

Synthesis, Spectroscopy and Crystal Structure of a New Copper Complex Built Up by Cationic (Dimethylphosphoryl)methanaminium Ligands

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Abstract: A new transition metal complex of the mono-protonated ligand (dimethylphosphoryl)methanamine ($dpmaH^+$) was obtained by equimolar reaction of copper(II) chloride dihydrate and $dpma$ in concentrated hydrochloric acid. The asymmetric unit of the title structure, $[CuCl_2(C_3H_{11}NOP)_4][CuCl_4]_2$, consists of one half of a fourfold charged *trans*-dichloridotetrakis[(dimethylphosphoryl)methanaminium]copper(II) complex with the copper atom located on an inversion centre and one tetrachloridocuprate(II) dianion found in a general position. The copper centre in the cationic complex shows a tetragonally distorted octahedral environment composed of four oxygen atoms in a square plane and two *trans*-coordinated chlorido ligands. This 4+2-coordination causes elongated Cu-Cl distances because of the Jahn-Teller effect. The geometry of the tetrachloridocuprate(II) dianion is best described as a seriously distorted tetrahedron. Analysis of the hydrogen bonding scheme by graph-set theory shows three patterns of rings in the title compound. The cationic copper complex reveals intramolecular hydrogen bonds between two aminium groups and the two axial chlorido ligands. Further hydrogen bonding among the cations and anions, more precisely between four aminium groups and the chlorido ligands of four adjacent tetrachloridocuprate(II) anions, lead to a chain-type structure. Comparing the coordination chemistry of the title structure with an analogue cobalt(II) compound only disclose differences in hydrogen bonding pattern resulting in an unusual chain propagation. Besides the crystal structure received spectroscopic data are in accordance with appropriate literature.

Keywords: Transition Metal Complex, Copper, Single Crystal, X-ray Diffraction, Hydrogen Bonding.

Introduction

Ionic and molecular units owing special shapes and functionalities have attracted much attention due to their ability to form supramolecular structures caused by weak attractive forces like hydrogen bonds. Such structural components are often named tectons^{1,2}. There are several examples which show the performance of the $dpmaH^+$ tecton (protonated (dimethylphosphoryl)methanaminium) to construct hydrogen bonded, one-dimensional polymers³⁻⁸. Moreover, hydrogen bonded three-dimensional networks with a highly complex architecture have been reported recently^{9,10}. In addition, the neutral $dpma$ ligand may act as a potent bidentate *N,O*-ligand in several metal complexes¹¹⁻¹³. Here, we report the crystal structure and spectroscopic data of a new transition metal complex of $dpmaH^+$, of which only two (Co^{2+} , Mn^{2+})^{14,15} are known until now.

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Results and Discussion

Amber-brown crystals of *trans*-Dichloridotetrakis[(dimethylphosphoryl)methanaminium- κO]-copper(II) bis(tetrachloridocuprate(II)) were obtained by slow evaporation of an equimolar solution of *dpma* and copper(II) chloride dihydrate in concentrated hydrochloric acid. The asymmetric unit of $[\text{CuCl}_2(\text{dpmaH}^+)_4][\text{CuCl}_4]$ contains one half of the *trans*-dichloridotetrakis[(dimethylphosphoryl)methanaminium]copper(II) tetracation with its copper atom on an inversion centre and one tetrachloridocuprate(II) counter dianion located on a general position. Details of crystal data and further parameters are given in Table 1.

Table 1: Crystal data and parameters for structure refinement

Empirical formula	$\text{C}_{12}\text{H}_{44}\text{Cl}_{10}\text{Cu}_3\text{N}_4\text{O}_4\text{P}_4$
Formula weight	977.54
Colour/Habit	Brown/Block
Wavelength (\AA)	0.71073
Crystal system/Space group	Triclinic/ $P \bar{1}$
Unit cell dimensions	$a = 8.1477(5)$ $\alpha = 101.801(5)$
	$b = 10.5002(7)$ $\beta = 108.700(5)$
	$c = 11.5049(6)$ $\gamma = 94.700(6)$
Volume (\AA^3)	900.99(10)
T (K)	290
Z	1
Density (g cm^{-3})	1.802
Absorption coefficient (mm^{-1})	2.701
Crystal size (mm^3)	$0.55 \times 0.35 \times 0.10$
T_{\min}/T_{\max}	0.334/1.000
Reflections collected	5213
Independent reflections	3083
Observed reflections [$I > 2\sigma(I)$]	2812
Absorption correction	Multi-scan
Final R indices [$I > 2\sigma(I)$]	$R(F) = 0.0345$; $wR(F^2) = 0.0887$
R indices (all data)	$R(F) = 0.0378$; $wR(F^2) = 0.0910$
Refinement method	Least-squares matrix
Data/restraints/parameters	3083/0/176
Goodness-of-fit on F^2	1.084
$\Delta\rho_{\max}/\Delta\rho_{\min}$ (e \AA^{-3})	0.804/-0.791
CCDC-number	994390

The d^9 -configuration of the cationic copper centre leads to a Jahn-Teller-distortion of its coordination polyhedron (Figure 1).

