

A Nitrilotriacetate Bridged Heteronuclear Co(II)-Na(I) Polymer: $\{[\text{CoNa}(\text{NTA})(\text{H}_2\text{O})_3] \cdot 2\text{H}_2\text{O}\}_n$

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A novel Co(II)-Na(I) heterometallic coordination polymer $\{[\text{CoNa}(\text{NTA})(\text{H}_2\text{O})_3] \cdot 2\text{H}_2\text{O}\}_n$ (NTA = nitrilotriacetate) was synthesized and characterized by elemental analysis and X-ray diffraction study. The electrochemical behavior in aqueous solution was measured by cyclic voltammetry, indicating a quasi-reversible process. The complex crystallizes in the orthorhombic space group *Pbca* with the cell parameters $a = 1.47276(3)$ nm, $b = 0.97280(3)$ nm, $c = 1.92946(6)$ nm, $V = 2.76434(13)$ nm³, $Z = 8$. In the title complex, there are two kinds of zigzag chains which interconnect together to form 2D network. One stretches along the *b*-axis, comprising Co(II) ions, the other stretches along the *c*-axis, comprising Na(I) ions.

Keywords nitrilotriacetate, cobalt(II) ion, crystal structure, heterometallic coordination polymer, electrochemical properties

Introduction

The nitrilotriacetic acid is one of the important derivatives of glycine. During the last decade, its trivalent anion (NTA), as a bridging ligand, has attracted wide attention and become one of the subject of intensive research for several reasons.¹⁻⁶ Each NTA has three carboxylate groups and each of them has five kinds of coordination modes,⁷ so that the complexes bridged by NTA possess many sorts of novel structural features.⁸ Moreover, NTA as a chelant can form stable coordination compounds with many metal ions, which is important for applications in medical science. For example, some toxic heavy metal ions can be eliminated from human body by forming complexes with NTA,⁹ and some NTA com-

plexes of radioactive metal ions can be used as the imaging agent¹⁰ for the diagnosis and therapy of some diseased organs.

We used sodium salt of NTA and Co(II) to prepare the title complex $\{[\text{CoNa}(\text{NTA})(\text{H}_2\text{O})_3] \cdot 2\text{H}_2\text{O}\}_n$, and report herewith its crystal structure and electrochemical properties.

Experimental

Preparation

The nitrilotriacetic acid (H_3NTA) (0.1915 g, 1.0 mmol) was dissolved in water (10 mL) at 80 °C and the pH value of the solution was adjusted to 6.0 with NaOH solution (0.2 mol/L), then aqueous solution (5 mL) of $\text{Co}(\text{CH}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$ (0.2498 g, 1.0 mmol) was added dropwise with stirring at room temperature. The resulting red solution was adjusted to pH = 5 and the reaction mixture was filtered. The filtrate stood for two months until the red single crystals were obtained.

Elemental analysis

C, H and N were analyzed using a Carlo-Erba 1112 Elemental Analyzer. Co was analyzed by complexometric titration with EDTA. Anal. calcd for $\{[\text{CoNa}(\text{NTA})(\text{H}_2\text{O})_3] \cdot 2\text{H}_2\text{O}\}_n$: C 19.99, H 4.44, N 3.89, Co 16.38; found C 19.68, H 4.64, N 3.76, Co 16.52.

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Received June 7, 2001; revised October 8, 2001; accepted November 23, 2001.

Project supported by the Education Commission of Zhejiang Province (No. 20010129) and "551" Distinguished Person Foundation of Wenzhou.

Crystal structure determination

A red single crystal (size 0.45 nm × 0.30 nm × 0.25 mm) of the title complex was mounted on a Rigaku AFC7R diffractometer. X-ray diffraction intensity data were collected up to 2θ value of 50.06° with graphite monochromated Mo K_α radiation (λ = 0.071069 nm) by the ω-2θ scan technique. A total of 6160 reflections were collected, of which 2373 reflections with [*I* > 2.0σ(*I*)] were considered as observed and used for the structure refinement. Usual LP and empirical absorption corrections were applied. The structure was solved by Patterson method followed by Fourier syntheses. Structure refinement was carried out by full-matrix least-squares procedures using the SHELX-93 program package. H atoms were located in a difference Fourier map, and their coordinates and thermal parameters were fixed during structure refinement. Anisotropic refinement in-

cluding all the non-H atoms converged at agreement factors *R* = 0.0501 and *wR* = 0.1278, where *w* = 1/σ²(*F*₀). Atomic scattering factors were taken from International Tables for X-ray crystallography. Crystal parameters and refinement results are summarized in Table 1.

