Metal-(phenylthio)acetic Acid Interactions. Part 2*: The Crystal Structure of Tetra-μ-[(phenylthio)acetato]bis[pyridinecopper(II)]

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Introduction

As an extension of the work on the mode of interaction of metal ions and phenoxyalkanoic acids, the metal complexes of the analogous (phenylthio)-acetic acid, [PTAH] are now being examined by single crystal X-ray diffractometry. The first part of this series [1] reported the crystal structures of the zinc and cadmium complexes, both metals having octahedral stereochemistry. *Trans*-diaquabis[(phenylthio)acetato]zinc(II) is monomeric with symmetric bidentate carboxylate ligands involved in coordination, in contrast to *catena*-aquabis[(phenylthio)acetato]cadmium(II) which is polymeric with both unidentate bridging and bidentate chelate thioacetate groups (involving carboxylate-O and thioether-S). In the present example, elemental analysis suggested the empirical formula [Cu(PTA)$_2$(py)]. This was found by X-ray analysis to be a tetracarboxylate bridged dimer similar to the pyridine adduct [Cu$_2$(2,4,5-T)$_4$(py)$_2$] [2].

Experimental

Preparation

The title compound, [Cu$_2$(PTA)$_4$(py)$_2$], was prepared by reacting an ethanolic solution of (phenylthio)acetic acid and pyridine with excess copper(II) carbonate, as previously described [3]. Crystals were obtained from the solution as green needles or plates. *Anal.* Found: C, 52.9; H, 4.09; N, 2.99%. Calc. for $C_{42}H_{38}Cu_2N_2O_8S_4$; C, 52.9; H, 4.01; N, 2.94%.

Crystal Data

$C_{42}H_{38}Cu_2N_2O_8S_4$, Mr = 954.1, triclinic, space group $P\bar{1}$ (C_i^1, No. 2), a = 7.139(1), b = 10.370(1), c = 15.386(1), α = 89.91(1), β = 107.95(1), γ = 103.63(1)°, V = 1050.0(3) Å^3, Z = 1, D_c = 1.509 g cm^{-3}, $F(000)$ = 490, μ(Mo-Kα) = 13.0 cm^{-1}.

Collection of X-ray Data and Structure Solution

Data were collected on a Nicolet R3m four-circle diffractometer using graphite monochromatized Mo-Kα radiation (λ = 0.71069 Å). 3043 unique reflections were collected up to $2\theta_{max}$ = 48°. Specimen size was 0.32 × 0.32 × 0.08 mm. The intensity data were processed with the learnt profile fitting procedure of Diamond [4], and 2636 observed reflections with $I > 2.5\sigma(I)$ were used in structure analysis. The structure was not immediately solved by the centrosymmetric direct methods procedure of SHELX-76 [5] but the origin of the cell was relocated to place the dimeric species about an inversion centre in the $P\bar{1}$ cell, after which the copper atom allowed the location of the remaining non-hydrogens *via* a weighted difference-Fourier synthesis. Blocked-matrix least-squares refinement with isotropic thermal parameters for all non-hydrogen atoms except Cu, Cl, S and the coordinated atoms [N(1)p, O(10) and O(11)] which were refined anisotropically, reduced R [$=\Sigma|Fo - Fc\|/\Sigma|Fo|$] to 0.055 and Rw [$=\Sigma w(\|Fo - Fc\|^2/\Sigma|Fo|^2)^{1/2}$] to 0.059. A value of $w = 5.19/[\sigma^2(Fo) + 0.00022(Fo)^2]$ was used. Hydrogens were located in a difference-Fourier synthesis and included in the refinement at fixed positions with their istropic U values set invariant at 0.05 Å^{-3}. Some disorder was apparent in carbon atoms of the phenyl ring of ligand B [C(4), C(5), C(6)], where isotropic thermal parameters [U] were 0.114, 0.163 and 0.123 Å^2 respectively. The data were corrected for absorption, but not extinction. All computations were carried out on the DEC-10 computer at the Queensland Institute of Technology using the SHELX-76 program set. Final atomic positional parameters are listed in Table I while bond distances and angles are given in Tables II and III. Lists of anisotropic thermal parameters and observed and calculated structure factors are available from the authors.

