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Hexaaquacobalt(II) and Hexaaquacadmium(II) 4-Nitro-2,3,5,6-Tetraoxopyridinates $[M(H_2O)_6](C_5HN_2O_6)_2 \cdot 2H_2O$ (M = Co and Cd): Synthesis, Structures, and Properties

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Abstract—The complexes $[Cd(H_2O)_6](C_5HN_2O_6)_2 \cdot 2H_2O$ (**I**) and $[Co(H_2O)_6](C_5HN_2O_6)_2 \cdot 2H_2O$ (**II**) were obtained in the crystalline state by reactions of cobalt chloride and cadmium chloride with ammonium 4-nitro-2,3,5,6-tetraoxopyridinate, $(NH_4)_2 \cdot (C_5HO_6N_2)_2$. Their cocrystallization gave the heterometallic complex $[Cd_{0.32}Co_{0.68}(H_2O)_6](C_5HN_2O_6)_2 \cdot 2H_2O$ (**III**). The crystal and molecular structures of complexes **I**–**III** were determined by X-ray diffraction. It was demonstrated that the complexation reactions occur by replacement of two ammonium cations 4-nitro-2,3,5,6-tetraoxopyridinate by the complex cations $[M(H_2O)_6]^{2+}$. The tetraoxopyridinate anions and the complex cations are hydrogen-bonded through the coordinated and crystallization water molecules as well as through the O atoms of the organic anion. The thermolysis of complexes **I** and **II** was examined by TGA.

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This work was intended to continue our many-year investigations of the structures and complexation reactions of tetraoxopyridines. For instance, ammonium 4-nitro-2,3,5,6-tetraoxopyridinate, $(NH_4)_2 \cdot (C_5HO_6N_2)_2$, is a precursor for the synthesis of coordination compounds containing the tetraoxopyridinate anion. Earlier, we have studied the structure of $(NH_4)_2 \cdot (C_5HO_6N_2)_2$ by X-ray diffraction [1], obtained the complexes $M(H_2O)_6(C_5HN_2O_6)_2 \cdot 2H_2O$ (M = Ni^{2+}, Cu^{2+}, Co^{2+}, and Zn^{2+}) in the crystalline state, and structurally identified the complex $Ni(H_2O)_6(C_5HN_2O_6)_2 \cdot 2H_2O$ [2]. Unusual solvatolytic decomposition of the pyridine ring of $(NH_4)_2 \cdot (C_5HN_2O_6)_2$ into 2-methyl-1,3-diazolium hydrobis(oxamate) has been studied in [3]. The crystal structures of sodium 4-nitro-2,3,5,6-tetraoxopyridinate trihydrate and ammonium sodium bis(4-nitro-2,3,5,6-tetraoxopyridinate) monohydrate have been examined in [4].

In the present work, we obtained hexaaquacadmium(II) and hexaaquacobalt(II) 4-nitro-2,3,5,6-tetraoxopyridinates, $[Cd(H_2O)_6](C_5HN_2O_6)_2 \cdot 2H_2O$ (**I**) and $[Co(H_2O)_6](C_5HN_2O_6)_2 \cdot 2H_2O$ (**II**), and the product of their cocrystallization, $[Cd_{0.32}Co_{0.68}(H_2O)_6](C_5HN_2O_6)_2 \cdot 2H_2O$ (**III**). In addition, we determined their crystal and molecular structures and studied their properties.

EXPERIMENTAL

Cobalt(II) and cadmium(II) chloride hydrates (reagent grade) were used; $(NH_4)_2 \cdot (C_5HO_6N_2)_2$ was prepared as described in [5, 6].

Synthesis of metal complexes. An appropriate metal chloride (5 mmol) was dissolved in ethanol (10–20 mL) and the resulting solution was brought to boiling. Then a hot solution of $(NH_4)_2 \cdot (C_5HO_6N_2)_2$ in acetonitrile was added dropwise. The reaction mixture was kept on a water bath for 30 min, cooled, and left for several days until precipitation occurred. The precipitates were filtered off, washed with ethanol, and dried to constant weights. The yields of the complexes were 30–45%. Yellow-brown single crystals suitable for X-ray diffraction were obtained by recrystallization from ethanol.