Cyclic voltammetry (CV) measurement

Cyclic voltammetry (CV) measurement was carried out in the potential range from 1.20 V to -0.38 V, using 0.10 mol/L KCl as the supporting electrolyte and water as the solvent. The working electrode was a spectrographic pure graphite electrode (diameter 3 mm). The auxiliary electrode was a platinum wire and the reference electrode was a saturated calomel electrode (SCE). Solutions were deoxygenated and blanketed with nitrogen gas. The concentration of the compounds in these measurements was 0.0010 mol/L. The scan rate was 50 mV/s.

Table 1 Crystallographic data for { [CoNa(NTA)(H₂O)₃] · 2H₂O }_n

Chemical Formula	C ₆ H ₁₆ CoNaNO ₁₁
Crystal system	orthorhombic
Space group	<i>Pbca</i>
<i>a</i> (nm)	1.47276(3)
<i>b</i> (nm)	0.97280(3)
<i>c</i> (nm)	1.92946(6)
<i>V</i> (nm ³)	2.76434(13)
<i>D</i> _c (g · cm ⁻³)	1.721
Formula weight	358.10
λ (nm)	0.071069
<i>Z</i>	8
<i>F</i> (000)	1464
Crystal size (nm)	0.45 nm × 0.30 nm × 0.25 nm
θ range (deg)	2.11 to 25.03
Index range	-16 ≤ <i>h</i> ≤ 17 - 6 ≤ <i>k</i> ≤ 10 - 13 ≤ <i>l</i> ≤ 22
μ, mm ⁻¹	1.326
<i>T</i> (K)	293
Reflections collected/unique	6160/2373 [<i>R</i> _{int} = 0.048]
Refinement method	Full-matrix least-squares on <i>F</i> ²
Parameters	182
Goodness-of-fit on <i>F</i> ²	1.183
Final <i>R</i> indices [<i>I</i> > 2.0σ(<i>I</i>)]	<i>R</i> ₁ = 0.0501 <i>wR</i> ₂ = 0.1278
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0353 <i>wR</i> ₂ = 0.0885,
Extinction coefficient	0.0031(4)
Largest diff. peak and hole	611 e ⁻ /nm ³ and -548 e ⁻ /nm ³
Maximum shift (Δ/σ) _{max}	0.00

Results and discussion

Selected bond distances and angles are listed in Table 2, and fractional atomic coordinates and equivalent isotropic thermal parameters for non-H atoms are summarized in Table 3. The molecular structure of the title complex with the atom numbering scheme is illustrated in Fig. 1.

In the title complex, there are two kinds of zigzag chains which interconnect together to form 2D network. One comprises Co(II) ions and stretches along the *b*-axis, the other comprises Na(I) ions and stretches along the *c*-axis. In the former chain, each Co(II) ion is coordinated by one nitrogen atom and three oxygen atoms from three carboxylate groups of one NTA, forming three five-members rings. Moreover the Co(II) ion is also coordinated by one oxygen atom from one carboxylate group of the adjacent NTA and one oxygen atom from the coordinated water, respectively. So the Co(II) ion is six-coordinated in an octahedral geometry. In the later chain,

the four oxygen atoms from the carboxylate groups of four NTAs and two oxygen atoms from the aqua ligands coordinate to the Na(I) ion to complete an octahedron around the Na(I) ion. In the title complex, the closest adjacent Co(II)—Na(I) distance is quite short [0.3364(19) nm].

It is worthy to note that the coordination modes of three carboxylate groups of each NTA are different. One acts using only one oxygen atom (O(5)) to ligate a pair of Co(II) and Na(I) ions in a bridging mode. Another one uses its two oxygen atoms, O(3) and O(4), to coordinate to a Co(II) and a Na(I) ion, respectively. The third one functions with each oxygen atom ligating a pair of Co(II) and Na(I) ions in a μ_4 -bridging mode. These bridging carboxylate groups extend the structure into 2D nets in the solid (Fig. 2). The crystal packing diagram along the *c*-axis is shown in Fig. 2.

Extensive hydrogen bonds have been found in the crystal. The H-bond exists between the carboxylate groups and water as verified by the O(1)—O(7) distance

Table 2 Selected interatomic distances (nm) and interbond angles ($^\circ$) for $\{[\text{CoNa}(\text{NTA})(\text{H}_2\text{O})_3] \cdot 2\text{H}_2\text{O}\}_n$

