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Synthesis and structural characterization of cadmium(II) complexes with chelating keto-hydroxy compounds: The X-ray molecular structure of $[Cd_2(nq)_4(H_2O)_4]\cdot 3H_2O$ (nqH = 2-hydroxynaphthoquinone)

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ABSTRACT

The reaction of cadmium(II) acetate dehydrate with the complexing agents tropolone (tropH), 2-hydroxynaphthoquinone (nqH), 1,2-dihydroxyanthraquinone (alizH$_2$), and 1,8-dihydroxyanthraquinone (chryzH$_2$), afforded the complexes $[Cd(trop)_2]$ **1**, $[Cd_2(nq)_4(H_2O)_4]\cdot 3H_2O$ **2**$\cdot 3H_2O$, $[Cd(alizH)_2(H_2O)_3]$ **3**, and $[Cd(chryzH)_2(H_2O)_2]$ **4**, respectively. The X-ray molecular structure of the dinuclear complex **2**$\cdot 3H_2O$ reveals that each cadmium(II) atom is seven-coordinated. The nature of water molecules (lattice or coordinated) was discerned by thermogravimetric studies. The ^{113}Cd NMR spectra were discussed in light of the chemical exchange.

1. Introduction

Complexes of naphthoquinone or anthraquinone derivatives with redox-active metal ions, like iron [1,2], copper [3], nickel [3], manganese [3], and ruthenium [4,5] have been thoroughly characterized. It is well known that 1,2-chelate polyhydroxyanthraquinones can display redox chemistry acting as semiquinone(−) or catecholate(2−) which means they are not innocent ligands [2]. In the redox-inactive aluminum–magnesium alizarinate or purpurinate compounds, the X-ray structures of their dimethylformamide/water solvate revealed tetranuclear complexes $[AlCa(OH)L_2]_2$ [L = alizarinate(2−) or purpurinate(2−)] [6]. The preparation of alizarinate complex containing other cations other than Ca^{2+} (Na^+, K^+, Ba^{2+}) in ethanol or water turned out to be dinuclear species based on solid-state ^{27}Al NMR studies and ESMS [7]. Within the zinc group, the structural characterizations of complexes with quinone derivatives are limited to zinc [3] and mercury [8,9]. In light of the versatility of coordination mode and prevalence in natural systems of hydroxynaphthoquinone (nqH), 1,2-dihydroxyanthraquinone (alizH$_2$), and 1,8-dihydroxyanthraquinone (chryzH$_2$), we found of interest to investigate their cadmium(II) complexes. Although the cadmium–tropolonate complex has been prepared previously [9], we have synthesized and characterized it by TG and ^{113}Cd NMR spectroscopy in order to use it as a probe, since structural complications, due to solvation, do not occur in this case [10].

Cadmium ^{113}NMR spectroscopy has been successfully used to investigate natural organic matter (NOM) [11] and to probe the active site of some metalloproteins [12]. The ^{113}Cd NMR spectra are dependent on the solvent, concentration, temperature and the magnetic field, the chemical exchange being the norm for this nucleus in solution [12].

To contribute in this field, we present here the synthesis and properties of three cadmium(II) complexes: $[Cd_2(nq)_4(H_2O)_4]\cdot 3H_2O$ **2**$\cdot 3H_2O$, $[Cd(alizH)_2(H_2O)_3]$ **3** and $[Cd(chryzH)_2(H_2O)_2]$ **4**.

2. Experimental

2.1. Reagents

The starting materials were used as received. Cadmium acetate dehydrate 98% (BDH), tropolone 99% (Fluka), 2-hydroxynaphthoquinone (lawsone) 95% (Sigma–Aldrich), 1,2-dihydroxyanthraquinone (alizarin) 97% (Merck), and 1,8-dihydroxyanthraquinone (chrysazin) 96% (Sigma–Aldrich).

