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Title
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Paul E. Riley, Salim F. Haddad, and Kenneth N. Raymond

July 1982

DISCLAIMER

The Preparation of Praseodymium(III) Chloranilate and the Crystal

Structures of $Pr_2(C_6Cl_2O_4)_3 \cdot 8C_2H_5OH$ and $Na_3[C_6H_2O(OH)(SO_3)_2] \cdot H_2O$

By

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Abstract

The crystal structure of $Pr_2(C_6Cl_2O_4)_3 \cdot 8C_2H_5OH$ (1), a complex obtained by slow hydrolysis of o-chloranil ($C_6Cl_4O_2$) in acidic ethanol solution, has been determined by single crystal X-ray diffraction techniques with data collected by counter methods. The structure of $Na_3[C_6H_2O(OH)(SO_3)_2] \cdot H_2O$ (2), the trianion of tiron, has also been determined by X-ray crystallography. Crystals of 1 form in triclinic space group $P\bar{1}$ with $a = 8.990(1)$, $b = 10.503(2)$, $c = 13.589(1)$ Å, $\alpha = 99.02(1)$, $\beta = 91.50(1)$, $\gamma = 94.44(1)°$. The observed density of 1.643 g cm^{-3} is in agreement with the calculated value of 1.671 g cm^{-3} for one unit of $Pr_2(C_6Cl_2O_4)_3 \cdot 8C_2H_5OH$ per unit cell. The crystal structure is a three-dimensional network of alternating $(C_6Cl_2O_4)^{2-}$ and Pr^{3+} ions in which the chloranilate rings lie about crystallographic inversion centers. The resulting coordination sphere about Pr^{3+} consists of six chloranilate oxygen atoms from three symmetry independent chloranilate ions and three ethanol oxygen atoms (six of the eight ethanol molecules in the full formula — the remaining two are simply in the crystal lattice), arranged in an approximately tricapped trigonal prismatic fashion. Full-matrix least-squares refinement of the structure has converged with R and R_w indices (on $|F|$) of 0.025 and 0.040 using 3057 symmetry-independent reflections with $F_o^2 > 3\sigma(F_o^2)$. Crystals of 2 form from aqueous solution in orthorhombic space group $Pnma$ with $a = 16.018(2)$, $b = 6.972(2)$, and $c = 9.700(1)$ Å. The $[C_6H_2O(OH)(SO_3)_2]^{3-}$ species exhibits rigorous C_s symmetry with only the two symmetry-related oxygen atoms of each SO_3 moiety lying out of the plane of the anion. There are no unusual aspects of the molecular geometry of 2. Full-matrix least-squares refinement of the structure has converged with R and R_w indices (on $|F|$) of 0.034 and 0.045 using the 805 observations with $F_o^2 > 3\sigma(F_o^2)$.

INTRODUCTION

We have a continuing interest in the coordination chemistry of lanthanide and actinide catecholate complexes and the question of whether such groups can be incorporated into multidentate sequestering agents.[2,3] Since we have observed that catecholates significantly stabilize higher oxidation states in the lanthanides $\{[Ce(cat)_4]^{4-}/[Ce(cat)_4]^{5-}$, $E^o \cong -0.45$ V; Ce^{4+}/Ce^{3+}, $E^o \cong +1.70$ V$\}$,[4] we have pursued the possibility of isolating a Pr(IV) complex with electronegative catecholates or their derivatives. To this end, o-chloranil ($C_6Cl_4O_2$), a chlorinated benzoquinone that is known[5-9] to be easily reduced to the semiquinone $(C_6Cl_4O_2)^-$ and the catecholate $(C_6Cl_4O_2)^{2-}$, was added to Pr^{3+} in order to learn if o-chloranil would oxidize Pr^{3+} or form a complex. Under the conditions used in this preparation the solvated praseodymium(III) chloranilate results from hydrolysis of o-chloranil. This hydrolysis is unusual under these conditions, since the amount of water present was only 0.3% at the start of the reaction and the pH was less than 2. For example, Ksenzhek et al.,[10] while studying the redox properties of the halide derivatives of benzoquinone, observed that p-chloranil and o-chloranil hydrolyze at pH 7 to p-chloranilic acid in aqueous media only to the extent of 40% and 60%, respectively. They also reported a pair of conjugate oxidation-reduction peaks corresponding to p-chloranilic acid imposed on the voltammogram of both p-chloranil and o-chloranil over the entire pH range studied (pH 0 - 10 for p-chloranil, pH 0 - 7 for o-chloranil). A number of crystalline hydrated alkali chloranilates have been prepared by addition of p-chloranil to aqueous alkali-metal hydroxide solutions.[11]

A survey of the literature reveals that although chloranilic acid was first prepared as the dihydrate as early as 1891 by Graebe,[12] very little is known of its structural chemistry in salts and complexes. Andersen reported the crystal structures of chloranilic acid,[13] its dihydrate,[14] and that of ammonium chloranilate monohydrate.[15] Herbstein and Kaftory[11] reported crystal data but no structural analyses for a number of hydrated alkali chloranilates. All of these complexes and salts are very water soluble. In contrast, the crystal structure reported here is that of an extremely water-insoluble, polymeric chloranilate, the preparation of which was achieved by slow hydrolysis of chloranil.

Chloranilic acid has found extensive use in analytical chemistry primarily because it forms numerous stable salts which are not soluble in water. For example, the Ca(II), U(IV), Nb(V), Mo(VI), W(VI), Zr(IV), Pb(II), and Hg(II) ions[16-23] all form water-insoluble complexes with chloranilate ion, which may then be analyzed spectrophotometrically or amperometrically. Perhaps the greatest use of a chloranilate salt is made in sulfate determination[24-29] in which barium chloranilate is used to precipitate $BaSO_4$. In a similar manner, copper(II) chloranilate is used in the analysis of sulfides,[30] lanthanum(III) chloranilate in the analysis of fluorides and oxalates,[31] and mercury(II) chloranilate in the analysis of cyanides mercaptobenzothiazoles, sulfides, sulfites, thiosulfates, and tetraphenylborates.[32-34] Mercury(II) chloranilate is also a reagent in the photometric determination of chloride in biological material.[35]

The above list of analytical uses of chloranilic acid is, although representative, by no means exhaustive. Yet despite their wide uses, chloranilic acid complexes and its water-insoluble salts have not been structurally characterized. Accordingly, we undertook the determination of the crystal structure of $Pr_2(C_6Cl_2O_4)_3 \cdot 8C_2H_5OH$ (1), which is a prototypical insoluble M^{3+} chloranilate.

In addition, we have also determined the crystal structure of the sodium salt of the substituted catecholate tiron, $Na_3[C_6H_2O(OH)(SO_3)_2] \cdot H_2O$ (2). This apparently is the first report of the structure of this ligand and hence provides a description of the geometry of an uncomplexed electronegative catecholate.

EXPERIMENTAL

Preparation of $Pr_2(C_6Cl_2O_4)_3 \cdot 8C_2H_5OH$ and $Ag_2(C_6Cl_2O_4)$

The praseodymium salt was prepared by heating $PrCl_3 \cdot 6H_2O$ (1 mmol) and tetrachloro-1,2-benzoquinone (o-chloranil) (5 mmol) in 40 mL of absolute ethyl alcohol in a dry atmosphere. Upon mixing, the solution became green-brown but changed gradually after half an hour of heating at reflux to red-brown. The chloranilate complex was then precipitated as a gray-purple powder by addition of water. Crystals suitable for X-ray diffraction were obtained by refluxing for 24 h and then allowing to stand for a few days. Large crystals were also obtained by slow evaporation of the refluxed solution in a dry atmosphere at reduced pressure. The crystals used for structure determination contain ethanol and could be stored under absolute alcohol. Slight exposure to water vapor causes the crystals to decompose and change color.