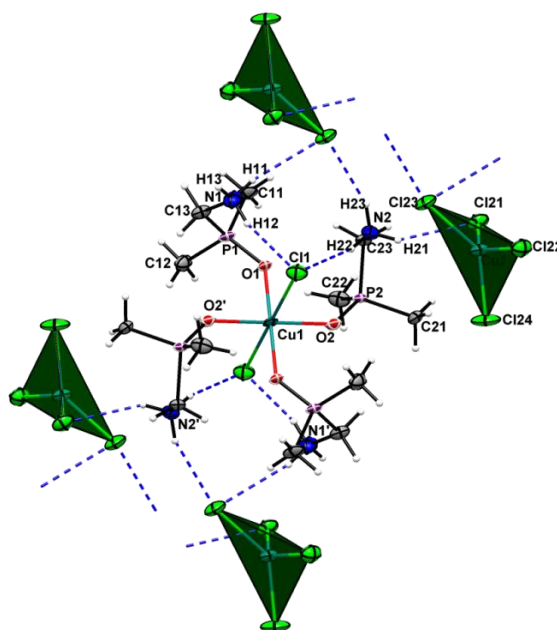


Figure 1: Title structure consisting of $[\text{CuCl}_2(\text{dpmaH}^+)_4]$ and tetrachloridocuprate(II) counter anions.²⁰

The tetragonally distorted octahedral coordination sphere around Cu1 consists of four oxygen atoms and two axial chlorido ligands. The oxygen atoms (O1, O2, O1', O2') form a square plane with angles amounting $89.26(9)^\circ$ and $90.74(9)^\circ$ and short Cu-O bond lengths of 1.962(2) and 1.965(2) Å. Whereas the distances of the axial Cu-Cl bonds (2.7978(9) Å) are significantly elongated, well-known for related compounds^{16,17}. The variance of the Cu-Cl bond lengths in the tetrachloridocuprate dianion (2.2000(10) Å to 2.3103(10) Å) and the Cl-Cu-Cl angles ranging from $94.91(4)^\circ$ to $139.12(5)^\circ$ indicate the typical distortion¹⁸ of this dianion (Table 2). All Cu-Cl and Cu-O bond lengths in both ions are in the expected ranges¹⁵.

Table 2: Selected atom distances and bond angles [Å, °]

Atoms	Distance	Atoms	Distance
Cu1–O1	1.965(2)	Cu1–Cl1	2.7978(9)
Cu1–O2	1.962(2)	P1–O1	1.502(2)
P2–O2	1.505(2)	P1–C11	1.777(3)
P1–C12	1.768(4)	P1–C13	1.810(4)
P2–C21	1.766(4)	P2–C22	1.774(4)
P2–C23	1.814(3)	N1–C13	1.478(5)
N2–C23	1.479(5)	Cu2–Cl21	2.2331(10)
Cu2–Cl22	2.2000(10)	Cu2–Cl23	2.3103(10)
Cu2–Cl24	2.2115(11)		
Atoms	Angle	Atoms	Angle
O1–Cu1–O2	89.26(9)	O1'–Cu1–O2'	90.74(9)
O1–P1–C11	110.22(16)	O1–P1–C12	115.38(16)
O1–P1–C13	109.59(15)	O2–P2–C21	109.63(15)
O2–P2–C22	114.96(16)	O2–P2–C23	112.20(15)
C11–P1–C12	108.08(19)	C11–P1–C13	108.50(18)
C12–P1–C13	104.77(18)	C21–P2–C22	108.7(2)
C21–P2–C23	105.76(17)	C22–P2–C23	105.08(17)
P1–C13–N1	113.4(2)	P2–C23–N2	113.0(2)
P1–O1–Cu1	136.07(14)	P2–O2–Cu1	132.05(13)
Cl21–Cu2–Cl22	139.10(4)	Cl21–Cu2–Cl23	94.91(4)
Cl21–Cu2–Cl24	96.94(4)	Cl22–Cu2–Cl23	95.36(4)
Cl22–Cu2–Cl24	100.67(4)	Cl23–Cu2–Cl24	139.12(5)
O1–P1–C13–N1	38.7(3)	O2–P2–C23–N2	41.2(3)

Symmetry code: ' = -x, -y, -z.

