

Contribution from the Department of Chemistry and Materials and Molecular Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720

Preparation of Praseodymium(III) Chloranilate and the Crystal Structures of $\text{Pr}_2(\text{C}_6\text{Cl}_2\text{O}_4)_3 \cdot 8\text{C}_2\text{H}_5\text{OH}$ and $\text{Na}_3[\text{C}_6\text{H}_2\text{O}(\text{OH})(\text{SO}_3)_2] \cdot \text{H}_2\text{O}$

PAUL E. RILEY, SALIM F. HADDAD,¹ and KENNETH N. RAYMOND*

Received September 8, 1982

The crystal structure of $\text{Pr}_2(\text{C}_6\text{Cl}_2\text{O}_4)_3 \cdot 8\text{C}_2\text{H}_5\text{OH}$ (**1**), a complex obtained by slow hydrolysis of *o*-chloranil ($\text{C}_6\text{Cl}_4\text{O}_2$) in acidic ethanol solution, has been determined by single-crystal X-ray diffraction techniques with data collected by counter methods. The structure of $\text{Na}_3[\text{C}_6\text{H}_2\text{O}(\text{OH})(\text{SO}_3)_2] \cdot \text{H}_2\text{O}$ (**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) Å, $b = 10.503$ (2) Å, $c = 13.598$ (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 $\text{Pr}_2(\text{C}_6\text{Cl}_2\text{O}_4)_3 \cdot 8\text{C}_2\text{H}_5\text{OH}$ per unit cell. The crystal structure is a three-dimensional network of alternating $(\text{C}_6\text{Cl}_2\text{O}_4)^{2-}$ 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 with use of 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) Å, $b = 6.972$ (2) Å, and $c = 9.700$ (1) Å. The $[\text{C}_6\text{H}_2\text{O}(\text{OH})(\text{SO}_3)_2]^{3-}$ 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 with use of 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 catecholates 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 $\{[\text{Ce}(\text{cat})_4]^{4-}/[\text{Ce}(\text{cat})_4]^{5-}, E^0 \cong -0.45 \text{ V}$, whereas $\text{Ce}^{4+}/\text{Ce}^{3+}, E^0 \cong +1.70 \text{ V}\}$,⁴ we have pursued the possibility of isolating a Pr(IV) complex with electronegative catecholates or their derivatives. To this end, *o*-chloranil ($\text{C}_6\text{Cl}_4\text{O}_2$), a chlorinated benzoquinone that is known⁵⁻⁹ to be easily reduced to the semiquinone $(\text{C}_6\text{Cl}_4\text{O}_2)^{\cdot-}$ and the catecholate $(\text{C}_6\text{Cl}_4\text{O}_2)^{2-}$, 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 Kaftory¹¹ 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 re-

ported 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 that 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) ions¹⁶⁻²³ 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 determination²⁴⁻²⁹ in which barium chloranilate is