The silver salt could be prepared by addition of 1 M Ag(NO$_3$) to the praseodymium salt. Heating silver chloranilate in 1 M HNO$_3$ precipitates AgCl.

The infrared spectrum of dried praseodymium(III) chloranilate in KBr shows a major band centered about 1500 cm^{-1} and exhibiting several shoulders. The infrared spectrum of silver(I) chloranilate shows a similar band centered about 1515 cm^{-1}. The IR spectra are very much like those reported for the Hg^{2+} and La^{3+} chloranilate salts.[36,37]

Anal. Calcd. for Pr$_2$(C$_6$Cl$_2$O$_4$)$_3$·8C$_2$H$_5$OH: C, 32.12; H, 3.81; Cl, 16.73. Found: C, 28.17; H, 3.63; Cl, 18.0.

Anal. Calcd. for Ag$_2$(C$_6$Cl$_2$O$_4$): C, 17.04; Cl, 16.78. Found: C, 16.74; Cl, 18.38.

X-Ray Crystallography

Pr$_2$(C$_6$Cl$_2$O$_4$)$_3$·8C$_2$H$_5$OH (1). Single crystals suitable for X-ray diffraction were wedged into 0.3 mm glass capillaries which were filled with absolute ethanol and were then sealed with a micro torch. Since the crystals tended to fracture, several were examined before one was found suitable for data collection. Precession photographs indicated the triclinic space groups P1 and P$\bar{1}$; the latter was confirmed subsequently. Intensity data were collected with an Enraf-Nonius CAD-4 diffractometer controlled by a DEC PDP-8/E computer in accordance with procedures outlined previously[38] and summarized in Table I. The measured intensities were reduced and assigned standard deviations with a p value given in Table I.[39]

The structure was solved by standard heavy atom methods and refined by full-matrix least-squares procedures in centric space group $P\bar{1}$ using the 3057 reflections with $\underline{F}_o^2 > 3\sigma(\underline{F}_o^2)$ as described previously.[40] Refinement of positional and anisotropic thermal parameters for all 31 nonhydrogen atoms converged to $\underline{R}$ and $\underline{R}_w$ indices[41] of 0.036 and 0.057, respectively. [Application of an absorption correction (see Table I) reduced the $\underline{R}$ index by 0.009.] Unequivocal assignment of hydrogen atom postiions was not possible due to high thermal motion of atoms of the ethanol molecules and accordingly hydrogen atoms were not included in the Fourier summation. The final difference Fourier map showed several residual peaks of about 0.3 e $\overset{\circ}{A}^{-3}$ in height, all of which were in the vicinity of the ethanol molecules and could be attributed to hydrogen atoms or minor disorder. Four reflections (110, $1\bar{1}1$, $01\bar{2}$, $21\bar{3}$) were rejected as poorly determined data. Inclusion of a correction for secondary extinction in the final refinement reduced $\underline{R}$ $(\underline{R}_w)$ to 0.025 (0.040). The final error in an observation of unit weight is 1.8.[41]

$\underline{Na_3[C_6H_2O(OH)(SO_3)_2]\cdot H_2O}$ ($\underline{\overset{\cdot}{\chi}}$). Single crystals of this salt were obtained during attempts to prepare crystalline samples of a transition metal tiron complex. Two well-formed, faintly purple prisms (from trace amounts of oxidized material) were obtained from a basic (NaOH) aqueous solution of tiron. Preliminary precession photographs with these crystals showed orthorhombic symmetry and yielded approximate unit cell constants, the values of which were confirmed by preliminary experiments with a CAD 4 diffractometer. Following accurate centering of three sets of eight symmetry-equivalent reflections with $24 < 2\theta < 28°$, intensity data were gathered, as summarized in Table I, and found to

exhibit systematic reflection absences consistent with space groups $Pna2_1$ and $Pnma$, the latter subsequently confirmed.

The structure was solved by direct methods (MULTAN)[39] in the centrosymmetric space group $Pnma$ and refined by full-matrix least-squares procedures using the 805 reflections with $F_o^2 > 3\sigma(F_o^2)$. All hydrogen atoms were readily located from a difference Fourier map computed near the end of refinement. In the final cycles of refinement, the anisotropic thermal parameters of all nonhydrogen atoms were refined and hydrogen atoms were maintained either at idealized positions[42] (phenyl ring atoms) or at positions determined from the difference map (water and hydroxyl atoms). At convergence, the R, R_w, and error in an observation of unit weight indices are 0.034, 0.045, and 2.58, respectively, for a model structure with 112 variables.[41] In the final cycle of refinement, the largest parameter shift was 0.16 of a corresponding esd. The largest peaks of a final difference electron density map were ~ 0.3 e Å^{-3} and thus were smaller than those previously attributed to the hydrogen atoms. There was no indication of secondary extinction in the data.

Tables II and III present positional parameters, with corresponding esd's as derived from the least-squares inverse matrices, of the nonhydrogen atoms of 1 and 2. Tabulations of anisotropic thermal parameters (Tables IV and V) and structure factor amplitudes (Tables VI and VII) are available.[43]

RESULTS AND DISCUSSION

$\underline{Pr_2(C_6Cl_2O_4)_3 \cdot 8C_2H_5OH}$ ($\underset{\sim}{\underline{1}}$)
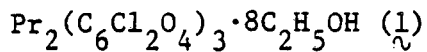
The crystal structure of $\underset{\sim}{1}$ is a prototype of M^{3+} complexes with

chloranilic acid. It consists, in part, of a polymeric three-dimensional

network of chloranilate ions alternating with Pr^{3+} ions. The two Pr^{3+}

ions in the unit cell are related by symmetry and are bridged by the

three independent chloranilate anions (A, B, C), each of which lies at a

crystallographic inversion center. These positions are, respectively,

(1/2, 1/2, 0), (0, 0, 0) and (0, 0, -1/2) for rings A, B and C and are

shown in Figure 1. Since bridging of oxy anions does not occur in this

structure, the 2:3 stoichiometry of Pr^{3+} to chloranilate ligand means

that the ortho-oxygen atoms of the anion only account for six coordination

sites of Pr^{3+}. Three more coordination sites are filled by oxygen atoms

from the solvent ethanol molecules, to complete a coordination number

of nine. A fourth ethanol molecule per Pr^{3+} occupies an interstitial

vacancy in the network. Bond lengths and bond angles are presented in

Table VIII, and the atom numbering scheme is shown in Figure 2. The

three coordinated and one interstitial ethanol molecules possess large

thermal motion (see Figure 1) and consequently are less satisfactorily

defined than the Pr^{3+}-chloranilate network. None of the hydrogen atoms

was located, although the hydrogen atom of each OH group could interact

with at least three nearby oxygen atoms (see Figure 1).