For $Cd(H_2O)_6(C_5HO_6N_2)_2 \cdot 2H_2O$ (**I**) ($M = 662.71$)

anal. calcd. (%):	C, 18.12;	N, 8.45;	H, 3.35;	Cd, 16.96.
Found (%):	C, 17.88;	N, 8.72;	H, 3.17;	Cd, 17.30.

For $Co(H_2O)_6(C_5HO_6N_2)_2 \cdot 2H_2O$ (**II**) ($M = 609.23$)

anal. calcd. (%):	C, 19.72;	N, 9.20;	H, 3.64;	Co, 9.67.
Found (%):	C, 20.14;	N, 9.24;	H, 3.01;	Co, 9.37.

The contents of the metals were determined by spectrophotometry. Chemical analyses for nitrogen

Table 1. Selected crystallographic parameters and the data collection and refinement statistics for structures **I–III**

Parameter	Value		
	I	**II**	**III**
Empirical formula	$C_5H_9N_2O_{10}Cd_{0.50}$	$C_5H_9N_2O_{10}Co_{0.50}$	$C_5H_9N_2O_{10}Cd_{0.16}Co_{0.34}$
M	313.34	286.61	295.16
Color, shape	Yellow, prism	Orange, prism	Dark yellow, prism
Crystal system, space group, Z	Triclinic, $P\bar{1}$, 2	Triclinic, $P\bar{1}$, 2	Triclinic, $P\bar{1}$, 2
a, Å	5.787(1)	5.687(1)	5.724(1)
b, Å	9.844(2)	9.825(2)	9.831(2)
c, Å	9.942(2)	9.847(2)	9.876(2)
α, deg	70.56(3)	70.03(3)	70.18(3)
β, deg	85.20(3)	78.78(3)	85.12(3)
γ, deg	77.81(3)	85.14(3)	78.33(3)
V, Å^3	521.98(18)	507.13(18)	511.9(2)
ρ_{calcd}, g/cm^3	1.994	1.877	1.915
μ_{Mo}, mm^{-1}	1.156	0.959	1.023
$F(000)$	314	293	300
Crystal dimensions, mm	0.50 × 0.30 × 0.10	0.50 × 0.40 × 0.25	0.50 × 0.40 × 0.25
θ scan range, deg	2.17–25.46	2.21–25.46	2.19–25.47
Ranges of h, k, and l indices	$-6 < h < 6, 0 < k < 11, -11 < l < 12$	$-6 < h < 6, 0 < k < 11, 11 < l < 11$	$0 < h < 6, 11 < k < 11, 11 < l < 11$
Number of measured reflections (N_0)/independent reflections (N) (R_{int})	2041/1920 (0.015)	1999/1881 (0.017)	2097/1892 (0.012)
Number of parameters refined	197	197	204
Completeness of data collection for $\theta = 25.46°$, %	100.0	100.0	100.0
R_1, wR_2 for N_0	0.0284, 0.0653	0.0369, 0.0789	0.0234, 0.0532
R_1, wR_2 ($I > 2\sigma(I)$)	0.0252, 0.0646	0.0267, 0.0765	0.0193, 0.0524
GOOF (F^2)	1.096	1.121	1.119
$\Delta\rho_{max}/\Delta\rho_{min}$, e/Å^3	0.722/–1.178	0.340/–0.306	0.274/–0.377

and carbon were carried out using micromethods. A qualitative reaction for chloride ions gave a negative result. The composition of complex **III** was confirmed by X-ray diffraction.

The IR spectra of the complexes under study were recorded on a Varian Excalibur HE 3100 instrument in the 4000–400 cm^{-1} range (KBr pellets). Polystyrene was used as a standard to check the calibration of the instrument.