- (1) On leave from the Chemistry Department, University of Jordan, Amman, Jordan.
- (2) Raymond, K. N.; Smith, W. L.; Weitl, F. L.; Durbin, P. W.; Jones, E. S.; Abu-Dari, K. *ACS Symp. Ser.* **1980**, No. 131, 143.
- (3) Raymond, K. N.; Harris, W. R.; Carrano, C. J.; Weitl, F. L. *ACS Symp. Ser.* **1980**, No. 140, 313.
- (4) Sofen, S. R.; Cooper, S. R.; Raymond, K. N. *Inorg. Chem.* **1979**, *18*, 1611.
- (5) Pierpont, C. G.; Downs, H. H.; Rukavina, T. G. *J. Am. Chem. Soc.* **1974**, *96*, 5573.
- (6) Pierpont, C. G.; Downs, H. H. *Inorg. Chem.* **1975**, *14*, 343.
- (7) Pierpont, C. G.; Downs, H. H. *J. Am. Chem. Soc.* **1975**, *97*, 2123.
- (8) Pierpont, C. G.; Downs, H. H. *J. Am. Chem. Soc.* **1976**, *98*, 4834.
- (9) Buchanan, R. M.; Kessel, S. L.; Downs, H. H.; Pierpont, C. G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1978**, *100*, 7894.
- (10) Ksenzhek, O. S.; Petrova, S. A.; Oleinik, S. V.; Kolodyazhnyi, M. V.; Moskovskii, V. Z. *Elektrokhimiya* **1977**, *13*, 48.
- (11) Herbstein, F. H.; Kaftory, M. *J. Appl. Crystallogr.* **1972**, *5*, 51.
- (12) Graebe, U. *Justus Liebigs Ann. Chem.* **1891**, *24*, 263.
- (13) Andersen, E. K. *Acta Crystallogr.* **1967**, *22*, 188.
- (14) Andersen, E. K. *Acta Crystallogr.* **1967**, *22*, 191.
- (15) Andersen, E. K. *Acta Crystallogr.* **1967**, *22*, 196.
- (16) Hostyn, L.; Hostynova, D. *Cesk. Patol.* **1973**, *9*, 105.
- (17) Chaplin, A. J.; Grace, S. R. *Histochemistry* **1976**, *47*, 263.
- (18) Marone, C. B.; Bianchi, G. *An. Chim.* **1973**, *69*, 205.
- (19) Frizanova, M.; Reis, A.; Hainberger, L. *Fresenius' Z. Anal. Chem.* **1972**, *261*, 400.
- (20) Poirier, J. M.; Verchere, J. F. *Talanta* **1979**, *26*, 349.
- (21) Floh, B.; Abrao, A.; Federgrun, L. *Inst. Energ. At. (Sao Paulo), Publ. IEA* **1976**, 427.
- (22) Cortinez, V. A.; Marone, C. B. *Quim. Anal.* **1976**, *30*, 33.
- (23) Baudino, O.; Cortinez, Marone, C. *Rev. Asoc. Bioquim. Argent.* **1976**, *41*, 212.
- (24) Howes, J. E.; Pesut, R. N.; Foster, J. F. American Society for Testing Materials, Method D 3226-73 T, 1976.
- (25) Kubadinow, N.; Forsthuber, J. *Zuckerindustrie (Berlin)* **1979**, *104*, 1019.
- (26) Driscoll, J. N.; Berger, A. W.; Becker, J. H.; Sommers, C. S. *Int. J. Environ. Anal. Chem.* **1974**, *3*, 293.
- (27) Murakawi, T.; Kamaya, M.; Shinozaki, J.; Kanari, Y. *Bunseki Kagaku* **1979**, *28*, 623.

* To whom correspondence should be addressed at the Department of Chemistry.

used to precipitate BaSO₄. 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 widespread use, chloranilic acid complexes and water-insoluble salts have not been structurally well characterized.³⁶ Accordingly, we undertook the determination of the crystal structure of Pr₂(C₆Cl₂O₄)₃·8C₂H₅OH (1), which is a prototypical insoluble metal(3+) chloranilate.

In addition, we have also determined the crystal structure of the sodium salt of the substituted catecholate, tiron, Na₃[C₆H₂O(OH)(SO₃)₂]₂·H₂O (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 Section

Preparation of Pr₂(C₆Cl₂O₄)₃·8C₂H₅OH and Ag₂(C₆Cl₂O₄). The praseodymium salt was prepared by heating PrCl₃·6H₂O (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 1/2 h 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 the solution 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(NO₃) to the praseodymium salt. Heating silver chloranilate in 1 M HNO₃ precipitates AgCl.

The infrared spectrum of dried praseodymium(III) chloranilate in KBr shows a major band centered about 1500 cm⁻¹, which exhibits 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 mercury(2+) and lanthanum(3+) chloranilate salts.^{37,38}

Anal. Calcd for Pr₂(C₆Cl₂O₄)₃·8C₂H₅OH: C, 32.12; H, 3.81; Cl, 16.73. Found: C, 28.17; H, 3.63; Cl, 18.0.

Anal. Calcd for Ag₂(C₆Cl₂O₄)₃: C, 17.04; Cl, 16.78. Found: C, 16.74; Cl, 18.38.

X-ray Crystallography. Pr₂(C₆Cl₂O₄)₃·8C₂H₅OH (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

Table I. Crystallographic Summary

	Pr ₂ (C ₆ Cl ₂ O ₄) ₃ ·8C ₂ H ₅ OH (1)	Na ₃ [C ₆ H ₂ O(OH)(SO ₃) ₂] ₂ ·H ₂ O (2)
<i>a</i> , Å	8.990 (1)	16.018 (2)
<i>b</i> , Å	10.503 (2)	6.972 (2)
<i>c</i> , 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
<i>V</i> , Å ³	1263.3 (6)	1083.3 (6)
<i>d</i> _{measd} , g cm ⁻³	1.643 ^a	<i>b</i>
<i>d</i> _{calcd} , g cm ⁻³	1.671	2.171
<i>Z</i>	2	4
mol formula	C ₁₇ H ₂₄ Cl ₃ O ₁₀ Pr	C ₆ H ₅ Na ₃ O ₉ S ₂
fw	635.64	354.19
cryst syst	triclinic	orthorhombic
systematic absences	none	0 <i>kl</i> , <i>k</i> + <i>l</i> = 2 <i>n</i> + 1; <i>hk</i> 0, <i>h</i> = 2 <i>n</i> + 1
space group	<i>P</i> $\bar{1}$ (No. 2)	<i>Pnma</i> (No. 62)
<i>p</i>	0.04	0.02
2θ range, deg	3.0-45.0	3.0-50.0
total reflns measd	3297	1038
data cryst dimens, mm	0.13 × 0.21 × 0.27	0.11 × 0.14 × 0.23
data cryst faces	($\bar{1}$ 10), ($\bar{1}$ 10), (010), (010), (001), (001)	(100), ($\bar{1}$ 00), (010), (010), (001), (001), (101), ($\bar{1}$ 01)
abs coeff ^c , μ(Mo Kα), cm ⁻¹	22.9	6.55