The three chloranilate ligands are planar and, as shown in Figure 3,

are similar in dimensions to the chloranilate ion found in the structure

of the NH_4^+ salt.[15] The Pr^{3+} ion does not lie in the plane of any of

these ligands but deviates by 0.019, 0.350, and 0.425 Å from the mean

planes of ligands A, B, and C, respectively. The average C-O bond distance here of 1.247 Å corresponds to a bond order of 1.5 when compared to the single C-OH bond (1.320 Å) and the double C=O bond (1.225 Å) in chloranilic acid. This average C-O bond distance agrees well with C-O bond distance found in insoluble oxalates such as in hydrated calcium oxalate (1.25 Å).[44] The major band in the infrared spectrum at approximately 1500 cm^{-1} is due mainly to the C-O stretch and is also consistent with a C-O bond order of 1.5. (The C=O stretch in tetrachloro-o-benzo-quinone is at 1175 cm^{-1}.[45]) The bond distances within the C_6 rings of A, B, and C are consistent with a bond order of 1.5 for the C(Cl)-C(O) bond (average 1.394 Å), and a bond order of 1 for the C(O)-C(O) bonds (average 1.528 Å).

The Pr-O(anion) distances are shorter than the Pr-O(neutral donor) distances, as expected: the average Pr-O(chloranilato) distance is 2.485 Å, while the average Pr-O(ethanol) distance is 2.553 Å (Table VIII). For comparison, the sum of ionic radii for Pr^{3+} and O^{2-} is 2.46 Å and the sum of crystal radii for Pr^{3+} (CN = 8) and O^{2-} (CN = 2) is 2.49 Å.[46] Characterization of this nine-coordinate Pr^{3+} complex contradicts what has been suggested by Albertsson and Oskarsson: that a lanthanide ion with metal-oxygen distances in the range 2.3 - 2.6 Å would be eight-coordinate.[47] Indeed, a survey of the literature shows that a coordination number of nine is preferred by Pr^{3+}, if the ligands are compact bidentate oxygen donors such as carboxylates or oxalates. For example, Pr(III) oxalate[48] is nine-coordinate, with an average Pr-O(oxalato) distance of 2.51 Å and an average Pr-O(water) distance of 2.55 Å; Pr(III) nitrilotriacetate[49] is nine-coordinate, with an average

Pr-O(acetato), Pr-O(water), and Pr-N distances of 2.51, 2.52, and 2.68 Å, respectively; Pr(III) iminodiacetate[50] is nine-coordinate, with an average Pr-O(acetato) distance of 2.48 Å and Pr-O(water) distance of 2.54 Å; and Pr(III) nicotinate[51] is nine-coordinate, with an average Pr-O(acetato) distance of 2.46 Å and Pr-O(water) distance of 2.49 Å.[52]

In contrast, the more bulky β-diketonates (which form six-membered chelate rings with the metal as compared to our membered rings for acetates and five membered rings for oxalates and chloranilate) tend to form complexes with Pr^{3+} which are less than nine-coordinate. This is particularly the case in the trifluoro-1-(2-thienyl)-1,3-butanedione complex (CN = 8).[53,54] However dimer formation through bridging ligands tends to increase the coordination number: the shift reagent 3-trifluoro-acetyl-d-camphor[53] is an asymmetric β-diketonato ligand which forms a dimeric Pr^{3+} complex with CN = 9. Other examples of this type are the dimeric complex with heptafluoro-7,7-dimethyl-4,6-octanedione, which contains two bridging carbonyl oxygen atoms and one bridging water oxygen (CN = 8),[55] and the dimeric complex with tetramethyl-3,5-heptane-dione that has two bridging carbonyl oxygen atoms (CN = 7).[56]

There are striking similarities between this ethanol-solvated Pr^{3+} chloranilate complex and the hydrated lanthanide oxalates.[57-60] In both cases the planar ligands ($C_6Cl_2O_4^{2-}$ and $C_2O_4^{2-}$) coordinate with two metal ions to form polymeric networks in which the metal ions bond to three $C_2O_2^-$ fragments and to three solvent molecules. There are solvent molecules which are held intersitially but which may be removed easily without loss of bulk crystallinity and are therefore difficult to define crystallographically. Grinding crystals of 1 in air results in complete

loss of alcohol and gradual absorption of moisture (as noted by IR spectroscopy), which explains the low value of carbon found by elemental analysis (see Experimental Section).

An analysis in terms of polyhedral shape-determining dihedral angles[61,62] of the coordination geometry formed by the nine oxygen atoms bound to Pr^{3+} is summarized in Table IX. As discussed in our recent study[63] of a nine-coordinate thorium complex, the two most plausible polyhedra are the tricapped trigonal prism ($\underline{D}_{3h}$) and the monocapped square antiprism ($\underline{C}_{4v}$). Although the geometry of this complex is, as shown in Table IX, intermediate between these two nearly equal energy[61] idealized polyhedra, it is clear that this coordination polyhedron has approximate $\underline{D}_{3h}$ symmetry. This is particularly apparent from the view provided by Figure 4. The two triangular faces defined by atoms O(1A), O(1B), O(2) and O(1), O(3), O(1C) which are approximately normal to the pseudo $\underline{C}_3$ axis of the complex are nearly parallel (dihedral angle = 6.6°) and are twisted about the vector joining their centroids by an average of 10.5° from the eclipsed conformation. Furthermore, the values of the equatorial bond angles at Pr^{3+} of this polyhedron [116.53(7), 121.43(6), and 122.04(6)°] support the view that the symmetry of this coordination geometry is closer to $\underline{D}_{3h}$ than $\underline{C}_{4v}$.
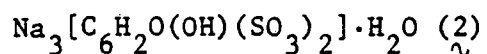
$\underline{Na_3[C_6H_2O(OH)(SO_3)_2]\cdot H_2O}$ (2)

Figure 5 is a drawing of the $[C_6H_2O(OH)(SO_3)_2]^{3-}$ ion and indicates the atom numbering scheme used herein. Selected bond lengths and angles are summarized in Table X.

The crystal structure consists of infinite sheets of $[C_6H_2O(OH)(SO_3)_2]^{3-}$ and Na(1) ions lying in the mirror planes at $y = \pm 1/4$ (see Figure 6). Each Na(1) ion is coordinated in the mirror plane with the phenolate atom O(1) and the phenol atom O(2) of one anion and with two sulfonate atoms O(3) and O(5) from a second anion. Two sulfonate atoms O(6) from two other anions, residing on opposite sides of the mirror plane complete a pseudo-octahedral environment about Na(1). The Na(1) - O distances and cis bond angles range from 2.254(2) to 2.598(2) Å [mean = 2.39(5) Å[64]] and from 73 to 110°. The Na(2) ions lie between these mirror planes and are octahedrally coordinated with O(1) and O(4) of one anion, three sulfonate atoms O(3), O(5), and O(6) of three other anions, and a water molecule O(7). The coordination geometry about Na(2) is less regular than that about Na(1): the five Na(2) - O distances, excluding the long Na(2) - O(7) distance, range from 2.322(2) to 2.480(2) Å [mean = 2.39(3) Å], while the cis bond angles at Na(2) fall between 72 and 118°. Water molecule O(7) exhibits four strong interactions — the aforementioned coordination with Na(2) and the formation of three hydrogen bonds, one along the mirror plane with the hydrogen atoms of O(2) (2.870 Å) and two on opposite sides of the mirror plane with atoms O(4) (2.892 Å).

