



对-氢醌金属配合物:合成,结构及电化学性质

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p-Hydroquinone-metal Complex: Synthesis, Crystal Structure and Electrochemical Property

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Abstract: A new Chromium(III) complex, $[\text{Cr}(\text{H}_4\text{cah})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$, where $\text{H}_4\text{cah} = 2\text{-}[N,N\text{-bis}(\text{carboxymethyl})\text{aminomethyl}] \text{hydroquinone}$ (H_4cah), has been synthesized and characterized using X-ray diffraction single crystal structure determination, IR and elemental analysis. The complex belongs monoclinic, space group $P2_1/c$, with $a=0.792\ 05(4)$ nm, $b=1.008\ 63(6)$ nm, $c=1.920\ 40(10)$ nm, $\beta=93.069(4)^\circ$, $V=1.531\ 98(14)$ nm³, and $Z=4$. The cyclic voltametric analysis shows that the electron transfer in the electrode reaction is irreversible for $\text{Cr(III)}/\text{Cr}_2\text{O}_7^{2-}$ and $\text{Cr(III)}/\text{Cr(II)}$ redox couples while reversible for process of interchange from *p*-Hydroquinone to *p*-semiquinones. CCDC: 666208.

Key words: chromium(III) complex; crystal structure; cyclic voltammetry

p-Hydroquinones along with their oxidation products, *p*-semiquinones and *p*-quinones, comprise perhaps the interesting organic electron and hydrogen transfer systems^[1]. For example, electron transfer reactions between transition metal centers and *p*-quinone cofactors are vital for all life^[2], occurring in key biological processes in the oxidative maintenance of biological amine levels^[3,4], tissue formation^[4,5], photosynthesis^[6] and aerobic respiration^[7].

The interaction of *p*-hydroquinones with Cr(III) presents more interest due to the participation of chromium(III) ions^[8,9]. However, the examples documented in the CSD of structurally characterized *p*-hydroquinone-metal compounds are surprisingly rare^[10]. A strate-

gy to prepare such species is to synthesize substituted, in the *o*-position, *p*-hydroquinones with substituents containing one or more donor atoms, thus enabling the metal atom to form chelate rings. In the article, we wish to report the synthesis, crystal structure and electrochemical property of the *p*-hydroquinone-metal compound with potentially chelate *o*-substituted ligand 2-[*N,N*-bis(carboxymethyl) aminomethyl] hydroquinone (H_4cah).

1 Experimental

1.1 Materials and physical measurements

The ligand 2-[*N,N*-bis(carboxymethyl) aminomethyl] hydroquinone was prepared according to literature^[11]. All chemicals were obtained from commercial sources

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and used without further purification. IR spectra were taken on a Perkin-Elmer spectrum One FTIR spectrometer in the $4\,000\sim400\text{ cm}^{-1}$ region with KBr pellets. Elemental analyses for C, H and N were carried out on a Model 2400 II, Perkin-Elmer elemental analyzer. Electrochemical measurement was made at $25\text{ }^{\circ}\text{C}$ using a BAS Epsilon Electrochemical workstation with a conventional three-electrode cell consisting of a glassy carbon working, a platinum wire auxiliary and a saturated calomel reference electrode (SCE). $0.1\text{ mol}\cdot\text{L}^{-1}$ KCl was used as supporting electrolytes in aqueous solution.

1.2 Preparation of $[\text{Cr}(\text{Hcch})(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}$

The title complex was synthesized by the addition of $\text{Cr}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ (0.5 mmol) to 20 mL methanol solution containing H_4cch (0.127 5 g, 0.5 mmol) and Et_3N (0.5 mmol). The resulting solution was stirred for 3 h at $60\text{ }^{\circ}\text{C}$ and then filtered. Red block single crystals were isolated from the solution at room temperature over several days. The product was isolated in 60% yield. Anal. Calcd. (%) for $\text{C}_{11}\text{H}_{18}\text{CrNO}_{10}$ (Found, %): C 35.49(35.11); H 4.12(4.82); N 3.58(3.72). IR: (KBr, cm^{-1}): 3 448.58(s), 3366.95 (m), 1 663.56 (vs), 1 492.00 (s), 1 451.05 (m), 1 364.94(s), 1 221.97(m), 925.22(w), 806.38 (w), 504.36 (m).