^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 $\chi = 90 \pm 10^\circ$ at approximately regular intervals ($\Delta 2\theta \approx 6-10^\circ$) within the 2θ range of data collection by the ψ -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).

photographs indicated the triclinic space groups *P*1 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 previously³⁹ and summarized in Table I. The measured intensities were reduced and assigned standard deviations with a *p* value given in Table I.⁴⁰

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 $F_o^2 > 3\sigma(F_o^2)$ as described previously.⁴¹ Refinement of positional and anisotropic thermal parameters for all 31 non-hydrogen atoms converged to *R* and *R_w* indices⁴² of 0.036 and 0.057, respectively. [Application of an absorption correction (see Table I) reduced the *R* index by 0.009.] Unequivocal assignment of hydrogen atom positions 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 Å⁻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, $\bar{1}\bar{1}1$, 01 $\bar{2}$, 21 $\bar{3}$) were rejected as poorly determined data. Inclusion of a correction for secondary extinction in the final refinement reduced *R* (*R_w*) to 0.025 (0.040). The final error in an observation of unit weight is 1.8.⁴²

Na₃[C₆H₂O(OH)(SO₃)₂]₂·H₂O (2). 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

(28) Khan, S. U.; Morris, G. F.; Hidiraglou, M. *Microchem. J.* **1979**, *24*, 291.

(29) Raber, H.; Likussar, W.; Gill, D. *Int. J. Environ. Anal. Chem.* **1976**, *4*, 251.

(30) Meditsch, J.; Coimbra, L. *Rev. Quim. Ind. (Rio de Janeiro)* **1970**, *39*, 458.

(31) Abe, S.; Kikuchi, H. *Mikrochim. Acta* **1975**, *4*, 379.

(32) Humphry, R. E.; Hinze, W. *Anal. Chem.* **1971**, *43*, 1100.

(33) Mehra, M. C.; O'Brien, P. *Mikrochim. Acta* **1976**, *2*, 603.

(34) Raber, H.; Gagliardi, E.; Meisterhofer, H. *Mikrochim. Acta* **1976**, *2*, 71.

(35) Novacek, L.; Semenkova, L.; Slovak, Z. *Cesk. Farm.* **1974**, *23*, 366.

(36) The structures of the Ni²⁺ and Cu²⁺ complexes of chloroanilate have been reported: Pierpont, C. G.; Francesconi, L. C.; Hendrickson, D. N. *Inorg. Chem.* **1977**, *16*, 2367.

(37) "The Aldrich Library of Infrared Spectra", 2nd ed.; Pouchert, C. J., Ed; Aldrich Chemical Co.: Milwaukee, WI, 1975; pp 240-241.

(38) Principal infrared bands (cm⁻¹): Pr₂(C₆Cl₂O₄)₃ 1615 m, 1500 vs, 1380 s, 1295 m, 1000 m, 950 s, 605 w, 580 m, 445 m, 385 w; Ag₂(C₆Cl₂O₄)₃ 1610 m, 1515 vs, 1380 w, 1275 w, 990 w, 830 s, 565 s, 355 w.

(39) Eigenbrot, C. W.; Jr.; Raymond, K. N. *Inorg. Chem.* **1982**, *21*, 2653.

(40) The computer program package used in this work is cited in ref 39.

(41) The function minimized in refinement is $\sum w(|F_o| - |F_c|)^2$, where the weight is $4F_o^2/\sigma^2(F_o^2)$, the reciprocal square of the standard deviation of each observation $|F_o|$.

(42) The error indices are $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$, and an error in an observation of unit weight = $[\sum w(|F_o| - |F_c|)^2 / (N_o - N_v)]^{1/2}$, where *N_o* is the number of observations $|F_o|$ and *N_v* is the number of variables in refinement.

