Polymeric 2,5-Dihydroxy-1,4-benzoquinone Transition Metal Complexes $\text{Na}_2(\text{H}_2\text{O})_{24}[\text{M}_2(\text{C}_6\text{H}_2\text{O}_4)_3]$ ($\text{M} = \text{Mn}^{2+}, \text{Cd}^{2+}$)

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Two-dimensional $[\text{M}_2(\text{C}_6\text{H}_2\text{O}_4)_3]^{2-}$ Complexes, Net-like Layers

The isotypic compounds $\text{Na}_2(\text{H}_2\text{O})_{24}[\text{M}_2(\text{C}_6\text{H}_2\text{O}_4)_3]$ ($\text{M} = \text{Mn}^{2+}, \text{Cd}^{2+}$) form infinite net-like layers. The transition metal ion is coordinated octahedrally. The dianion of 2,5-dihydroxy-1,4-benzoquinone, consisting of two allyl systems interlinked by two long C–C distances (152–153 pm), acts as a chelating ligand. Adjacent layers are connected by hydrogen bonds. The stacking sequence of these layers, $\cdots\text{AAA}\cdots$, leads to channels, which are filled by hydrated Na^+ ions. The Na^+ ions are coordinated in a distorted octahedral fashion, with neighbouring octahedra sharing common faces.

Introduction

2,5-Dihydroxy-1,4-benzoquinone is an acid of moderate strength [1]; it can form a dianion which is stabilized by resonance:

Hence it possesses four partially negatively charged oxygen atoms capable of coordinating metal ions. This property has already been studied [2] and used for analytical purposes [3]. The crystal structure of 2,5-dihydroxy-1,4-benzoquinone was solved by Semmingsen [4]. He found that the molecule has to be described principally as quinoid with some degree of conjugation, indicated by the bond lengths between C–C and C–O, respectively. Kulpe [5] investigated the crystal structure of $\text{K}_2\text{C}_6\text{H}_2\text{O}_4$ and found, that the dianion could be described as two allyl systems connected by C–C single bonds, thus confirming the existence of resonance effects.

Structure reports concerning the molecular structure and the coordination effects in transition metal complexes were lacking. This may be due to difficulties arising from characterization of polymeric compounds, whose properties are considerably depending on the molecular weight. The products described hitherto were frequently obtained as extremely fine precipitates, ill-defined by chemical analyses. The

varying composition is partially affected by cation exchange properties. We succeeded in growing well defined macroscopic crystals by gel crystallization in silica gel.

The present paper deals with isotypic complex compounds of the formula $\text{Na}_2(\text{H}_2\text{O})_{24}[\text{M}_2(\text{C}_6\text{H}_2\text{O}_4)_3]$ ($\text{M} = \text{Mn}^{2+}, \text{Cd}^{2+}$).

Preparation and Properties of the Compound

Single crystals were grown by gel crystallization in silica gel according to the following method: 2.3 ml 2 M $\text{Na}_2\text{H}_2\text{SiO}_4$ solution were added dropwise to a mixture of 6 ml 2 M acetic acid and 3 ml water while stirring. Afterwards 3 ml 0.08 M $\text{Na}_2\text{C}_6\text{H}_2\text{O}_4$ solution were added and the mixture was poured into a test tube. Within 24 h a gel was formed, on top of which 3 ml 1 M aqueous $\text{M}(\text{NO}_3)_2$ solution ($\text{M} = \text{Mn}^{2+}, \text{Cd}^{2+}$) were placed. Within three weeks small, dark red crystals grew to a size of 0.4 mm. The trigonal crystals were bounded by {100} and {001} faces.

The above stated formula is based on results of the well refined single crystal X-ray structure determination. Chemical analyses showed values which indicated a slightly lower water content (Table I). This water evaporates while adhering silica gel is removed

Table I. Results of chemical analyses.

Mn compound [%]			Cd compound [%]		
	found	calcd		found	calcd
Mn	12.4	10.9	Cd	18.3	20.1
C	23.1	21.5		21.6	19.3
H	5.1	5.4		5.3	4.8
Na	4.3	4.5		4.2	4.1

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from the crystal surface. The water molecules are weakly bound in the channels, out of which they can easily escape.

The crystals were examined by Guinier-, rotating crystal and Weissenberg photographs, from which the crystallographic properties were deduced. Intensities were collected on a Siemens four-circle diffractometer. The phase problem was solved by interpreting the Patterson map from which the positions of

the transition metal and the Na⁺ ions could be obtained. Subsequent difference Fourier maps revealed the lighter atoms except hydrogen. Anisotropic least squares refinement converged at $R = 5.3\%$ (Mn compound) and $R = 3.7\%$ (Cd compound), respectively.

Atomic parameters are listed in Table II, crystallographic data in Table III. Tables containing F_o/F_c values can be requested from the authors.

