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Complexes with Substituted 2,5-Dihydroxy-*p*-benzoquinones: A Neutron Diffraction Study on $BaC_6(C_6H_5)_2O_4 \cdot 4H_2O$*

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Orthorhombic crystals of $BaC_6(C_6H_5)_2O_4 \cdot 4H_2O$ were grown from aqueous silica gel. Lattice constants: $a = 1791.7(4)$ pm, $b = 926.5(2)$ pm, $c = 1121.2(2)$ pm, $Z = 4$, space group *Pbcn*. Anisotropic refinement of neutron diffraction data converged at $R_w = 0.0305$. Ba^{2+} has CN 8. It is surrounded by four oxygen atoms of the bis-chelating polyporate dianions and four water molecules in a distorted, dodecahedral fashion. The connection of Ba^{2+} with the dianions leads to folded, infinite chains extending along [001]. Adjacent chains are interlinked by asymmetric hydrogen bonds thus forming layers parallel (100). Only one hydrogen atom of each of the two crystallographically independent water molecules is involved in hydrogen bonding. The polyporate dianion is centrosymmetric with phenyl rings inclined to the quinone ring plane. Only the oxygen atom of the quinone ring which is less strongly bound to Ba^{2+} acts as proton acceptor. However, the resulting C–O and C–C bond lengths do not indicate a system of alternating double bonds in the quinone ring; rather, they indicate extensively delocalized π-electrons.

Introduction

2,5-Dihydroxy-*p*-benzoquinone (Scheme 1) is an acid of moderate strength since its dianion is stabilized by resonance effects (*1*). Thereby four negatively charged oxygen atoms result which are in principle equivalent for the coordination of cations. By introduction of various substituents in 3,6-position it is possible to modify the acid strength within a wide range (*1*). This should have an important influence on the complexing properties of the resulting dianions. Furthermore steric effects of the substituents have to be taken into consideration.

For the investigation of these effects 2,5-dihydroxy-3,6-diphenyl-*p*-benzoquinone was employed to form coordination polymers with alkaline–earth metals. 2,5-Dihydroxy-3,6-diphenyl-*p*-benzoquinone is also called polyporic acid as Stahlschmidt (*2*)

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* Dedicated with best wishes to Prof. Dr. A. Rabenau on the occasion of his 65th birthday.

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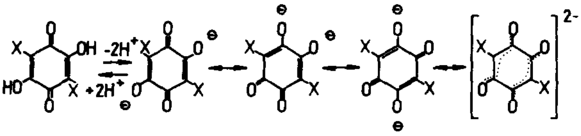

SCHEME 1

discovered it first in the fungus polyporus rutilans. Stahlschmidt has already reported on sparingly soluble alkaline–earth polyporates crystallizing as tetrahydrates. However, it is not possible to decide whether his samples were identical to our $BaC_6(C_6H_5)_2O_4 \cdot 4H_2O$ since highly polymeric complex compounds often show considerable differences in their chemical and structural properties even with identical net formulas (*3–5*). The X-ray structure determination showed that chains consisting of Ba^{2+} and the bis-chelating polyporate dianions are the main structural feature of $BaC_6(C_6H_5)_2O_4 \cdot 4H_2O$ (*6*). The coordination sphere of Ba^{2+} is completed by water molecules to yield CN 8. Interatomic distances indicated that these chains are interlinked by hydrogen bonds. Thereby the water molecules are coordinated in an unusual fashion as only one hydrogen atom of each water molecule is involved in hydrogen bonding as indicated by IR spectroscopy and peaks in difference Fourier maps obtained by X-ray diffraction (*6*) of the isotypic Sr compound. In order to obtain detailed information on this system of hydrogen bonds a neutron diffraction study was carried out. This should give valuable insight into the polymeric structure which is to a considerable extent determined by hydrogen bonding (*7–10*).

Experimental Details and Structure Refinement

Dark-violet single crystals of $BaC_6(C_6H_5)_2O_4 \cdot 4H_2O$ in a size suitable for neutron diffraction work were grown in aqueous silica gel as described in (*6*), employing glass tubes of 1.5 cm diameter and 45 cm length.