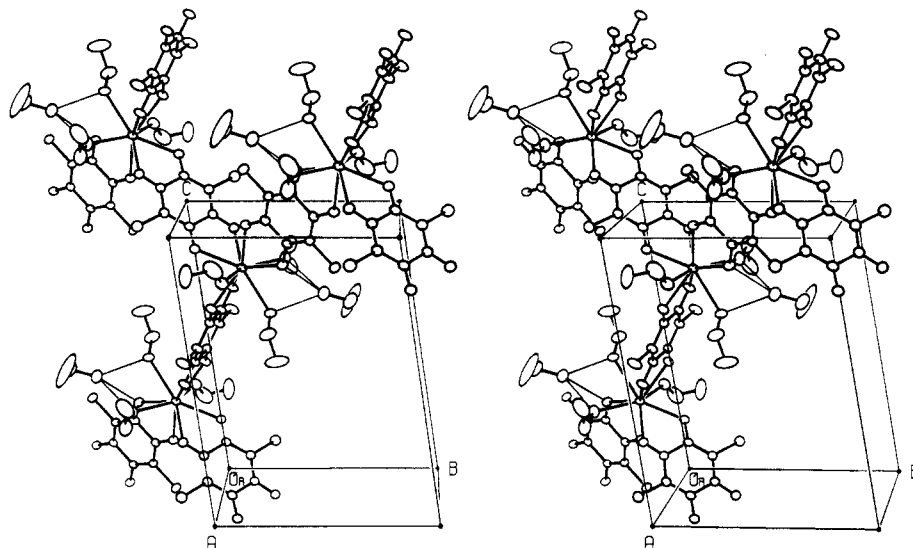


Figure 1. Packing of the $\text{Pr}_2(\text{C}_6\text{Cl}_2\text{O}_4)_3(\text{C}_2\text{H}_5\text{OH})_6$ units. Atoms are shown as ellipsoids of 15% probability. Hydrogen atoms (of the $\text{C}_2\text{H}_5\text{OH}$ molecules) have been omitted for clarity. Hydrogen bonds are drawn as thin lines.

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 $24^\circ < 2\theta < 28^\circ$, 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)⁴⁰ 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 non-hydrogen atoms were refined and hydrogen atoms were maintained either at idealized positions⁴³ (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.⁴² 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 $\sim 0.3 \text{ e } \text{\AA}^{-3}$ 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 non-hydrogen atoms of **1** and **2**. Tabulations of anisotropic thermal parameters (Tables IV and V) and structure factor amplitudes (Tables VI and VII) are available.⁴⁴

Results and Discussion

$\text{Pr}_2(\text{C}_6\text{Cl}_2\text{O}_4)_3 \cdot 8\text{C}_2\text{H}_5\text{OH}$ (1**).** The crystal structure of **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, $(\frac{1}{2}, \frac{1}{2}, 0)$, $(0, 0, 0)$, and $(0, 0, -\frac{1}{2})$ 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

Table II. Fractional Coordinates of the Non-Hydrogen Atoms of $\text{Pr}_2(\text{C}_6\text{Cl}_2\text{O}_4)_3 \cdot 8\text{C}_2\text{H}_5\text{OH}$ (**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.

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 praseodymium(III) chloranilate network. None of the hydrogen atoms were 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

(43) The C-H bonds were constrained to 0.95 Å in accordance with a previous study: Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213.

(44) Supplementary material.

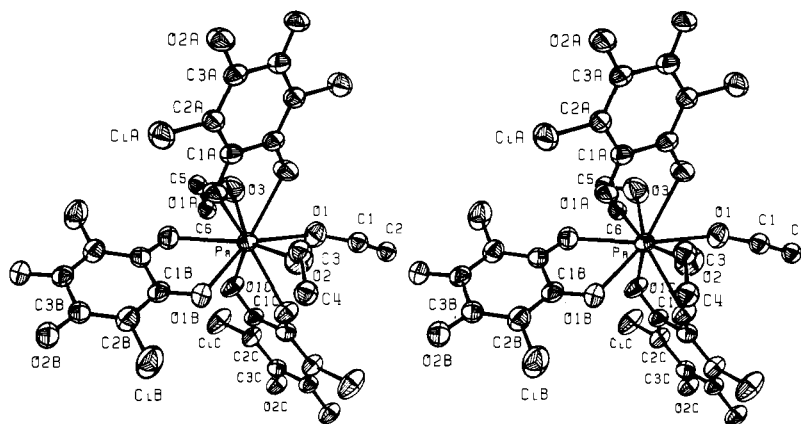


Figure 2. Stereoscopic view of the Pr³⁺ complex illustrating the atom numbering scheme. Atoms are drawn as spheres of 50% probability. The thermal motion of the ethanol carbon atoms has been artificially reduced, and hydrogen atoms have been omitted for clarity.

