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Structural Investigation of the Cu(II) Chelate of *N*-Phosphonomethylglycine. X-ray Crystal Structure of Cu(II)[$O_2CCH_2NHCH_2PO_3$]·$Na(H_2O)_{3.5}$

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Abstract

The structure of the metal chelate formed between Cu(II) and *N*-phosphonomethylglycine (PMG) has been determined by single crystal X-ray diffraction methods. The Cu(II) cation is five-coordinate with donor atoms in a distorted square pyramidal geometry for which the basal plane involves a tridentate combination of the carboxylate oxygen, one of the phosphonate oxygen atoms and the monoprotonated secondary amine nitrogen atom to form two adjacent chelate rings, together with a second phosphonate oxygen atom from an adjacent ligand. The complex is capped and further extended by coordination to one of the basal phosphonate oxygen atoms of yet another adjacent ligand. The phosphonate group of the ligand bridges between three Cu(II) centers through a monodentate O2 and a bidentate O1. Each Cu(II) cation is coordinated by all ligand donor atoms, carboxylate oxygen, nitrogen and phosphonate oxygen, in addition to the two bridging phosphonate oxygens of ligands which are primarily associated with adjacent chelate molecules. The Cu(II) conplex is monoclinic, space group $C2$, with cell parameters $a = 21.980(2)$, $b = 4.779(2)$, $c = 10.017(2)$ Å, $\beta = 93.86(1)°$, $V = 1049.9(4)$ Å^3 and $Z = 4$. The structure was solved by direct methods and refined by a modification of direct difference and least-squares techniques to $R = 0.072$ with 715 independent reflections, $I > 3\sigma(I)$, and 62 variables.

Introduction

We have recently reported on the crystal structure of a Ca(II) complex of *N*-phosphonomethylglycine (PMG) [1], the crystals of which were obtained during an investigation of the chelating behavior of this ligand with divalent metal ions in aqueous solutions. This investigation, employing potentiometric equilibrium measurements [2], established the tendency of divalent alkaline-earth and transition metals to form 1:1 and 2:1 metal chelates with PMG in solution. The nature of any metal complex with PMG recently became an issue in a patent infringement proceeding, in view of the first report of PMG by Toy and Whing [3], and its description as a chelating agent. Our report of the crystal structure of the protonated Ca(II) complex of PMG describes it as a polymeric complex which involves seven-coordination of Ca(II) to monodentate carboxylate and phosphonate oxygen atoms, two water molecules, and two phosphonate oxygen atoms of one PMG phosphonate donor which forms an unusual four-membered chelate ring. The protonated secondary amine nitrogen atom is not available for metal ion coordination and thus cannot participate in chelate ring formation as it would if it were not protonated. An independent report [4] of a virtually identical structure of the Ca(II)–PMG complex claims that Ca(II) forms a salt of PMG.

In the present study, the first clear evidence for a metal PMG chelate of a divalent transition metal in the solid state is reported. The crystal and molecular structure of the Cu(II) complex of PMG crystallized from aqueous solution at pH 7.1 has been determined and the presence of two chelate rings involving the divalent metal ion, the secondary amino, the carboxylate and the phosphonate groups is demonstrated.

Experimental

PMG (500 mg, 3.0 mmol, Stauffer), 99.34% purity by titration [2] and $Cu(NO_3)_2 \cdot 2.5H_2O$ (700 mg, 3.0 mmol, Baker Analyzed), were dissolved in a minimum of hot water. The pH of the solution was adjusted to 7.1 by addition of 1 M NaOH. Thin fibrous blue crystals of small size were grown by slow evaporation over a period of 12 months, but none of the crystals were suitable for mounting after this period of growth. Subsequently, the bulk suspension was taken down to dryness by rapid evaporation without separation of the amorphous salts that were present in the bulk solid. *Anal.* (Galbraith Laboratories,

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Knoxville, TN): Calc. for Cu(II)[$O_2CCH_2NHCH_2PO_3$]·Na$(H_2O)_{3.5}$: C, 11.41; H, 3.80; N, 4.44; Cu, 20.13; P, 9.83; Na, 7.29. Found: C, 9.26; H, 3.0; N, 6.64; Cu, 14.26; P, 7.02; Na, 13.18%.

