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Structural study of copper (II) complexes with *N,N,N',N",N"*-pentamethyl-diethylenetriamine and dicarboxylic acids

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ABSTRACT

This paper presents the synthesis of coordination compounds of Cu (II) using *N,N,N',N",N"*-Pentamethyl-diethylenetriamine (pmdt) as tridentate chelate ligand and mono-aromatic carboxylic acids as ligand connectors. The crystals of these compounds exhibit a regular pyramid with a square base geometry in the first coordination sphere of copper (II). When 4-aminobenzoic acid is used, intermolecular interactions via hydrogen bonds generate a double strand 1-D polymer. Otherwise, when 2-naphthoic acid and 2, 3-dimethylbenzoic acid was used no supramolecular structure was observed. It was attributed to different factors such as the coordination of aquo ligands in apical position, and intramolecular interaction.

INTRODUCTION

Currently, the creation of polymeric metal complexes (PMCs) with special geometrical and topological arrangements is an attractive topic in materials sciences, particularly in the field of "crystal engineering"[1]. It is known that in PMCs, metal sites induce certain chemical and physical characteristics that make them interesting for many scientific and industrial applications. Applications range from molecular recognition processes in biological systems and medicine[2]; hydrogen storage[3], gas adsorption[4], catalysis[5], electrical conductivity[6], nonlinear optics[7], and magnetism[8]. The nature of metal centers and the selection of ligands with special features such as flexibility, versatile binding modes, and formation of hydrogen bonds are crucial properties in the construction of PMCs[9].

Polycarboxylate assemblies and rigid ligands derived from symmetric and asymmetric aromatic multicarboxylic acids are promising candidates for construction of novel PMCs[8,10]. Carboxylic acid groups may be either completely or partially deprotonated: depending on the number of deprotonated groups, carboxylic groups can be H-bond acceptors or donors. As demonstrated in previous reports[11], the geometry of copper (II) coordination sphere varies from penta-coordinated square pyramid to trigonal bi-pyramid. Tridentate ligands form two flat chelate rings with five members, it favoring the geometry of square pyramid.

In a previous report[12], it was found that the tridentate chelate ligand diethylenetriamine (dien) induce formation of square pyramid PMCs. In this work, a different ligand is used, the *N,N,N',N",N"*-Pentamethyl-diethylenetriamine (pmdt); in comparison with dien, it is less flexible and voluminous. The construction of supramolecular structures using pmdt is shown thorough crystallographic studies.

EXPERIMENTAL SECTION

Experimental procedure

$[Cu(pmdt)(H_2O)_2](ClO_4)_2$ was prepared from copper (II) perchlorate hexahydrate (7.4g, 20 mmol) and 1,1,4,7,7-Pentamethyl-diethylenetriamine (3.5 g, 20 mmol) in 50 ml of water and 50 ml of ethanol. The compounds I, II and III were synthesized from $[Cu(pmdt)(H_2O)_2](ClO_4)_2$ (1mmol) and equimolar amounts of the corresponding carboxylic acid (2,3-dimethylbenzoic (I), 2-naphthoic (II), and 4-aminobenzoic acids(III)) dissolved in 5 mL of hot water. The reaction was stirred for thirty minutes at 40 ºC. The resulting blue solutions were covered with pin-holed parafilm and stored at room temperature. After one or two weeks, stable single-crystals of suitable dimensions for X-ray analysis were obtained.

Synthesis of $[Cu(pmdt)(2,3\text{-dimethylbenzoate})(H_2O)](ClO_4)$ (Compound I)

Aqua(2,3-dimethylbenzoate-*O*)-(1,1,4,7,7-pentamethyl-diethylenetriamine-*N*, *N*', *N*'')-copper (II), perchlorate.