Table III. Fractional Coordinates of the Atoms of Na₃[C₆H₂O(OH)(SO₃)₂]₂·H₂O (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	0.3330 (5)
C(6)	0.1215 (3)	1/4	0.3940 (5)
H(O2)	-0.1439	1/4	0.5972
H(O7)	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.

in the structure of the NH₄⁺ salt.¹⁵ The Pr³⁺ 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 the C—O bond distance found in insoluble oxalates such as in hydrated calcium oxalate (1.25 Å).⁴⁵ 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*-benzoquinone is at 1175 cm⁻¹.⁴⁶) The bond distances within the C₆ rings of A, B, and C are consistent with a bond order of 1.5 for the C(Cl)—C(O) bonds (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,

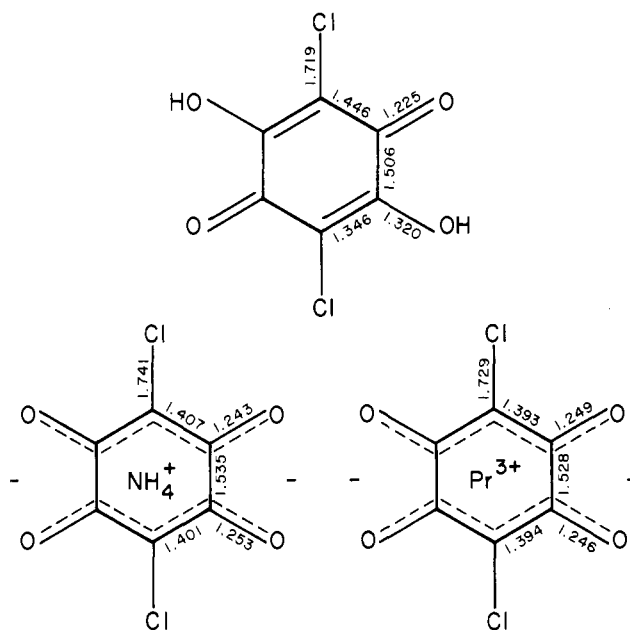


Figure 3. Comparison of the molecular geometry of chloranilate ligand as the uncomplexed and neutral molecule, as the NH₄⁺ salt,¹⁵ and in the Pr³⁺ complex.

the sum of ionic radii for Pr³⁺ (CN = 8) and O²⁻ (CN = 2) is 2.48 Å and for Pr³⁺ (CN = 9) is 2.53 Å.⁴⁷ Characterization of this nine-coordinate Pr³⁺ 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.⁴⁸ Indeed, a survey of the literature shows that a coordination number of nine is preferred by Pr³⁺, if the ligands are compact bidentate oxygen donors such as carboxylates or oxalates. For example, praseodymium(III) oxalate⁴⁹ 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; praseodymium(III) nitrilotriacetate⁵⁰ is nine-coordinate, with an average Pr—O(acetato), Pr—O(water), and Pr—N distance of 2.51, 2.52, and 2.68 Å, respectively; praseodymium(III) iminodiacetate⁵¹ is nine-coordinate, with an average Pr—O(acetato) distance of 2.48 Å and Pr—O(water) distance of 2.54 Å; and praseodymium(III) nicotinate⁵² is nine-coor-

(45) Sterling C. *Acta Crystallogr.* **1965**, *18*, 917.

(46) Sofen, S. R. Ph.D. Dissertation, The University of California, Berkeley, CA, 1979.

(47) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *A32*, 751.

(48) Albertsson, J.; Oskarsson, A. *Acta Chem. Scand.* **1968**, *22*, 1700.

(49) Ollendorff, W.; Weigel, F. *Inorg. Nucl. Chem. Lett.* **1969**, *5*, 263.

(50) Martin, L. L.; Jacobson, R. A. *Inorg. Chem.* **1972**, *11*, 2785.

(51) Albertsson, J.; Oskarsson, A. *Acta Chem. Scand., Ser. A* **1974**, *A28*, 347.

(52) Aslanov, L. A.; Abdul'minev, I. K.; Porai-Koshits, M. A. *Zh. Strukt. Khim.* **1972**, *13*, 468.