Crystallographic and experimental details: orthorhombic cell with $a = 1791.7(4)$ pm, $b = 926.5(2)$ pm, $c = 1121.2(2)$ pm, $V = 1861.2 \times 10^6$ pm^3 (calculated from single-crystal X-ray data, 293 K, $\lambda = 71.07$ pm), space group *Pbcn* (No. 60), $Z = 4$, $M_r = 499.68$ g/mol, $D_x = 1.78$ Mg m^{-3}. Neutron data collection carried out with the D9B four circle diffractometer at the ILL, 296 K, $\lambda = 84.90$ pm (H3 beam tube), Cu(220) monochromator in transmission, $\lambda/2$ contamination filtered by 0.62-mm erbium foil, $\mu = 1.31$ cm^{-1} (calculated), crystal dimensions $1.5 \times 0.7 \times 2.3$ mm, numerical absorption correction, isotropic extinction correction, ω-2θ scan, θ limit 30°, 2787 reflections recorded, 1599 unique, merging $R = 0.037$, refinement on $|F|$ using program system PROMETHEUS (*11*), quantity minimized $\Sigma w(|F_o| - |F_c|)^2$, weights $1/\sigma^2_{|F|}$ from counting statistics, scattering lengths from Ref. (*12*), reflections with $I < 2\sigma_I$ considered as unobserved (1086 observed).

Starting parameters for the refinements were obtained from the results of the X-ray structure determination (*6*). H positions as found in difference Fourier maps (X-ray data) of the isotypic Sr compound were refined successfully. Refinement converged at $R = 0.0384$, $R_w = 0.0305$ (observed reflections only) and at $R = 0.0696$, $R_w = 0.0359$ (all reflections), respectively. Goodness of fit 1.07; 205 parameters. Final atomic parameters are listed in Table I. Ad-

TABLE I

PARAMETERS FOR $BaC_6(C_6H_5)_2O_4 \cdot 4H_2O$

Atom	X	Y	Z	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ba	0	.09355(34)	.25	.0340(16)	.0186(14)	.0266(16)	0	.0015(14)	0
W(1)	.10559(20)	.02564(32)	.90717(27)	.0534(19)	.0398(17)	.0465(16)	.0039(14)	−.0011(15)	−.0160(14)
W(2)	.91278(25)	.10808(46)	.86745(40)	.1120(30)	.0664(24)	.0450(21)	.0461(23)	.0038(21)	−.0070(19)
O(1)	.93268(13)	.67664(23)	.65257(22)	.0319(12)	.0269(11)	.0506(14)	−.0061(10)	.0130(11)	−.0152(11)
O(2)	.05517(13)	.76424(22)	.55150(20)	.0421(13)	.0231(10)	.0350(12)	−.0085(9)	.0103(10)	−.0064(9)
C(1)	.96194(9)	.58871(18)	.58421(16)	.0233(8)	.0180(9)	.0280(9)	−.0005(7)	.0020(8)	−.0052(8)
C(2)	.96658(10)	.36045(19)	.47872(16)	.0287(8)	.0174(8)	.0252(9)	−.0026(7)	.0007(8)	−.0022(7)
C(3)	.93113(10)	.44915(18)	.56193(16)	.0247(8)	.0200(8)	.0264(9)	−.0020(7)	.0016(8)	−.0025(7)
C(4)	.86275(10)	.40344(18)	.62506(16)	.0277(9)	.0233(9)	.0257(9)	−.0013(7)	.0013(8)	−.0019(8)
C(5)	.80448(11)	.33396(21)	.56503(19)	.0269(10)	.0386(11)	.0296(12)	−.0063(8)	.0015(8)	−.0033(9)
C(6)	.74097(12)	.28825(25)	.62547(20)	.0269(11)	.0473(13)	.0452(12)	−.0078(10)	.0037(10)	.0008(11)
C(7)	.73281(12)	.31372(25)	.74663(21)	.0352(12)	.0499(13)	.0431(12)	−.0019(10)	.0099(10)	.0101(11)
C(8)	.78963(12)	.38454(25)	.80688(20)	.0469(13)	.0462(13)	.0315(12)	−.0027(11)	.0119(10)	.0042(10)
C(9)	.85393(12)	.42761(22)	.74759(18)	.0407(12)	.0373(10)	.0272(10)	−.0062(10)	.0035(10)	−.0033(9)
H(5)	.80938(26)	.31558(60)	.46995(42)	.0541(28)	.0855(35)	.0367(27)	−.0218(24)	.0023(21)	−.0177(23)
H(6)	.69646(29)	.23261(71)	.57827(53)	.0457(26)	.0979(41)	.0719(33)	−.0253(29)	−.0044(26)	−.0129(34)
H(7)	.68287(30)	.27618(68)	.79139(53)	.0540(30)	.0946(40)	.0748(36)	−.0162(30)	.0241(29)	.0146(32)
H(8)	.78434(34)	.40556(77)	.90163(44)	.0943(38)	.1064(49)	.0341(26)	−.0208(35)	.0222(25)	−.0020(26)
H(9)	.89823(29)	.48230(65)	.79587(43)	.0666(29)	.0875(36)	.0419(24)	−.0260(30)	−.0027(25)	−.0152(26)
H(11)	.90652(28)	.88489(54)	.04860(44)	.0713(30)	.0410(25)	.0523(26)	.0061(23)	−.0044(23)	−.0089(24)
H(12)	.84594(40)	.96528(85)	.11689(65)	.0695(40)	.1133(60)	.0790(41)	−.0060(38)	.0087(37)	−.0338(38)
H(21)	.09874(43)	.09194(80)	.55200(68)	.1272(54)	.0996(49)	.0504(36)	−.0509(43)	.0101(36)	.0090(36)
H(22)	.11190(54)	.18653(101)	.65965(70)	.1617(79)	.0990(54)	.0895(50)	−.0709(59)	−.0035(49)	−.0063(45)