The reaction of $[Cu(pmdt)(H_2O)_2](ClO_4)$ with 150 mg of 2,3-dimethylbenzoic acid generated the compound I. Yield: 372 mg, 74%. Elemental analysis: C, 42.74, H, 7.05; N, 8.27%. Formula: $C_{18}H_{35}ClCuN_3O_7$, C, 42.85, H 6.99, N, 8.33%. IR spectrum (with KBr): wide (w); weak (k); strong (s); shoulder (h), medium (m). 3298s (-OH water), 2960s (C-H aromatic ring), 2872m, 1634m (Cu^{2+}-OH_2), 1603s, 1564s (R-NH-), 1465m (R-NH-), 1387s (Ar-CO_2^-), 1085s, 1063s (ClO_4^-), 773m, 617m cm^{-1}.

Synthesis of $[Cu(pmdt)(2\text{-naphthoate})(H_2O)](ClO_4)$ (Compound II)

Aqua(2-naphthoate-*O*)-(1,1,4,7,7-pentamethyl-diethylenetriamine-*N*, *N*', *N*'')-copper (II), perchlorate.

The reaction of $[Cu(pmdt)(H_2O)_2](ClO_4)$ with 172 mg of 2-naphthoic acid generated the compound II. Yield: 380 mg, 73%. Elemental analysis: C, 45.67, H, 6.09; N, 7.96%. Formula: $C_{20}H_{32}ClCuN_3O_7$, C, 45.71, H 6.14, N, 8.00%. IR spectrum (with KBr): 3292s (-OH water), 2975m (C-H aromatic ring), 1631m (Cu^{2+}-OH_2), 1561s (R-NH-), 1466s (R-NH-), 1389s (Ar-CO_2^-), 1086s, 1061m (ClO4-), 781m, 621m cm^{-1}.

Synthesis of $[Cu(pmdt)(NO_2C_6H_4CO_2)(H_2O)](ClO_4)$ (Compound III)

Aqua(4-aminobenzoate-*O*)-(1,1,4,7,7-pentamethyl-diethylenetriamine-*N*,*N*',*N*'')copper(II), perchlorate

The reaction of $[Cu(pmdt)(H_2O)_2](ClO_4)$ with 166 mg of 4-aminobenzoic acid generated the compound III. Yield: 348 mg, 71%. Elemental analysis: C, 39.12, H, 6.43; N, 11.39%. Formula: $C_{16}H_{31}ClCuN_4O_7$, C, 39.18, H 6.37, N, 11.42%. IR spectrum (with KBr): 3286s (-OH water), 2972m (C-H aromatic ring), 2995k, 1633m (Cu^{2+}-OH_2), 1557s (R-NH-), 1464m (R-NH-), 1387s (Ar-CO_2^-), 1343h, 1078s, 1063m (ClO_4^-), 782m, 624m cm^{-1}.

Crystallographic analysis

The obtained single-crystals were mounted in random orientation on the tip of a glass fiber. Crystallographic data were collected on a Brucker SMART APEX CCD-based three-circle diffractometer, using mono-chromatic Mo-Kα ($\lambda = 0.71073$ Å) radiation at 293 K with SMART software[13]. The data were corrected using the SAINT-Plus analytical method[13] using indexed face correction, and the space group was determined through XPREP[13]. The structures were solved by direct methods (SHELXS-97)[14] and refined by all dates for least squares of full matrix using SHELXL[15]. All atoms except hydrogen were located from difference electron density map and refined anisotropically. Hydrogen atoms were placed in geometrically in idealized positions with 0.96 Å for C-H and attached to the parent atom (Uiso(H) = 1, 2 UeqC and 1.5 UeqC, and refined using the riding model. The geometric calculations were done with Platon[16]. The molecular and supramolecular graphs were done using XP and X-seed[17].

RESULTS

The crystallographic details of the compounds are presented in the TABLE 1. The geometry for compound is presented with thermal ellipsoids at 50% probability level; see Figures 1 to 3. For clarity, the figures show the cationic structure only.

Molecular description of compounds I, II and III

The compounds are ionic with an asymmetric unit as cationic complex and a perchlorate anion. The complexes exhibit slightly distorted square pyramidal pentacoordinated geometry; an (4+1) elongation causes the distortion. The basal plane is formed by the N atoms of pmdt, and an O atom of the carboxylate, and an aquo ligand is located at the elongated apical position.