Thermogravimetric analysis (TGA) was carried out on a CDT Q 600 derivatograph by heating complexes **I** (24.50 mg) and **II** (11.44 mg) from 20 to 700°C.

A single-crystal X-ray diffraction study of complexes **I–III** was carried out at 293 K on an Enraf-Nonius CAD-4 diffractometer (MoK_α radiation, $\omega/2\theta$ scan mode, β-filter). The crystallographic parameters and the data collection and refinement statistics for structures **I–III** are given in Table 1; the corresponding hydrogen bonding parameters are given in Tables 2–4. The structures were solved by direct methods and refined anisotropically (for the non-hydrogen atoms) by the full-matrix least-squares method. The H atoms were located in difference electron-density maps and refined with fixed coordinates and thermal parameters. All calculations were performed with the SHELX-97 program [7]. The atomic coordinates and other parameters of structures **I–III** have been deposited with the Cambridge Crystallographic Data Centre (nos. 888700–888702 for **I–III**, respectively; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

According to the elemental analysis data, complexes **I** and **II** can be formulated as

Table 2. Geometrical parameters of the hydrogen bonds in structure **I***

Hydrogen bond D–H···A	Distance, Å			Angle DHA, deg
	D–H	H···A	D···A	
N(1)–H(1)O(1)$^{\#3}$	0.75(3)	2.15(3)	2.892(3)	167(3)
O(7)–H(71)O(2)$^{\#4}$	0.73(4)	2.04(4)	2.738(3)	162(4)
O(7)–H(72)O(10)$^{\#2}$	0.81(4)	1.84(4)	2.650(3)	179(4)
O(8)–H(81)O(2)$^{\#5}$	0.73(4)	2.15(4)	2.771(3)	144(4)
O(8)–H(82)O(6)$^{\#6}$	0.76(4)	2.16(4)	2.892(3)	162(4)
O(9)–H(91)O(3)$^{\#1}$	0.74(4)	2.09(5)	2.781(3)	156(4)
O(10)–H(101)O(3)$^{\#2}$	0.69(4)	2.23(5)	2.853(3)	151(5)
O(10)–H(102)O(4)$^{\#7}$	0.76(5)	2.11(5)	2.869(3)	174(5)

* The symmetry operation codes are: $^{\#1}$ $-x, -y, -z$; $^{\#2}$ x, y, z; $^{\#3}$ $-x, -y-1, -z+2$; $^{\#4}$ $x+1, y, z-1$; $^{\#5}$ $-x-1, -y, -z+1$; $^{\#6}$ $x+1, y, z$; $^{\#7}$ $-x+1, -y-1, -z+1$.

Table 3. Geometrical parameters of the hydrogen bonds in structure **II***

Hydrogen bond D–H···A	Distance, Å			Angle DHA, deg
	D–H	H···A	D···A	
N(1)–H(1)O(1)$^{\#3}$	0.83(3)	2.05(3)	2.879(3)	174(2)
O(7)–H(71)O(10)$^{\#2}$	0.80(4)	1.87(4)	2.666(3)	176(3)
O(7)–H(72)O(2)$^{\#4}$	0.71(4)	2.03(4)	2.720(2)	163(3)
O(8)–H(81)O(2)$^{\#5}$	0.65(3)	2.17(3)	2.757(3)	151(4)
O(8)–H(82)O(6)$^{\#2}$	0.78(4)	2.10(4)	2.870(3)	169(3)
O(9)–H(91)O(7)$^{\#6}$	0.73(3)	2.19(4)	2.923(3)	173(3)
O(9)–H(92)O(3)$^{\#6}$	0.77(4)	2.06(4)	2.786(3)	159(3)
O(10)–H(101)O(4)$^{\#7}$	0.77(4)	2.13(4)	2.869(3)	160(3)
O(10)–H(102)O(3)$^{\#8}$	0.66(4)	2.24(4)	2.836(3)	151(4)

* The symmetry operation codes are: $^{\#1}$ $-x, -y, -z$; $^{\#2}$ x, y, z; $^{\#3}$ $-x+2, -y+2, -z-1$; $^{\#4}$ $x, y-1, z$; $^{\#5}$ $-x, -y+1, -z$; $^{\#6}$ $-x+1, -y, -z$; $^{\#7}$ $-x+2, -y+1, -z-1$; $^{\#8}$ $x-1, y, z$.