Six out of twelve hydrogen atoms of the four aminium groups of the cationic copper complex form hydrogen bonds to chlorine atoms of $[\text{CuCl}_4]^{2-}$ counter anions causing the linkage to a polymeric one-dimensional strand of the structure (Figure 1). One hydrogen atom of each aminium group is involved in an intramolecular hydrogen bond with one of the chlorido ligands. The distances between donor and acceptor ($\text{N-H}\cdots\text{Cl}$) vary from 3.126(6) Å to 3.470(4) Å, which are characteristic for medium to weak hydrogen bonding (Table 3). The existing network (ring motifs within the one-dimensional polymer) can be analysed using so-called graph-set descriptors¹⁹. The two intramolecular rings are described as $S_1^1(7)$ whereas the intermolecular ones are delineated as $R_4^4(11)$ and $R_4^2(8)$ (Figure 2).

Table 3: Hydrogen bond parameters [Å, °]

D–H \cdots A	d (D–H)	d (H \cdots A)	d (D–H \cdots A)	< (DHA)
N1–H11 \cdots Cl1	0.89	2.25	3.122(4)	167.2
N1–H12 \cdots Cl21	0.89	2.81	3.470(4)	132.6
N1–H12 \cdots Cl24	0.89	2.82	3.442(4)	127.9
N1–H13 \cdots Cl23	0.89	2.61	3.465(4)	161.2
N2–H21 \cdots Cl1	0.89	2.25	3.121(3)	165.1
N2–H22 \cdots Cl23	0.89	2.39	3.198(3)	151.5
N2–H23 \cdots Cl21	0.89	2.48	3.253(3)	145.1

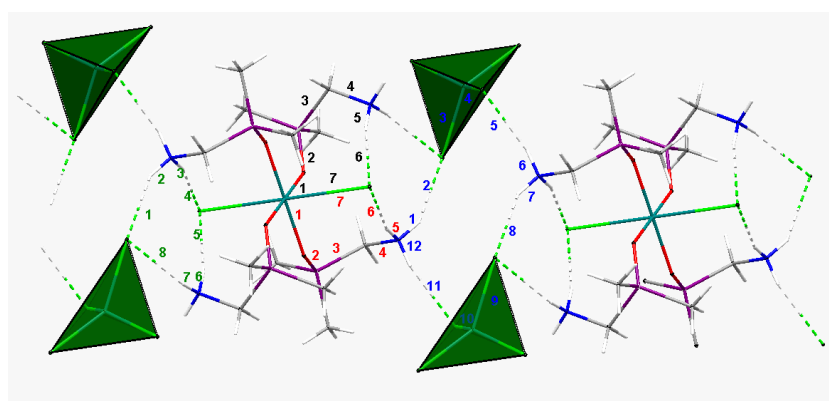


Figure 2: Part of a hydrogen bonded chain of the title structure (graph-sets descriptors (colour code):

$R_4^4(12)$ (blue), $R_4^2(8)$ (green), $S_1^1(7)$ (black and red)²⁰.

The comparable cobalt compound¹⁴ offers related bond lengths for the $dpmaH^+$ ligands. The same setting exists in the tetrachloridocuprate anion, although the tetrahedral coordination sphere in the cobalt equivalent is less distorted. The bond lengths between the transition metal and the chlorido ligands in the cationic complexes change from 2.7978(9) Å in the copper compound to 2.4525(3) Å in the analogue cobalt complex. Consequently, the hydrogen bond lengths $\text{NH}\cdots\text{Cl}$ vary in a similar manner. The main difference between these structures is the absence of hydrogen bonds between the aminium donors and the oxygen acceptors in the title structure in contrast to the cobalt compound (Figure 3). In the title structure one of the aminium groups (N1) in the $dpmaH^+$ ligand occupies a different position compared to the cobalt complex. This disparity can be described as a rotation about the P1–C13 bond axis leading to a drift in bond angles P1–C13–N1 from 113.4(2)° for the copper structure to 108.03(6)° for the related cobalt complex. This geometry causes a different position of the tetrachloridocuprate anions in the vicinity of the complex cation, which thereby directs towards an alternative chain-propagation. Whereas the polymeric strand in the

cobalt structure is formed along the crystallographic *b*-axis, the propagation in the title structure proceeds across the unit cell.