TABLE 1 shows the distances and angles of the bonds which describe the geometry of the compounds. The trigonal distorisión rate τ[18] confirms that the molecular geometry of the compounds is a regular square pyramid. The dihedral angle between the basal plane around Cu (II) and the apex of the pyramid is close to the ideal (90°).

The perpendicular distance between the basal plane and Cu (II) for the three compounds indicates that the central Cu (II) is slightly below the mean baseline level composed of N and O atoms of the pmdt and carboxylate ligands, respectively, see TABLE 2. Furthermore, for the three compounds an intramolecular interaction via hydrogen bonds is observed, it is between the aquo ligad in the apical position and the O of the carbonyl coordinated in the basal position. The parameters for these hydrogen bonds are presented in TABLE 3. This interaction forms a very stable six-membered ring, which can be described by graph set as $R_1^1(6)$[19]. Finally, Figure 1 shows the structure of I; Figure 2 the structure of II, and Figure 3 shows the structure of III. For the figures, the molecular geometry is represented with thermal ellipsoids at 50% probability level.

TABLE 1 : Data collection and refinements for compounds I, II, and III.

Compound	I	II	III
Empirical formula	$C_{18}H_{34}ClCuN_3O_4$	$C_{20}H_{32}ClCuN_3O_3$	$C_{16}H_{31}ClCuN_4O_7$
Formula weight, mol^{-1}	503.48	525.49	490.45
System	Orthorhombic	Monoclinic	Orthorhombic
Space group	*P*21	*P*21/c	*P*21
a, Å	8.3212(11)	15.6886(10)	10.0220(6)
b, Å	13.5457(17)	11.7644(7)	13.4586(8)
c, Å	20.944(3)	15.0806(9)	17.1128(11)
α, °	90	90	90
β, °	90	116.2080(10)	90
γ, °	90	90	90
H	-10, 10	-18, 18	-11, 11
K	-16, 16	-13, 13	-16, 15
L	-21, 21	-17, 17	-20, 20
V, Å3	2358.9(5)	2498.7(3)	2308.2(2)
Z	4	4	4
T (K)	291(2)	291	291
μ(MoKα), mm^{-1}	1.081	1.024	1.103
Dcalc (mg/m3)	1.418	1.397	1.411
Crystal size (mm)	0.34x0.14x0.06	0.08x0.26x0.34	0.08x0.10x0.26
θmax (°)	30.94	25.0	25.0
Data collected	16952	19941	19022
Unique reflections/Rint	0.0576	0.049	0.060
Parameters	573	308	271
Goodness-of-fit on F2	0.950	0.98	0.96
*R*1	0.0654	0.0475	0.0498
*wR*2	0.1630	0.1077	0.1053
Residual density (e/Å3)	0.496/-0.450	0.45/-0.44	0.47/-0.25

TABLE 2 : Bond distances (Å) and angles (degrees) of the synthesized compounds.

Compound I							
Cu1-N1	2.0473	Cu1-O1	1.9512	O3-Cu1-N1	103.84	O3-Cu1-O1	94.82
Cu1-N2	2.0348	Cu1-O3	2.2282	O3-Cu1-N2	96.09	N1-Cu1-N3	151.65
Cu1-N3	2.0544			O3-Cu1-N3	104.15	N2-Cu1-O2	169.05
Compound II							
Cu-N1	2.054(3)	Cu-O1	1.958(3)	O3-Cu-N1	109.43(12)	O1-Cu-O3	94.05(12)
Cu-N2	2.034(5)	Cu-O3	2.205(3)	O3-Cu-N2	97.49(14)	N1-Cu-N3	150.00(12)
Cu-N3	2.062(3)			O3-Cu-N3	100.19(12)	N2-Cu-O1	168.43(14)
Compound III							
Cu1-N1	2.046(5)	Cu1-O1	1.950(4)	O3-Cu1-N1	111.3(2)	O1-Cu1-O3	94.82(17)
Cu1-N2	2.030(5)	Cu1-O3	2.203(5)	O3-Cu1-N2	94.8(2)	N1-Cu1-N3	146.4(2)
Cu1-N3	2.069(6)			O3-Cu1-N3	101.8(2)	N2-Cu1-O1	170.4(2)

TABLE 3 : Structural geometric parameters of the synthesized compounds.