Table 4. Geometrical parameters of the hydrogen bonds in structure **III***

Hydrogen bond D–H···A	Distance, Å			Angle DHA, deg
	D–H	H···A	D···A	
N(4)–H(4)O(3)$^{\#3}$	0.86(2)	2.03(2)	2.881(2)	172(2)
O(1*w*)–H(11)O(3*w*)$^{\#4}$	0.81(3)	2.09(3)	2.899(2)	174(3)
O(1*w*)–H(12)O(6)$^{\#5}$	0.82(3)	2.00(3)	2.783(2)	160(3)
O(2*w*)–H(21)O(7)$^{\#6}$	0.82(3)	2.07(3)	2.875(2)	167(2)
O(2*w*)–H(22)O(2)$^{\#2}$	0.83(3)	2.04(3)	2.756(2)	144(2)
O(3*w*)–H(31)O(2)$^{\#2}$	0.87(3)	1.89(3)	2.7217(2)	160(2)
O(3*w*)–H(32)O(4*w*)$^{\#7}$	0.87(3)	1.79(3)	2.661(2)	178(3)
O(4*w*)–H(41)O(5)$^{\#8}$	0.86(3)	2.02(3)	2.866(2)	165(2)
O(4*w*)–H(42)O(6)$^{\#9}$	0.81(3)	2.10(3)	2.837(2)	151(3)

* The symmetry operation codes are: $^{\#1}$ $-x+1, -y+1, -z+1$; $^{\#2}$ x, y, z; $^{\#3}$ $-x-1, -y+2, -z+1$; $^{\#4}$ $-x, -y+1, -z+1$; $^{\#5}$ $-x, -y+1, -z+2$; $^{\#6}$ $-x+1, -y+1, -z+2$; $^{\#7}$ $-x, -y+2, -z+1$; $^{\#8}$ $x+1, y, z$; $^{\#9}$ $-x-1, -y+2, -z+2$.

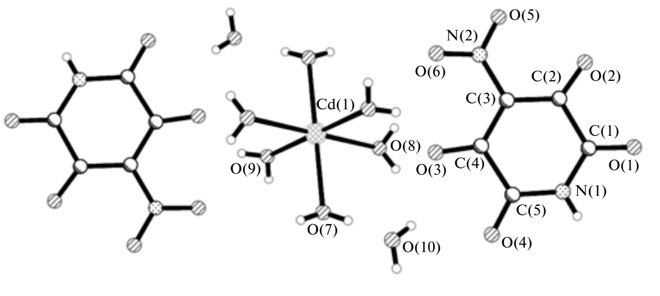

Fig. 1. Structure **I**.

$M(H_2O)_6(C_5HO_6N_2)_2 \cdot 2H_2O$ (M = Co (**I**) and Cd (**II**)). They are formed by replacement of two ammonium cations in $(NH_4)_2 \cdot (C_5HO_6N_2)_2$ by the hexaaqua cation of the corresponding metal. Cocrystallization of complexes **I** and **II** yielded the complex $[Cd_{0.32}Co_{0.68}(H_2O)_6](C_5HN_2O_6)_2 \cdot 2H_2O$ (**III**); in its crystal lattice, 32% of the cobalt atoms are replaced by cadmium ones. Structurally, complexes **I–III** are built from the centrosymmetric complex cations $[M(H_2O)_6]^{2+}$, the 4-nitro-2,3,5,6-tetraoxopyridinate anions, and crystallization water molecules (X-ray diffraction data).

