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Metal–(Phenylthio)acetic Acid Interactions.
Part 1. The Crystal Structures of (Phenylthio)acetic Acid, Diaquabis[(phenylthio)acetato]zinc(II), and *Catena*{aquabis[(phenylthio)acetato] cadmium(II)}

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Crystal structures of (phenylthio)acetic acid (PTAH) (1), and the zinc(II) and cadmium(II) complexes of PTAH have been determined by X-ray diffraction. The acid, PTAH, is monoclinic, space group $P2_1/n$, *with* $Z = 4$ *in a cell of dimensions* a = 7.666(1), b = 5.638(1), c = 18.939(2) Å, β = 99.33(1)°. *The molecules are planar and exist as centrosymmetric hydrogen bonded cyclic dimers. The thioacetic side chain has synplanar–synplanar conformation. The Zn(II) complex,* $[Zn(PTA)_2(H_2O)_2]$, *(2), is monoclinic, space group* $C2/c$, *with* $Z = 4$, *in a cell of dimensions,* a = 32.048(11), b = 5.314(2), c = 10.725(3) Å, β = 101.20(2)°. *(2) is monomeric with a distorted octahedral* MO_6 *coordination involving four oxygens from two symmetrical bidentate PTA carboxyl groups [Zn–O, 2.176(4), 2.204(3) Å] and two form* cis-*related waters [Zn–O, 2.002(4)].* $[Cd(PTA)_2(H_2O)]_n$ *(3) is orthorhombic, space group* $Pca2_1$, $Z = 4$, *with* a = 33.826(8), b = 5.119(1), c = 9.872(3) Å, *having an octahedral* MO_5S *coordination sphere consisting of one water [Cd–O, 2.294(10) Å], an oxygen and a sulphur from one PTA ligand [Cd–O, 2.335(10) Å, Cd–S, 2.738(5) Å] and an oxygen from the second PTA ligand [Cd–O, 2.276(10) Å]. The second carboxyl oxygen from each PTA ligand completes the fifth and sixth coordination sites [Cd–O, 2.263(12), 2.254(10) Å] and bridges adjacent complex centres giving a polymeric structure.*

Introduction

Metal(II)–phenoxyalkanoic acid complexes have interesting and sometimes unusual stereochemistry and complexing modes (Part 1, [1] to Part 11 [2]). A number of the acids are commercial herbicides [2,4-dichlorophenoxyacetic acid (2,4-D); 2,4,5-trichlorophenoxyacetic acid (2,4,5-T); 4-chloro-2-methylphenoxyacetic acid (MCPA); and their 2-propionic acid analogues, 2,4-DP, 2,4,5-TP, and MCPP], and as such provide readily available ligands which differ not only in the position and type of the phenyl ring substituent but also in the length of the oxoalkanoic acid side-chain. The study has now been extended to determine the effect of replacing the ether oxygen by sulphur or nitrogen. So far in work with phenoxy complexes, it is uncommon (except for the copper(II) series) to have this ether-O coordinated to the metal. In the case of copper(II) coordination, the tetragonal distortion inherent in the metal coordination sphere probably allows accommodation of the slightly longer O(ether)···O(carboxyl) 'bite' distance of the chelate ring. An analogous bis-(O,S) chelate complex of copper(II) [diaquabis(isopropylthioacetato)copper(II) [3]] supports the contention that thioether-S should also enter into coordination for phenylthioacetates of metals having a larger radius. The ligand selected to initiate this project was (phenylthio)acetic acid [PTAH, (thiophenoxy)-acetic acid]. This report deals with the crystal structure of (phenylthio)acetic acid and the zinc(II) and cadmium(II) complexes of this acid, so as to

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TABLE I. Comparative Crystal Data for PTAH, (*1*), $[Zn(PTA)_2(H_2O)_2]$, (*2*) and $[Cd(PTA)_2(H_2O)]_n$, (*3*).