Table VIII. Bond Lengths (Å) and Bond Angles (deg) for Pr₂(C₆Cl₂O₄)₃·8C₂H₅OH (1)^a

	chloranilate A	chloranilate B	chloranilate C	av
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	av
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	av 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 Pr³⁺ Coordination Sphere to Those of the Idealized D_{3h} and C_{4v} Polyhedra^a

type of faces	position	idealized δ	face 1 ^b	face 2 ^b	determined δ
D _{3h} Tricapped Trigonal Prism					
opposed (\perp)	\perp threefold axis	180	O(1A), O(1B), O(2)	O(1), O(3), O(1C)	173.4
opposed (\parallel)	\parallel 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 (\parallel)	\parallel 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
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 (\perp)	\perp 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 62. ^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 $1-x$, $1-y$, z ; \bar{x} , \bar{y} , \bar{z} ; and \bar{x} , \bar{y} , $-1-z$ for O(2A)', O(2B)', and O(2C)', respectively.

dinate, with an average Pr-O(acetato) distance of 2.46 Å and Pr-O(water) distance of 2.49 Å.⁵³

In contrast, the more bulky β -diketonates (which form six-membered chelate rings with the metal as compared to four-membered rings for acetates and five-membered rings for oxalates and chloranilate) tend to form complexes with Pr³⁺ that are less than nine-coordinate. This is particularly the case in the trifluoro-1-(2-thienyl)-1,3-butanedione complex (CN = 8).^{54,55} However dimer formation through bridging ligands tends to increase the coordination number: the shift reagent 3-trifluoroacetyl-*d*-camphor⁵⁴ is an asymmetric β -diketonato ligand that forms a dimeric Pr³⁺ complex with CN = 9. Other examples of this type are the dimeric complex with hepta-

fluoro-7,7-dimethyl-4,6-octanedione, which contains two bridging carbonyl oxygen atoms and one bridging water oxygen (CN = 8),⁵⁶ and the dimeric complex with tetramethyl-3,5-heptanedione that has two bridging carbonyl oxygen atoms (CN = 7).⁵⁷

There are striking similarities between this ethanol-solvated praseodymium(3+) chloranilate complex and the hydrated lanthanide oxalates.⁵⁸⁻⁶¹ In both cases the planar ligands (C₆Cl₂O₄²⁻ and C₂O₄²⁻) coordinate with two metal ions to form polymeric networks in which the metal ions bond to three

(53) One Pr-O(acetato) distance of 2.90 Å in this complex is not averaged with the other Pr-O(acetato) distances since the oxygen atom is shared by two Pr³⁺ ions.

(54) Cunningham, J. A.; Sievers, R. E. *J. Am. Chem. Soc.* **1975**, *97*, 1586.

(55) Lalancette, R. A.; Cefola, M.; Hamilton, W. C.; La Placa, S. J. *Inorg. Chem.* **1967**, *6*, 2127.

(56) De Villiers, J. P. R.; Boeyens, J. C. A. *Acta Crystallogr., Sect. B* **1971**, *B27*, 692.

(57) Erasmus, C. S.; Boeyens, J. C. A. *Acta Crystallogr., Sect. B* **1970**, *B26*, 1843.

(58) Weigel, V. F.; Ollendorff, W.; Scherer, V.; Hagenbruch, R. Z. *Anorg. Allg. Chem.* **1966**, *345*, 119.

(59) Hansson, E.; Albertsson, J. *Acta Chem. Scand.* **1968**, *22*, 1682.

(60) Hansson, E. *Acta Chem. Scand.* **1970**, *24*, 2969.

(61) Hansson, E. *Acta Chem. Scand.* **1973**, *27*, 2852.

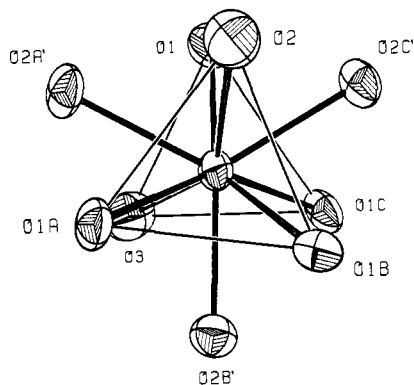


Figure 4. Projection normal to the plane formed by the vectors between atoms O(2A)' and O(2B)' and O(2A)' and O(2C)', i.e., approximately down the pseudo-C₃ axis of the Pr³⁺ coordination polyhedron. Primed atoms are related to the correspondingly named unprimed atoms of Table II by the symmetry operations given in the caption of Table IX.

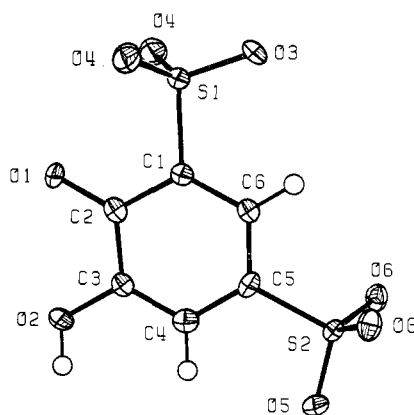


Figure 5. Perspective drawing of the [C₆H₂O(OH)(SO₃)₂]³⁻ ion indicating the atom numbering scheme. Non-hydrogen atoms are drawn as ellipsoids of 50% probability and hydrogen atoms as spheres of radius 0.1 Å.