Note. W = water oxygen; anisotropic temperature factors according to $\exp(-2\pi^2(U^{11}h^2a^{*2} + \ldots + 2U^{12}hka^*b^* + \ldots))$.

ditional material has been deposited with the NAPS.[1]

Results and Discussion

The previous X-ray results (*6*) are in good agreement with the neutron diffraction structure refinement. The eight-coordinated Ba^{2+} is situated on a twofold axis of space group *Pbcn*. The coordination polyhedron is a distorted dodecahedron formed by four oxygen atoms of the bis-chelating polyporate dianions (2 × O(1), 2 × O(2)) and four water molecules (2 × *W*(1), 2 × *W*(2); *W* = water oxygen) (see Table II and Fig. 1). O(2) (Ba–O(2) 276.9 pm) is much more remote from Ba^{2+} than O(1) (Ba–O(1) 268.0 pm). The Ba–water distances show smaller differences. The connection of Ba^{2+} with the dianions leads to infinite, folded chains extending along [001]. Thereby the plane of the phenyl substituents is almost parallel to (010) and the C(4)–C(7) diagonal is rather well aligned along [101]. Adjacent chains are interlinked by hydrogen bonds thus forming layers parallel to (100) (Fig. 2). Neighboring coordination polyhedra are connected by two unique asymmetric hydrogen bonds. One bond occurs between *W*(1) and O(2) via H(11). The other is formed between *W*(2) and *W*(1) via H(21). The remaining water hydrogen atoms (H(12) and H(22)) are not involved in hy-

TABLE II

THE COORDINATION OF Ba^{2+}

Distances (pm)	Ba–O(1)	268.0(3)	2×	Ba–*W*(2)	276.9(5)	2×
	Ba–O(2)	276.9(3)	2×	Ba–*W*(1)	281.1(4)	2×

Note. *W* = water oxygen.

