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Metal–(Phenylthio)acetic Acid Interactions. Part 3[a]. The Crystal Structures of Anhydrous Barium (Phenylthio)acetate and the Potassium (Phenylthio)acetate–(Phenylthio)acetic Acid Adduct

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The crystal structures of barium and potassium complexes of (phenylthio)acetic acid (PTAH) have been determined using X-ray diffraction. The barium analogue, $[Ba(PTA)_2]_n$ *(1) is monoclinic, space group C2 with* $Z = 2$, $a = 7.219(4)$, $b = 5.894(2)$, $c = 19.272(2)$ *Å,* $\beta = 91.57(4)°$. $[K(PTA)(PTAH)]_n$ *(2) is triclinic, space group* $P\bar{1}$ *with* $Z = 2$, $a = 6.272(1)$, $b = 7.222(1)$, $c = 18.459(3)$ *Å,* $\alpha = 97.23(1)$, $\beta = 93.64(1)$, $\gamma = 97.31(1)°$. *The structures of (1) and (2) were refined to residuals of 0.047 and 0.053 for 844 and 2628 'observed' reflections respectively. The* MO_8 *coordination about Ba in (1) is distorted 'cubic' with four oxygens from two bidentate carboxylate groups [Ba–O, 2.86, 2.97(3) Å] and four oxygens from adjacent carboxylates [Ba–O, 2.68, 2.69(2) Å] forming an infinite 2-dimensional polymer structure. (2) is polymeric and has bonded PTA as well as adducted PTAH species. There are seven K–O contacts ranging from 2.729–3.034(3) Å from both PTA and PTAH species in an irregular coordination.*

Introduction

The Zn^{II} and Cd^{II} complexes of (phenylthio)acetic acid (PTAH) [1] were reported in Part 1 of this series. In the case of the Cd^{II} analogue, the metal coordination involved carboxyl oxygens and a sulphur atom in an octahedral MO_5S coordination sphere. It was anticipated that with the 'larger' metals, S would be involved in the coordination, resulting in higher coordination numbers. This paper (Part 3) reports on the barium and potassium complexes of PTAH, $[Ba(PTA)_2]_n$ and $[K(PTA)(PTAH)]_n$. The potassium analogue was of particular interest since elemental analysis indicated the presence of 'adducted' molecules of PTAH.

Experimental

Preparation

Complexes were prepared by reacting (phenylthio)acetic acid in aqueous ethanol with an excess of metal carbonate. After digesting for one hour at 70–90 °C, the excess carbonate was removed by filtration (*1*), and the solutions, on standing at room temperature, yielded crystals of the complexes.

Analysis: For (*1*), found: C, 41.0; H, 3.43%. Calc. for $C_{16}H_{14}BaO_4S_2$: C, 40.7; H, 2.99%. For (*2*), found: C, 51.1; H, 3.96%. Calc. for $C_{16}H_{15}KO_4S_2$: C, 51.3; H, 4.01%.

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*) and (*2*). Data were processed using the profile fitting procedure of Diamond [3] and were corrected for absorption. Structure solution and refinement were completed using SHELX-76 [4] on a DEC-10 computer. In the case of structure (*1*), the two phenyl rings which are required by the space group C2 to be related by crystallographic two-fold symmetry, were found to be rotationally disordered about the C(1)–C(4) ring axis. This same phenomenon was previously observed for another PTA complex, $[Zn(PTA)_2(H_2O)_2]$ [1]. The site occupancy factors of the atoms C(2), C(3), C(5) and C(6) were determined to be close to 0.5 and this figure was then used in subsequent refinement of

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[a] Part 1. [(Phenylthio)acetic and the Zn^{II} and Cd^{II} (phenylthio)acetate complexes] [1]. Part 2. [The (phenylthio)-acetato-copper(II)monopyridine dimer] [2].

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TABLE I. Crystal Data for $[Ba(PTA)_2]_n$, (*1*) and $[K(PTA)(PTAH)]_n$, (*2*).