C₂O₂⁻ fragments and to three solvent molecules. There are solvent molecules that are held interstitially but that 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^{62,63} of the coordination geometry formed by the nine oxygen atoms bound to Pr³⁺ is summarized in Table IX. As discussed in our recent study⁶⁴ of a nine-coordinate thorium complex, the two most plausible polyhedra are the tricapped trigonal prism (*D*_{3h}) and the monocapped square antiprism (*C*_{4v}). Although the geometry of this complex is, as shown in Table IX, intermediate between these two nearly equal energy⁶² idealized polyhedra, it is clear that this coordination polyhedron has approximate *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-C₃ 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 confor-

Table X. Bond Lengths (Å) and Bond Angles (deg) for Na₃[C₆H₂O(OH)(SO₃)₂]-H₂O (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 $x, \frac{1}{2} - y, z$.

mation. Furthermore, the values of the equatorial bond angles at Pr³⁺ 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 *D*_{3h} than *C*_{4v}.

Na₃[C₆H₂O(OH)(SO₃)₂]-H₂O (2). Figure 5 is a drawing of the [C₆H₂O(OH)(SO₃)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 [C₆H₂O(OH)(SO₃)₂]³⁻ and Na(1) ions lying in the mirror planes at $y = \pm 1/4$ (shown in Figure 6).⁴⁴ 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 pseudooctahedral 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) Å⁶⁵] 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.⁶⁶ 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

(62) Guggenberger, L. J.; Muettterties, E. L. *J. Am. Chem. Soc.* **1976**, *98*, 7221.

(63) Robertson, B. E. *Inorg. Chem.* **1977**, *16*, 2735.

(64) Riley, P. E.; Abu-Dari, K.; Raymond, K. N. *Inorg. Chem.*, in press.

(65) A mean bond length is given by $\bar{l} = \sum l_i/n$ and its standard deviation by $\{[\sum (l_i - \bar{l})^2 / (n(n-1))]\}^{1/2}$, where n is the number of equivalent bonds.

(66) Couldwell, C.; Prout, K.; Robey, D.; Taylor, R. *Acta Crystallogr., Sect. B* **1978**, *B34*, 1491.

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).

Acknowledgment. We thank Dr. Fred Hollander of the Berkeley CHEXRAY Diffraction Facility (supported in part by the National Science Foundation) for assistance and Susan J. Barclay for helpful suggestions during the preparation of

this manuscript. This work was supported in part by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy, under Contract No. DE-AC03-76SF00098.

Registry No. 1, 86709-65-1; 2, 86709-67-3; $\text{Ag}_2(\text{C}_6\text{Cl}_2\text{O}_4)$, 86709-66-2; *o*-chloranil, 2435-53-2.

Supplementary Material Available: Listings of anisotropic thermal parameters and observed and calculated structure factor amplitudes (Tables IV-VII) and a stereoscopic view of **2** (Figure 6) (22 pages). Ordering information is given on any current masthead page.

Contribution from the Departments of Chemistry, University of California, Berkeley, California 94720, and University of Vermont, Burlington, Vermont 05405

Siderophilin Metal Coordination. 3. Crystal Structures of the Cobalt(III), Gallium(III), and Copper(II) Complexes of Ethylenebis[*o*-hydroxyphenyl]glycine]¹

