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The Crystal and Molecular Structure of Tris(*ortho*-aminobenzoato)aquoyttrium(III), $Y(H_2NC_6H_4COO)_3 \cdot H_2O$

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Tris(*ortho*-aminobenzoato)aquoyttrium(III), $Y(H_2NC_6H_4COO)_3 \cdot H_2O$, crystallizes in the monoclinic space group, $C2/c$, with eight molecules in a unit cell of dimensions: a = 30.89(1) Å, b = 9.09(1) Å, c = 14.85(1) Å, and β = 109.3(1)°. The structure was determined using three-dimensional X-ray diffraction data gathered on multiple-film equi-inclination, integrated Weissenberg, and precession photographs taken about two crystal axes. The structure, excluding the hydrogen atoms, was solved from Patterson and electron density maps and refined by least-squares methods to a final R of 0.081. The coordination about the yttrium atom is sevenfold, best described by a capped trigonal prism. Each *ortho*-aminobenzoate ligand acts as a bridging bidentate ligand, resulting in six *ortho*-aminobenzoate residues coupled to each yttrium atom. The water molecule occupies the seventh position. This bonding configuration generates a structure in which each yttrium atom in (100) is attached to two other yttrium atoms via carboxylate bridges to give parallel sets of polymeric chains coincident with (100). It is suggested that this polymeric character accounts for the extreme insolubility of $Y(H_2NC_6H_4COO)_3 \cdot H_2O$.

Introduction

Ortho-aminobenzoic acid (anthranilic acid) is an important precursor to tryptophan, one of the biologically important α-amino acids. The acid also forms stable, highly insoluble compounds with a variety of divalent and trivalent metals and can be used as a reagent for quantitative determinations of these metals (*1*). The complexes may be of interest in connection with ^{14}N nuclear quadrupole resonance studies.

Single crystals of a number of divalent and trivalent metal complexes have been grown, comparable in quality to those used for the structural determination of the bis(*ortho*-aminobenzoato)copper(II) (*2*). The yttrium compound was the only member of the synthesized series which was hydrated, a fact contrary to the composition reported by Surgutskii *et al.* (*3*). Its crystal structure has been determined. Work on the zinc and lanthanum complexes is in progress.

Experimental

Single crystals of $Y(H_2NC_6H_4COO)_3 \cdot H_2O$ were prepared by a diffusion reaction (*4*). The resulting needle-shaped, tan crystals of yttrium anthranilate were subjected to thermal and elemental analysis. The complex exhibited an endothermic peak between 105 and 125° and a weight loss of 3.30%. Theoretical weight loss for

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1 mole of water is 3.49%. *Anal.* Calcd. for $Y(H_2NC_6H_4COO)_3 \cdot H_2O$: Y, 17.26; C, 48.95; H, 3.91; N, 8.15. Found: Y, 17.34; C, 48.30; H, 3.94; N, 8.24. Preliminary Weissenberg photographs and intensity statistics indicated the space group $C2/c$. The unit cell dimensions were determined using zero level Weissenberg and rotation photographs taken about [010]. In addition, zero level precession and cone axis photographs were recorded of the a*b* and b*c* reciprocal nets. Measurements were recorded with nickel-filtered copper radiation (λ = 1.54178 Å). The pertinent crystal data are given in Table I. The density measurements were obtained by flotation of a single crystal in a solution of carbon tetrachloride/dichloromethane.

Intensity data for $Y(H_2NC_6H_4COO)_3 \cdot H_2O$ were gathered with nickel-filtered Cu$K\alpha$ radiation using multiple-film, equi-inclination, integrated Weissenberg photographs for layers 0–5 of a crystal mounted on the *b* axis, and multiple-film integrated precession photographs for layers 0–2 of the a*b* reciprocal net. Five Kodak No-Screen medical X-ray films were used for each individual layer, the average film absorption factor being 3.8(2). The crystal used for data collection was a fragment of dimensions 0.05 × 0.45 × 0.09 mm cut from a larger rodlike crystal. The intensities of the reflections were measured with a Welch Densichron for which an 0.5 mm aperture was made.