All atoms of the anion except O(4) and O(6) are rigorously coplanar. The S-O and S-C bond lengths are in excellent agreement with distances recently reported for aromatic sulfonates.[65] The O(1) - C(2) bond is significantly shorter (by 0.07 Å) than the O(2) - C(3) bond because the O(2) atom is protonated. The shortening of the O(1) - C(2) bond is indicative of multiple bonding, which in turn promotes a small degree of localization of the π bonds of the phenyl ring. Hence, the C-C bonds

formed with C(2) [C(1) - C(2) and C(2) - C(3)] are 1.438(4) and 1.415(4) Å and as such are substantially longer than the remaining four bonds in the ring which average 1.377(5) Å. Accordingly, this distribution of bond lengths suggests that a small contribution to the stability of this anion is made by some S-C multiple bonding (and inductive electron withdrawal), which localizes double bond character at C(3) - C(4) and also at C(5) - C(6) and C(1) - C(6).

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SUPPLEMENTARY MATERIAL

Ordering information is given on any current masthead page.

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37. Principal infrared bands (cm^{-1}): $Pr_2(C_6Cl_2O_4)_3$ 1615m, 1500vs, 1380s, 1295m, 1000m, 950s, 605w, 580m, 445m, 385w. $Ag_2(C_6Cl_2O_4)$ 1610m, 1515vs, 1380w, 1275w, 990w, 830s, 565s, 355w.

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41. The error indices are: $\underline{R} = \Sigma||\underline{F}_{\underline{o}}| - |\underline{F}_{\underline{c}}||/\Sigma|\underline{F}_{\underline{o}}|$, $\underline{R}_{\underline{w}} = [\Sigma \underline{w}(|\underline{F}_{\underline{o}}| - |\underline{F}_{\underline{c}}|)^2/\Sigma \underline{w}\underline{F}_{\underline{o}}^2]^{1/2}$, and an error in an observation of unit weight $= [\Sigma \underline{w}(|\underline{F}_{\underline{o}}| - |\underline{F}_{\underline{c}}|)^2/(\underline{N}_{\underline{o}} - \underline{N}_{\underline{v}})]^{1/2}$, where $\underline{N}_{\underline{o}}$ is the number of observations $|\underline{F}_{\underline{o}}|$ and $\underline{N}_{\underline{v}}$ is the number of variables in refinement.

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Table I. Crystallographic Summary

	$Pr_2(C_6Cl_2O_4)_3 \cdot 8C_2H_5OH$ (1)	$Na_3[C_6H_2O(OH)(SO_3)_2] \cdot H_2O$ (2)
$\underline{a}$, Å	8.990(1)	16.018(2)
$\underline{b}$, Å	10.503(2)	6.972(2)
$\underline{c}$, Å	13.598(1)	9.700(1)
α, deg	99.02(1)	90
β, deg	91.50(1)	90
γ, deg	94.44(1)	90
V, Å^3	1263.3(6)	1083.3(6)
$\underline{d}_{measd}$ g cm^{-3}	1.643[a]	---[b]
$\underline{d}_{calcd}$ g cm^{-3}	1.671	2.171
Z	2	4
Molecular formula	$C_{17}H_{24}Cl_3O_{10}Pr$	$C_6H_5Na_3O_9S_2$
Fw	635.64	354.19
Crystal system	triclinic	orthorhombic
Systematic absences	none	$0k\underline{l}$, $\underline{k}+\underline{l} = 2\underline{n} + 1$; $hk0$, $\underline{h} = 2\underline{n} + 1$
Space group	$P\bar{1}$ (no. 2)	$Pnma$ (no. 62)
$\underline{p}$ value	0.04	0.02
2θ range, deg	3.0–45.0	3.0–50.0
Total reflections measured	3297	1038
Data crystal dimensions, mm	0.13 x 0.21 x 0.27	0.11 x 0.14 x 0.23
Data crystal faces	$(\bar{1}10)$, $(1\bar{1}0)$, (010), $(0\bar{1}0)$, (001), $(00\bar{1})$	(100), $(\bar{1}00)$, (010), $(0\bar{1}0)$, (001), $(00\bar{1})$, (101), $(\bar{1}0\bar{1})$
Absorption coefficients,[c] $\mu(MoK_\alpha)$, cm^{-1}	22.9	6.55

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[a] Flotation in an ethanol-dibromomethane mixture. [b] Since only two crystals were isolated (see text), an experimental density was not determined. [c] Examination of reflections with $\chi = 90 \pm 10°$ at approximately regular intervals ($\Delta 2\theta \approx 6-10°$) within the 2θ range of data collection by the psi scan technique indicated a variation of 13% in the diffracted beam intensity for the Pr-containing crystal but of only 5% for the tiron-containing crystal. Hence, an absorption correction was applied only to the data set for the more highly absorbing material (see text).

Table II. Fractional Coordinates of the Nonhydrogen

Atoms of $Pr_2(C_6Cl_2O_4)_3 \cdot 8C_2H_5OH$ (1)[a]

Atom	x	y	z
Pr	0.19991(2)	0.22649(2)	-0.21794(1)
Cl(A)	0.4343(1)	0.3231(1)	0.16502(8)
Cl(B)	0.2115(1)	-0.2240(1)	-0.06518(9)
Cl(C)	-0.3160(1)	0.1028(1)	-0.44976(9)
O(1A)	0.3166(3)	0.2842(3)	-0.0463(2)
O(2A)	0.6272(3)	0.5714(3)	0.1827(2)
O(1B)	0.1800(3)	0.0201(3)	-0.1521(2)
O(2B)	-0.0045(3)	-0.2015(3)	0.0962(2)
O(1C)	-0.0305(3)	0.1469(3)	-0.3232(2)
O(2C)	-0.2270(3)	-0.0577(3)	-0.6354(2)
O(1)	0.2451(3)	0.3288(3)	-0.3774(2)
O(2)	0.4589(3)	0.1465(3)	-0.2370(2)
O(3)	0.0550(4)	0.4242(3)	-0.2030(3)
O(4)	0.2297(5)	0.5913(4)	-0.3073(3)
C(1A)	0.4031(4)	0.3831(3)	-0.0193(3)
C(2A)	0.4697(4)	0.4198(4)	0.0748(3)
C(3A)	0.5647(4)	0.5316(3)	0.0990(3)
C(1B)	0.0988(4)	0.0038(4)	-0.0810(3)
C(2B)	0.0955(4)	-0.1029(4)	-0.0310(3)
C(3B)	0.0022(4)	-0.1113(4)	0.0487(3)
C(1C)	-0.0247(4)	0.0788(4)	-0.4067(3)
C(2C)	-0.1435(4)	0.0459(4)	-0.4760(3)
C(3C)	-0.1268(4)	-0.0201(3)	-0.5686(3)
C(1)	0.3781(7)	0.3131(7)	-0.4333(5)
C(2)	0.3626(10)	0.3341(13)	-0.5355(6)
C(3)	0.5761(8)	0.1269(9)	-0.1730(6)
C(4)	0.6287(12)	0.0050(8)	-0.1872(8)
C(5)	-0.0980(7)	0.4469(6)	-0.1732(6)
C(6)	-0.2024(9)	0.4206(9)	-0.2644(8)
C(7)	0.1965(11)	0.7075(7)	-0.3399(6)
C(8)	0.0446(13)	0.7038(10)	-0.3617(10)

[a]Numbers in parentheses are the estimated standard deviation in the

least significant digits. See Figure 2 for identity of the atoms.

