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Inorganic Chemistry
Note

Synthesis and Structural Characterization of $[Na_2M(C_5O_5)_2(H_2O)_2]\cdot 4H_2O$ ($M = Ni^{II}$, Cu^{II})

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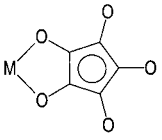
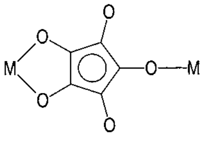
Introduction

Monocyclic aromatic oxocarbon dianions $[C_nO_n]^{2-}$ ($n = 3-5$), characterized by extensive π electron delocalization all over the ring of carbon and oxygen atoms, can serve as polydentate ligands to bind the metal ions via various bonding modes, especially for the squarate ($n = 4$) and croconate ($n = 5$) dianion ligands.[1−14] So far, only a few structures of croconate ($C_5O_5^{2-}$) hydrate metal complexes with first row transition metal ions in the formula $[M(C_5O_5)(H_2O)_3]$ ($M = Zn^{II}$, Cu^{II}, Co^{II}, Fe^{II}, Mn^{II})[8−10,12] and some rare earth metal ions are known.[8−14] Available structural conformations for the transition metal ions with croconate ligand show that croconate ligand can act either as a terminal as form **I**[15−17] or as a bridging ligand as form **II** or **III**.[8−14]



I



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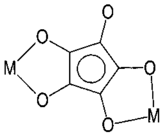
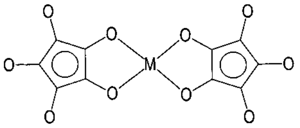


III

In the present study, a symmetric bonding mode as form **IV** of croconate ligands coordinating to a metal ion is introduced as the formula $[Na_2M(C_5O_5)_2(H_2O)_2]\cdot 4H_2O$ (M = Ni, **1** and Cu, **2**). The preparation and structural characterization of these two complexes are presented herein. The three-dimensional framework constructed by the $[M(C_5O_5)_2(H_2O)_2]^{2-}$ moieties and sodium ions is described in detail.



IV

Experimental Section

Reactants and Physical Techniques. All chemicals were of reagent grade and were used as commercially obtained without further purification. The infrared spectra were recorded on a Nicolet Fourier transform IR, MAGNA-IR 500 spectrometer in the range 500−4000 cm^{-1} using the KBr disk technique. The temperature-dependent magnetic susceptibility of complex **2** was measured on the SQUID system with 10000 G external magnetic field. Molar magnetic susceptibility was recorded every 5 K in the range 5−300 K.

Preparation of $[Na_2Ni(C_5O_5)_2(H_2O)_2]\cdot 4H_2O$ (1). An aqueous solution (5 mL) of anhydrous $NiCl_2$ (32.4 mg, 0.2 mmol) was added to an aqueous solution (1 mL) of $Na_2C_5O_5$ (69.7 mg, 0.375 mmol) in a tube at room temperature. Slow evaporation at room temperature of the resulting green solution gave green crystals of complex **1** after two weeks (yield 2.94%). Anal. Calcd of **1**: C, 24.37; H, 2.45. Found: C, 23.26; H, 2.44. IR (KBr) $\nu/cm^{-1} = 1506$ (vs), 1592 (s), 1646 (m) (C═C and C═O for $C_5O_5^{2-}$).

Preparation of $[Na_2Cu(C_5O_5)_2(H_2O)_2]\cdot 4H_2O$ (2). An aqueous solution (1 mL) of $CuCl_2\cdot 2H_2O$ (42.6 mg, 0.2 mmol) was added to an aqueous solution (1 mL) of $Na_2C_5O_5$ (69.7 mg, 0.375 mmol) in a tube at room temperature. Slow evaporation at room temperature of the resulting yellow solution gave two colors of crystals in the solution. One is a red crystal which has been identified as the formula $[Cu(C_5O_5)\cdot 3H_2O]$ in the previous literature;[10] the other is