1.3 Crystal structure determination

A red block single crystal of the title compound with dimensions of $0.40\text{ mm}\times 0.35\text{ mm}\times 0.30\text{ mm}$ was put on a Bruker SMART CCD diffractometer equipped with a graphite-monochromatic $\text{Mo K}\alpha$ ($\lambda=0.071\,073\text{ nm}$) by using an ω scan mode at $294(2)\text{ K}$. Out of the total 12 824 reflections collected in the $2.12^{\circ}\leq\theta\leq 27.67^{\circ}$ range, 3 571 were independent with $R_{\text{int}}=0.044$, of which 2 623 were considered as observed $I>2\sigma(I)$.

The crystal structure was solved by direct methods with SHLXS-97 program and refined by full-matrix least-squares techniques on F^2 using SHLXTL-97 program^[12]. All non-hydrogen atoms were assigned anisotropically. The H atoms of the water molecules were located in a difference Fourier map and the H atoms on O1 and all C atoms were positioned geometrically ($\text{C-H}=0.093\text{ nm}$ for $\text{C-H}_{\text{aromatic}}$, $\text{C-H}=0.097\text{ nm}$ for $\text{C-H}_{\text{aliphatic}}$ and $\text{O1-H1}=0.082\text{ nm}$). All the hydrogen atoms were refined with a common isotropic thermal parameter. The final cycle of refinement converged at $R=0.039\,6$, $wR=0.091\,1$ ($w=1/[\sigma^2(F_o^2)+(0.041\,8P)^2+0.717\,1P]$, where $P=(F_o^2+2F_c^2)/3$).

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2 Results and discussion

2.1 Structure

The selected bond distances and bond angles are given in Table 1 and the molecular structure of the title complex are shown in Fig.1. The crystal structure of the title complex shows that the Cr (III) atom in the asymmetric unit is coordinated by one tetradentate Hcch ligand and two coordinated water molecules complete a distorted octahedral CrNO_5 coordination environment, with bond distance of Cr-O lies in the $0.192\,4\sim0.199\,3\text{ nm}$ range, and Cr-N is $0.207\,1\text{ nm}$ which is similar to that reported^[13]. The best equatorial plane is defined by O2, N1, O3 and O1w, while O5 and O2w occupy the apical sites. The mononuclear structure of the complex is similar to the hydroquinonate complex of Mo(VI) ^[14], Cu(II) ^[15], Mg(II) ^[16], Fe(III) ^[17] and Ga(III) ^[18]. In the title complex, the most important intermolecular interaction in the crystal packing is formation of the infinite 1D chain (Fig.2) through hydrogen bonds ($\text{O1w-H1A}\cdots\text{O3}^{\#2}$, $\text{O1w-H1B}\cdots\text{O2}^{\#3}$, Table 2) among

Table 1 Selected bond lengths (nm) and bond angles ($^{\circ}$) of the title complex

Cr1-O2	0.192 39(16)	Cr1-O1w	0.199 03(19)	Cr1-O5	0.196 35(16)
Cr1-O3	0.199 28(17)	Cr1-O2w	0.197 35(19)	Cr1-N1	0.207 1(2)
O2-Cr1-O5	90.66(7)	O2w-Cr1-O3	86.60(8)	O2-Cr1-O2w	88.21(8)
O1w-Cr1-O3	94.88(8)	O5-Cr1-O2w	176.53(8)	O2-Cr1-N1	93.52(7)
O2-Cr1-O1w	91.81(8)	O5-Cr1-N1	83.46(7)	O5-Cr1-O1w	90.55(8)
O2w-Cr1-N1	93.34(9)	O2w-Cr1-O1w	92.76(9)	O1w-Cr1-N1	172.02(8)
O2-Cr1-O3	171.71(8)	O3-Cr1-N1	80.36(7)	O5-Cr1-O3	94.16(7)

Table 2 Hydrogen bond lengths and bond angles in complex 1

D-H...A	D-H / nm	H...A / nm	D...A / nm	D-H...A / (°)
O1-H1...O5 ^{#1}	0.082	0.192	0.271 5(3)	162
O1w-H1A...O3 ^{#2}	0.080	0.194	0.273 8(3)	176(3)
O1w-H1B...O2 ^{#3}	0.087	0.176	0.262 6(3)	175(3)
O2w-H2A...O4w ^{#3}	0.084	0.175	0.257 8(3)	170(3)
O2w-H2B...O3w	0.083	0.178	0.260 7(4)	174(3)
O3w-H3A...O1 ^{#4}	0.084	0.213	0.295 6(4)	167(6)
O3w-H3B...O6 ^{#5}	0.086	0.223	0.271 1(4)	115(6)
O4w-H4A...O4 ^{#2}	0.083	0.192	0.273 3(3)	166(3)
O4w-H4B...O1 ^{#6}	0.082	0.202	0.283 4(3)	172(3)