Compound	Center	τ^a	Dihedral^b angleb	Distance^c	Geometry	Symmetry
I	Cu1	29.0	89	0.3419	SP	C_4v
II	Cu	30.7	87	0.3621	SP	C_4v
III	Cu1	40.0	86	0.3755	SP	C_4v

[a]τ (%) The ideal value for Square pyramid (C_4v symmetry) is 0 and for a trigonal bipyramid (D_3h symmetry) is 100; [b]Dihedral angle between the equatorial plane around Cu (II) and the apex of the pyramid (°); [c]Perpendicular distance between the basal plane and Cu (II) (Å).

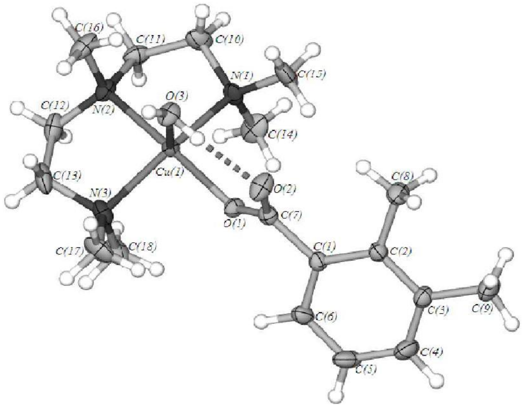

Figure 1 : Molecular geometry of the cation of compound I.

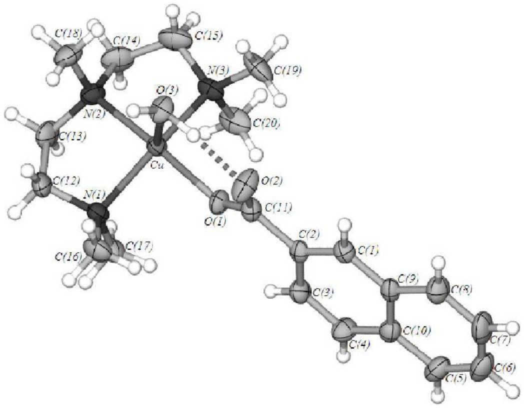

Figure 2 : Molecular geometry of the cation of compound II.

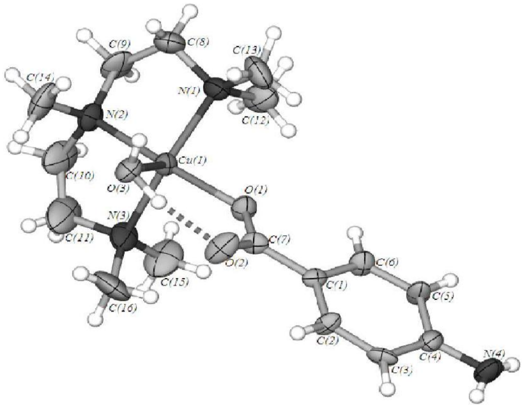

Figure 3 : Molecular geometry of the cation of compound III.