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Table 1. Crystallographic Data for Complexes **1** and **2**

	1	**2**
chemical formula	$C_{10}H_{12}Na_2NiO_{16}$	$C_{10}H_{12}Na_2CuO_{16}$
fw	492.89	497.72
space group	$P\bar{1}$	$P\bar{1}$
a (Å)	6.922(1)	6.392(1)
b (Å)	7.938(1)	7.971(2)
c (Å)	8.703(2)	8.820(2)
α (deg)	100.54(2)	84.70(2)
β (deg)	111.74(2)	83.27(2)
γ (deg)	99.62(2)	70.82(2)
V (Å^3)	422.0(1)	420.9(2)
Z	1	1
T (K)	295(2)	295(2)
λ (Mo Kα) (Å)	0.71073	0.71073
D_{calcd} (kg m^{-3})	1.939	1.964
μ (mm^{-1})	1.290	1.439
$R(F_o)^a$ $(I > 2\sigma(I))$	0.0250	0.0459
$R_w(F_o)^b$ $(I > 2\sigma(I))$	0.0683	0.1217
F(000)	250	250
reflns collected	2454	2445
unique reflns	2182	1886
abs correction	semiempirical from ψ-scans	semiempirical from ψ-scans
refinement on	F^2	F^2
params refined	157	157
GOF on F^2	1.073	1.024

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R_w = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{1/2}$.

a yellow-green crystal of complex **2** (yield 12.62%). Anal. Calcd of **2**: C, 24.13; H, 2.44. Found: C, 23.82; H, 2.37. IR (KBr) ν/cm^{-1} = 1506(vs), 1592(s), 1646(m), 1727(m) (C=C and C=O for $C_5O_5^{2-}$).

Crystallographic Procedure. Suitable single crystals of complexes **1** and **2** were selected under a microscope and mounted in glass capillaries. All the measurements were made on an Enraf-Nonius CAD4 diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The data were collected at room temperature using the $\omega-2\theta$ scan technique to maximum 2θ of 60°. The cell parameters were determined using 25 reflections in the 2θ ranges of $14.72° \leq 2\theta \leq 32.76°$ for **1** and $14.72° \leq 2\theta \leq 27.28°$ for **2**, respectively. Three intensity-control reference reflections monitored every 3600 s throughout the data collection showed no significant decay. The intensity data were corrected for Lorentz and polarization effects, and refinement was performed using the counting statistics weighting scheme. An empirical absorption correction based on three azimuthal scans was also applied. Both of the structures were solved by the direct methods with the SHELX-93[19] program and refined by full-matrix least-squares methods on F^2 with SHEXLTL-PC V 5.03.[19] All of the non-hydrogen atomic positions were located in difference Fourier maps and refined anisotropically. Hydrogen atoms were placed in their geometrically generated positions. The detailed data collection and refinement parameters of complexes **1** and **2** are summarized in Table 1. Selected bond distances and angles of complexes **1** and **2** are listed in Table 2. Other crystallographic data are given as Supporting Information. All calculations were carried out on the VAX Alpha station.

Result and Discussion

Synthesis. Reaction of sodium croconate ($Na_2C_5O_5$) and the corresponding metal chloride in aqueous solution resulted in the formation of $Na_2[M(C_5O_5)_2(H_2O)_2]\cdot4H_2O$ (M = Ni **1**, Cu **2**). The IR spectra of **1** and **2** both show a strong and broad band centered at around 1506 cm^{-1}, which is attributed to vibrational modes representing mixtures of C−O and C−C stretching and is the characteristic of the $(CO)_n^{2-}$ salts.[18]