In the complex cation (Fig. 1), the metal atom is coordinated by the O atoms of six water molecules arranged in an octahedral pattern. The M–O bond lengths are 2.247–2.314 Å for **I** and 2.044–2.134 Å for **II**; the angles in the equatorial plane of the octahedron are 77°–85°. Structure **III** shows partial replacement of the cobalt atoms by cadmium ones. This does not change the general scheme of crystal formation, so complexes **I–III** are isostructural. In turn, they are isostructural to the complex $Ni(H_2O)_6(C_5HN_2O_6)_2 \cdot 2H_2O$ [5]. The parameter *a* increases in the order Co < Ni < Co/Cd < Cd; the parameters *b* and *c* increase in the order Ni < Co < Co/Cd < Cd.

In the anion containing the organic ligand $(C_5HN_2O_6)^-$, the heterocyclic framework is nearly planar (the average deviation of the atoms from their mean-square plane is 0.0178 Å). The ring is not aromatic: the imine (OC–NH–CO) and β-diketone fragments (OC–C(NO_2)–CO) are linked by the single C–C bonds. The nitro group of the ligand is not coplanar with the framework (the corresponding angle is 10.6°). The endo- and exocyclic N atoms show trigonal bond orientations (the sums of their bond angles are 359.1° and 360°, respectively). The geometrical parameters of the organic anion in structures **I–III** are close to those in $(NH_4)_2 \cdot (C_5HO_6N_2)_2$ [3]. The main difference is that the organic anions in $(NH_4)_2 \cdot (C_5HO_6N_2)_2$ form in pairs charge-transfer complexes and each monoanion simultaneously acts as both an electron donor and an electron acceptor with respect to its partner in the associate (the electron-withdrawing diketone fragment is above the electron-donating imine fragment). In complexes **I–III**, the organic anions are spatially oriented in a different way: the diketone fragment is above the diketone fragment and the imine fragment is above the imine fragment. Complexes **I–III** have layered crystal structures (Figs. 2a–2c). Each layer consists of alternating cation- and anion-containing stacks aligned with the axis *x*. In stacks, the complex cations are hydrogen-bonded to form infinite chains (Tables 2–4). The shortest Cd···Cd distance in the chain of complex **I** is 5.787 Å; analogous Co···Co and Co/Cd···Co/Cd distances in structures **II** and **III** are 5.687 and 5.724 Å, respectively. The shortest distances between the adjacent organic anions in stacks (3.158 Å for C(3)···O(5) and