	(*1*)	(*2*)	(*3*)
Formula	$C_8H_8O_2S$	$C_{16}H_{18}O_6S_2Zn$	$C_{16}H_{16}CdO_5S_2$
Mr	168.2	435.8	464.8
a (Å)	7.666(1)	32.048(11)	33.826(8)
b	5.638(1)	5.314(2)	5.119(1)
c	18.939(2)	10.725(3)	9.872(3)
β (°)	99.33(1)	101.20(2)	
V (Å^3)	807.7(2)	1791.7(9)	1709.4(8)
Z	4	4	4
ρ_c (g cm^{-3})	1.383	1.616	1.806
ρ_f (g cm^{-3})	1.38	1.62	1.87
Space Group	$P2_1/n(C_{2h}^5$, No. 14)	$C2/c(C_{2h}^6$, No. 15)	$Pca2_1(C_{2v}^5$, No. 29)
μ (cm^{-1})	3.29	16.54	15.28
F(000)	352	896	928
Data Collection			
a. diffractometer	Nicolet R3m	Nicolet R3m	Nicolet R3m
b. radiation	Mo Kα	Mo Kα	Mo Kα
c. $2\theta_{max}$	50	52	46
d. unique reflections measured	1394	1621	1267
e. crystal size (mm)	0.40 × 0.36 × 0.18	0.32 × 0.30 × 0.06	0.20 × 0.16 × 0.03
Structure Solution, Refinement			
a. method used	Direct methods [6]	Direct methods [6]	Patterson
b. R	0.038	0.049	0.042
c. R_w	0.042	0.053	0.040
d. w^a A	0.75	1.71	1.33
B	2.5×10^{-4}	6.7×10^{-4}	4.5×10^{-4}
e. data used	1048	1205	951
f. discrimination	I > 2.5σ(I)	I > 2.5σ(I)	I > 2.5σ(I)

[a] $w = A/[\sigma^2(F_o) + B(F_o^2)]$.

provide a comparison of the conformational features of both the uncomplexed and complexed ligand.

Experimental

Preparation

Crystals of (phenylthio)acetic acid, PTAH, (*1*), (m.p. 64 °C; lit. 63.5 °C [4]) suitable for X-ray analysis were obtained by recrystallisation of the commercial acid (Tokyo Kasei) from ethanol.

Complexes (*2*) and (*3*) were prepared by reacting PTAH in aqueous ethanol with a suspension of excess metal carbonate (in aqueous ethanol), and digesting for one hour at 70–90 °C. The excess carbonate was removed by filtration. The filtrate, on standing at room temperature, yielded crystals which were re-crystallised from absolute ethanol as flat needles or plates. Analysis: for (*2*), found C, 44.6; H, 4.23; S, 14.2%. Calc. for $C_{16}H_{18}O_6S_2Zn$: C, 44.1; H, 4.16; S, 14.7%. For (*3*), found: C, 41.4; H, 3.54%. Calc. for $C_{16}H_{16}CdO_5S_2$: C, 41.30; H, 3.44%.

Crystal Data, X-ray Data Collection and Structure Refinement

Table I contains details of unit cell parameters, data acquisition and structure solution for compounds (*1*), (*2*) and (*3*). Data were processed using the profile fitting procedure [5]. Structures were solved and refined using the SHELX-76 program set [6]. In the case of (*1*), the structure was refined by full matrix least squares, and for (*2*) and (*3*) by blocked matrix. With (*2*), atoms C(2) to C(6) of the two phenyl rings (A and B) were found to be

TABLE II. Atomic Coordinates ($\times 10^4$) for Phenylthioacetic Acid, (PTAH) (*1*), [Zn(PTA)$_2$(H$_2$O)$_2$], (*2*) and [Cd(PTA)$_2$(H$_2$O)]$_n$, (*3*). For (*2*) the Primed Carbons Represent the Atoms of the Rotationally Disordered Phenyl Ring. (Ring B). [Hydrogens $\times$ 10^3].