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complexes **1** and **2**

Complex **1**			
Bond Lengths			
Ni(1)−O(1)	2.121(1)	Ni(1)−O(2)	2.054(1)
Ni(1)−O(6)	2.020(1)		
C(1)−O(1)	1.265(2)	C(1)−C(2)	1.435(2)
C(2)−O(2)	1.259(2)	C(2)−C(3)	1.451(2)
C(3)−O(3)	1.229(2)	C(3)−C(4)	1.488(2)
C(4)−O(4)	1.235(2)	C(4)−C(5)	1.484(2)
C(5)−O(5)	1.241(2)	C(5)−C(1)	1.453(2)
Bond Angles			
O(1)−Ni(1)−O(1)	180.0	O(1)−Ni(1)−O(2)	83.30(4)
O(1)−Ni(1)−O(6)	92.23(5)	O(2)−Ni(1)−O(2)	180.0
O(2)−Ni(1)−O(6)	87.50(5)	O(6)−Ni(1)−O(6)	180.0
O(1)−C(1)−C(2)	122.0(1)	O(1)−C(1)−C(5)	129.1(1)
O(2)−C(2)−C(3)	127.8(1)	O(2)−C(2)−C(1)	122.1(1)
O(3)−C(3)−C(4)	127.2(1)	O(3)−C(3)−C(2)	126.7(1)
O(4)−C(4)−C(5)	126.0(1)	O(4)−C(4)−C(3)	125.9(1)
O(5)−C(5)−C(1)	127.1(1)	O(5)−C(5)−C(4)	126.1(1)
C(1)−C(2)−C(3)	110.1(1)	C(2)−C(3)−C(4)	106.1(1)
C(3)−C(4)−C(5)	108.0(1)	C(4)−C(5)−C(1)	106.8(1)
C(5)−C(1)−C(2)	108.9(1)		
Complex **2**			
Bond Lengths			
Cu(1)−O(1)	2.459(2)	Cu(1)−O(2)	1.987(2)
Cu(1)−O(6)	1.935(2)		
C(1)−O(1)	1.243(3)	C(1)−C(2)	1.453(3)
C(2)−O(2)	1.264(3)	C(2)−C(3)	1.464(3)
C(3)−O(3)	1.235(3)	C(3)−C(4)	1.476(3)
C(4)−O(4)	1.246(3)	C(4)−C(5)	1.467(3)
C(5)−O(5)	1.244(3)	C(5)−C(1)	1.452(3)
Bond Angles			
O(1)−Cu(1)−O(1)	180.0	O(1)−Cu(1)−O(2)	78.74(7)
O(1)−Cu(1)−O(6)	92.7(1)	O(2)−Cu(1)−O(2)	180.0
O(2)−Cu(1)−O(6)	88.73(9)	O(6)−Cu(1)−O(6)	180.0
O(1)−C(1)−C(2)	123.9(2)	O(1)−C(1)−C(5)	128.5(2)
O(2)−C(2)−C(3)	126.8(2)	O(2)−C(2)−C(1)	123.5(2)
O(3)−C(3)−C(4)	126.6(2)	O(3)−C(3)−C(2)	126.7(2)
O(4)−C(4)−C(5)	125.7(2)	O(4)−C(4)−C(3)	125.8(2)
O(5)−C(5)−C(1)	126.6(2)	O(5)−C(5)−C(4)	126.2(2)
C(1)−C(2)−C(3)	109.8(2)	C(2)−C(3)−C(4)	106.7(2)
C(3)−C(4)−C(5)	108.5(2)	C(4)−C(5)−C(1)	107.2(2)
C(5)−C(1)−C(2)	107.6(2)		

Structural Description. Both of the two structures are made of a discrete dianionic mononuclear $[M(C_5O_5)_2(H_2O)_2]^{2-}$ moiety, two sodium ions, and four hydrate water molecules. The molecular structure of complex **1**, $[Na_2Ni(C_5O_5)_2(H_2O)_2]\cdot4H_2O$, is shown in Figure 1, and selected bond distances and angles are listed in Table 2. The nickel atom is located at the inversion center and surrounded by six oxygen atoms of which four are from croconate ligands and two are from water molecules. Each croconate dianion ($C_5O_5^{2-}$) acts as a bidentate ligand as form **IV**, with Ni−O(croconate) bond distances of 2.054(1) and 2.121(1) Å. A slightly distorted octahedral geometry of Ni ion is observed with two short $Ni-O_{water}$ bond lengths of 2.020(1) Å. The sodium atoms are six-coordinated surrounded by three croconate oxygen atoms (one O(1) and two O(4)) and three water oxygen atoms (one O(7) and two O(8)) with Na⋯O bond distances varying in the range 2.361(1)−2.563(1) Å building a distorted octahedral environment. In the ligand part, the lengthening