Discussion

The complex [Cu$_2$(PTA)$_2$(py)$_2$] consists of centrosymmetric tetracarboxylate bridged dimers of

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*Part 1. The crystal structures of the Zn^{II} and Cd^{II} analogues [1].

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TABLE I. Atomic Coordinates ($\times 10^4$) and Isotropic/Equivalent Isotropic Thermal Parameters (Å^2, $\times 10^3$). [$U_{eq}{}^* = (U_{11} \cdot U_{22} \cdot U_{33})^{1/3}$].

	x/a	*y/b*	*z/c*	$U_{eq}{}^*$/iso		*x/a*	*y/b*	*z/c*	$U_{eq}{}^*$/iso
Cu	1479(1)	1115(1)	96(1)	30.1(4)*	H(2)p	3530	3668	1438	50
N(1)p	4132(7)	2755(4)	430(3)	33(3)*	H(3)p	6341	5607	1757	50
C(2)p	4471(9)	3771(6)	1043(4)	42(1)	H(4)p	8935	5577	1035	50
C(3)p	6207(10)	4791(6)	1294(4)	47(2)	H(5)p	8518	3673	15	50
C(4)p	7677(10)	4796(6)	892(4)	48(2)	H(6)p	5114	1964	−418	50
C(5)p	7368(10)	3758(6)	259(4)	48(2)					
C(6)p	5603(10)	2762(6)	59(4)	43(1)					
		ligand A					*ligand B*		
C(1)	−1487(10)	3543(5)	−2885(4)	43(1)		1482(10)	1330(6)	3574(5)	48(2)
C(2)	−330(10)	2679(7)	−2967(4)	50(2)		2929(12)	1808(7)	3171(5)	62(2)
C(3)	1036(12)	3025(7)	−3461(5)	62(2)		4981(14)	2292(9)	3672(6)	78(2)
C(4)	1259(12)	4218(8)	−3835(6)	71(2)		5683(18)	2301(11)	4604(8)	114(3)
C(5)	162(13)	5060(8)	−3753(6)	69(2)		4191(23)	1963(14)	5052(10)	163(5)
C(6)	−1266(11)	4751(7)	3289(5)	59(2)		1991(19)	1389(11)	4523(8)	123(4)
S(7)	−3235(3)	3261(2)	−2264(1)	52(1)*		−1121(2)	663(2)	3020(1)	50(1)*
C(8)	−3705(10)	1520(6)	−2087(4)	42(1)		−1699(10)	1494(6)	1980(4)	42(1)
C(9)	−2230(9)	1051(5)	−1270(4)	38(1)		−1125(9)	947(6)	1219(4)	38(1)
O(10)	−509(6)	1793(4)	−892(3)	39(2)*		300(6)	1677(4)	988(3)	42(2)*
O(11)	2935(6)	79(4)	1056(3)	40(2)*		2101(6)	203(4)	−867(3)	46(2)*
H2	−523	1760	−2718	50		2402	2105	2458	50
H3	1352	2248	−3604	50		6184	2802	3345	50
H4	2463	4340	−4179	50		[a]			
H5	331	6075	−3905	50		4392	1007	4888	50
H6	−2123	5277	−3146	50		805	1779	4814	50
H(81)	−5179	1334	−2043	50		−1104	2413	2061	50
H(82)	−3725	1039	−2594	50		−3070	1405	1761	50

*Anisotropic. [a]Not located.