Supramolecular description of compound III

The crystal structures of compounds I and II did not show any intermolecular interaction. However, for compound III, additionally to the intramolecular interaction where six-membered rings are formed; there are intermolecular hydrogen bonds between the amine groups of 4-aminobenzoate, and the uncoordinated O atoms of carbonyl ligands. In addition, hydrogen bonds are observed between O of the perchlorate ion, which acts as a bridge between the O of the aquo ligand, and the N of 4-aminobenzoate ligand. Both interactions via hydrogen bonds may generate a double strand 1-D polymer, see Figure 4. For reference, the main parameters of the hydrogen bonds are shown in TABLE 4

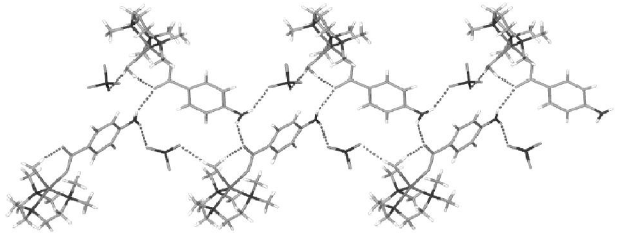

Figure 4 : 1D chain via hydrogen bonds of compound III.

Similar to the synthesized structures, most of the reported structures of Cu(II) with pmdt and carboxilate ligands[20], do not exhibit supramolecular arrangements. Through X-ray diffraction analysis, the intramolecular interactions via hydrogen bonds is only observed in these structures. However, only the structure III exhibit a self-assembled structure showing the formation of a PMC structure.

DISCUSSION

According to the τ parameter, the compounds synthesized here have a percentage between 29 and 40%, which corresponds to a square pyramid geometry, see TABLE 2. It is observed that τ values are higher than those found in complexes where other ligads are used instead pmdt[12]. I can be observed that the structures reported here and similar reported structures exhibit intramolecular interaction between the aqueous binder in apical position and the second uncoordinated O of the carboxylate ligand in the basal position. The diagram shown in Figure 5 represents a systematic construction of the synthesized compounds.

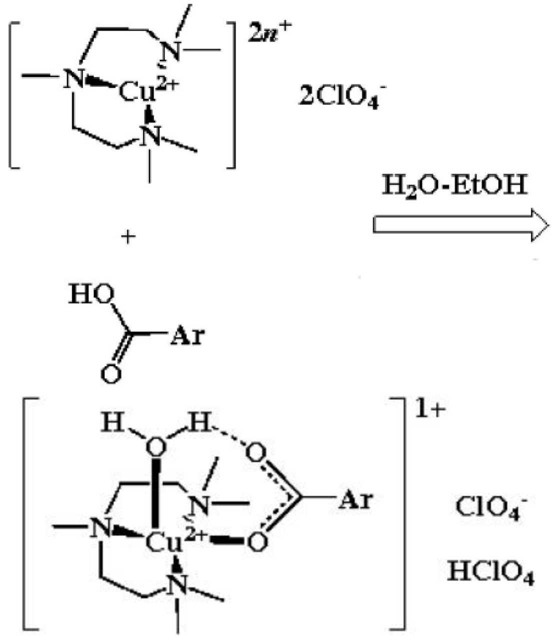

Figure 5 : Schematic construction of coordination compounds with pmdt.

The intramolecuar interaction exhibited by the compounds is favored by the steric hindrance due to the methyl groups of the pmdt ligand. I was observed that pmdt presents a greater steric hindrance than diethylentriamine when it is coordinated to Cu(II)[12]. Different factors such as the coordination of the aquo ligand in apical position, and the intramolecular interaction avoid the formation of 1-D coordination polymers. However, the compound III, where the tecton present an additional group such as the amine in the 4-aminobenzoate ligand, the formation of a PMC. The 1-D chain is constructed by self-complementary hydrogen bonds between tectons, see Figure 4.

CONCLUSIONS

At molecular level, Cu (II) complexes with pmdt and carboxylic acids exhibited a slightly distorted regular pyramid with a square base. The use of a tridentate ligand such as pmdt prevents the formation of supramolecular structures, it is because the steric hindrance that is promoted by the pmdt ligand. However, when the 4-aminobenzoate ligand was used; intermolecular hydrogen bonds between its amine group and the uncoordinated O atoms of carbonyl ligands are formed. In addition, the formation of other hydrogen bonds act as bridges. These interactions generated a double strand 1-D polymer in compound III.

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