Atom	PTAH, (*1*)					[Zn(PTA)$_2$(H$_2$O)$_2$], (*2*)			
	x/*a*	y/*b*	z/*c*	x/*a*	y/*b*	z/*c*	x/*a*	y/*b*	z/*b*
Zn				0	6832(1)	2500		(ring B)	
Ow				–411(1)	4461(7)	3069(3)			
C(1)	2569(4)	2788(5)	8665(1)	1509(2)	11554(11)	4140(5)			
C(2), C(2)′	1295(5)	1181(6)	8767(2)	1517(3)	9182(22)	3492(10)	1529(4)	12973(22)	2945(10)
C(3), C(3)′	–371(4)	1277(7)	8368(2)	1862(4)	8225(25)	3086(13)	1843(3)	11977(27)	2283(14)
C(4), C(4)′	–776(4)	3012(6)	7853(2)	2233(4)	9152(27)	3465(13)	2070(4)	9924(27)	2746(15)
C(5), C(5)′	468(4)	4625(6)	7754(2)	2303(4)	11314(24)	4179(11)	2015(5)	8665(26)	3864(14)
C(6), C(6)′	2153(4)	4553(6)	8150(2)	1961(4)	12371(22)	4614(11)	1703(3)	9740(22)	4497(11)
S(7)	4668(1)	2377(1)	9197(4)	1114(0)	13030(3)	4793(1)			
C(8)	5841(4)	5022(7)	9038(2)	816(2)	10454(11)	5252(5)			
C(9)	7636(4)	4995(6)	9486(1)	509(1)	9175(10)	4211(4)			
O(10)	8137(3)	3436(4)	9915(1)	469(1)	9782(7)	3073(3)			
O(11)	8589(3)	6815(5)	9363(1)	281(1)	7451(7)	4521(3)			
H(2)	153(4)	–4(6)	913(2)						
H(3)	–121(4)	20(5)	845(1)						
H(4)	–198(4)	305(5)	762(1)						
H(5)	25(5)	580(7)	740(2)						
H(6)	293(5)	565(6)	870(2)						
H(81)	526(4)	627(6)	916(1)						
H(82)	606(5)	514(6)	853(2)						
H(11)	966(5)	671(7)	959(2)						

	[Cd(PTA)$_2$(H$_2$O)]$_n$, (*3*)					
Atom	x/*a*	y/*b*	z/*c*	x/*c*	y/*b*	z/*c*
Cd	332(0)	2308(1)	0			
Ow	–85(3)	–701(17)	960(11)			
		ligand A			ligand B	
C(1)	1498(5)	–928(29)	–3644(15)	1283(5)	2984(29)	1693(16)
C(2)	1657(7)	935(36)	–4444(22)	1507(5)	2404(35)	601(16)
C(3)	2049(8)	1778(45)	–4113(33)	1845(6)	3764(42)	279(18)
C(4)	2263(6)	709(46)	–3083(27)	1952(6)	5729(38)	1115(29)
C(5)	2088(7)	–926(50)	–2319(23)	1748(7)	6390(44)	2246(22)
C(6)	1705(7)	–1944(37)	–2584(20)	1399(4)	5050(29)	2493(16)
S(7)	1023(1)	–2073(9)	–4171(5)	826(1)	989(8)	1982(5)
C(8)	833(5)	–3980(30)	–2752(15)	599(4)	2420(26)	3374(16)
C(9)	667(4)	–2489(28)	–1544(17)	302(4)	4636(25)	3051(16)
O(10)	595(4)	–48(19)	–1718(13)	156(3)	4724(18)	1913(11)
O(11)	606(3)	–3748(19)	–508(11)	224(3)	6101(21)	4052(10)
H(2)	142	239	–500	142	122	1
H(3)	218	260	–502	200	201	–30
H(4)	*			220	696	115
H(5)	218	–153	–123	184	800	305
H(6)	161	–369	–205	122	552	333
H(81)	64	–371	–305	80	291	389
H(82)	104	–474	–266	41	71	351
Hw(1)	–1	713	116			
Hw(2)	*					

*not located.

TABLE III. Bond Distances (A) andAngles (degrees) for (*2*) and (*3*) Compared with the Uncomplexed Acid (*1*).

a. Distances

Coordination Sphere

(*2*)		(*3*)	
Zn–O(10)	2.176(4)	Cd–O(10A)	2.263(12)
Zn–O(11)	2.204(3)	Cd–O(10B)	2.335(10)
Zn–Ow	2.002(4)	Cd–O(11A)′	2.276(10)
		Cd–O(11B)″	2.254(10)
		Cd–S(7B)	2.738(5)
		Cd–Ow	2.294(10)