2.2. Instrumentation

Elemental analyses (C, H, N) were performed on a Perkin Elmer/Series II 2400 analyser. The cadmium content of compounds

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2·$2H_2O$, **3** and **4** was determined by atomic absorption spectroscopy (AAS). The NMR spectra were recorded on a Varian MERCURY plus spectrometer, 7.05 T, operating at 300.07 MHz for ^1H, 75.46 MHz for ^{13}C, and 66.56 MHz for ^{113}Cd. Chemical shifts (δ) are given in ppm relative to $SiMe_4$ (internal reference for ^1H and ^{13}C) and 0.1 M D_2O solution of $Cd(ClO_4)_2$ ($\delta = 0$) (external reference for ^{113}Cd) [13,14]. The infrared spectra (KBr pellets, 4000–400 cm^{-1}) were recorded on a BOMEM BM 100 FT-IR spectrometer. Thermal studies were performed on a Shimadzu Thermogravimetric Analyzer TGA-50 in platinum crucibles at a heating rate of 10 °C/min under a helium atmosphere.

2.3. Crystallographic determination of **2**·$3H_2O$

Data were collected with a Bruker APEX II CCD area-detector diffractometer and graphite-monochromatized Mo Kα radiation. The structure was solved by direct methods using SHELXS [15]. Subsequent Fourier-difference map analyses yielded the positions of the non-hydrogen atoms. Refinements were carried out with the SHELXL package [15]. All refinements were made by full-matrix least-squares on F^2 with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were included in the refinement in calculated positions. Crystal data and more details of the data collections and refinements are contained in Table 1.

2.4. Preparation of complexes

2.4.1. $[Cd_2(nq)_4(H_2O)_4]\cdot 3H_2O$ **2**·$2H_2O$

To a hot methanol solution (10 mL) containing 1,2-hydroxynaphthoquinone (174.0 mg, 1 mmol), a water solution (5 mL) of cadmium acetate dihydrate, $Cd(CH_3COO)_2\cdot 2H_2O$ (133.01 mg, 0.5 mmol) was added under continuous stirring. The red suspension was maintained under reflux for 3 h. The red solid was filtered of while hot and washed with water (5 mL) and methanol (5 mL), respectively. The product was recrystallized in a dimethylsulfoxide/methanol (1:3) mixture. Yield 86% (225 mg). M.p. 198–200 °C. *Anal.* Calc. for $C_{40}H_{32}O_{18}Cd_2$: C, 46.85; H, 3.15; Cd, 21.92. Found: C, 46.85; H, 3.10; Cd, 22.15%. NMR ^1H δ 7.95–7.92 (m, 8H, C5H and C8H), 7.80 (ddd, ^3J, 7.5; ^4J, 1.5 Hz, 4H, C6H), 7.67 (ddd, ^3J, 7.5; ^4J, 1.5 Hz, 4H, C7H); $^{13}C\{^1H\}$ δ 187.3, 182.8, 166.9, 134.9, 134.4, 131.5, 130.3, 125.9, 125.2, 107.6. IR 3400–3200m, 1650m, 1615m, 1587s, 1557s, 1478w, 1381m, 1337m, 1270s, 1220w, 1122w, 989m, 845w, 781w, 735m, 667w.

Table 1
Crystal data and structure refinement for **2**·$3H_2O$.

Empirical formula	$C_{40}H_{34}Cd_2O_{19}$
Formula weight	1043.47
T (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	tetragonal
Space group	$I\ 41/a$
Unit cell dimensions	
a (Å)	16.3417(2)
c (Å)	29.2014(9)
V (Å^3)	7798.3(3)
Z	8
Density (calculated) (Mg/m^3)	1.778
Absorption coefficient (mm^{-1})	1.176
$F(0\,0\,0)$	4176
Crystal size (mm^3)	0.199 × 0.193 × 0.19
θ Range for data collection (°)	2.44–28.35
Index ranges	$-21 \leqslant h \leqslant 21$, $-21 \leqslant k \leqslant 21$, $-38 \leqslant l \leqslant 38$
Reflections collected	68 863
Independent reflections	4858 [$R_{int} = 0.0479$]
Completeness to $\theta = 28.35°$	99.9%
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	4858/0/252
Goodness-of-fit (GOF) on F^2	1.106
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0337$, $wR_2 = 0.0972$
R indices (all data)	$R_1 = 0.0464$, $wR_2 = 0.1046$
Largest difference in peak and hole (e Å^{-3})	2.090 and −0.594