TABLE I

CRYSTAL DATA

Monoclinic	D_m = 1.74 g cm^{-3}
a = 30.89(1) Å	D_c = 1.737 g cm^{-3}
b = 9.09(1) Å	$\mu(CuK\alpha)$ = 46.97 cm^{-1}
c = 14.85(1) Å	Observation conditions
β = 109.3(1)°	hkl: $h + k = 2n$
v = 3940.1 Å^3	$h0l$: $l = 2n$; $(h = 2n)$
Z = 8	$0k0$: $(k = 2n)$
$F(000)$ = 2096	Space group $C2/c$ (15)

The intensities were corrected for Lorentz and polarization factors, and the two sets of relative intensities were cross scaled and correlated. In view of the small magnitude of $\mu(CuK\alpha)$, no absorption correction was applied. A scale factor to place the reduced intensity data on an absolute scale and an overall temperature factor, B, were derived from a Wilson plot. Reflections were measured to an upper limit of sin θ equal to 0.70 and resulted in a final data set of 1393 reflections, 915 of these being nonzero reflections, a nonzero reflection being defined as a diffraction spot visible on any film.

Structure Determination and Refinement

The yttrium atoms were located from a three-dimensional Patterson function. Three cycles of block diagonal refinement using isotropic temperature factors gave R = 0.374. The remaining nonhydrogen atoms were then located on three-dimensional Fourier maps. Further refinement, using full matrix least-squares calculations with anisotropic temperature factors for all nonhydrogen atoms and yttrium scattering factors corrected for anomalous dispersion, lowered R to 0.081. A final difference map showed a number of peaks of intensity 0.85–1.2 $\Delta e/Å^3$. The quality and size of the data set did not permit accurate assignment of these to hydrogen positions, and the inclusion of all 1393 reflections, observed and unobserved, did not improve the R factor. An error analysis of the final structure showed no systematic errors in F_{obs} as a function of $\sin^2 \theta$. The error analysis also indicated that all but eight reflections had $||F_{obs}| - |F_{calc}|| / |F_{obs}|$ less than twice the final R value, or $|F_{obs}| - |F_{calc}|$ less than one-half the $|F_{obs}|$ value of the weakest reflection. A check of the noncentrosymmetric space group, Cc, resulted in a correlation matrix showing strong correlation

TABLE II

FINAL POSITIONAL PARAMETERS[a] FOR $Y(H_2NC_6H_4COO)_3 \cdot H_2O$

Atom	Positional parameters		
	x	y	z
Y	0.2516(1)	0.4884(3)	0.2057(2)
O(7)	0.2552(6)	0.5216(29)	0.0547(12)
Ligand 1			
C(1)	0.197(1)	0.673(4)	0.385(1)
C(2)	0.154(1)	0.611(4)	0.435(1)
C(3)	0.153(1)	0.469(4)	0.477(1)
C(4)	0.111(1)	0.401(4)	0.516(2)
C(5)	0.071(1)	0.478(4)	0.526(2)
C(6)	0.074(1)	0.621(5)	0.486(2)
C(7)	0.114(1)	0.692(4)	0.445(2)
O(1)	0.2276(4)	0.6075(20)	0.3422(8)
O(2)	0.1983(6)	0.8160(25)	0.3836(11)
N(1)	0.1917(8)	0.3809(27)	0.4663(15)
Ligand 2			
C(8)	0.331(1)	0.745(4)	0.204(2)
C(9)	0.378(1)	0.724(4)	0.187(2)
C(10)	0.400(1)	0.820(4)	0.234(2)
C(11)	0.448(1)	0.802(6)	0.218(3)
C(12)	0.470(1)	0.736(5)	0.147(3)
C(13)	0.451(2)	0.617(5)	0.100(3)
C(14)	0.401(1)	0.617(5)	0.115(2)
O(3)	0.3113(6)	0.6374(18)	0.1739(11)
O(4)	0.3022(5)	0.8290(20)	0.2529(11)
N(2)	0.379(1)	0.888(4)	0.315(2)
Ligand 3			
C(15)	0.311(1)	0.270(2)	0.305(2)
C(16)	0.355(1)	0.335(3)	0.311(1)
C(17)	0.356(1)	0.462(3)	0.357(1)
C(18)	0.400(1)	0.513(4)	0.363(2)
C(19)	0.438(1)	0.423(3)	0.323(2)
C(20)	0.436(1)	0.302(4)	0.277(2)
C(21)	0.394(1)	0.257(4)	0.274(2)
O(5)	0.2821(6)	0.3623(16)	0.3044(12)
O(6)	0.3069(5)	0.1391(17)	0.3030(11)
N(3)	0.3201(8)	0.5619(30)	0.3992(15)