Table III. Fractional Coordinations of the Atoms

of $Na_3[C_6H_2O(OH)(SO_3)_2] \cdot H_2O$ (2)[a]
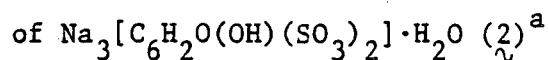
Atom	x	y	z
S(1)	0.22480(7)	1/4	0.6164(1)
S(2)	0.03679(8)	1/4	0.1526(1)
Na(1)	-0.07020(12)	1/4	0.8658(2)
Na(2)	0.35659(9)	-0.0212(2)	0.3866(1)
O(1)	0.0613(2)	1/4	0.7597(3)
O(2)	-0.0924(2)	1/4	0.6364(3)
O(3)	0.2873(2)	1/4	0.5061(3)
O(4)	0.2307(1)	0.0763(4)	0.6996(2)
O(5)	-0.0528(2)	1/4	0.1212(3)
O(6)	0.0779(1)	0.0792(4)	0.1015(2)
O(7)	0.2543(2)	1/4	0.0171(4)
C(1)	0.1269(3)	1/4	0.5365(5)
C(2)	0.0550(3)	1/4	0.6252(5)
C(3)	-0.0222(3)	1/4	0.5543(5)
C(4)	-0.0279(3)	1/4	0.4141(5)
C(5)	0.0435(3)	1/4	0.333((5)
C(6)	0.1215(3)	1/4	0.3940(5)
H(02)	-0.1439	1/4	0.5972
H(07)	0.2793	0.1660	0.0547
H(4)	-0.0817	1/4	0.3710
H(6)	0.1709	1/4	0.3374

[a]Numbers in parentheses are the estimated standard deviations in the least significant figures. See Figure 5 for identity of the atoms.

Table VIII. Bond Lengths (Å) and Bond Angles (deg) for $Pr_2(C_6Cl_2O_4)_3 \cdot 8C_2H_5OH$ (1)[a]

	chloranilate A	chloranilate B	chloranilate C	average
Pr–O(1)	2.497(2)	2.462(2)	2.498(2)	2.486(2)
Pr–O(2)	2.507(2)	2.452(2)	2.483(2)	2.481(2)
O(1)–C(1)	1.247(3)	1.253(3)	1.248(3)	1.249(3)
O(2)–C(3)	1.252(3)	1.236(3)	1.251(3)	1.246(3)
Cl–C(2)	1.731(3)	1.723(3)	1.732(3)	1.729(3)
C(3)'–C(1)	1.527(4)	1.529(4)	1.527(4)	1.528(4)
C(1)–C(2)	1.390(4)	1.402(4)	1.389(4)	1.394(4)
C(2)–C(3)	1.387(4)	1.401(4)	1.390(4)	1.393(4)
	ethanol 1	ethanol 2	ethanol 3	
Pr–O	2.601(2)	2.543(2)	2.516(2)	2.553(2)
O–C	1.437(5)	1.399(5)	1.463(5)	1.433(5)
C–C	1.435(7)	1.384(8)	1.490(9)	1.436(8)
O(1)–Pr–O(2)'	62.82(6)	63.85(6)	63.12(6)	63.26(6)
O(1)–C(1)–C(3)'	115.9(2)	115.1(3)	115.5(2)	115.5(2)
O(2)–C(3)–C(1)'	115.4(2)	115.8(2)	115.7(2)	115.6(2)
O(1)–C(1)–C(2)	125.3(2)	125.5(3)	125.6(2)	125.5(2)
O(2)–C(3)–C(2)	125.2(3)	125.0(3)	125.2(2)	125.1(3)
Cl–C(2)–C(1)	119.1(2)	119.7(2)	119.8(2)	119.5(2)
Cl–C(2)–C(3)	119.1(2)	118.8(2)	118.2(2)	118.7(2)
C(2)–C(1)–C(3)'	118.8(2)	119.5(3)	118.9(2)	119.1(2)
C(2)–C(3)–C(1)'	119.4(2)	119.1(3)	119.1(2)	119.2(2)
C(1)–C(2)–C(3)	121.8(2)	121.4(3)	122.0(2)	121.7(2)
	alcohol 1	alcohol 2	alcohol 3	average 1,2,3
O–C–C	115.8(4)	117.1(5)	107.9(5)	113.6(5)

[a] Prime refers to atoms related to those in Table II by inversion through the ring centroid. See Figure 2 for identity of the atoms. Numbers in parentheses are the esd's in the least significant figures.

Table IX. Comparison of dihedral angles δ (deg) formed by the oxygen atoms of the Pr^{3+} coordination sphere to those of the idealized $\underline{D}_{3h}$ and $\underline{C}_{4v}$ polyhedra[a]

Type of faces	Position	Idealized δ	Face 1[b]	Face 2[b]	Determined δ
			$\underline{D}_{3h}$ tricapped trigonal prism		
Opposed (⊥)	⊥ threefold axis	180	O(1A), O(1B), O(2)	O(1), O(3), O(1C)	173.4
Opposed (∥)	∥ threefold axis	146.4	O(1), O(2), O(2A)'	O(2B)', O(1C), O(1B)	154.2
			O(2A)', O(3), O(1A)	O(1C), O(1B), O(2C)'	145.1
			O(3), O(1A), O(2B)'	O(2C)', O(1), O(2)	157.4
Vicinal (∥)	∥ threefold axis	26.4	O(1), O(2), O(2C)'	O(1), O(2), O(2A)'	28.7
			O(3), O(1A), O(2A)'	O(3), O(1A), O(2B)'	21.7
			O(1C), O(1B), O(2B)'	O(1C), O(1B), O(2C)'	30.5
			$\underline{C}_{4v}$ monocapped square antiprism		
Opposed	1 vertex on square face	163.5	O(1A), O(2), O(1B)	O(3), O(1), O(1C)	173.4
			O(2B)', O(1B), O(1C)	O(2A)', O(2), O(1)	154.2
Opposed	2 vertices on square face	138.2	O(1A), O(2B)', O(1B)	O(2A)', O(3), O(1)	128.4
			O(2B)', O(3), O(1C)	O(1A), O(2A)', O(2)	144.6
Vicinal (⊥)	⊥ fourfold axis	0	O(1A), O(2A)', O(3)	O(1A), O(2B)', O(3)	21.7
			O(2A)', O(1A), O(2B)'	O(2A)', O(3), O(2B)'	24.8

[a]Shape-determining dihedral angles for these idealized polyhedra and definition of face type as given in Ref. 61. [b]See Figures 2 and 4 for identity of atoms. Primed atoms are related to the positions of the correspondingly numbered unprimed atoms of Table II by transformations 1-$\underline{x}$, 1-$\underline{y}$, $\bar{\underline{z}}$, $\bar{\underline{x}}$, $\bar{\underline{y}}$, $\bar{\underline{z}}$, and $\bar{\underline{x}}$, $\bar{\underline{y}}$, -1-$\underline{z}$ for O(2A)', O(2B)', and O(2C)', respectively.