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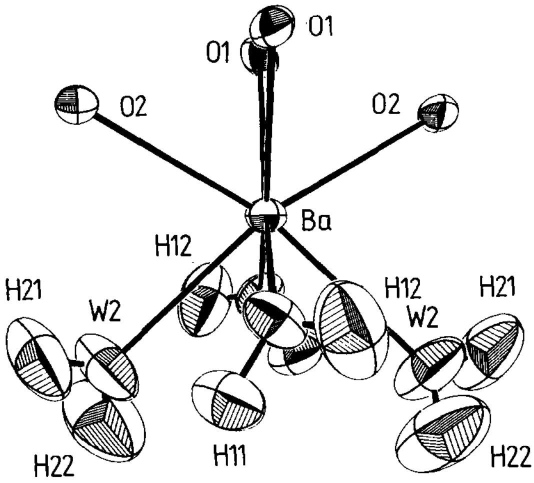

FIG. 1. Distorted, dodecahedral coordination of Ba^{2+} (W = water oxygen).

drogen bonding. Among the oxygen atoms of the dianion only O(2) which is more weakly bound to Ba^{2+} than O(1) occurs as proton acceptor. The chelate moiety formed by Ba, O(1), O(2), C(1), and C(2) is approximately planar and inclined to the quinone ring plane by 10°. H(11), however, is considerably out of the former plane (deviation 34 pm). The hydrogen atoms show a high thermal smearing, in particular those atoms which do not participate in the hydrogen bonding (root mean square displacements are listed in Table III). The O–H bond lengths were corrected employing a riding model. The corresponding values are compared in Table IV. The longest O–H bond involves H(11) which forms the strongest hydrogen bond. The remaining O–H bonds are identical within the limits of experimental error. Greater differences show up concerning the HOH angles. The angle with $W(1)$ resembles the value found in free water molecules whereas $W(2)$ shows an angle very close to tetrahedral. The hydrogen bonds are considerably bent, in particular the one involving H(21) ($W(2)$–H(21)–$W(1)$ 154.16(71)°).

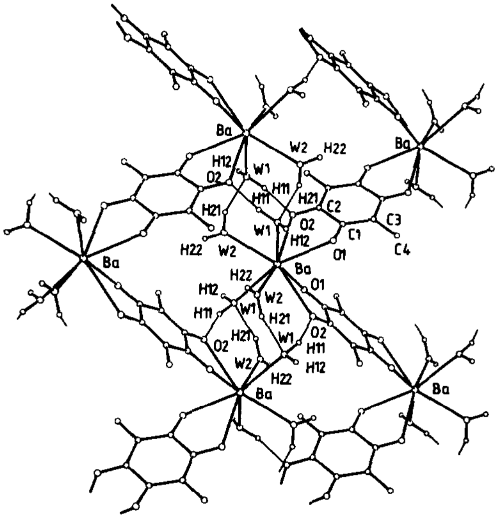

FIG. 2. Connection of adjacent chains by asymmetric hydrogen bonds (W = water oxygen; arbitrary atomic radii).

C–O and C–C bond lengths in the dianion reflect the different coordination of O(1) and O(2) (Table V). C(1)–O(1) is somewhat shorter than C(2)–O(2). The same is true with C(2)–C(3) and C(1)–C(3). However, the differences (approx 3 pm) are too small to indicate a system of alternating double bonds. Rather they confirm an extensive delocalization of the π-electrons. The phenyl ring as well as the quinone ring do not show significant deviations from planarity (maximum deviation 3 pm). The normals to the two least-squares planes are inclined by 43.84° with respect to each other.

TABLE III

ROOT MEAN SQUARE DISPLACEMENTS FOR WATER HYDROGEN ATOMS (pm)

	H(11)	H(12)	H(21)	H(22)
Axis 1	19	24	20	23
Axis 2	23	26	26	30
Axis 3	27	37	41	46
Along O–H bond	19	26	24	23

TABLE IV

WATER AND HYDROGEN BONDS

Distances (pm)	Uncorrected	Riding model	
W(1)–H(11)	99.0(6)	99.8	
W(1)–H(12)	91.3(8)	97.4	
H(11)–O(2)	172.6(5)	174.1	
W(2)–H(21)	93.8(9)	96.5	
W(2)–H(22)	90.3(1.0)	96.9	
H(21)–*W*(1)	195.9(8)	199.0	
W(1)–*W*(2)	283.4(5)		
W(1)–O(2)	268.8(4)		
Angles (degrees)			
H(11)–*W*(1)–H(12)	106.21(65)	H(12)–*W*(1)–Ba	119.40(52)
H(11)–*W*(1)–Ba	119.69(38)		
H(21)–*W*(2)–H(22)	110.14(83)	H(22)–*W*(2)–Ba	131.23(62)
H(21)–*W*(2)–Ba	118.32(56)		
O(2)–H(11)–*W*(1)	162.73(49)	*W*(2)–H(21)–*W*(1)	154.16(71)

Note. *W* = water oxygen.