[a] Estimated standard deviations are given in parentheses.

(coefficients of 0.9–1.0) between parameters of the supposedly unrelated yttrium atoms, leading back to the original $C2/c$ space group.

In both the block diagonal and full matrix least-squares procedure the function minimized was $\Sigma W(|F_0| - |F_c|)^2$; $W = 1/\sigma^2(|F_0|)$. The atomic scattering factors for the nonhydrogen atoms were taken from those tabulated by Hanson *et al.* (*5*). Corrections for anomalous dispersion were made only for yttrium, and the values of $\Delta f'$ and $\Delta f''$ (−0.70 and 2.3) were those found in the International Tables (*6*). The values of the refined parameters and their estimated standard deviations are listed in Table II. A list of the observed and calculated structure factors is available from the authors.

Results and Discussion

The molecular geometry and the numbering scheme for the light atoms are shown in Fig. 1. The yttrium atom exhibits a common coordination for yttrium and lanthanide complexes—seven coordinate. Each yttrium atom is bonded to seven oxygen atoms, contributed by the aminobenzoate groups and one water molecule. Each *ortho*-aminobenzoate group functions as a bridging bidentate ligand, resulting in a total of six *ortho*-aminobenzoate residues associated with each yttrium atom. This is similar to the oxygen bonding found in the bis(*ortho*-aminobenzoato)copper(II) compound (*2*).

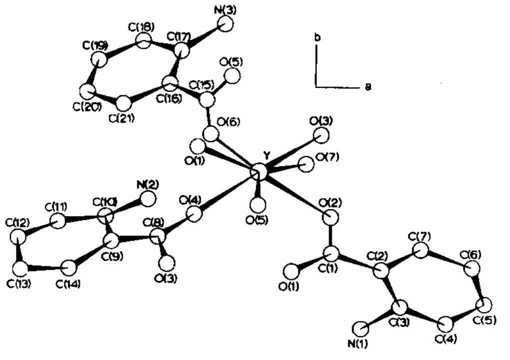

FIG. 1. Molecular geometry of $Y(H_2NC_6H_4COO)_3 \cdot H_2O$.

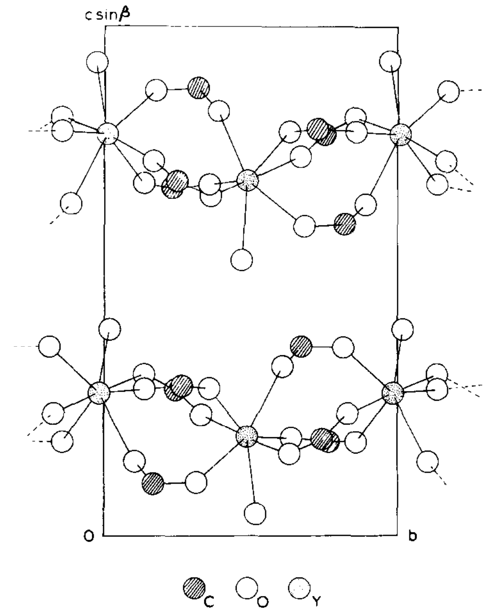

FIG. 2. Polymeric structure in $Y(H_2NC_6H_4COO)_3 \cdot H_2O$.