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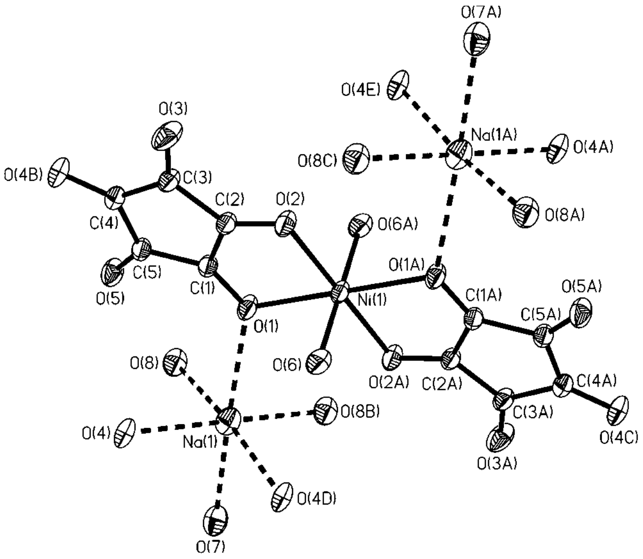

Figure 1. Molecular structure of $[Na_2Ni(C_5O_5)_2(H_2O)_2]\cdot4H_2O$, **1**. Ellipsoids are drawn at the 30% probability level.

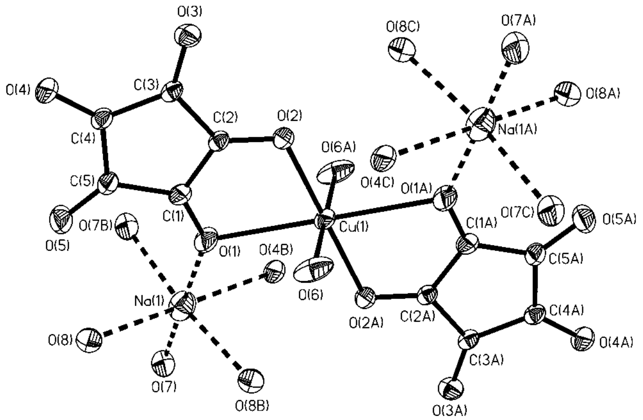

Figure 2. Molecular structure of $[Na_2Cu(C_5O_5)_2(H_2O)_2]\cdot4H_2O$, **2**. Ellipsoids are drawn at the 30% probability level.

of the C(1)−O(1) and C(2)−O(2) bonds (1.265(2), 1.259(2) Å) versus the mean of the three remaining C−O bond distances (1.235 Å) is in agreement with a concurrent shortening of the C(1)−C(2) bond length (1.435(2) Å) compared to the other C−C distances (1.451(2)−1.488(2) Å). Such structural features support an enediol form for the bidentate croconate.[11]