TABLE II. Bond Distances (Å).

a. *Coordination sphere*

Cu–O(10)A	1.989(4)	Cu–O(11)B′	1.973(5)
Cu–O(11)A′	1.998(4)	Cu–N(1)p	2.151(4)
Cu–O(10)B	1.969(5)		

b. *Intraligand*

N(1)p–C(2)p	1.342(8)	C(4)p–C(5)p	1.384(10)
C(2)p–C(3)p	1.376(8)	C(5)p–C(6)p	1.378(8)
C(3)p–C(4)p	1.372(11)	C(6)p–N(1)p	1.340(10)

	ligand A	*ligand B*		*ligand A*	*ligand B*
C(1)–C(2)	1.384(11)	1.360(12)	C(1)–S(7)	1.766(8)	1.754(6)
C(2)–C(3)	1.396(12)	1.397(11)	S(7)–C(8)	1.793(7)	1.797(7)
C(3)–C(4)	1.360(11)	1.365(15)	C(8)–C(9)	1.533(8)	1.506(10)
C(4)–C(5)	1.332(14)	1.417(23)	C(9)–O(10)	1.247(6)	1.262(8)
C(5)–C(6)	1.395(13)	1.502(18)	C(9)–O(11)	1.248(6)	1.257(7)
C(6)–C(1)	1.395(10)	1.389(12)			

TABLE III. Bond Angles (degrees).

a. *Coordination sphere*

N(1)p–Cu–O(10)A	102.3(2)	O(10)A–Cu–O(11)A′	166.9(1)
N(1)p–Cu–O(10)B	96.6(2)	O(10)A–Cu–O(11)B′	88.1(2)
N(1)p–Cu–O(11)A′	90.8(2)	O(10)B–Cu–O(11)A′	88.4(2)
N(1)p–Cu–O(11)B′	96.7(2)	O(10)B–Cu–O(11)B′	166.7(2)
O(10)A–Cu–O(10)B	89.1(2)	O(11)A′–Cu–O(11)B′	91.4(2)
C(2)p–N(1)p–Cu	123.2(4)	C(6)p–N(1)p–Cu	120.1(4)

b. *Intraligand*

C(2)p–N(1)p–C(6)p	116.5(5)	C(3)p–C(4)p–C(5)p	118.5(6)
N(1)p–C(2)p–C(3)p	123.7(7)	C(4)p–C(5)p–C(6)p	118.8(7)
C(2)p–C(3)p–C(4)p	119.0(6)	C(5)p–C(6)p–N(1)p	123.4(6)

	ligand A	*ligand B*		*ligand A*	*ligand B*
C(2)–C(1)–C(6)	119.8(7)	120.2(5)	C(5)–C(6)–C(1)	118.3(8)	116.3(9)
C(2)–C(1)–S(7)	124.7(5)	126.9(5)	C(1)–S(7)–C(8)	105.6(3)	105.1(3)
C(6)–C(1)–S(7)	115.5(6)	112.8(5)	S(7)–C(8)–C(9)	118.6(4)	114.7(5)
C(1)–C(2)–C(3)	119.4(6)	122.7(7)	C(8)–C(9)–O(10)	119.4(5)	117.5(5)
C(2)–C(3)–C(4)	119.9(6)	122.2(7)	C(8)–C(9)–O(11)	113.8(5)	117.3(5)
C(3)–C(4)–C(5)	121.0(9)	116.4(8)	O(10)–C(9)–O(11)	126.8(4)	125.2(5)
C(4)–C(5)–C(6)	121.5(8)	121.3(12)			

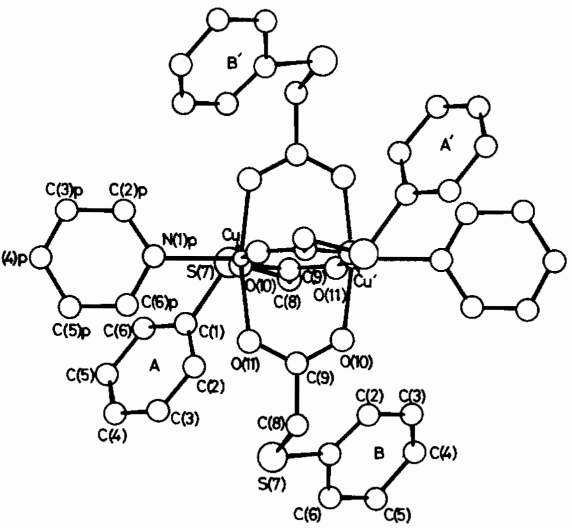

Fig. 1. Complex stereochemistry and atom naming scheme for $[Cu_2(PTA)_2(py)_2]$. The primed section of the molecule is generated by an inversion operation.