Table X. Bond Lengths (Å) and Bond Angles (deg)

for $Na_3[C_6H_2O(OH)(SO_3)_2]\cdot H_2O$ (2)[a]

C(1)-C(2)	1.438(4)	S(1)-O(3)	1.466(2)
C(2)-C(3)	1.415(4)	S(1)-O(4)	1.458(2)
C(3)-C(4)	1.363(5)	S(2)-C(5)	1.762(3)
C(4)-C(5)	1.382(5)	S(2)-O(5)	1.466(2)
C(5)-C(6)	1.378(4)	S(2)-O(6)	1.448(2)
C(6)-C(1)	1.385(4)	C(2)-O(1)	1.308(4)
S(1)-C(1)	1.749(3)	C(3)-O(2)	1.378(4)

C(2)-C(1)-C(6)	123.1(3)	C(4)-C(5)-S(2)	120.8(2)
C(2)-C(1)-S(1)	116.9(2)	S(2)-C(5)-C(6)	118.5(2)
C(6)-C(1)-S(1)	119.9(2)	C(5)-C(6)-C(1)	118.6(3)
C(1)-C(2)-C(3)	114.2(3)	C(1)-S(1)-O(3)	106.8(1)
C(1)-C(2)-O(1)	122.3(3)	C(1)-S(1)-O(4)	107.6(1)
O(1)-C(2)-C(3)	123.5(3)	O(3)-S(1)-O(4)	111.1(1)
C(2)-C(3)-C(4)	122.9(3)	O(4)-S(1)-O(4)'	112.3(1)
C(2)-C(3)-O(2)	115.6(3)	C(5)-S(2)-O(5)	105.4(1)
O(2)-C(3)-C(4)	121.5(3)	C(5)-S(2)-O(6)	108.3(1)
C(3)-C(4)-C(5)	120.4(3)	O(5)-S(2)-O(6)	112.0(1)
C(4)-C(5)-C(6)	120.8(3)	O(6)-S(2)-O(6)'	110.6(1)

[a]Numbers in parentheses are the estimated standard deviations in the least significant digits. See Figure 5 for identity of the atoms. O(4)' and O(6)' are related to the coordinates given for O(4) and O(6) in Table III by the symmetry operation x, 1/2-y, z.

FIGURE CAPTIONS

Figure 1. Packing of the $Pr_2(C_6Cl_2O_4)_3(C_2H_5OH)_6$ units. Atoms are shown as ellipsoids of 15% probability. Hydrogen atoms (of the C_2H_5OH molecules) have been omitted for clarity. Hydrogen bonds are drawn as thin lines.

Figure 2. Stereoscopic view of the Pr^{3+} complex illustrating the atom numbering scheme. Atoms are drawn as spheres of 50% probability. The thermal motion of the ethanol carbon atoms has been artificially reduced and hydrogen atoms omitted for clarity.

Figure 3. Comparison of the molecular geometry of chloranilate ligand as the uncomplexed and neutral molecule, as the NH_4^+ salt,[15] and in the Pr^{3+} complex.

Figure 4. Projection normal to the plane formed by the vectors between atoms (O2A)' and O(2B)' and O(2A)' and O(2C)'; that is, approximately down the pseudo-$\underline{C}_3$ axis of the Pr^{3+} coordination polyhedron. Primed atoms are related to the correspondingly names unprimed atoms of Table II by the symmetry operations given in the caption of Table IX.

Figure 5. Perspective drawing of the $[C_6H_2O(OH)(SO_3)_2]^{3-}$ ion indicating the atom numbering scheme. Nonhydrogen atoms are drawn as ellipsoids of 50% probability, and hydrogen atoms as spheres of radius 0.1 Å.
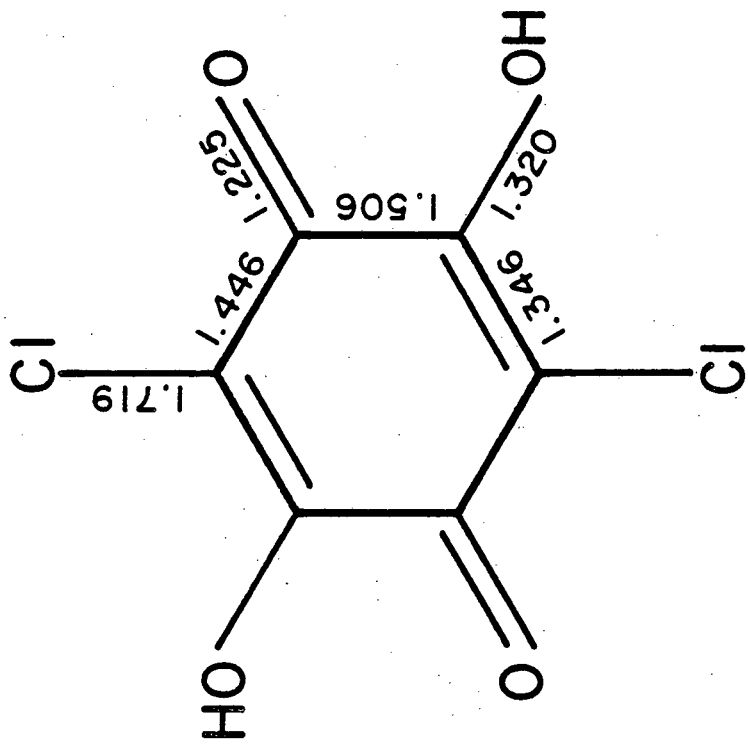
Figure 6. Stereoscopic view of the packing of the $[C_6H_2O(OH)(SO_3)_2]^{3-}$ ions, Na^+ ions (partially shaded), and H_2O molecules of $\underset{\sim}{2}$. Atoms are drawn as ellipsoids of 15% probability; hydrogen atoms have been omitted for clarity. Hydrogen bonds and Na^+-O bonds are drawn as thin lines.