Symmetry codes: ^{#1} $x+1, y-1/2, -z+1/2$; ^{#2} $x, -y+1, -z+1$; ^{#3} $-x+1, -y+1, -z+1$; ^{#4} $x-1, -y-1/2, z-1/2$; ^{#5} $x, -y-1/2, z-1/2$; ^{#6} $-x+1, y+1/2, -z+1/2$.

the coordinated carboxylate oxygen atoms. The coordinated phenolate oxygen atoms and coordinated water molecules, which are parallel, connected to each other and extended to a 3D hydrogen-bonded network.

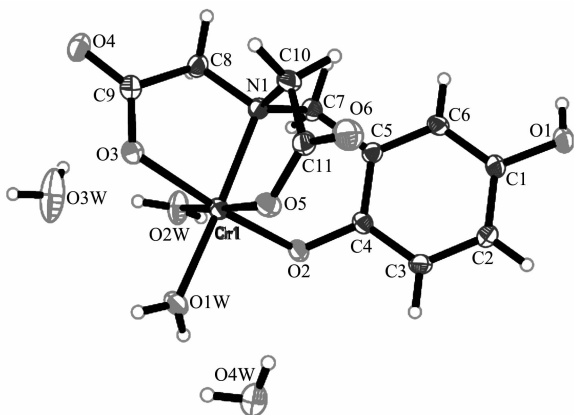
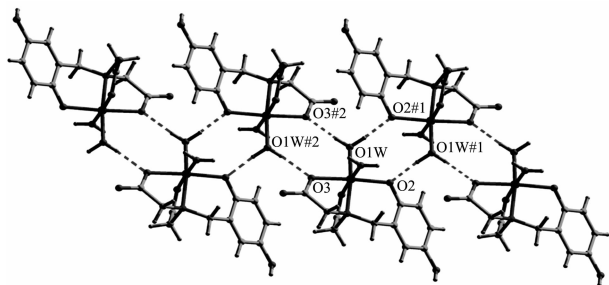


Fig.1 Asymmetric unit of the title complex



#1: $x+1, y-1/2, -z+1/2$, #2: $x, -y+1, -z+1$

Fig.2 1D chain structure in the complex linked by the hydrogen bonds shown as dashed lines

2.2 Cyclic voltammetry (CV) discussion

Cyclic voltammogram (CV) of the Chromium(III) complex (Fig.3) was measured with a conventional three electrode cell in aqueous solution with complex condensation of $1.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$. The measurement

was carried out at room temperature with scanning range of $-1.500 \sim 1.750 \text{ V}$ and scanning rate of $100 \text{ mV} \cdot \text{s}^{-1}$. The result shows that one irreversible oxidative and one irreversible reductive response at 1.420 and -0.377 V due to $\text{Cr(III)}/\text{Cr}_2\text{O}_7^{2-}$ and $\text{Cr(III)}/\text{Cr(II)}$ redox couples, respectively^[19,20]. However, only one reversible redox wave was observed at $E_{1/2} = 0.292 \text{ V}$ ($\Delta E_p = 260 \text{ mV}$, $I_{pa}/I_{pc} = 1.54$) corresponding to the process of interchange from *p*-hydroquinone to *p*-semiquinones^[2].

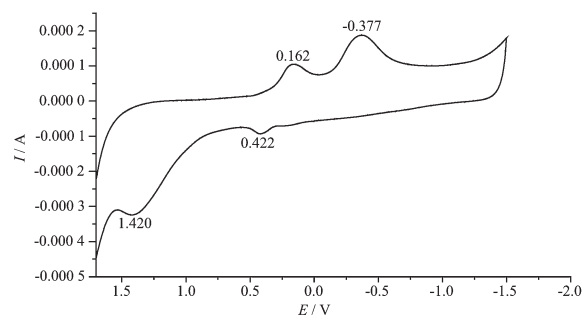


Fig.3 Cyclic voltammogram of the title complex

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