The result of this mode of coordination is that each yttrium atom is attached to two other yttrium atoms via carboxylate bridges to give sets of polymeric parallel chains. Figure 2 is a view along [100], showing the orientation of these parallel chains. The aromatic rings of the *ortho*-aminobenzoate ligands extend nearly perpendicularly on either side of the polymeric chains and may provide lateral stability. This polymeric arrangement probably is the source of the compound's extreme insolubility.

The bond distances and angles found in tris(*ortho*-aminobenzoato)aquoyttrium(III) are listed in Table III. The average Y–$O_{chelate}$ = 2.42(2) Å. Corresponding average values of 2.36(6) Å and 2.323(8) Å have been measured in the few reported yttrium(III) complexes with amino acids (*7*, *8*). The C–O distances in the carbonyl group are significantly different, especially in ligands 1 and 2. This is an indication that the *pi* delocalization between the two bonds is not equal—possibly as a consequence of the bonding arrangement. The average C–C distance in the aromatic rings is 1.49(5) Å, somewhat higher than the idealized C–C bond of 1.395 Å. The difference map indi-

TABLE III

BOND DISTANCES AND ANGLES IN $Y(H_2NC_6H_4COO)_3 \cdot H_2O$[a,b]

Y—O(1)	2.61(1) Å	Y···O(4)	2.55(2) Å	Y···N(1)	3.64(3) Å
Y···O(2)	2.82(2)	Y—O(5)	1.86(2)	Y···N(2)	4.03(2)
Y—O(3)	2.46(2)	Y···O(6)	2.24(2)	Y···N(3)	3.23(2)
		Y—O(7)	2.30(2)		

C(1)–O(1)	1.30(4) Å
C(1)–O(2)	1.43(3)
C(8)–O(3)	1.15(4)
C(8)–O(4)	1.41(4)
C(15)–O(5)	1.23(3)
C(15)–O(6)	1.19(3)

$C\text{–}C_{Average}$ = 1.49(5)

O(2)–Y–O(7)	53.5(7)°
O(3)–Y–O(7)	57.9(7)
O(6)–Y–O(7)	98.9(7)
O(2)–Y–O(3)	69.7(5)
O(3)–Y–O(6)	107.2(6)
O(2)–Y–O(6)	150.6(6)
O(1)–Y–O(4)	69.0(5)
O(4)–Y–O(5)	71.1(7)
O(1)–Y–O(5)	81.0(7)
O(5)–Y–O(6)	127.4(7)

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[a] Estimated standard deviations are given in parentheses and are calculated from those derived for the positional parameters.

[b] The dotted line represents a bond between a yttrium atom and the carbonyl oxygen of a ligand attached to a different yttrium atom, or the distance between yttrium and a nitrogen atom.

cated no other possible locations for the assigned atoms, but the high standard deviations of the parameters reflect the less than ideal quality of the data set. The significant deviation from the idealized bond lengths of an aromatic ring may be contributed in part by the quality of the data set. It should be noted that in the parent anthranilic acid there is also a considerable (and significant) variation among individual C–C distances in the phenyl rings (*9*).

The polyhedron formed by the coordinated oxygen atoms about yttrium may be described as a distorted capped trigonal prism with O(5) capping the lateral face O(2)–O(3)–O(1)–O(4). However, this polyhedron is severely distorted from ideal C_{2v} symmetry (*10, 11*). A capped trigonal prism has also been observed in the structure of ytterbium acetylacetonate monohydrate (*12*). Description is also possible in terms of the capped octahedron which has been found in chelate structures of tris(1-phenyl-1,3-butanedionato)aquoyttrium(III) (*13*) and tris(diphenyl-propanedionato)aquoholmium) (*14*). The capping ligand in this case would be O(7) of the water molecule and the deviations from ideal C_{3v} symmetry would be large (*10*). As a consequence of the distortion, distinction between the two polyhedral forms cannot be unequivocal (*10*). This yttrium amino acid complex is unique in that both oxygens of the carboxylate are active in bonding and that each of the six bonding chelate oxygens of the distorted trigonal prism belong to a different *ortho*-aminobenzoate ligand. Based on the available data taken from photographic techniques, the authors feel that the gross structural features of the complex represent the best current model, considering the large number of light atoms in the compound.

Acknowledgments

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