The molecular structure of complex **2**, $[Na_2Cu(C_5O_5)_2(H_2O)_2]\cdot4H_2O$, shown in Figure 2, is slightly different from that of complex **1**. However, because of the severe Jahn−Teller distortion, a tetragonally distorted octahedral geometry of **2** is much more obvious than that of **1**. Selected bond distances and angles are listed in Table 2. One of the Cu−O(croconate) bond distances (2.459(2) Å) is much longer than the other two Cu−O bond distances (Cu−$O_{croconate}$ 1.987(2), Cu−O_{water} 1.935(2) Å). The environment of the sodium ion in **2** is also distorted octahedral, but it is surrounded by two croconate oxygen (O(1) and O(4)) and four water oxygen atoms (two O(7) and two O(8)) with Na···O bond distances varying in the range 2.382(3)−2.478(2) Å. The C(2)−O(2) distance of 1.264(3) Å with the short Cu(1)−O(1) distance (1.987(2) Å) is obviously longer than the other C(1)−O(1) distance of 1.243(3) Å and other three uncoordinated C−O distances of 1.235(2)−1.246(2) Å. The main difference in structure between these two complexes is the location of sodium atoms as shown in Figure 3. Two four-membered Na_2O_2 rings are found both in complexes **1** and **2**. In complex **1**, two croconate O(4) atoms and two water O(8) atoms are acting as the bridging atoms to connect the sodium ions. The sodium ions are aligned linearly (Figure 3a) with the Na−Na−Na angle being 175.10(4)°. But in the case of **2**, the sodium ions are bridged by two O(7) and two O(8) atoms of water molecules to form a zigzag chain (Figure 3b) with the Na−Na−Na angle being 132.64(8)°. The sodium−sodium separations within the Na_2O_2 rings are 3.398(1), 3.531(1) for **1** and 3.402(3), 3.577(1) Å for **2**, respectively.

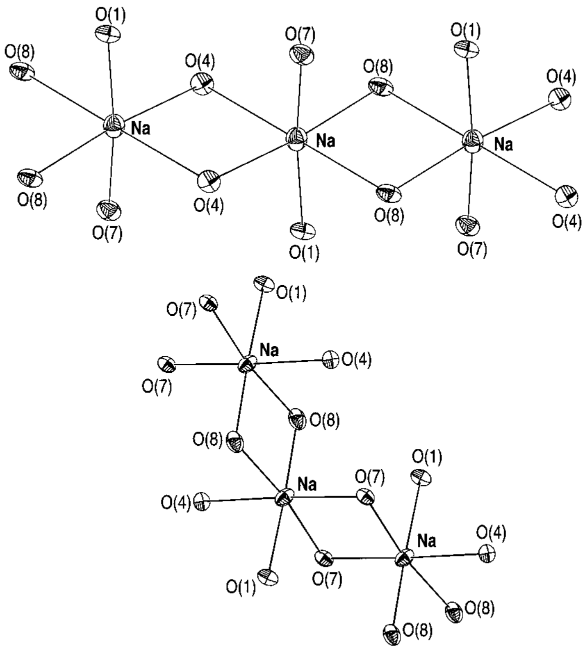

Figure 3. Sodium ion arrangement of complex **1** (a) and **2** (b).

Both complexes **1** and **2** appear to be self-assembled from $[M(C_5O_5)_2(H_2O)_2]^{2-}$ and aqueous sodium cations to form a three-dimensional structure. Because of the different arrangement of sodium ions described previously, the three-dimensional framework is also different. In complex **1**, the $[Ni(C_5O_5)_2(H_2O)_2]^{2-}$ moieties are interconnected in two ways, one is via the interactions of O(1)···Na···4(1), and the other is via the interactions of O(4)···Na···O(4) to construct a one-dimensional chain. But in complex **2**, the $[Cu(C_5O_5)_2(H_2O)_2]^{2-}$ moieties are connected only via the interactions of O(1)···Na···O(4). The shortest intersheet M···M distances of $[M(C_5O_5)_2(H_2O)_2]^{2-}$ moieties are 6.922(4) and 6.392(4) Å for complexes **1** and **2**, respectively. The metal−sodium distances via bridging a croconato group are 3.979 Å for nickel−sodium and 4.227 Å for copper−sodium. A honeycomb-like structure shown in Figure 2 of the Supporting Information constructed by the croconate ligands and sodium ions is found both in complexes **1** and **2** as viewed along the *c*-axis.