Intraligand

	(*2*)		(*3*)		(*1*)
	ring A	ring B*	ligand A	ligand B	
C(1)–C(2)	1.44(1)	1.50(2)	1.35(2)	1.35(2)	1.369(4)
C(1)–C(6)	1.50(2)	1.17(2)	1.36(2)	1.38(2)	1.394(4)
C(1)–S(7)	1.747(2)		1.79(2)	1.77(2)	1.770(3)
C(2)–C(3)	1.36(2)	1.44(2)	1.43(3)	1.38(3)	1.376(5)
C(3)–C(4)	1.28(2)	1.35(2)	1.36(4)	1.35(3)	1.381(5)
C(4)–C(5)	1.38(2)	1.41(2)	1.27(3)	1.36(3)	1.353(5)
C(5)–C(6)	1.39(2)	1.43(2)	1.42(3)	1.39(3)	1.385(5)
S(7)–C(8)	1.792(2)		1.82(2)	1.79(2)	1.792(4)
C(8)–C(9)	1.500(8)		1.52(2)	1.55(2)	1.495(4)
C(9)–O(10)	1.245(6)		1.28(2)	1.23(2)	1.216(4)
C(9)–O(11)	1.256(6)		1.23(2)	1.27(2)	1.302(4)

b. Angles

Coordination Sphere

(*2*)		(*3*)			
Ow–Zn–Ow′	102.3(1)	Ow–Cd–O(10A)	101.1(4)	O(10B)–Cd–O(11B)″	86.1(4)
Ow–Zn–O(10)′	145.0(1)	Ow–Cd–O(10B)	82.2(4)	O(10B)–Cd–S(7B)	73.7(3)
Ow–Zn–O(11)	87.8(1)	Ow–Cd–O(11A)′	159.5(4)	O(11A)–Cd–O(11B)″	85.8(4)
Ow–Zn–O(11)′	103.1(1)	Ow–Cd–O(11B)″	84.3(4)	O(11A)′–Cd–S(7B)	96.3(3)
O(10)–Zn–O(11)	59.1(1)	Ow–Cd–S(7B)	86.7(3)	O(11B)″–Cd–S(7B)	158.8(3)
O(10)–Zn–O(11)′	107.3(1)	O(10A)–Cd–O(11A)′	98.5(4)	Cd–O(10A)–C(9A)	120(1)
O(10)–Zn–O(10)′	87.8(1)	O(10A)–Cd–O(10B)	171.4(4)	Cd–O(11A)′–C(9A)′	136(1)
O(11)–Zn–O(11)′	162.8(1)	O(10A)–Cd–O(11B)″	102.1(4)	Cd–O(10B)–C(9B)	128(1)
Zn–O(10)–C(9)	91.4(1)	O(10A)–Cd–S(7B)	98.5(3)	Cd–O(11B)″–C(9B)″	135(1)
Zn–O(11)–C(9)	89.8(1)	O(10B)–Cd–O(11A)′	79.2(4)		

−x, −y, z

O′ x, 1 + y, z

O″ −x, 1 − y, −½ + z

Intraligand

	(*2*)		(*3*)		(*1*)
	ring A	ring B*	ligand A	ligand B	
C(2)–C(1)–C(6)	108(1)	126(1)	121(2)	118(1)	118.9(2)
C(2)–C(1)–S(7)	131.9(6)	105.7(6)	115(1)	117(1)	115.9(1)
C(6)–C(1)–S(7)	117.4(6)	128.2(6)	124(1)	125(1)	125.1(1)
C(1)–C(2)–C(3)	125(1)	113(1)	117(2)	123(2)	121.1(2)
C(2)–C(3)–C(4)	121(1)	120(1)	123(2)	117(2)	119.9(2)
C(3)–C(4)–C(5)	123(1)	123(1)	117(2)	123(2)	119.4(2)
C(4)–C(5)–C(6)	118(1)	115(1)	124(2)	117(2)	121.4(2)
C(5)–C(6)–C(1)	123(1)	123(1)	118(2)	121(2)	119.2(2)

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*disordered ring.

(continued on facing page)

TABLE III. *(continued)*

	ring A	ring B*	ligand A	ligand B	
C(1)–S(7)–C(8)	103.5(3)		106(2)	107(1)	103.3(2)
S(7)–C(8)–C(9)	116.7(4)		118(2)	118(1)	109.7(2)
C(8)–C(9)–O(10)	122.7(5)		117(1)	118(2)	123.3(1)
C(8)–C(9)–O(11)	117.7(4)		117(1)	114(2)	112.4(1)
O(10)–C(9)–O(11)	119.6(4)		126(1)	127(1)	124.2(1)

*disordered ring.