	(*1*)	(*2*)
Formula	$C_{16}H_{14}BaO_4S_2$	$C_{16}H_{15}KO_4S_2$
Mr	471.8	374.1
a (Å)	7.219(4)	6.272(1)
b (Å)	5.894(2)	7.222(1)
c (Å)	19.272(2)	18.459(3)
α (°)		97.23(1)
β (°)	91.57(4)	93.64(1)
γ (°)		97.31(1)
V ($Å^3$)	819.7(6)	820.0(3)
Z	2	2
ρ_c (g cm^{-3})	1.911	1.516
ρ_f (g cm^{-3})	1.91	1.52
F(000)	460	388
μ (cm^{-1})	26.8	5.82
λ (Å)	0.7107	0.7107
Space group	$C2(C_2^3$, No. 5)	$P\bar{1}(C_i^1$, No. 2)
Data collection		
a. diffractometer	Nicolet R3m	Nicolet R3m
b. radiation	Mo Kα	Mo Kα
c. $2\theta_{max}$ (°)	52	52
d. unique reflections measured	852	3186
e. crystal size (mm)	0.32 × 0.28 × 0.04	0.44 × 0.40 × 0.09
Structure solution, refinement		
a. method used	Heavy-atom/ Fourier	Patterson
b. R	0.047	0.053
c. R_w	0.047	0.058
d. w^a A	1.5	2.9
B	2.5×10^{-3}	8.1×10^{-4}
e. data used	844	2628
f. discrimination	$I > 2.5\sigma(I)$	$I > 2.5\sigma(I)$

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

the atoms of the two rings. In all structures, blocked matrix anisotropic refinement was used. Hydrogens were located from difference-Fourier syntheses and were included in the refinement at fixed positions with their isotropic *U*'s set invariant at 0.05 $Å^2$. Residuals R and Rw are defined as: $R = \Sigma[|F_o - F_c|]/\Sigma F_o$ and $Rw = (\Sigma w[|F_o - F_c|]^2/\Sigma w|F_o|^2)^{1/2}$. Neutral atom scattering factors were used [5]. 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

The complexes, $[Ba(PTA)_2]_n$ (*1*) and $[K(PTA)(PTAH)]_n$ (*2*) crystallize as anhydrous solids. Carboxylates of Group IA metals are often devoid of water of crystallization when grown from aqueous media, but those of Ba^{II} usually involve water and complete an irregular coordination sphere with coordination numbers ranging from 6 to 12 [6, 7]. In bis(phenylthioacetato)barium(II) (*1*), the Ba coordination consists of four oxygens from two almost symmetrical bidentate carboxylate ligands [Ba–O, 2.86(2), 2.97(3) Å] related by the space group imposed two-fold rotation operator. Coordination number 8 is satisfied by four oxygens from adjacent carboxylates [Ba–O(10)'(1/2 + x, 1/2 + y, z), 2.68(2) Å; Ba–O(11)'(1/2 + x, 1/2 + y, z), 2.69(2) Å] resulting in an infinite 2-dimensional polymeric structure [Figs. 1, 2a]. The thioether-S is not involved in coordination. The stereochemistry about Ba is distorted cubic, which is consistent with energy calculations for $M(bidentate)_2(unidentate)_4$ systems [8] although the 'unidentate' ligands must be considered more 'shared' than free in coordination in the polymer structure of (*1*). Although cubic stereochemistry is rare among eight-coordinate complexes, another example is also a Ba^{II} complex, tetraaquabis(1,10-phenanthroline)barium(II) perchlorate:1,10-phenanthroline(1/2) [6], which is isostructural with its Sr^{II} analogue. In these complexes, the 'square' coordination is possible because of the longer metal to donor atom distances associated with Ba and Sr [M–N, 2.96 and 2.80 Å (mean) respectively] which allows the *trans*-bis(1,10-phenanthroline) arrangement, the only examples of this known among coordination complexes. A comparable system is found for (*1*), but with the Ba–O distance [2.86, 2.97 Å] shorter, less symmetrical and the ligand 'bite' smaller (O---O, 2.21 Å, *cf.* 2.74 Å for the N---N distance in the *phen* ligand), resulting in a contracted intraligand angle of 44.5° for (*1*) (*cf.* 55.1° in the *phen* complex).

Potassium (phenylthio)acetate (phenylthio)acetic acid (1/1) (*2*) has ionic PTA ligands and adducted PTAH acid molecules. These species are bound in an irregular coordination sphere with seven K–O distances shorter than 3.1 Å [2.729(3)–3.034(3) Å; mean 2.903(3) Å] (Fig. 2b). The S atom of the PTA ligand is not involved in coordination. This is different from potassium 2,4-dichlorophenoxyacetate hemi-hydrate [9] where the potassium is surrounded by an irregular sphere of one chlorine and eight oxygens; two from water molecules, five from carboxyl oxygens of the 2,4-D anions, and one from the phenoxy oxygen. In (*2*), the carboxyl proton of the free acid is linked to a complexed acid *via* short hydrogen bonds [O(11A)---O(10B)', 2.494(5) Å, O–H--O, 172.4(2)°] (Fig. 2b). A comparable adduct system is found in the potassium salt of the dicarboxylic acid *o,o'*-catecholdiacetic acid, $[K(CDAH)(CDAH_2)]$ [10] with both anion and free acid involved in 'coordination' to K [K–O distances, 2.78–2.96 Å]. The higher coordination number (10),

TABLE II. Atomic Positional Parameters ($\times 10^4$). Atom Numbering Scheme is that used for the Parent (Phenylthio)acetic Acid [1].