Qualitative tests were performed to explain the excess amounts of Na, N and C in the bulk solid. An FT-IR spectroscopic analysis of the free PMG ligand and the recovered Cu complex, performed with an IBM IR/40S spectrometer using KBr pellets, showed characteristic frequencies for $NaHCO_3$ [5] at 662 and 698 cm^{-1} in the spectrum of the solid recovered by evaporation. These bands were absent from the IR pattern of the free ligand. The IR analysis could not be utilized to prove the presence of NO_3^- since the characteristic frequencies for $NaNO_3$ overlap those of the PMG ligand. Therefore a powder diffraction pattern of the bulk sample was obtained with Cu Kα radiation on a Seifert-Scintag PAD II computer-automated powder diffractometer and was compared to the calculated pattern for the CuPMG complex based on the structure determination obtained from the single crystal X-ray diffraction experiment. The powder diffraction pattern contains a peak of strong intensity at 29.36° 2θ which agrees with that reported for $NaNO_3$. Thus the difference between the calculated and observed analysis is attributed to the presence of $NaNO_3$ and $NaHCO_3$ in the bulk sample.

Crystallographic Study

A light blue cylindrical shaped crystal of approximate dimensions 0.005 mm diameter × 0.30 mm long was mounted with the cylinder axis parallel to ϕ. Diffraction data were obtained on an AFC5R diffractometer using Mo Kα radiation and CONTROL software [6]. Data collection parameters are presented in Table 1. Data were collected by using ω-profile scans over 1.5°ω. Each scan was measured at 4°ω/min and partitioned into 32 steps. The digitized scans were then processed by a modified Lehmann–Larsen algorithm to determine the background contribution and to optimize the signal to noise ratio [6]. This method of data collection was chosen to optimize the poor diffracting power of the crystal. Intensity was calculated from the Lehmann–Larsen algorithm as was the intensity error, $\sigma(I)$. A total of 2277 reflections were collected and averaged to yield 1659 unique data with 715 having $I > 3\sigma(I)$. Solution of the structure was accomplished by direct methods [7, 8]. The atoms were refined isotropically with the refinement based on F with sigma weights, $1/\sigma^2(F_o)$.

The final cycle of full-matrix least-squares refinement was based on 715 observed reflections with $I > 3\sigma(I)$ and 62 variable parameters and converged (largest parameter shift was 0.3 times its e.s.d.) with unweighted and weighted agreement factors of:

$$R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.072$$

$$R_w = [(\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2)]^{1/2} = 0.075$$

TABLE 1. Collected single crystal data and analysis parameters for the Cu(II) chelate of phosphonomethylglycine (PMG)

Empirical formula	$CuPNO_{8.5}C_3H_{12}Na$
Formula weight	315.64
Crystal system	Monoclinic
Lattice parameters	$a = 21.980(2)$ Å $b = 4.779(2)$ Å $c = 10.017(2)$ Å $\beta = 93.86(1)°$ $V = 1049.9(4)$ Å^3
Space group	C2 (No. 5)
Z value	4
D_{calc}	2.00 g/cm^3
$F(000)$	524
μ(Mo Kα)	22.40 cm^{-1}
Radiation	Graphite-monochromated Mo Kα ($\lambda = 0.71069$)
Temperature	23 °C
2θ range for data collection	$0° < 2\theta$(Mo Kα) $< 50°$
Data collected	$\pm h, \pm k, \pm l$
Total no. data collected	2277
Total no. unique data	1659
No. unique observations with $I > 3.0(I\sigma)$	715
No.variables	62
Residuals: R, R_w	0.072; 0.075
Goodness of fit indicator	1.43
Maximum shift in final cycle	0.04
Largest shift in final cycle	1.04 e/Å
Standards, h, k, l	(511), (710), (112)