PAUL E. RILEY,^{2a} VINCENT L. PECORARO,^{2a} CARL J. CARRANO,^{2b} and KENNETH N. RAYMOND*^{2a}

Received August 24, 1982

The structures of the Co(III), Ga(III), and Cu(II) complexes of the hexadentate ligand ethylenebis[*o*-hydroxyphenyl]glycine (EHPG) have been determined by single-crystal X-ray diffraction techniques using data collected by counter methods. These complexes are used as models for the metal binding site of the human iron transport protein transferrin. While solutions of the complexed metals were composed of mixtures of racemic and mesomeric ligands, for all three metal complexes the only crystals obtained were those of the racemic isomer of EHPG. Deep red prisms of $[\text{Co}(\text{H}_2\text{O})_6][\text{Co}(\text{EHPG})]_2 \cdot 4\text{H}_2\text{O}$ (**1**) crystallize in the monoclinic space group $P2_1/n$ with $a = 14.818$ (2) Å, $b = 16.991$ (2) Å, $c = 8.414$ (1) Å, and $\beta = 91.32$ (1)°. The calculated density of 1.676 g cm⁻³ for $Z = 2$ compares satisfactorily with the measured value of 1.61 (3) g cm⁻³. Large, irregular, pale orange crystals of $[\text{Mg}(\text{H}_2\text{O})_6][\text{Ga}(\text{EHPG})]_2 \cdot 3\text{H}_2\text{O}$ (**2**) form in the monoclinic space group $C2/c$ with $a = 20.946$ (4) Å, $b = 13.010$ (1) Å, $c = 17.002$ (3) Å, and $\beta = 114.75$ (1)° and are isostructural with $[\text{Mg}(\text{H}_2\text{O})_6][\text{Fe}(\text{EHPG})]_2 \cdot 3\text{H}_2\text{O}$, which was reported earlier. The value of the calculated density of 2 of 1.639 g cm⁻³ for $Z = 4$ is in agreement with the measured value of 1.56 (3) g cm⁻³. Deep blue-green prisms of $\text{Na}_2[\text{Cu}(\text{EHPG})] \cdot 5.5\text{H}_2\text{O}$ (**3**) crystallize in the orthorhombic space group $Pbcn$ with $a = 14.195$ (1), $b = 22.607$ (3), and $c = 14.242$ (1) Å. The calculated density of 1.641 g cm⁻³ for $Z = 8$ agrees well with the measured density of 1.61 (3) g cm⁻³. In each structure, the metal ion is bound by the two nitrogen atoms, the two phenolate oxygen atoms, and the two carboxylate oxygen atoms, so as to describe a pseudooctahedral geometry about the metal with the carboxylate ligands trans to each other. Each complex displays virtual C_2 symmetry. In contrast, in the previously reported structure of the Na^+ salt of the meso complex of $[\text{Fe}(\text{EHPG})]^-$ (which cannot have C_2 symmetry because it possesses both *R* and *S* centers in the ligand), the three pairs of chemically equivalent donor atoms are mutually cis. Although the structure of **3** suffers from disorder of the Na^+ ions over several similar coordination environments, the structure of the $[\text{Cu}(\text{EHPG})]^{2-}$ species is satisfactorily determined and exhibits an anticipated tetragonal elongation (by 0.4-0.5 Å) of the axial Cu-O(carboxylate) bonds. As a consequence of the cation disorder, the resultant Na^+ content per unit cell, as ascertained by least-squares refinement of Na^+ occupancy parameters, is 13.9 (2) ions rather than the 16 ions required by stoichiometry. Full-matrix least-squares refinements of the structures have converged with conventional (and weighted) *R* indices (on $|F|$) of 0.025 (0.031), 0.033 (0.035), and 0.052 (0.064) for **1**, **2**, and **3**, respectively, using (in the same order) 3536, 3778, and 2508 observations of $|F_o|$ with $F_o^2 > 3\sigma(F_o^2)$.

Introduction

The mechanisms of iron exchange, assimilation, transport, and utilization by immature red blood cells are of critical interest in the field of iron metabolism. The subsequent implications of these processes with respect to the treatment of various blood disorders are especially significant. A key component of mammalian iron biochemistry is the serum protein transferrin, which shuttles iron from points of absorption and storage to the reticulocytes for utilization in heme synthesis.³ Therefore, a thorough understanding of transferrin chemistry is prerequisite to a detailed description of iron metabolism.

Human serum transferrin is a glycoprotein of molecular weight 80 000, which is capable of binding two ferric ions

tightly but reversibly.⁴ Although the area of transferrin chemistry has been studied extensively for many years, several important questions still remain unanswered. One of the most important of these is the nature and number of ligating groups that comprise the metal binding sites.

Recently we have begun to gain further insight into these questions by the examination of suitable small-molecule model compounds that mimic the physical properties of the iron binding sites of transferrin.^{1,5,6} Presently these models are based on ethylenebis[*o*-hydroxyphenyl]glycine (EHPG) (Figure 1), which incorporates the ligating groups previously implicated in the metal binding sites.⁴ On the basis of its optical and resonance Raman spectra, $\text{Fe}^{\text{III}}\text{EHPG}$ has long been recognized as a potential model for the iron binding site of transferrin.^{7,8} One area of our current interest has been

(1) Previous paper in this series: Pecoraro, V. L.; Harris, W. R.; Carrano, C. J.; Raymond, K. N. *Biochemistry* 1981, 20, 7033.

(2) (a) University of California, Berkeley. (b) University of Vermont.

(3) Crichton, R. R., Ed. "Problems of Iron Storage and Transport in Biochemistry and Medicine"; North Holland Publishing Co.: Amsterdam, 1975.

(4) Chasteen, N. D. *Coord. Chem. Rev.* 1977, 22, 1.

(5) Harris, W. R.; Carrano, C. J.; Pecoraro, V. L.; Raymond, K. N. *J. Am. Chem. Soc.* 1981, 103, 2231.

(6) Patch, M. G.; Simolo, K. S.; Carrano, C. J. *Inorg. Chem.* 1982, 21, 2972.