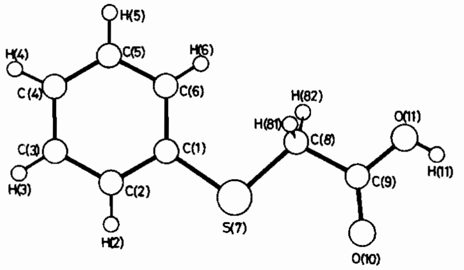

Fig. 1a. Molecular conformation and atom numbering scheme for (phenylthio)acetic acid (PTAH) (*1*).

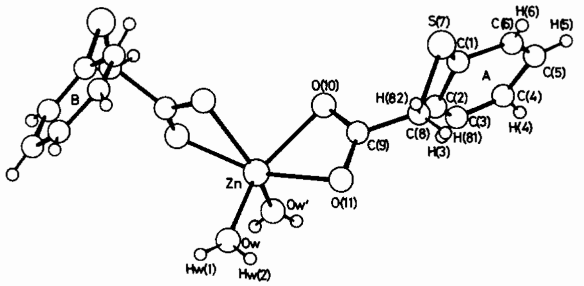

Fig. 1b. [Zn(PTA)$_2$(H$_2$O)$_2$] (*2*).

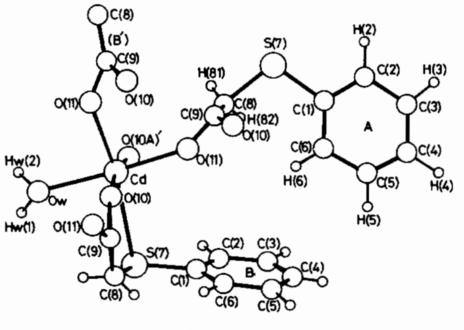

Fig. 1c. [Cd(PTA)$_2$(H$_2$O)]$_n$ (*3*).

rotationally disordered in the centrosymmetric space group C2/c, while those of the remainder of the molecule had the symmetry required two-fold rotation. The phenyl carbons were located in the space group Cc after which they were refined as disordered groups with half occupancy in C2/c. For (*2*) the atoms of the rotationally disordered rings were refined isotropically while the remaining atoms were refined anisotropically. Hydrogens were located from difference-Fourier syntheses and in (*2*) and (*3*) were included in the refinement at fixed positions with their isotropic U's set invariant at 0.05 Å^2. For (*1*), both positional and thermal parameters were allowed to refine. Residuals R and Rw are defined as:

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

and

$$Rw = (\Sigma w \| F_o | - | F_c \|^2 / \Sigma w | F_o |^2)^{1/2}$$

Data for (*3*) only were corrected for absorption. Neutral atom scattering factors were used [7], the metal and sulphur being corrected for anomalous dispersion [7]. Final atomic parameters are listed in Table II, while lists of anisotropic thermal parameters and observed and calculated structure factors are available from the authors. Bond distances and angles are given in Table III.

Discussion

(Phenylthio)acetic acid (*1*) (Fig. 1a) is essentially planar (the preferred conformation of the unsubstituted and monosubstituted phenoxyacetic acids [16]) and exists in the solid state as the usual centrosymmetric hydrogen bonded cyclic dimers [O–H··· O, 2.660(3) Å] known for the phenoxyacetic acids [15] (Fig. 2a). The conformation of the thioacetic acid side-chain is also synplanar-synplanar (as for the phenoxy acids), placing the 'carbonyl' oxygen 2.847(3) Å from the sulphur atom.

The zinc and cadmium complexes of (phenylthio)acetic acid [Zn(PTA)$_2$(H$_2$O)$_2$], (*2*) and [Cd(PTA)$_2$(H$_2$O)]$_n$ (*3*) have few common features beyond the distorted six coordination about the central metal atom. Complex (*2*) has an extremely distorted MO$_6$ octahedral stereochemistry consisting of two *cis*-related waters [Zn–O, 2.002(4) Å] and four oxygens