Bonds distances (nm)			
N—Co(1)	0.2148(4)	Co—O(2) # 2	0.2066(3)
Na—O(1)	0.2358(4)	Na—O(8)	0.2362(4)
Na—O(5) # 1	0.2402(4)	Na—O(2) # 2	0.2434(4)
Na—O(9)	0.2430(4)	Na—O(4) # 3	0.2434(4)
Co—O(3)	0.2051(3)	Co—O(7)	0.2134(3)
Co—O(5)	0.2083(3)	O(1)—C(2)	0.1252(5)
O(2)—C(2)	0.1258(5)	O(3)—C(4)	0.1261(6)
O(4)—C(4)	0.1246(6)	O(5)—C(6)	0.1251(5)
O(6)—C(6)	0.1248(5)	O(1)—O(7)	0.2874(5)
O(8)—OW(2) # 1	0.2774(6)	OW(2)—OW(1) # 4	0.2822(6)
OW(1)—O(3)	0.2793(5)	Co—Na	0.3364(19)
Bond angle ($^\circ$)			
O(1)-Na-O(8)	176.81(17)	O(9)-Na-O(4) # 3	164.03(16)
O(5) # 1-Na-O(2) #	164.87(14)	O(1)-Na-O(9)	81.17(13)
O(8)-Na-O(4) # 3	99.98(17)	O(8)-Na-O(9)	95.92(16)
O(1)-Na-O(4) # 3	82.90(14)	O(8)-Na-O(2) # 2	105.59(14)
O(1)-Na-O(5) # 1	89.41(12)	O(1)-C(2)-O(2)	124.9(4)
O(4)-C(4)-O(3)	124.4(5)	O(6)-C(6)-O(5)	124.6(4)
O(5)-Co-O(1)	154.85(13)	O(3)-Co-O(7)	174.99(14)
O(2) # 2-Co-N	164.62(13)	O(3)-Co-N	82.55(13)
O(2) # 2-Co-O(7)	87.42(13)	O(7)-Co-N	101.31(14)
O(3)-Co-O(2) # 2	89.53(13)	O(5)-Co-N	80.03(13)
O(2) # 2-Co-O(1)	89.97(12)		

Table 3 Atomic coordinates and equivalent isotropic displacement parameters [$\times 10^4 \text{ nm}^2$] for $[\text{CoNa}(\text{NTA})(\text{H}_2\text{O})_3] \cdot 2\text{H}_2\text{O}$. $U(\text{eq})$ is defined as one third of the trace of orthogonalized U_{ij} tensor

Atom	X	Y	Z	U(eq)
N	0.6122(2)	0.3294(4)	0.3733(2)	2.3(1)
Na	0.4601(1)	0.3208(2)	0.1507(1)	3.2(1)
Co	0.5535(1)	0.1958(1)	0.2968(1)	2.3(1)
O(1)	0.5122(2)	0.3916(3)	0.2606(2)	3.1(1)
O(8)	0.4135(3)	0.2588(4)	0.0379(2)	5.9(1)
O(2)	0.4910(2)	0.6079(3)	0.2946(2)	2.7(1)
OW(2)	0.6749(3)	-0.4567(5)	0.5277(2)	6.6(1)
O(3)	0.6837(2)	0.1948(4)	0.2591(2)	3.8(1)
OW(1)	0.7089(3)	-0.0306(5)	0.1715(2)	5.8(1)
O(4)	0.8245(2)	0.2590(4)	0.2843(2)	4.6(1)
O(9)	0.6085(2)	0.4070(4)	0.1171(2)	4.9(1)
O(5)	0.5885(2)	0.0520(3)	0.3723(2)	3.2(1)
O(6)	0.6411(3)	0.0278(4)	0.4790(2)	4.4(1)
O(7)	0.4175(2)	0.1781(4)	0.3339(2)	3.9(1)
C(1)	0.5550(3)	0.4533(5)	0.3758(2)	2.7(1)
C(2)	0.5176(3)	0.4865(5)	0.3043(2)	2.4(1)
C(3)	0.7043(3)	0.3609(6)	0.3484(3)	3.6(1)
C(4)	0.7408(3)	0.2626(5)	0.2938(2)	3.0(1)
C(5)	0.6146(4)	0.2533(5)	0.4396(3)	3.7(1)
C(6)	0.6156(3)	0.0993(5)	0.4289(2)	2.8(1)