The standard deviation of an observation of unit weight was 1.43. Plots of $\Sigma w(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $\sin\theta/\lambda$, and various classes of indices showed no unusual trends. Although the linear absorption coefficient of Mo Kα was 23.1 cm^{-1}, no reflections suitable for azimuthal scans were available. The absorption correction was therefore calculated using DIFABS [9]. The data were also corrected for Lorentz and polarization effects. Neutral atom scattering factors were taken from Cromer and Waber [10]. Anomalous dispersion effects were included [11] and the values for $\Delta f'$ and $\Delta f''$ were taken from Cromer [12]. All calculations were performed with the TEXSAN single crystal package [9]. The final positional and isotropic thermal parameters for the Cu(II)–PMG chelate are presented in Table 2.

Results and Discussion

Refinement of the Cu(II)–PMG crystal structure could not be carried further than that reported here because of the extremely small size of the crystal. Anisotropic refinement of the non-hydrogen atoms was attempted but was not successful. Inclusion of

TABLE 2. Positional parameters and isotropic thermal parameters for the Cu(II) chelate of phosphonomethylglycine (PMG)

Atom	x/a	y/b	z/c	B_{iso} (A^2)
Cu[a]	0.2241(1)	0.6407	0.6292(3)	1.34(7)
P	0.3482(2)	0.634(3)	0.5385(5)	1.0(1)
Na	0.0732(3)	0.620(4)	0.6506(8)	2.1(2)
O1	0.2920(7)	0.828(3)	0.542(1)	1.1(3)
O2	0.1614(7)	0.907(4)	0.571(2)	1.2(3)
O3	0.4062(7)	0.785(3)	0.529(2)	1.6(3)
O4	0.1713(7)	0.492(4)	0.759(2)	2.0(4)
O5[b]	0	0.889(5)	0.5	2.2(5)
O6	0.1722(8)	0.224(4)	0.944(2)	2.8(5)
O7	0.0790(7)	0.559(4)	1.051(2)	2.7(4)
O8	−0.0117(7)	0.392(4)	0.742(2)	1.9(4)
O9	0.0628(7)	0.953(4)	0.832(2)	2.6(5)
N	0.2839(8)	0.368(4)	0.709(2)	1.1(4)
C1	0.349(1)	0.455(5)	0.705(2)	0.8(4)
C2	0.265(1)	0.282(5)	0.848(2)	0.7(5)
C3	0.199(1)	0.333(6)	0.846(3)	2.0(5)

[a] The origin in the monoclinic space group C2 was fixed by the y parameter of Cu. [b] Special position.

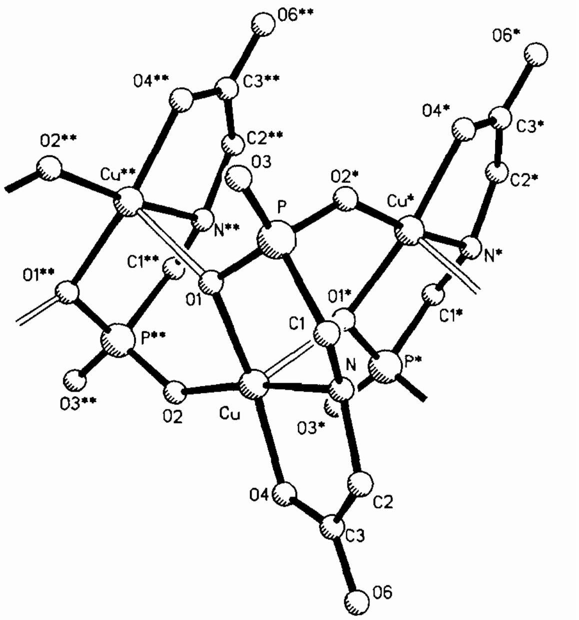

Fig. 1. Molecular representation of the Cu(II) chelate of phosphonomethylglycine with the atom numbering scheme. The weak axial Cu–O1 bond is emphasized by the open-shaded bond.

calculated hydrogen atom positions as a fixed contribution did not measurably improve the refinement.