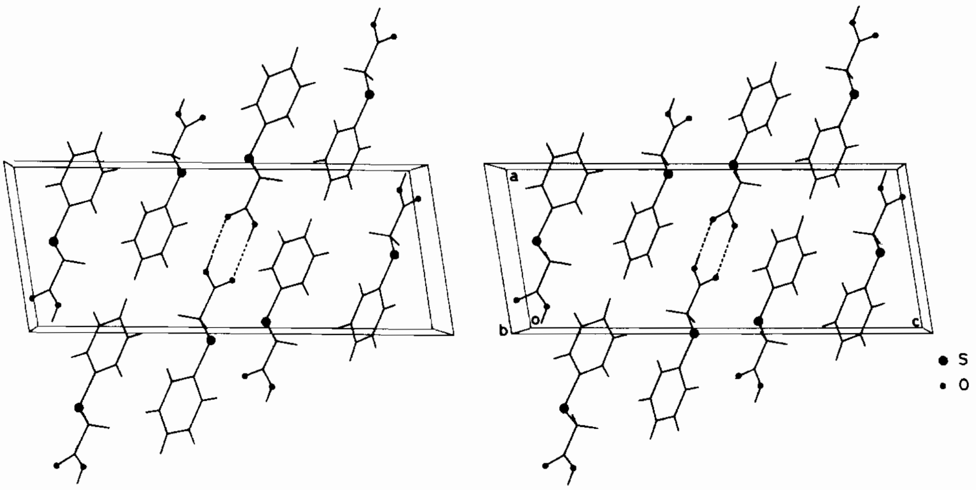

Fig. 2a. Stereoview of PTAH down the *b* axis.

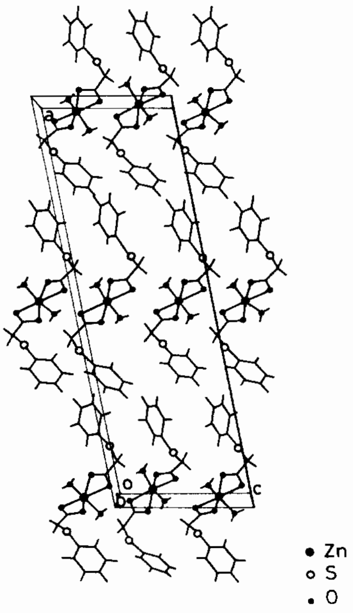

Fig. 2b. Molecular packing for $[Zn(PTA)_2(H_2O)_2]$ in the cell perpendicular to *ac*.

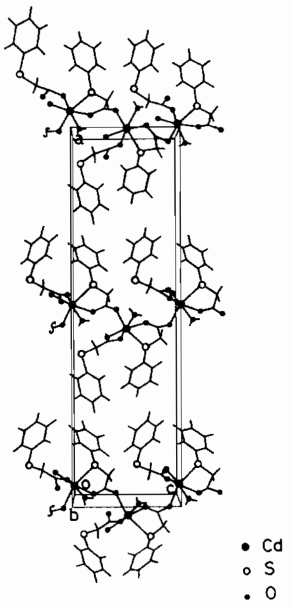

Fig. 2c. Molecular packing for $[Cd(PTA)_2(H_2O)]_n$ in the cell viewed perpendicular to *ac*.

from two bidentate carboxylate groups of the PTA ligands [Zn–O, 2.176(4), 2.204(4) Å] (Fig. 1b). The complex has crystallographic two-fold rotational symmetry relating all atoms except C(2) to C(6) of the phenyl rings. These show disorder arising from rotation about the S(7)–C(1) bonds. The analogous complex, zinc acetate dihydrate [8], devoid of the extension provided by the thiophenyl group in (*2*), has closely similar structural features, including the symmetrical bidentate carboxylate groups [Zn–O, 2.14, 2.17 Å] and the same crystallographic two-fold rotational symmetry required by the C2/c space group. When the analogy is extended to zinc phenoxyacetate dihydrate [1], it is found that asymmetry is generated within the carboxyl–Zn coordination [Zn–O, 2.20, 2.34 Å], although the two-fold rotation symmetry is retained. It is conceivable therefore that in the case of (*2*), the longer C–S bonds [1.747, 1.792(6) Å] compared to the C–O values of 1.366 and 1.415(3) Å in the phenoxyacetate analogue, relieve the steric strain and allow a symmetrical mode of interaction. In the more sterically hindered zinc benzoates, this expected increased asymmetry is also observed, *e.g.* zinc ethoxybenzoate

TABLE IV. Torsion Angles about Side-Chains in the PTA Ligands in *(2)* and *(3)* Compared with PTAH *(1)*. Estimated Standard Deviations are about 1°.