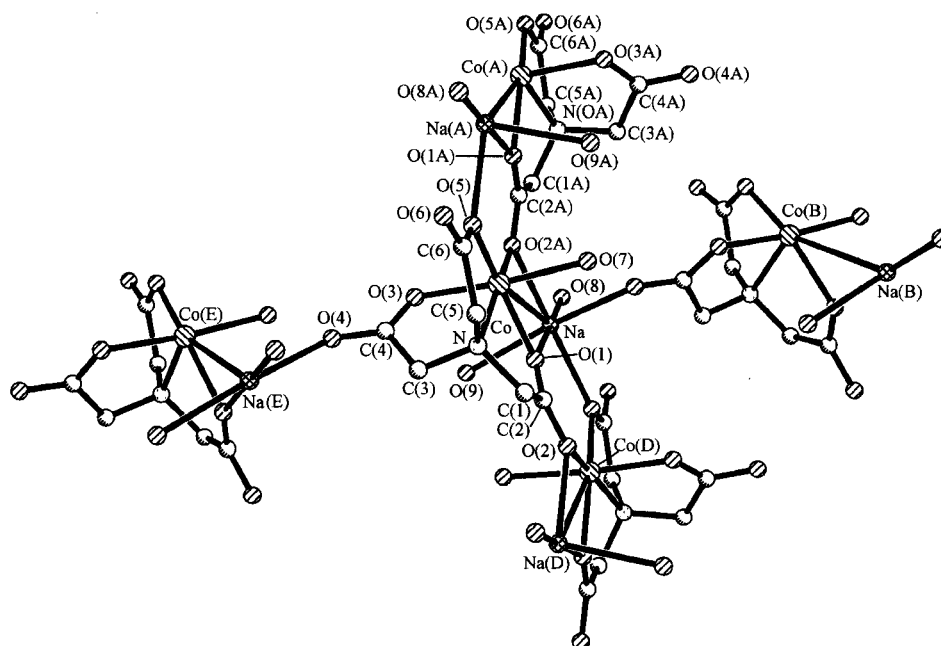


Fig. 1 Coordination environments of the metal ions.

of 0.2874(5) nm and OW(1)—O(3) distance of 0.2793(5) nm, between the aqua ligands and lattice water molecules as verified by the O(8)—OW(2) [$-x + 1, y + 1/2, -z + 1/2$] distance of 0.2774(6) nm,

especially between the two lattice water molecules as verified by the OW(2)—OW(1) [$x, -y - 1/2, z + 1/2$] distance of 0.2822(6) nm. Therefore, these hydrogen bonds result in the final three-dimensional network.

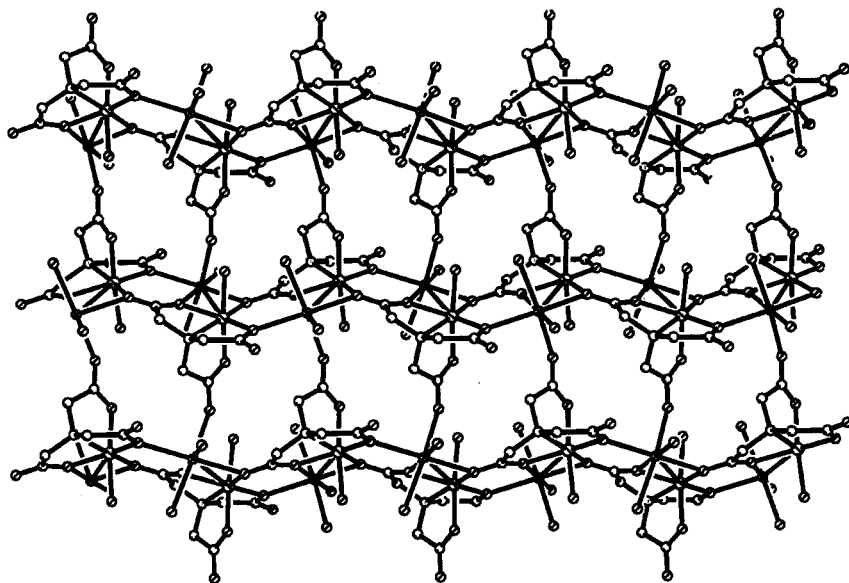


Fig. 2 2D network viewed along the *c*-axis.

Cyclic voltammetry (Fig. 3) of the title complex in aqueous solution shows a pair of redox waves with the oxidation and reduction peaks at 0.96 V and -0.067 V versus SCE, respectively, and the difference of 1.027 V indicates a quasi-reversible redox process.¹¹ The CV behavior is different from those of simple Co(III)/Co(II) chelate complexes which usually demonstrate reversible electrochemical behavior.^{12,13} The quasi-reversible redox behavior may be possibly due to the formation of hydroxide Co(III) species in the solution.

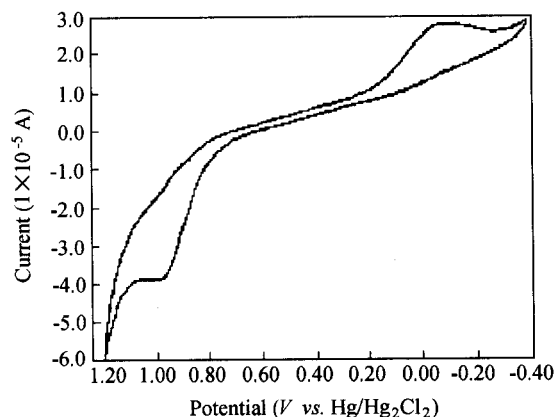


Fig. 3 Cyclic voltammogram of the title complex in water. Concentration of the sample; 0.001 mol/L; Scan rate; 50 mV/s.

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