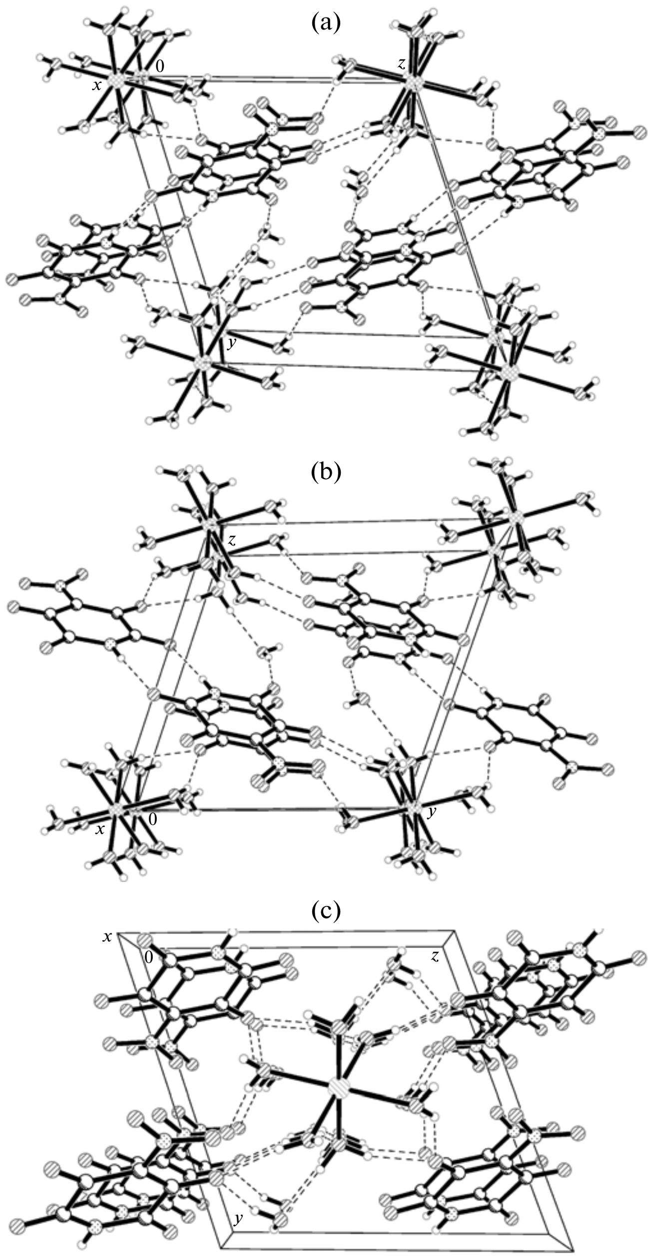

Fig. 2. Molecular packing in the crystals of complexes (a) **I**, (b) **II**, and (c) **III** along the crystallographic axis *x*.

Table 5. TGA data for complexes **I** and **II**

Complex	*T*, °C	Effect	Weight loss, %	Process	Theoretical weight loss, %
I	108	Endo	18.49	$-7H_2O$	19.01
	163	Endo	1.56	$-0.5H_2O$	1.36
	225	Endo	1.06	$-0.5H_2O$	1.36
	345	Exo	59.02	Burning of the organic mass (CdO as a solid residue)	59.50
II	125	Endo	8.98	$-3H_2O$	8.86
	162	Endo	13.36	$-3H_2O$	11.81
	205	Endo	1.98	$-H_2O$	2.95
	344	Exo	37.72	Burning of the organic mass (Co_3O_4 as a solid residue)	36.97

2.900 Å for O(5)···O(5)) are close to the sums of the van der Waals radii of the corresponding atoms (3.17 and 2.80 Å, respectively [4]).

In stacks A, each organic anion is hydrogen-bonded by the carbonyl and nitro groups to two cations of an adjacent stack (O(9)–H(7)···O(3) and O(8)–H(4)···O(6)). In addition, the organic anion is hydrogen-bonded through the imine N atom and the carbonyl group to an anion of an adjacent stack A (N(1)–H(1)···O(1)). Layers are united through hydrogen bonds formed by the carbonyl group of an anion in one layer and a water molecule in a different layer. The layers are interlaid with crystallization water molecules which are also hydrogen-bonded to the organic anions and complex cations of adjacent layers (Tables 2–4, Fig. 2).

The IR spectra of complexes **I–III** retain the absorption bands of the carbonyl groups at 1740–1690 cm^{-1}, which is characteristic of compounds containing the outer-sphere 4-nitro-2,3,5,6-tetraoxopyridinate anion [5]. The bands at 3235–3080 (N–H stretching vibrations in NH_4^+) and 1400 cm^{-1} (N–H bending vibrations in NH_4^+) disappear. The very intense, wide band at 3450–3600 cm^{-1} is due to the stretching vibrations of coordinated and crystallization water molecules.

According to TGA data (Table 5), complexes **I** and **II** at 108–125°C release their crystallization water and part of their coordinated water. The other water molecules are successively eliminated up to 225°C. From 344 to 700°C, the organic component decomposes and Co^{2+} partially oxidizes into Co^{3+} (the final thermolysis product for **II** is Co_3O_4). For complex **I**, the final thermolysis product is CdO.

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