(*1*) $[Ba(PTA)_2]_n$

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
Ba	0	0	0				
C(1)	5535(16)	2801(22)	2910(6)				
C(2)	6481(37)	4640(37)	3151(13)	C(2)B†	5109(37)	4121(200)	3350(13)
C(3)	7058(39)	4650(47)	3850(12)	C(3)B†	5740(38)	4578(75)	4056(15)
C(4)	6672(20)	2759(28)	4287(7)				
C(5)	5756(47)	1017(53)	4026(13)	C(5)B†	7080(37)	871(51)	3838(12)
C(6)	5166(42)	935(48)	3336(12)	C(6)B†	6443(50)	984(64)	3134(16)
S(7)	4658(5)	3061(6)	2032(2)				
C(8)	4616(18)	223(66)	1724(5)				
C(9)	3617(11)	187(64)	1010(5)				
O(10)	3107(30)	1953(40)	734(8)				
O(11)	3330(38)	-1787(44)	753(12)				
H(2)	7101	5008	2628				
H(3)	7646	4981	4302				
H(4)	6978	2474	4799				
H(5)	*						
H(6)	4068	-9	2988				
H(81)	3879	180	2146				
H(82)	6188	79	1343				

(*2*) $[K(PTA)(PTAH)]_n$

	PTA ligand (*B*)			PTAH ligand (*A*)		
	x/a	y/b	z/c	x/a	y/b	z/c
K	2166(1)	2969(1)	243(0)			
C(1)	186(7)	10387(6)	12457(2)	5356(5)	4460(4)	6862(2)
C(2)	-1657(8)	11144(7)	12660(3)	7280(6)	4795(5)	6535(2)
C(3)	-1983(9)	11602(8)	13392(3)	7397(6)	4081(5)	5807(2)
C(4)	-488(10)	11271(8)	13933(2)	5652(7)	3040(5)	5408(2)
C(5)	1311(10)	10496(8)	13738(3)	3800(7)	2677(6)	5740(2)
C(6)	1679(8)	10056(8)	13001(3)	3622(6)	3380(5)	6467(2)
S(7)	462(2)	9941(2)	11507(1)	5394(1)	5593(1)	7775(0)
C(8)	2795(7)	8740(6)	11477(2)	2801(5)	4696(5)	8059(2)
C(9)	3285(7)	8056(6)	10701(2)	2351(5)	5736(4)	8788(2)
O(10)	4443(5)	6819(4)	10613(1)	847(4)	5056(3)	9108(1)
O(11)	2450(5)	8846(4)	10185(2)	3531(4)	7326(3)	9000(1)
H(2)	-2676	11296	12284	8561	5184	6812
H(3)	-3422	11950	13470	9099	4111	5618
H(4)	-744	11753	14534	5549	2627	4815
H(5)	2565	10244	14052	2313	2364	5482
H(6)	3128	9630	12846	2051	3272	6648
H(81)	4004	9617	11705	2850	3428	8132
H(82)	2530	7889	11772	1702	4857	7726
H(11)	–	–		2932	7942	9547

*Not located. †Atoms of the disordered phenyl ring.

the more regular coordination polyhedron (distorted pentagonal antiprism) and the involvement of the phenoxy oxygen in coordination to the metal, may be attributed to the nature of the ligand which has many more potential coordinating sites than the monofunctional phenyloxy- and phenylthio-acids. Adducted free acids were also found in a Mn^{II}–2,4,5-trichlorophenoxyacetate (2,4,5-T) chemical poly-

TABLE III. Comparative Bond distances (Å) and Angles (°) for $[Ba(PTA)_2]_n$ (*1*), and $[K(PTA)(PTAH)]_n$ (*2*). Primed atoms are symmetry generated.

