(1) or Cl(1′) to complete its distorted octahedron and extend the chain.

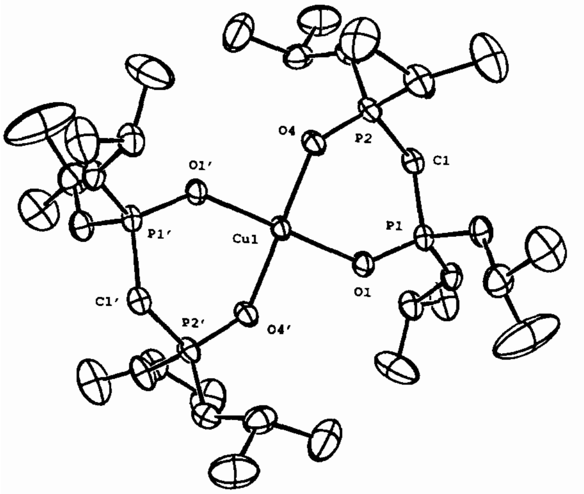

Fig. 2. The $Cu(MBP)_2^{2+}$ cation. The axial bonds to the two Cls have been omitted for clarity.

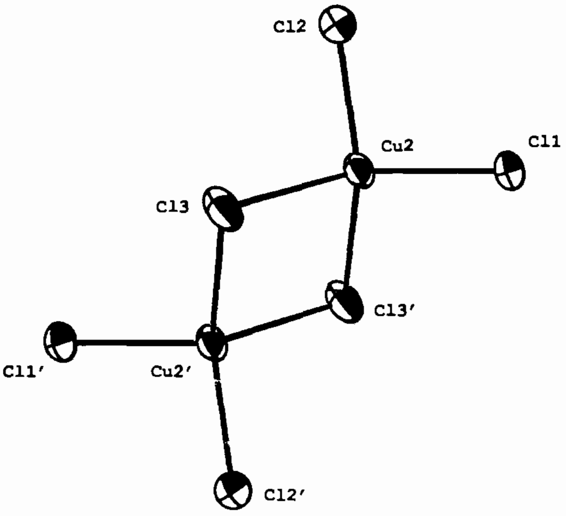

Fig. 3. The $Cu_2Cl_6^{2-}$ anion. Bridging to the cation occurs through bonds to Cl(1) and Cl(1′) (not shown).

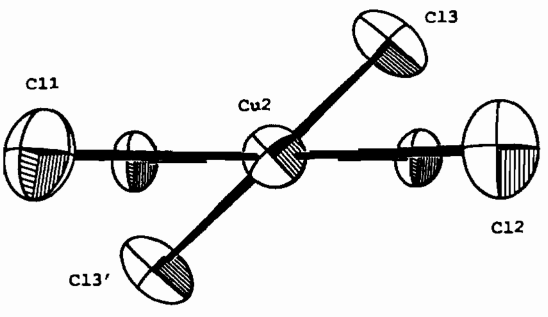

Fig. 4. The $Cu_2Cl_6^{2-}$ anion looking down the Cu–Cu axis.

bridge (Fig. 3). The geometry is almost exactly halfway between that of square planar and tetrahedral, with an angle of 44.34(2)° between the bridge plane and the terminal plane (Fig. 4). All of the Cu(2)–Cl bond lengths are different. Not surprisingly, the bridge bonds within the dimer are the longest (Cu(2)–Cl(3) = 2.287; Cu(2)–Cl(3′) = 2.305 Å). Of the two terminal bonds, the one to Cl(1), which bridges to the cation, is the longer (2.211 versus 2.194 Å).

The details of the structure of the dimeric anion appear to be highly sensitive to the environment. Although the dimeric anion in $[Cu(MBP)_2][Cu_2Cl_6]$ bridges to the cation, it is more similar in bond lengths and angles to the discrete anion in $[Ph_4Sb]_2[Cu_2Cl_6]$ [5] and the corresponding As compound [4] than to the bridging anion in $[Cu(TMSO)_4][Cu_2Cl_6]$ [9]. On the other hand, the anion in the $[CuL_3]^{2+}$ compound, which is non-bridging and well isolated, is more distorted and is not centrosymmetric [8]. The distortion was ascribed to crystal packing forces in the last compound. In the compounds in which there is bridging between anions to give five- or six-coordinate Cu centers, structural variability is perhaps not surprising.