XBL 829-9627
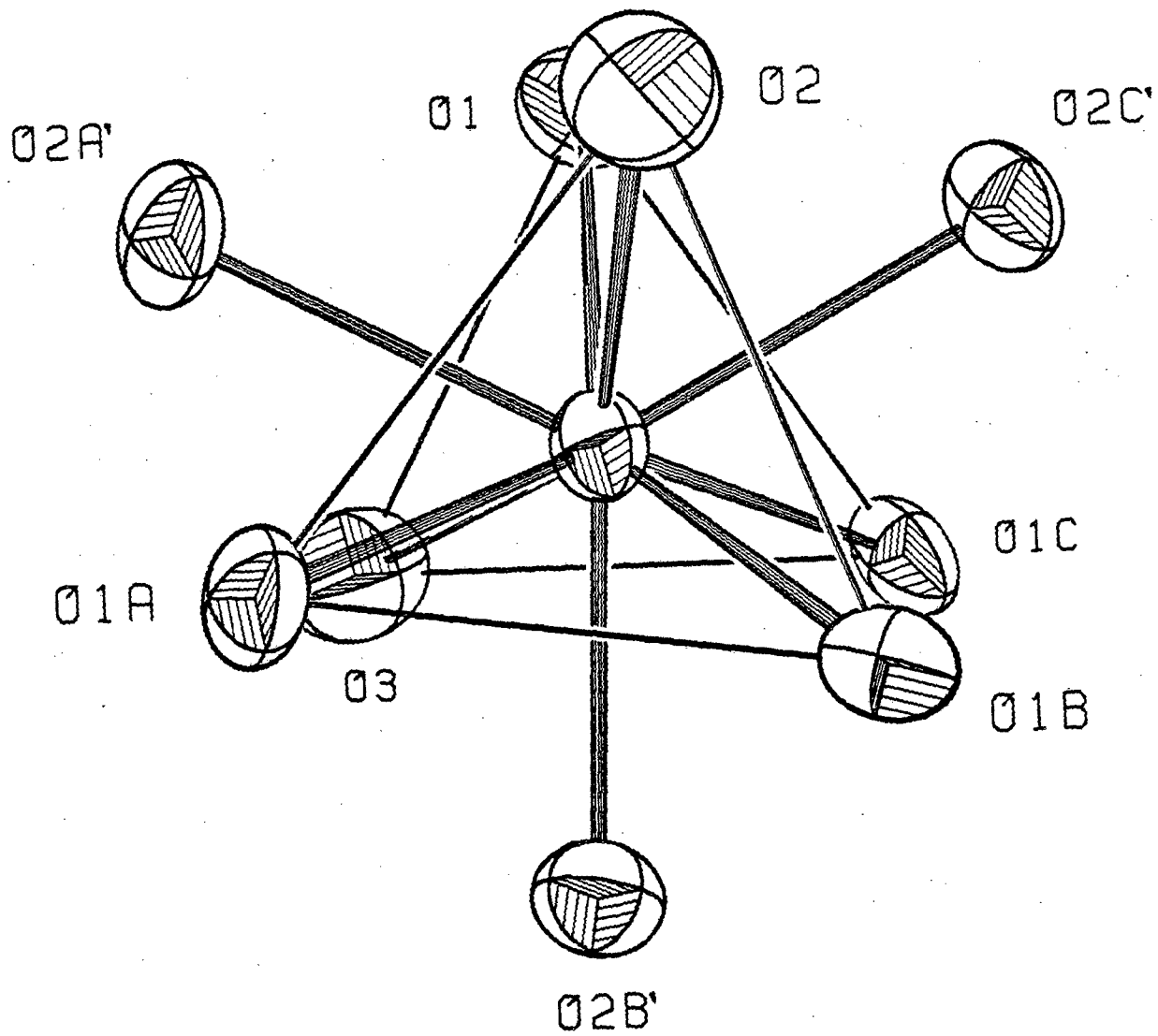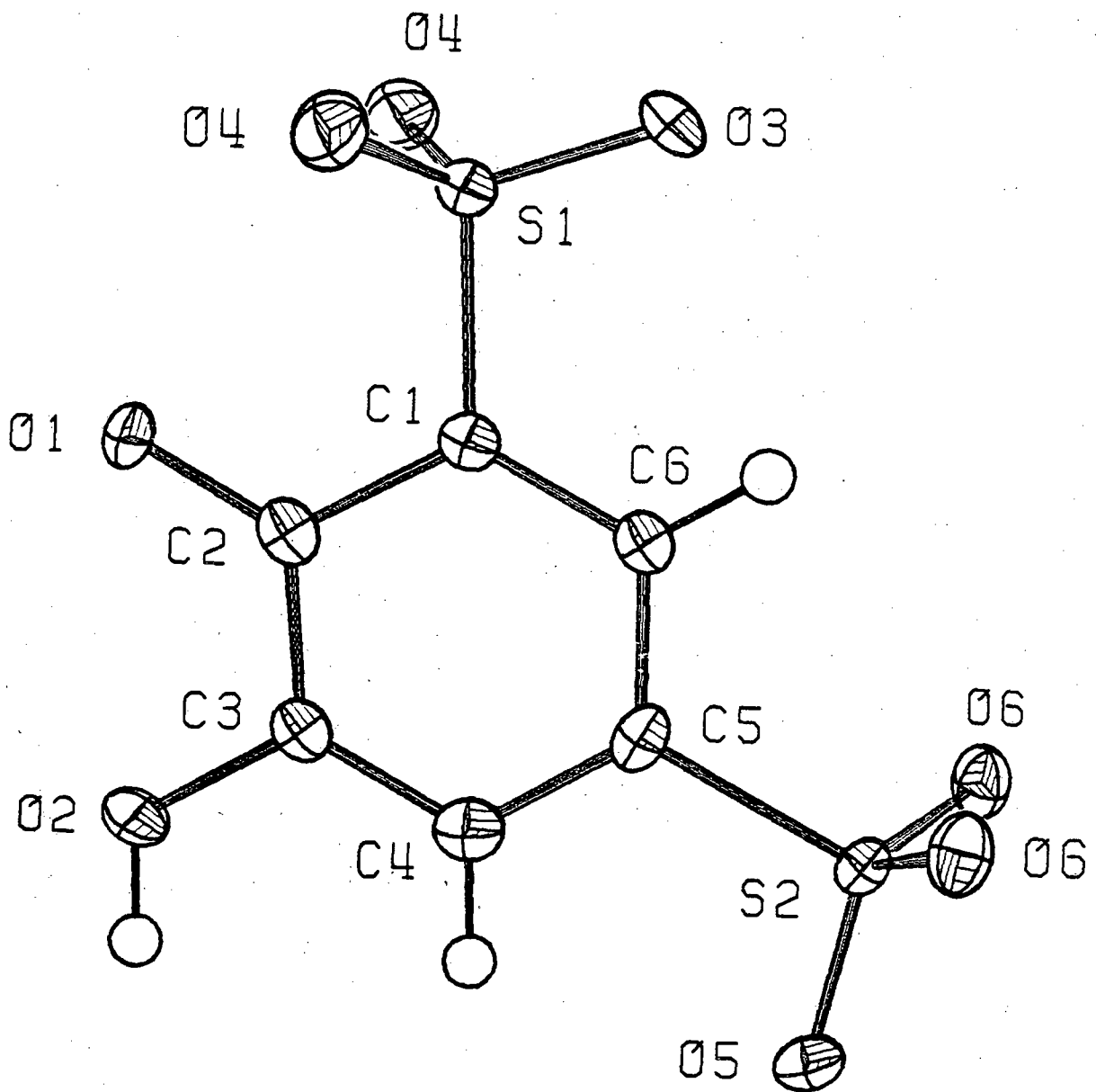
O2A' O1 O2 O2C'
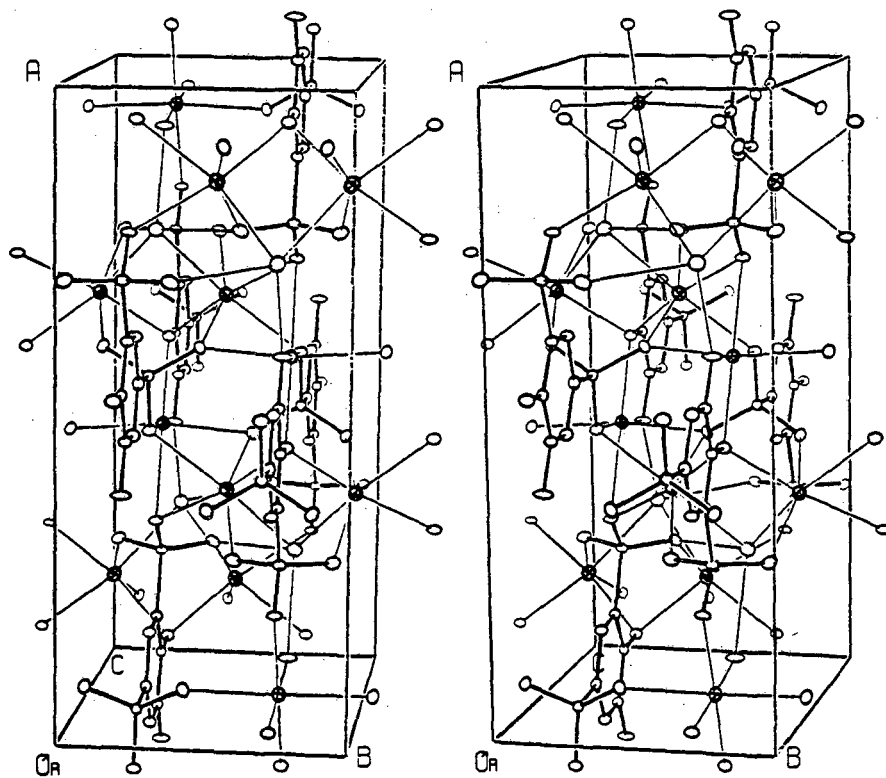
O1A