(a) Coordination sphere

(i) distances

(*1*)		(*2*)	
Ba–O(10)	2.86(2)	K–O(10)A	2.870(3)
Ba–O(11)	2.97(3)	K–O(11)A	3.004(3)
Ba–O(10)′	2.68(2)	K–O(10)B	3.034(3)
Ba–O(11)′	2.69(3)	K–O(11)B	2.729(3)
		K–O(10)A′	2.754(3)
		K–O(10)B′	2.995(3)
		K–O(11)B′	2.936(3)

(ii) angles

(*1*)		(*2*)	
O(10)–Ba–O(11)	44.6(7)	O(11)A–K–O(10)A	133.3(1)
O(10)–Ba–O(10)′	132.5(6)	O(11)A–K–O(10)A′	123.2(1)
O(10)–Ba–O(10)″	114.4(6)	O(11)A–K–O(10)B	147.2(1)
O(10)–Ba–O(10)‴	97.2(6)	O(11)A–K–O(10)B′	73.7(1)
O(10)–Ba–O(11)′	176.9(6)	O(11)A–K–O(11)B	64.6(1)
O(10)–Ba–O(11)″	78.9(7)	O(11)A–K–O(11)B′	72.9(1)
O(10)–Ba–O(11)‴	68.0(7)	O(10)A–K–O(10)A′	77.8(1)
		O(10)A–K–O(10)B	77.6(1)
O(11)–Ba–O(10)″	85.5(7)	O(10)A–K–O(10)B′	129.8(1)
O(11)–Ba–O(10)‴	66.6(7)	O(10)A–K–O(11)B	75.7(1)
O(11)–Ba–O(11)′	138.4(6)	O(10)A–K–O(11)B′	73.3(1)
O(11)–Ba–O(11)″	110.8(6)	O(10)A′–K–O(10)B	66.5(1)
O(11)–Ba–O(11)‴	98.3(6)	O(10)A′–K–O(10)B′	127.5(1)
O(10)″–Ba–O(10)‴	96.0(6)	O(10)A′–K–O(11)B	144.7(1)
		O(10)A′–K–O(11)B′	76.2(1)
		O(10)B–K–O(10)B′	76.8(1)
O(10)″–Ba–O(11)″	86.8(7)	O(10)B–K–O(11)B	128.3(1)
O(10)″–Ba–O(11)‴	175.9(7)	O(10)B–K–O(11)B′	136.6(1)
O(11)′–Ba–O(11)″	98.3(7)	O(10)B′–K–O(11)B	87.6(1)
O(11)″–Ba–O(11)‴	90.5(7)	O(10)B′–K–O(11)B′	146.4(1)
		O(11)B–K–O(11)B′	74.1(1)

(b) Intraligand

(i) distances

	(*1*)	(*2*)	
		(A)	(B)
C(1)–C(2)	1.36(3)	1.391(7)	1.393(5)
C(1)–C(6)	1.40(3)	1.366(6)	1.393(5)
C(1)–S(7)	1.80(1)	1.774(3)	1.767(3)
C(2)–C(3)	1.40(3)	1.386(7)	1.385(5)
C(3)–C(4)	1.43(3)	1.362(7)	1.390(5)
C(4)–C(5)	1.31(3)	1.360(8)	1.371(6)
C(5)–C(6)	1.39(3)	1.389(7)	1.398(5)
S(7)–C(8)	1.78(3)	1.807(3)	1.793(4)
C(8)–C(9)	1.53(1)	1.519(6)	1.519(5)
C(9)–O(10)	1.22(3)	1.226(5)	1.223(4)
C(9)–O(11)	1.28(3)	1.285(5)	1.287(4)

(ii) angles

	(*1*)	(*2*)	
		(A)	(B)
C(2)–C(1)–C(6)	122(2)	119.3(5)	119.1(3)
C(2)–C(1)–S(7)	115(1)	114.8(5)	116.3(2)
C(6)–C(1)–S(7)	123(1)	125.9(5)	124.6(3)
C(1)–C(2)–C(3)	118(2)	119.9(4)	120.6(3)
C(2)–C(3)–C(4)	120(2)	120.8(5)	120.1(4)
C(3)–C(4)–C(5)	119(2)	118.8(5)	119.7(3)
C(4)–C(5)–C(6)	122(2)	121.9(5)	120.9(4)
C(5)–C(6)–C(1)	119(2)	119.3(5)	119.7(4)
C(1)–S(7)–C(8)	104(1)	103.4(4)	102.3(2)
S(7)–C(8)–C(9)	108(2)	111.8(4)	112.8(3)
C(8)–C(9)–O(10)	121(2)	118.3(4)	118.2(3)
C(8)–C(9)–O(11)	115(2)	116.2(4)	116.8(3)
O(10)–C(9)–O(11)	124(2)	125.4(4)	125.0(3)