The structure determination is, however, sufficient to elucidate the nature of the chelate. The chelate is in a five-coordinate distorted square pyramidal geometry about the Cu(II) cation. A high degree of twisting of the bonds about the P–C–N axes precludes a strictly planar configuration for the Cu(II) basal plane. Each Cu(II) cation is coordinated to the amine nitrogen atom, the carboxylate oxygen atom, one phosphonate oxygen atom of the same ligand, and a monodentate phosphonate oxygen of one adjacent ligand complex in the basal plane (Fig. 1). The distorted square pyramidal geometry is capped by a bidentate phosphonate oxygen atom of a second adjacent ligand complex. No atoms are bound to the remaining axial site from behind the basal plane.

Within the basal plane, the phosphonate and carboxylate O–Cu bond distances have a narrow range of values from 1.92(2) to 1.99(2) Å and the N–Cu coordinate bond length is 2.00(2) Å. The bond angles of O1–Cu–O2 (95.5(7)°), O1–Cu–N (88.5(7)°) and O2–Cu–N (174.2(8)°) are distorted from square geometry. The plane is capped by the bidentate O1* at a bond distance of 2.28(2) Å, which represents a weak Cu–O bond. This distance is considerably less than the sum of the van der Waals radii of 2.90 Å [13]. The apical O1* lies almost directly above the basal plane and makes bond angles with Cu(II) and its basal donor atoms within a range of 86.2(8) to 101.8(7)°. Below the basal plane, a nitrogen and an O2 atom are separated from Cu(II) at non-bonding contact distances of 3.78(2) and 3.79(8) Å, respectively. Table 3 contains intramolecular bond distances and angles.

A least-squares analysis of the Cu(II)–PMG coordination plane shows that O1 and O4 are raised less than 0.1 Å above the plane, whereas O2 and N are lowered about 0.10 to 0.12 Å below the plane. The Cu(II) ion resides about 0.18 Å below the plane on the same side as the O2 and N donor atoms (Table 4). The mean deviation from the plane is approximately 0.10 Å.

The structure is described as being a chain of Cu(II)–PMG chelates which arises in a zigzag pattern (Fig. 1), for which the nitrogen atom and a carboxylate oxygen form a five-membered chelate ring, and the nitrogen atom and a phosphonate oxygen form a second five-membered chelate ring. The fourth and fifth coordination sites of the Cu(II) cation are filled by a second and third PMG ligand such that when three Cu(II) complexes are aligned in a head-to-tail fashion, discrete dimerization is prevented by formation of an extended PMG complex in the form of a continuous chain.

The unit cell contains four Cu(II)–PMG complexes as shown in the packing diagram (Fig. 2). Aquated Na^+ ions stabilize the chains by association with phosphonate oxygen atoms O2 (2.56(2) Å) and O3 (2.46(2) Å) of adjacent ligands and also with the carboxylate oxygen O4 (2.44(2) Å) and water molecules of crystallization. The water molecule at O5 is shared between two Na^+ ions and has an O–Na

TABLE 3. Intramolecular bond distances and bond angles for the Cu(II) chelate of PMG