As a result of Cu–Cu interactions, the $Cu_2Cl_6^{2-}$ anion has been found to exhibit either antiferromagnetic or ferromagnetic behavior, depending upon the bond angles within the dimer [2, 13]. Of particular importance in determining the magnetic properties are the dihedral angle (ϕ) between the dimer bridge and terminal Cls, and the Cu(2)–Cl(3)–Cu(2) bridge angle. Typically, the behavior is antiferromagnetic for square planar Cu geometry ($\phi = 0°$) and ferromagnetic for pseudotetrahedral geometry ($\phi = 44–51°$) [13]. The angle determines whether a singlet or a triplet electronic ground state occurs for the Cu–Cu dimer. The nature of the ground state has been related to the d orbital overlap for the two Cu ions [2]. The MBP compound has a ϕ of 44.34(2)°, in the range for ferromagnetic behavior. However, in both the MBP compound and the TMSO compound [9], there is the possibility of Cu(cation)–Cu(anion) electronic interaction as well as that within the dimer. In $[Cu(TMSO)_4][Cu_2Cl_6]$, $\phi = 51.0°$, ferromagnetic exchange coupling was observed for both interactions down to 1.4 K, with the Cu(cation)–Cu(anion) being the weaker [9]. The magnetic moment of $[Cu(MBP)_2][Cu_2Cl_6]$ at 20 °C is 2.10 BM (recalculated from ref. 10 with a corrected *MW*). This is higher than that normally observed for magnetically well-isolated Cu(II) centers in octahedral or tetragonal environments at room temperature [14a]. It is also higher than the average μ of 1.92 BM for $CuCl_4^{2-}$ in Cs_2CuCl_4 [15]. The anion in this compound is of pseudotetrahedral geometry, like $Cu_2Cl_6^{2-}$, but is monomeric [1]. Thus it is likely that ferromagnetic interactions are occurring within the $Cu_2Cl_6^{2-}$ anion. A careful temperature-dependent susceptibility study is required to determine the magnetic properties of this compound.

The Cu–Cl–Cu bridge within the dimeric anion has been found to be less than 95° in $Cu_2Cl_6^{2-}$ ions which exhibit ferromagnetic behavior [9]. This angle is 93.96(3)° in the MBP compound and very close to the 93.4° found for the TMSO compound [9].

The absorption spectrum between 33 000 and 10 000 cm^{-1} of $[Cu(MBP)_2][Cu_2Cl_6]$ consists of bands at 21 100 ($\epsilon = 444$ M^{-1} cm^{-1}) and 11 800 ($\epsilon = 134$ M^{-1} cm^{-1}) cm^{-1} [10]*. The first of these has been attributed to a ligand to metal charge transfer band which is specific to dimeric Cu(II) clusters [1]. The position shifts from near 21 000 to 19 000 cm^{-1} as the geometry of the dimeric cluster changes from pseudotetrahedral to square planar [1]. The frequency of this band in the MBP compound is at the high end of this range, in agreement with its pseudotetrahedral structure. Because of the rather low intensity of the band, Bencini and Gatteschi [2] have alternatively proposed that it might possibly be a double electron excitation rather than a charge transfer band. The lower energy band at 11 800 cm^{-1} is in such a location that it could be a d–d transition from either the distorted octahedral cation or from the $Cu_2Cl_6^{2-}$ anion. The observed intensity is quite high for it to arise from an octahedral cation, especially since the distortion from O_h does not remove the center of symmetry [12]. Therefore it is assigned as a transition from the $^2B_2$ ground state to the ^2E state of the dimeric anion [14b, 16]. This absorption is broad and without splitting or asymmetry at room temperature. At low temperatures, this band has been observed to split into two components ($^2A_1$ and $^2B_1$) for compounds such as $[Ph_4P]_2[Cu_2Cl_6]$ and the corresponding Sb compound [4, 5, 17]. The d–d transition expected in the same spectral region for the octahedral cation must be of considerably lesser intensity and well buried beneath the anion band.

The visible–near IR spectrum and other physical properties of $[Cu(MBP)_2][Cu_2Cl_6]$ are consistent with its crystal structure and with the properties of other compounds containing the $Cu_2Cl_6^{2-}$ ion. With its chains of alternating cations and dimeric anions linked together by an additional chloride bridge it is very similar to $[Cu(TMSO)_4][Cu_2Cl_6]$. The existence of other compounds with the same type of structure seems likely.

Supplementary Material

Tables of calculated hydrogen positions, anisotropic thermal parameters, and observed and calculated structure factors are available from the authors.

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*The spectrum was obtained on a 3.88×10^{-4} M acetone solution in 1 cm cells.

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