O3

O1C

O1B

O2B'
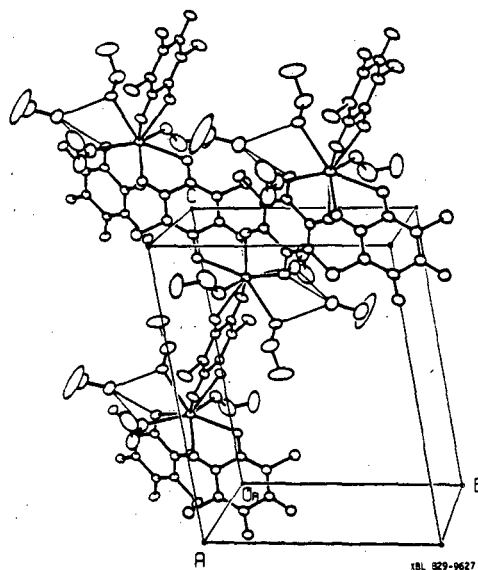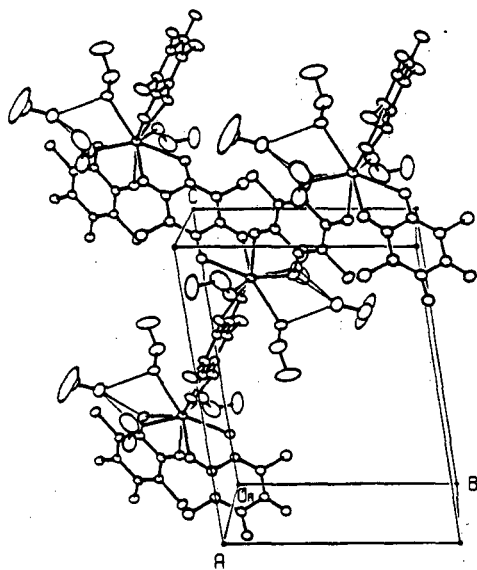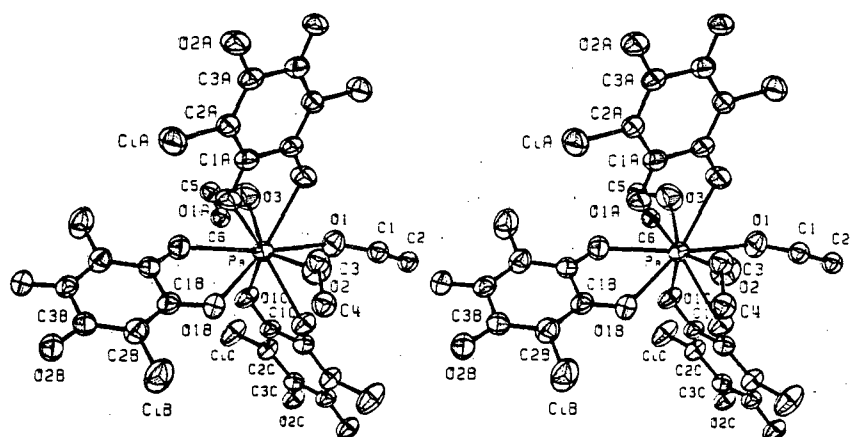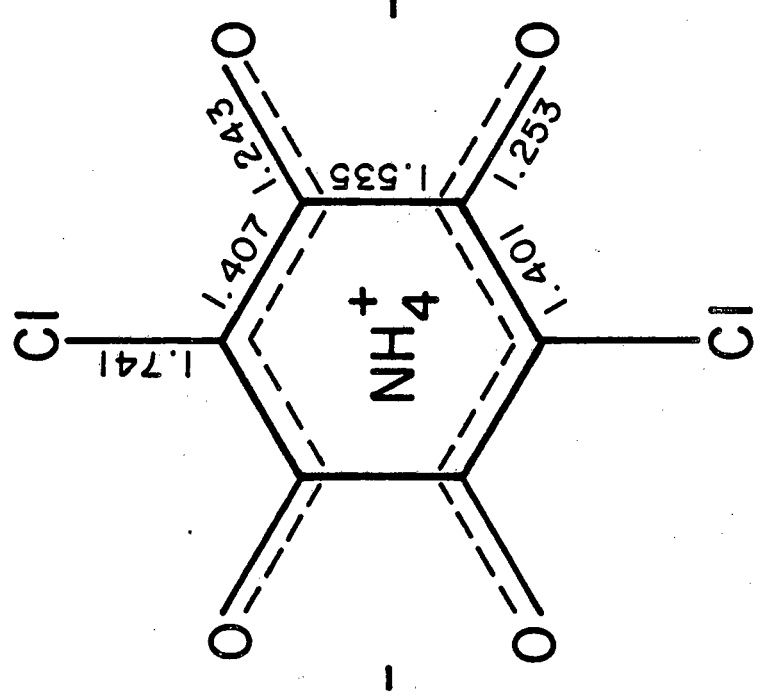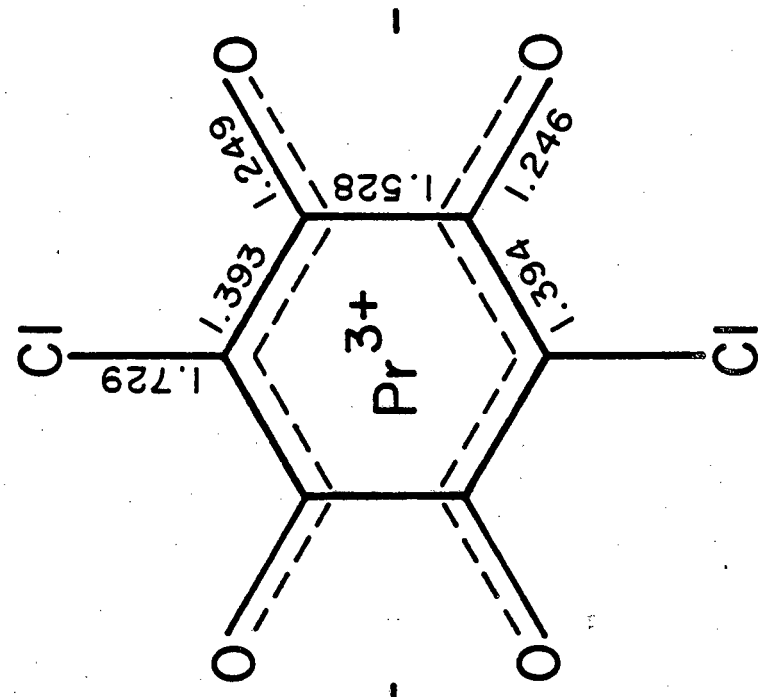
XBL 829-9625

XBL 818-11488