the copper(II) acetate monohydrate [6] and copper(II) acetate monopyridine [7. 8] type (Fig. 1). The four equatorial Cu–O (carboxylate) distance [1.969(5)–1.998(4) Å: 1.982(4) Å mean] are similar and vary little among the entire series of this type of copper(II) dimer [mean, 1.96 Å [2, 9]. The axial Cu–N (pyridine) distance [2.151(4) Å] is normal for pyridine adducts in the series [2.13–2.19 Å]. The variation in this distance with change in the nature of the axial group has been shown to be related to the Cu---Cu distance and to the Cu-to-basal plane distance, *i.e.* the distance which the Cu lies above the equatorial O_4 plane. This Cu–Cu distance varies markedly among the examples [2.563 Å $[Cu_2(C_2H_5\cdot COO)_4(dioxane)]$ [10]] to 2.886 Å $[Cu_2(F_3C\cdot COO)_4(quinoline)_2]$ [11]], compared with 2.685(1) Å for the present example (in the phenoxy/pyridine dimer $[Cu_2(2,4,5\text{-}T)_4(py)_2]$ the Cu–Cu distance is 2.716(7) Å). No correlation is found between this distance and the base strength of the axial group or the magnetic moment for the complex but the latter two are related [9].

To date, apart from the 2,4,5-T/pyridine dimer [2], the present complex is the only other known example among the phenyloxy- or phenylthiocarboxylate/pyridine dimers which is discretely dimeric. In contrast, the two complexes, $[Cu(phenoxyacetato)_2(py)_2(H_2O)]$ and $[Cu(MCPA)_2(py)_2(H_2O)]$, [13] are monomeric five-coordinate with the axial group of the square pyrimidal coordination sphere occupied by a water molecule lying on a molecular two-fold rotational axis. The steric influence of the larger acid residues in both $[Cu_2(PTA)_4(py)_2]$ and $[Cu_2(2,4,5\text{-}T)_4(py)_2]$ may be instrumental in forcing the pyridine molecule into the axial position rather than the equatorial, with subsequent dimer formation. The conformation of the PTA ligands are considerably

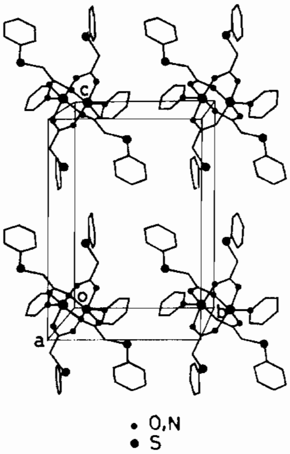

Fig. 2. Packing of the complex in the unit cell viewed perpendicular to *bc*.

changed compared to the free acid [1] [torsion angle C(1)–S(7)–C(8)–C(9), +84°(A); +80°(B) *cf.* +117° for PTAH]. Also, the S(7)- - -O(carboxyl) interactive distance is considerably different for the two ligands [3.068(A), 3.249 Å(B)] and different from the value for PTAH (2.847 Å). This parameter is also variable among the other complexes of PTA [Zn (3.029 Å) and Cd (3.009, 3.060 Å) [1]; Ba (2.79 Å) and K (2.84, 2.88 Å) [14]], in contrast to the relatively invariable O(7)- - -O(carboxyl) distance in the phenoxyalkanoic acids and their complexes. The packing of the dimers in the unit cell (Fig. 2) follows a trend common among the series of non-association between the complex dimers. No intermolecular contacts less than 3 Å are found involving oxygens.

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