TABLE V

THE POLYPORATE DIANION

Bond lengths (pm)			
Uncorrected			
C(1)–O(1)	123.5(3)	C(5)–H(5)	108.3(5)
C(2)–O(2)	126.5(3)	C(6)–H(6)	108.7(6)
C(1)–C(2)	153.6(2)	C(7)–H(7)	108.3(6)
C(1)–C(3)	142.8(2)	C(8)–H(8)	108.4(6)
C(2)–C(3)	139.6(3)	C(9)–H(9)	108.6(6)
C(3)–C(4)	147.7(3)		
Corrected for libration			
C(4)–C(5)	141.4(3)	C(5)–H(5)	109.5
C(4)–C(9)	141.6(3)	C(6)–H(6)	109.8
C(5)–C(6)	140.2(3)	C(7)–H(7)	109.2
C(6)–C(7)	140.1(3)	C(8)–H(8)	109.6
C(7)–C(8)	140.1(3)	C(9)–H(9)	109.7
C(8)–C(9)	140.0(3)		
Angles (degrees)			
O(1)–C(1)–C(2)	115.89(17)	C(5)–C(6)–C(7)	120.79(20)
O(1)–C(1)–C(3)	122.80(18)	C(5)–C(6)–H(6)	120.50(36)
C(3)–C(1)–C(2)	121.30(15)	C(7)–C(6)–H(6)	118.71(36)
O(2)–C(2)–C(1)	114.44(17)	C(6)–C(7)–C(8)	118.71(20)
O(2)–C(2)–C(3)	125.18(19)	C(6)–C(7)–H(7)	119.10(37)
C(1)–C(2)–C(3)	120.38(15)	C(8)–C(7)–H(7)	122.18(38)
C(2)–C(3)–C(1)	118.30(16)	C(7)–C(8)–C(9)	120.78(21)
C(2)–C(3)–C(4)	121.93(15)	C(7)–C(8)–H(8)	119.87(39)
C(4)–C(3)–C(1)	119.77(15)	C(9)–C(8)–H(8)	119.34(39)
C(5)–C(4)–C(3)	121.36(17)	C(8)–C(9)–C(4)	121.14(19)
C(9)–C(4)–C(5)	117.46(17)	C(8)–C(9)–H(9)	120.11(32)
C(9)–C(4)–C(3)	121.18(17)	C(4)–C(9)–H(9)	118.74(32)
C(4)–C(5)–C(6)	121.09(19)		
C(4)–C(5)–H(5)	119.04(31)		
C(6)–C(5)–H(5)	119.88(32)		

A rigid body analysis (TLS (*13*)) unambiguously indicates some motional independence of the phenyl and quinone ring: The quinone part shows a roughly three times smaller librational displacement, whereas the translational displacements are very similar. Uncorrected C–H bond lengths (approx. 108 pm) correspond well to values quoted in the literature (*14*). Application of a rigid body model bond length correction leads to slightly longer bond distances in the range between 109 and 110 pm (Table V). The O(1)–C(1)–C(2) and O(2)–C(2)–C(1) bond angles are markedly smaller than 120°. This could be partly due to a contracting influence of Ba^{2+} in the chelate moiety. However, bond angles similar to those have been observed in free dihydroxy-*p*-benzoquinones as well (*15–18*). Probably this angle deformation is caused by repulsive steric interactions between the substituent bound to C(3) and O(1) and O(2), respectively. Angle deformations from the ideal 120° are also observed with the phenyl ring (Table V).

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