2.4.2. $[Cd(alizH)_2(H_2O)_3]$ **3**

To a hot orange 2-propanol solution (20 mL) of alizarin, (240.21 mg, 1 mmol), a water solution (5 mL) of cadmium acetate dihydrate, (133.01 mg, 0.5 mmol) was added at once at continuous stirring. The purple suspension was maintained at reflux for 3 h. The product was filtered of under reduced pressure and washed with water (5 mL) and methanol (5 mL), respectively. Yield 54% (174 mg). The solid does not melt up to 350 °C. *Anal.* Calc. for $C_{28}H_{20}O_{11}Cd$: C, 52.15; H, 3.13; Cd, 17.43. Found: C, 52.22; H, 2.87; Cd, 15.35%. NMR ^1H δ 8.19 (s, 2H, C8H), 8.14 (s, 2H, C5H), 7.89 (s, 4H, C6H and C7H), 7.62 (s, 2H, C3H), 7.21 (s, 2H, C4H); $^{13}C\{^1H\}$ δ 188.6, 180.4, 153.0, 150.8, 134.9, 134.4, 133.9, 133.5, 132.8, 126.4, 123.5, 121.1, 120.7, 116.1. IR 3440vs(br), 1630vs, 1586m, 1562m, 1510m, 1440m, 1410m, 1345s, 1258s, 1209w, 1187w, 1154w, 1042w,1019w, 815m, 764m, 715s, 663m.

2.4.3. $[Cd(chryzH)_2(H_2O)_2]$ **4**

The complex **4** was prepared following the same procedure adopted for **3**. Yield 45% (282 mg). M.p. 235–238 °C. *Anal.* Calc. for $C_{28}H_{18}O_{10}Cd$: C, 53.65; H, 2.89; Cd, 17.93. Found: C, 54.56; H, 2.87; Cd, 20.12%. NMR ^1H δ 7.53 (br, CH_{arom}), 7.01 (br, CH_{arom}); $^{13}C\{^1H\}$ δ 188.6, 182.1, 161.7, 161.1, 135.3, 133.5, 126.4, 124.1(br), 116.9. IR 3447s(br), 1675w, 1617vs, 1523w, 1478m, 1420m, 1347m, 1305m 1287s, 1220m, 1197m, 1160w, 1146w, 1085w, 1063w, 987w, 844m, 745s, 672w, 628m, 593w.

3. Results and discussion

3.1. Syntheses

While the 2-hydroxynaphthoquinone complex has been prepared in high yield, the complexes with dihydroxyanthraquinone have been prepared in moderate yields.

$$Cd(OOCCH_3)_2 + 2LH \rightarrow [CdL_2(H_2O)_n] + 2CH_3COOH \qquad (1)$$

L = alizH, $n = 3$ (**3**); L = chryzH, $n = 2$ (**4**).

In our studied complexes, the keto-hydroxy groups are acting as monoanionic chelating ligands. Although the X-ray diffraction and TG studies are convergent to **2**·$3H_2O$, the complex **2** has been analyzed as **2**·$2H_2O$ (Section 2.4). The complexes **2**–**4** are deeply colored and indefinitely stable in the solid-state.

3.2. X-ray molecular structure of **2**·$3H_2O$

High quality crystals of **2**·$3H_2O$ for X-ray analysis were obtained by dissolving an as isolated sample in water giving a rough concentration of 1 mM. The solution was left to stand on a bench top for 15 days when red crystals were collected by filtration. The most relevant bond lengths [Å] and bond angles [°] are seen in Table 2. The structure of compound **2**·$3H_2O$ features an isolated dimeric unit $[Cd_2(nq)_4(H_2O)_4]$ (Fig. 1). There is a unique cadmium(II) ion per asymmetric unit of **2**. The coordination polyhedral about each cadmium(II) atom is close to that found in bis(μ$_2$-o-hydroxybenzoato)bis(*o*-hydroxybenzoato)tetraaquodicadmium(II), described as pentagonal–bipyramidal [16]. The largest angle O–Cd–O 173.24(6) is between coordinated water molecules; the smallest angle 67.89(8) is from the chelate-bridging *o*-hydroxynaphthoquinonato ligand. The plane comprised by O(4)O(5)O(1)(O(2′)O(1′) bound to Cd (RMS deviation of fitted atoms 0.1803) and the corresponding plane formed by the oxygen atoms bound to Cd′ form an