Table II. Atomic parameters (anisotropic temperature factors according to $\exp(-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{12}hka^*b^* + \dots))$).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂
Mn compound									
Mn	.3333	.6667	.0000	.0250(7)	.0250(7)	.0433(11)	.0000	.0000	.0125(3)
Na(1)	.0000	.0000	.0000	.0535(31)	.0535(31)	.0470(42)	.0000	.0000	.0267(15)
Na(2)	.0000	.0000	.5000	.0575(31)	.0575(31)	.0376(38)	.0000	.0000	.0287(15)
C(1)	.4321(4)	.9026(4)	.8916(6)	.0298(31)	.0353(28)	.0320(23)	.0025(23)	-.0041(23)	.0148(26)
C(2)	.4607(5)	.0000	.7925(10)	.0400(32)	.0285(40)	.0405(40)	.0000	-.0077(31)	.0142(20)
O	.3712(3)	.5630(3)	.1850(5)	.0465(23)	.0451(24)	.0474(21)	.0115(18)	.0175(17)	.0329(22)
H ₂ O(1)	.2301(2)	.7699(2)	.5000	.0628(29)	.0628(29)	.0501(30)	-.0112(27)	-.0112(27)	.0387(35)
H ₂ O(2)	.0000	.1265(4)	.7448(9)	.0692(46)	.0526(65)	.0584(34)	.0000	.0028(56)	.0263(32)
H ₂ O(3)	.3191(3)	.2059(4)	.8153(6)	.0731(33)	.0788(33)	.0681(28)	.0131(26)	.0132(26)	.0411(28)
Cd compound									
Cd	.3333	.6667	.0000	.0209(3)	.0209(3)	.0452(5)	.0000	.0000	.0104(1)
Na(1)	.0000	.0000	.0000	.0478(27)	.0478(27)	.0357(43)	.0000	.0000	.0239(12)
Na(2)	.0000	.0000	.5000	.0446(25)	.0446(25)	.0344(40)	.0000	.0000	.0223(12)
C(1)	.0961(3)	.5285(3)	.1099(8)	.0236(20)	.0279(24)	.0355(28)	.0073(21)	-.0008(20)	.0120(19)
C(2)	.0000	.4632(5)	.2082(12)	.0275(32)	.0551(77)	.0407(44)	.0000	-.0234(55)	.0276(38)
O	.3745(3)	.5616(3)	.8069(6)	.0435(20)	.0424(21)	.0426(22)	-.0412(18)	-.0177(18)	.0314(18)
H ₂ O(1)	.2276(2)	.7724(2)	.5000	.0557(27)	.0557(27)	.0464(33)	.0156(31)	.0156(31)	.0357(32)
H ₂ O(2)	.0000	.1241(4)	.2508(10)	.0598(42)	.0312(49)	.0541(37)	.0000	.0003(60)	.0155(25)
H ₂ O(3)	.3122(4)	.2000(4)	.1872(9)	.0570(29)	.0699(33)	.0716(34)	-.0173(29)	-.0147(27)	.0340(27)

Crystal system	trigonal
Space group	P3̄1m (No. 162)
Conditions limiting possible reflections:	none
Cell dimensions	<i>a</i> = 1415.0(2) pm <i>c</i> = 656.5(2) pm
Volume of unit cell	<i>U</i> = 1138.5 · 10 ⁶ pm ³
Molecular weight	1001.92 g/mol
Density	<i>D_x</i> = 1.55 g/cm ³ <i>D_m</i> = 1.53 g/cm ³ (floatation method)
Formulas per unit cell	<i>Z</i> = 1
<i>μ</i> (cm ⁻¹ , CuKα)	54.77
<i>θ</i> -range	<i>θ</i> < 45°
unique reflections	415 (out of 799)
<i>R</i> _{int.}	2%
Corrections applied	LP- and absorption correction
Parameters	51
Ratio unique refl./param.	N/NP = 8.1
Residuals	<i>R</i> = 5.3% <i>R_w</i> = 5.1% <i>R_g</i> = 5.6%
max. diff. Fourier peaks	+2.5/-2.6 el · 10 ⁻⁶ pm ⁻³
(10 reflections obviously affected by extinction, therefore not used in the last stages of refinement: 001, 120, 003, 010, 020, 240, 221, 011, 223, 221)	

Table III. Crystallographic data for Na₂(H₂O)₂₄[Mn₂(C₆H₂O₄)₃]*.

* Cd compound: *a* = 1444.5(2) pm, *c* = 647.4(2) pm, *U* = 1169.9 · 10⁶ pm³, *M_r* = 1116.8 g/mol, *D_x* = 1.58 g/cm³, *D_m* = 1.61 g/cm³, *μ* = 80.48 cm⁻¹ (CuKα), unique refl. 495, N/NP = 9.7, *R* = 3.7%, *R_w* = 3.7%, *R_g* = 4.5%.