Atom	Atom	Distance (Å)	Atom	Atom	Distance (Å)
Cu	O2	1.92(2)	O2	Na	2.56(2)
Cu	O4	1.96(2)	O3	Na	2.46(2)
Cu	O1	1.99(2)	O4	Na	2.44(2)
Cu	O1*	2.28(2)	O5	Na	2.49(2)
Cu	N	2.00(2)	O8	Na	2.43(2)
P	N	2.61(2)	O9	Na	2.42(3)
P	O3	1.48(2)	N	C1	1.48(3)
P	O2	1.54(2)	N	C2	1.55(3)
P	O1	1.56(2)	C2	C3	1.48(3)
P	C1	1.84(2)	O6	O7	2.86(4)
O4	C3	1.27(3)	O8	O7	2.75(2)
O6	C3	1.27(3)	O9	O7	2.89(2)

Atom	Atom	Atom	Angle (°)	Atom	Atom	Atom	Angle (°)
O2	Cu	O4	90.7(7)	Cu	O4	Na	99.3(7)
O2	Cu	O1	95.5(7)	Na	O5	Na	118(1)
O2	Cu	O1*	97.9(7)	O9	Na	O8	83.5(7)
O2	Cu	N	174.2(8)	O9	Na	O4	86.5(7)
O4	Cu	O1	163.6(7)	O9	Na	O3	174.4(7)
O4	Cu	O1*	101.8(7)	O9	Na	O5	92.2(9)
O4	Cu	N	84.4(8)	O9	Na	O2	90.5(8)
N	Cu	O1*	86.2(8)	O8	Na	O4	112.8(8)
O1	Cu	N	88.5(7)	O8	Na	O3	99.2(9)
O1	Cu	O1*	92.5(4)	O8	Na	O5	89.2(6)
O3	P	O2	112(1)	O8	Na	O2	174.0(9)
O3	P	O1	114(1)	O4	Na	O3	87.9(7)
O3	P	C1	110(1)	O4	Na	O5	157.6(9)
O2	P	O1	110.4(9)	O4	Na	O2	66.9(6)
O2	P	C1	108(1)	O3	Na	O5	92.8(7)
O1	P	C1	102(1)	O3	Na	O2	86.8(6)
P	O1	Cu	112(1)	O5	Na	O2	90.7(7)
P	O1*	Cu	117.2(8)	C1	N	C2	117(2)
P	O2	Cu	137(1)	C1	N	Cu	112(1)
P	O2	Na	121.9(8)	C2	N	Cu	110(1)
Cu	O1*	Cu	122.7(7)	N	C1	P	103(1)
Cu	O2	Na	95.2(7)	C3	C2	N	106(2)
P	O3	Na	124(1)	O4	C3	O6	122(2)
C3	O4	Cu	114(2)	O4	C3	C2	122(2)
C3	O4	Na	145(2)	O6	C3	C2	115(2)

e.s.d.s in the least significant figure are given in parentheses.

TABLE 4. Least-squares plane[a] atom deviations (Å) from the plane[b]

Atom	Δ(atom)	e.s.d.
O_1	0.067	0.017
O_2	−0.102	0.020
O_4	0.088	0.021
N	−0.129	0.023
Cu	−0.179	

[a] $AX + BY + CZ - D = 0$ with $A = 4.7697$; $B = 3.0027$; $C = 7.3208$; $D = 7.7776$. [b] $\chi^2 = 88.476$, mean deviation = 0.097 Å.

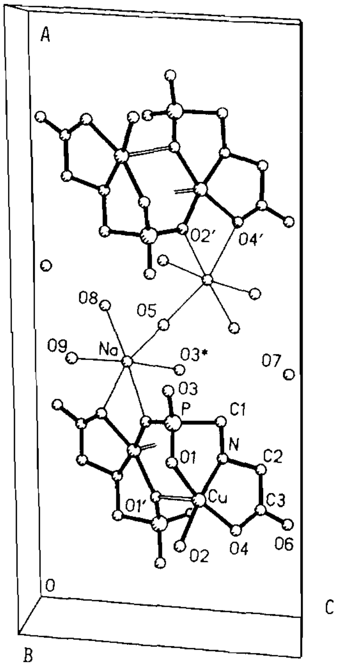

Fig. 2. Packing diagram of the Cu(II) chelate of PMG.

bond length of 2.49(2) Å. Water molecules O8 and O9 are bonded to Na^+ at distances of 2.43(2) and 2.42(3) Å, respectively. The water molecule O7 is associated with the carbonyl oxygen O6 and with O8 and O9 by hydrogen-bonding with bond distances of 2.86(4), 2.75(2) and 2.89(2) Å, respectively.