	(1)	*(2)*		*(3)*	
		Ring A	Ring B	Ligand A	Ligand B
C(2)–C(1)–S(7)–C(8)	–170	+29	+136	–167	–174
C(1)–S(7)–C(8)–C(9)	+177	–78		+77	+86
S(7)–C(8)–C(9)–O(10)	–4	+2		+14	+25
C(8)–C(9)–O(10)–M		+178		+178	–10
C(8)–C(9)–O(11)–M		–178			
C(8)–S(7)–Cd–O(10)				+13	

*disordered ring.

monohydrate [9] [2.05, 2.32 Å]; zinc salicylate dihydrate [10] [2.03, 2.53 Å]; zinc *p*-aminobenzoate 1.5 hydrate [11] [1.98, 2.49 Å]. The extreme case is realised in zinc 2,4-dichlorophenoxyacetate trihydrate [12] in which both tetrahedral [Zn(2,4-D)$_2$(H$_2$O)$_2$] and octahedral [Zn(2,4-D)$_2$(H$_2$O)$_4$] species are found, each with unidentate carboxyls.

The non-involvement of S in the coordination is a feature of the structure of *(2)* and in this respect differs from the only other analogous Zn complex, tetraaquazinc(II) thiodiglycollate hydrate [13] in which both O and S are coordinated. However, in this example, the thiodiglycollic acid ligand tends to impose the tridentate (O, S, O) coordination upon the Zn. It might be reasoned again that in *(2)* steric effects are responsible for forcing O rather than S coordination.

With the cadmium analogue *(3)*, greater steric freedom would be expected with the increased ionic radius of the Cd ion relative to Zn. The effect is not completely realised since the coordination found has both a bidentate chelate (S, O) ring and a unidentate carboxylate system. The octahedral MO$_5$S coordination sphere (Fig. 1c) consists of an oxygen and a sulphur from ligand B [Cd–O, 2.335(10); Cd–S, 2.738(5) Å], a single water [Cd–O, 2.294(10) Å] and an oxygen from the carboxyl group of ligand A [Cd–O, 2.276(10) Å]. The second carboxyl oxygen from each of ligands A and B acts as a bridging atom between complex centres, completing the fifth and sixth (*cis*) positions of the coordination spheres, [Cd–O(10)A, 2.263(12) Å; Cd–O(11)B″, 2.254(10) Å]. The result is a two dimensional polymeric structure which extends down the *c* direction of the cell (Fig. 2c). Stability in the packing of the structure is enhanced by a number of intermolecular hydrogen bonding interactions *via* the coordinated water and the carboxyl groups, *e.g.* Ow–O(10)A, 2.89 Å, Ow–O(10)B, 2.65 Å. In contrast *(2)* derives little stability in this manner (Fig. 2b) having only two hydrogen bonding associations [Ow–O(10), 2.762 Å]. However, in many respects the packing of *(2)* and *(3)* in their respective cells is similar, if one overlooks the larger number of intermolecular associations and the polymeric nature of *(3)*. The Cd–S and Cd–O distances in *(3)* are very similar to those for the comparable polymer structure cadmium thiodiacetate hydrate [14] [2.663, 2.274 Å (average) respectively].

The PTA ligand undergoes various conformational changes upon being complexed (Table IV). In the complexed state the S(thioether)···O(carboxyl) distance has increased from 2.847(3) Å in the uncomplexed ligand to 3.029 Å in *(2)* and 3.006, 3.060 Å in *(3)*, although the conformation varies. This is different from the phenoxy series where coordination results in little change in the O(ether)- - -O(carboxyl) interactive distance [1]. Also associated with the *syn–syn* conformation in the phenoxyacetic acids and their complexes is a discrete angular difference between the C–C–O (carboxyl) and C–C–O (hydroxyl) values [16]. This phenomenon is also observed for PTAH [C–C–O(10), 123.3(1)°, C–C–O(11), 112.4(1)° and C–O(10), 1.216(4), C–O(11), 1.302(4) Å. Retention of this difference on complexation (indicating also retention of the *syn–syn* side chain conformation) allows recognition of the origin of the carboxyl oxygen as 'hydroxyl' or 'carbonyl'. For *(2)*, the angles are 122.7(5), 117.7(4)° (retention of conformation), and distances 1.245(6), 1.256(6) Å, while for *(3)* the angles and distances are 117(1), 117(1)°, 1.28(2), 1.23(2) Å (ligand A, no retention), and 118(2), 114(2)°, 1.23(2), 1.27(2) Å (ligand B, no retention).

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