Discussion

The dianions are almost planar with bond lengths characteristic of resonance stabilization (Fig. 1, Table IV). The oxygen atoms coordinate the transition metal ions in a distorted octahedral fashion (Table V). The triangular faces are rotated around the threefold axis of the octahedron *versus* a trigonal prism; this tendency is more pronounced in the Cd compound. The O–Mn–O angle is 73.74(11)°, (O–Cd–O 72.14(13)°). The dianions are linked together by the transition metal ions forming infinite net-like layers [M₂^{II}(C₆H₂O₄)₃]^{2–} with excess of negative charge (Fig. 2). The stacking sequence corresponds to ...AAA.... Thereby long channels are built up in *c*-direction (Fig. 3). Those channels contain the Na⁺ ions. One Na⁺ ion lies in the layer, the other is

Fig. 1. The dianion of the Mn compound with numbering of atoms and deviations from least squares plane in pm (Cd compound: O: ±1.5, C(1): ±1.0, C(2): ±1.6).

Table IV. Bond lengths and angles in the dianion.

Mn compound		Cd compound	
C(1)–O	127.6(6)	127.2(4)	in pm
C(2)–C(1)	138.9(6)	138.3(7)	
C(1)′–C(1)	152.3(5)	153.1(7)	
C(1)′–C(1)–C(2)	120.71(44)	119.62(37)	in degrees
C(1)′–C(1)–O	114.98(40)	116.46(33)	
O–C(1)–C(2)	124.29(40)	123.90(50)	
C(1)–C(2)–C(1)′	118.50(53)	120.76(60)

Fig. 2. The dianions coordinate the Mn²⁺ cations, acting as bis-chelating tetradentate ligands, thereby two-dimensional layers are formed parallel to the *ab*-plane.

Table V. Bond lengths and angles in the coordination polyhedra of the cations.

Mn compound			Cd compound		
Mn–O	216.8(3) pm	6×	Cd–O	226.3(3) pm	6×
angle O–Mn–O			angle O–Cd–O		
108.26(11)°	distance O–O		109.00(11)°	distance O–O	
73.74(11)°	351.3 pm	3×	72.14(13)°	368.5 pm	
91.68(12)°	260.1 pm	3×	92.43(13)°	266.5 pm	
155.28(14)°	311.0 pm	6×	153.69(10)°	326.8 pm	
	423.5 pm	3×		440.8 pm	
Na(1)–H ₂ O(2)	242.2(5) pm	6×		241.9(5) pm	
angle H ₂ O(2)–Na(1)–H ₂ O(2)					
78.44(15)°	dist. H ₂ O(2)–H ₂ O(2)				
101.56(15)°	310.0 pm	6×	79.86(16)°	310.5 pm	
180.00°	379.9 pm	6×	100.14(16)°	370.9 pm	
	490.3 pm	3×	180.00°	483.7 pm	
Na(2)–H ₂ O(2)	240.6(5) pm	6×		241.2(5) pm	
angle H ₂ O(2)–Na(2)–H ₂ O(2)					
80.24(15)°	dist. H ₂ O(2)–H ₂ O(2)				
99.76(17)°	310.0 pm	6×	80.14(16)°	310.5 pm	
180.00°	367.9 pm	6×	99.86(16)°	369.1 pm	
	481.1 pm	3×	180.00°	482.3 pm	
Na(1)–Na(2)	328.3 pm			323.7 pm	

midway between two layers. The water molecules coordinate the Na^+ ions and tie the layers together.

Three species of water can be distinguished. The first kind coordinates the Na^+ ions by forming distorted octahedra which share common faces. This leads to quite close $\text{Na}^+ - \text{Na}^+$ contacts (328.3 pm in the Mn compound and 323.7 pm in the Cd compound, respectively). Na^+ coordination octahedra sharing common faces are not found frequently, similar coordination is known in the structure of $\text{Na}_2\text{HAsO}_4 \cdot 7 \text{H}_2\text{O}$ [6].

Another water shell is arranged around the chains of $[\text{Na}(\text{H}_2\text{O})_3]_n^{n+}$ -octahedra, which is shown in Fig. 4

Fig. 3. The layers are stacked identically above each other, thus forming channels parallel *c*.

Fig. 4. Distribution of H_2O between the layers. The dotted lines indicate probable hydrogen bonds.

as hatched circles. Together with $\text{H}_2\text{O}(1)$ and $\text{H}_2\text{O}(2)$ they form distorted tetrahedra (Fig. 5). The distances between the central molecule and the others are 275–288 pm, which are typical values for hydrogen bonding. Six at a time of those 12 water molecules are situated in a common plane. The third kind of water ($\text{H}_2\text{O}(1)$) is shown in Fig. 6. It interlinks the layers, probably by hydrogen bonding.

Fig. 5. $\text{H}_2\text{O}(3)$ is surrounded by four other water molecules in a distorted tetrahedral fashion.

Fig. 6. Model for the interlinkage of adjacent layers by hydrogen bonding (the contribution of these H atoms to R is not significant).

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