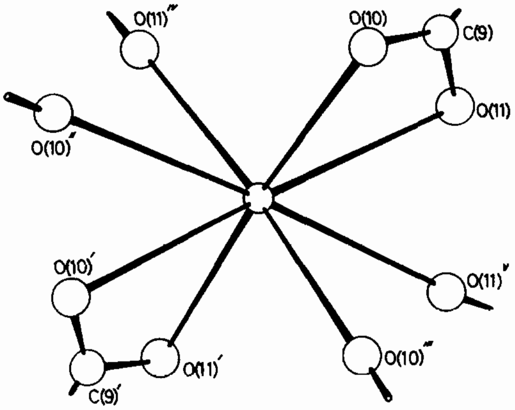
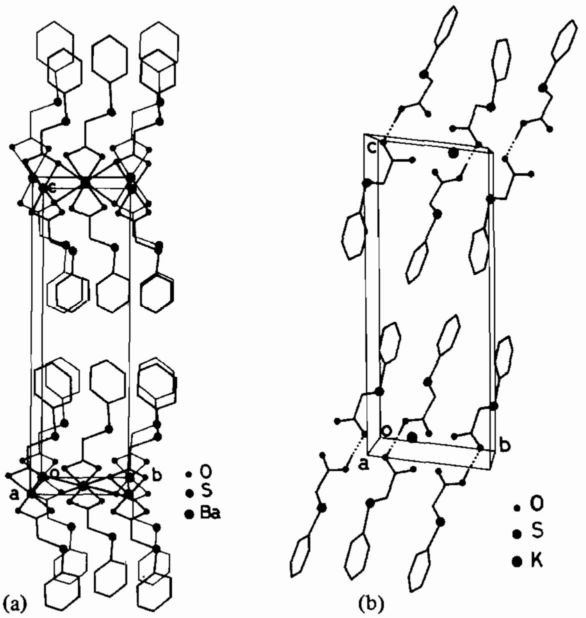


Fig. 1. Coordination polyhedron of $[Ba(PTA)_2]_n$ (*1*).



(a) (b)

Fig. 2. Molecular packing for $[Ba(PTA)_2]$ (*1*) and [K(PTA)-(PTAH)] (*2*). a) (*1*) $[Ba(PTA)_2]_n$ viewed perpendicular to *bc*. b) (*2*) $[K(PTA)(PTAH)]_n$ viewed perpendicular to *bc*.

TABLE IV. Comparative Torsion Angles for the PTA Ligands in (*1*) and (*2*) compared with PTAH [1].

	(*1*)	(*2*)	PTAH
C(2)–C(1)–S(7)–C(8)	–209.0	–174.6, –173.3	–170
C(1)–S(7)–C(8)–C(9)	+171.7	+189.33, +175.6	+177
S(7)–C(8)–C(9)–O(10)	+4.2	–166.8, –161.0*	–4
*S(7)–C(8)–C(9)–O(11)		+16.6, +19.6	

morph {Type 1, $[Mn(2,4,5\text{-}T)_2(H_2O)_4]\cdot 2(2,4,5\text{-}TH)$, [11]}, where adducted 2,4,5-TH acid molecules form regular layers with 2,4,5-T ligands through short hydrogen bonds (2.459 Å) giving a stable complex network. The coordination is inherently more regular with Mn^{II} and so comparison with the potassium compound is not appropriate. Furthermore the discrete layering, a feature of both Mn^{II}–2,4,5-T polytypes and potassium 2,4-dichlorophenoxyacetate hemi-dydrate [9] is absent in the structure of (*2*). This effect is presumably due to the planar nature of the substituted chlorinated ring system.

The structural and conformational aspects of the (phenylthio)acetate ligand, (PTA) and the adducted (or complexed) (phenylthio)acetic acids (PTAH) are also of interest when compared with the structure of PTAH itself [1]. The important intraligand structural features are compared in Table IV. In (*2*), the two independent PTA species are conformationally different, with the anion being planar and the adduct having a synclinal side-chain. The anion is planar in (*1*) with the S(7)–O(10) side-chain distances for (*1*) and (*2*) 2.79 Å and 2.84 (A), 2.88 (B) Å respectively, compared with 2.85 Å in the free acid [1] and 3.03 Å and 3.01, 3.06 Å respectively for the zinc and cadmium complexes of PTA [1]. At this stage, it is not understood why the S---O distances in (*1*) and (*2*) are less perturbed than for the other complexes but it tends to be the expected phenomenon when an analogy is made to the phenoxyalkanoic acids and their complexes. The O---O distance, without exception, shows little variation among the free acids or their metal complexes [12, 13].

The discrete difference between the two C–C–O angles is also retained in all the complexes completed so far as well as for the free acid. In the current work these angles are 115, 121(2)° (*1*) and 116.2, 118.3(3)° (*2*A), 116.8, 118.2(3)° (*2*B).

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