Hydrogen Bonding. It is worth mentioning that there are relatively strong inter- and intramolecular hydrogen bonds

Table 3. Hydrogen Bonds for Complexes **1** and **2**

donor-H (Å)	donor···acceptor (Å)	H···acceptor (Å)	∠donor-H···acceptor (deg)
Complex **1**[a]			
O(6)−H(6a)	O(6)···O(3)$_{i}$	H(6a)···O(3)$_{i}$	∠O(6)−H(6a)···O(3)$_{i}$
0.817(3)	2.642(3)	1.844(3)	165.0(1)
O(6)−H(6b)	O(6)···O(7)$_{ii}$	H(6b)···O(7)$_{ii}$	∠O(6)−H(6b)···O(7)$_{ii}$
0.818(3)	2.689(3)	1.903(3)	160.9(1)
O(7)−H(7a)	O(7)···O(6)$_{iii}$	H(7a)···O(6)$_{iii}$	∠O(7)−H(7a)···O(6)$_{iii}$
0.786(3)	2.963(3)	2.292(3)	143.8(1)
O(7)−H(7b)	O(7)···O(5)$_{i}$	H(7b)···O(5)$_{i}$	∠O(7)−H(7b)···O(5)$_{i}$
0.738(3)	2.791(3)	2.058(3)	172.3(1)
O(8)−H(8b)	O(8)···O(1)$_{iii}$	H(8b)···O(1)$_{iii}$	∠O(8)−H(8b)···O(1)$_{iii}$
0.759(3)	2.761(3)	2.059(3)	156.0(1)
Complex **2**[b]			
O(6)−H(6a)	O(6)···O(4)$_{iv}$	H(6a)···O(4)$_{iv}$	∠O(6)−H(6a)···O(4)$_{iv}$
0.844(4)	2.736(4)	1.898(4)	172.4(2)
O(6)−H(6b)	O(6)···O(5)$_{v}$	H(6b)···O(5)$_{v}$	∠O(6)−H(6b)···O(5)$_{v}$
0.728(3)	2.610(4)	1.887(4)	172.4(2)
O(7)−H(7a)	O(7)···O(3)	H(7a)···O(3)	∠O(7)−H(7a)···O(3)
0.822(4)	2.800(4)	1.978(4)	178.2(3)
O(7)−H(7b)	O(7)···O(2)$_{vi}$	H(7b)···O(2)$_{vi}$	∠O(7)−H(7b)···O(2)$_{vi}$
0.800(4)	2.927(4)	2.134(4)	170.7(3)
O(8)−H(8b)	O(8)···O(3)$_{v}$	H(8b)···O(3)$_{v}$	∠O(8)−H(8b)···O(3)$_{v}$
0.786(4)	2.770(5)	1.988(4)	173.7(3)

[a] Equivalent positions. i: $+x, -1 + y, +z$. ii: $2 - x, 1 - y, 2-z$. iii: $+x, +y, 1 + z$. [b] Equivalent positions. iv: $-1 - x, 1 - y, -z$. v: $+x, -1 + y, +z$. vi: $+x, +y, -1 + z$.

in both complexes. The related O−H and O···O bond distances and ∠O−H···O angles are listed in Table 3. These hydrogen bonds exist between water molecules and the oxygen atoms of croconate ligands and may well be the main cause for the form of such a beautiful network.

Conclusion

In this work, we have presented the syntheses and crystal structures of two metal−croconate hydrate complexes, $[Na_2Ni(C_5O_5)_2(H_2O)_2]\cdot 4H_2O$ (**1**) and $[Na_2Cu(C_5O_5)_2(H_2O)_2]\cdot 4H_2O$ (**2**). Their structural characterization shows a symmetric coordinate mode of croconate ligands bonded to the metal center. The $[M(C_5O_5)_2(H_2O)_2]^{2-}$ moieties act as dianionic templates, and sodium acts as an interconnecting cation to build up a three-dimensional framework. The hydrogen bonds among the croconate ligands and water molecules play an important role to hold up such a novel network.

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Supporting Information Available: Packing pictures of complexes **1** and **2**. X-ray crystallographic files for both **1** and **2** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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