The structure of the Cu(II)–PMG chelate differs greatly from that of the N-protonated Ca(II) complex previously reported [1] in that Cu(II) is coordinated to the amino nitrogen atom as well as the carboxylate and phosphonate oxygen atoms. The Cu–N bond distance is 2.00(2) Å and compares well with distances observed for aliphatic amino complexes of Cu(II). By way of reference, trinuclear anions of $[(CuEDTA)_2Cu(en)_2]^{2-}$ contain six-coordinate units of CuEDTA with tetragonal bipyramidal geometry in which the Cu(II) ion is bonded to two imine nitrogen atoms and four carboxylate oxygen donors. The mean Cu–N bond distance was found to be 2.01(6) Å [14].

The Cu–O bond distances for the carboxylate and phosphonate groups of the ligand are virtually the same (1.96(2) to 1.99(2) Å), and are about 0.50 Å shorter than the corresponding Ca–O bonds reported by Rudolf *et al.* [1] and show less variation in bond length. By way of comparison, the bidentate phosphonate Ca–O bond distances for the Ca(II)–PMG complex are 2.500(2) to 2.510(2) Å whereas the monodentate phosphonate Ca–O bond lengths are 2.361(2) and 2.367(2) Å, and the carboxylate Ca–O bond distance is 2.359(2) Å. The carboxylate Cu–O bond distance determined for the complex of PMG is comparable to those in the aliphatic complexes mentioned above. In addition, the phosphonate Cu–O coordinate bond distances are normal and compare with those in the copper(II) and zinc(II) complexes of aminomethylphosphonic acid [15, 16].

Stabilization of the network in the crystal structures of the free ligand of PMG and its Ca(II) complex were influenced by hydrogen bonding between the carbonyl oxygen and coordinated water [1, 4, 17], but these hydrogen bonding influences are much less extensive in the Cu(II) chelate. Stabilization in the Cu(II)–PMG complex is primarily effected by bonding of phosphonate oxygen atoms to partially aquated Na^+ counter ions. Stabilization of polymeric strands by metal counter ions is common in other structures and has been described for complexes with carboxylic functional groups in MgEDTA [18] and also for sheets of lanthanide complexes of polyaza–polycarboxylate macrocyclic compounds which alternate with aquated alkali cations [19]. The stability imparted to the Cu(II) chelate of PMG by Na^+ can be inferred from the size of the isotropic thermal parameters (Table 2); these are of the order of the thermal parameters reported for the hydrogen bonded Ca(II)–PMG complex [1]. The Ca(II) and Cu(II) complexes of PMG differ primarily in that the Ca(II)–PMG complex is best described as a polymeric bidentate phosphonate complex whereas Cu(II)–PMG contains two discrete chelate rings around each metal ion, with members of the chain held together by unidentate and bidentate coordination to a bridging phosphonate group.

It is suggested that in aqueous solution under the conditions employed in the potentiometric investigation of the metal chelates of PMG [2], the complex retains the two chelate rings, but loses the bridging phosphonate oxygens, resulting in a terdentate structure with a water molecule coordinated to the fourth approximately planar position, and perhaps more distant water molecules coordinated at the axial sites. In concentrated aqueous solution one might expect some bridging through phosphonate oxygens, a polymerization process which would go to completion on crystallization.

Supplementary Material

Tables of atomic parameters, isotropic thermal parameters, bond distances and angles, and observed versus calculated structure amplitudes are available from the authors.

Acknowledgements

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