Additionally, the title compound was characterized by IR and UV/Vis spectroscopic methods. The vibrational frequencies and the spectral reflectance curve were as expected. The vibrational modes are comparable with the assignments of the cobalt analogue. An assignment and a short discussion on the typical Infrared and Raman bands of the *dpma* ligand and the *dpmaH*⁺ cation have been reported recently³.

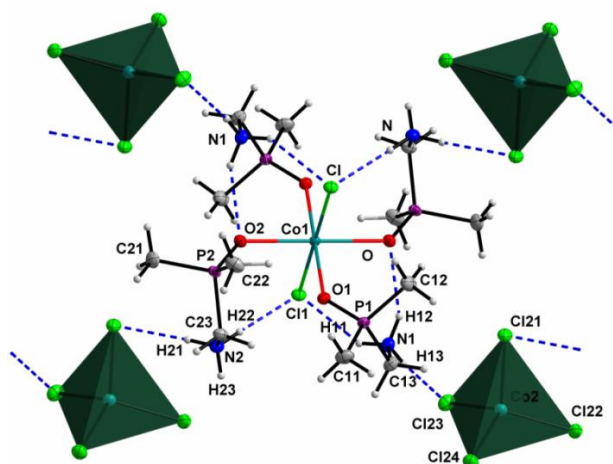


Figure 3: $[\text{CoCl}_2(\text{dpmaH}^+)_4]$ and $[\text{CoCl}_4]^{2-}$. Displacement ellipsoids are drawn with a probability level of 70% on the left and 70% on the right²⁰.

Conclusion

A new copper complex was successfully synthesized using the promising tecton *dpmaH*⁺. The title crystal structure is closely related to the recently reported Co^{2+} analogue. Both structures offer one-dimensional polymeric strands as the most striking structural elements. Slightly deviating hydrogen bonding schemes results in a different crystallographic orientation. Hence, the presented structure is a further example for the ability of the *dpmaH*⁺ tecton to form extended hydrogen bonded polymers.

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Experimental Section

The title compound was synthesised by the reaction of equimolar amounts of *dpma* and copper(II) chloride dihydrate in concentrated hydrochloric acid. After slow evaporation at room temperature hard, amber-brown crystals grown from the dark green mother liquor were obtained.

UV/Vis reflectance spectra of the crystalline sample were obtained using a SPECORD 210 PLUS spectrophotometer with an integrating sphere (Analytic Jena). In the near ultraviolet and visible region the title compound show a strong reflectance between 550 and 650 nm with a local maximum at 600 nm, which verifies the colouring. Moreover the spectrum is featureless with a reflectance of 20% relative to Spectralon®. The infrared spectrum data

were recorded on a *Digilab FT3400* spectrometer equipped with a MIRacle ATR unit (Pike Technologies), 4000-560 cm^{-1} : 3389(s), 3074(vs), 3003(vs), 2985(vs), 2977(vs), 2947(s), 2907(s), 2817(s), 2760(s), 2637(m), 2606(m), 2557(m), 2539(m), 2525(m), 1920(vw), 1604(m), 1578(m), 1493(s), 1429(w), 1413(m), 1330(vw), 1309(m), 1299(m), 1113(vs), 1070(m), 1013(vw), 951(m), 920(w), 889(vs), 784(w), 767(w), 733(m), 658(w).

Elemental analysis (C, H, N) was performed with the *Euro EA3000 Analyzer* from HEKA tech GmbH. $[\text{CuCl}_2(\text{C}_3\text{H}_{11}\text{NOP})_4][\text{CuCl}_4]$ (977.58): calcd. C 14.74, H 4.54, N 5.73; found C 14.48, H 4.54, N 5.38.

X-ray diffraction: A Xcalibur diffractometer (Agilent) operating with Mo K_α -radiation and equipped with an EOS detector was used for the data collection²¹. Structure solution using Direct Methods and refinement of the structure was performed with the SHELX program system²². The hydrogen atoms of the CH_2 groups were positioned geometrically and allowed to ride on their parent atoms ($U_{\text{iso}} = 1.2U_{\text{eq}}(\text{C})$). The hydrogens atoms of the aminium groups and of the methyl groups were geometrically restrained and additionally allowed to rotate about the N-C and C-C bonds, respectively. Their U_{iso} values were set to $1.5U_{\text{eq}}$ of the parent atom.

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