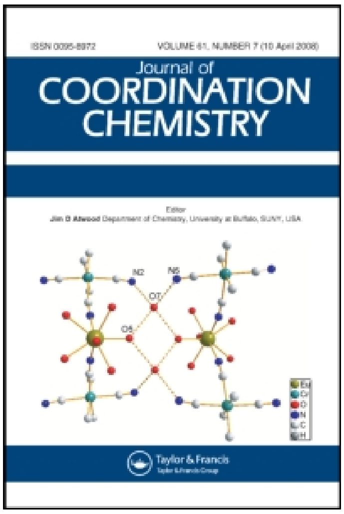

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Synthesis and characterization of some metal(II) and sodium ions with cyclopentane-1,2,3,4-tetracarboxylate anion

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New divalent metal cyclopentane-1,2,3,4-tetracarboxylate (CPTC) hydrates of empirical formula $M_2C_5H_6(COO)_4 \cdot nH_2O$, where M = Ni, Co, Cu, or Zn and $n = 3-6$, and sodium CPTC $Na_3C_5H_6COOH(COO)_3 \cdot 7H_2O$ have been prepared and characterized by elemental analysis, magnetic measurements, thermal, and infrared spectral studies. For the sodium salt, a single crystal ($Na_3C_5H_6COOH(COO)_3 \cdot 8H_2O$) was also obtained. IR spectra of the metal(II) complexes indicate the coordination of metal ions through all carboxylates. For the sodium compound, a band at 1681 cm^{-1} indicates that some carboxylic groups have not been deprotonated. The presence of protonated carboxylic group was also confirmed by an X-ray single crystal analysis. On heating in air atmosphere, all complexes lose water molecules and next anhydrous compounds decompose to corresponding metal oxides and sodium carbonate.

Keywords: Cyclopentane-1,2,3,4-tetracarboxylates; Metal complexes; Thermal analysis; FTIR; X-ray diffractometry

1. Introduction

Much attention has been focused on the design, synthesis, and characterization of 1-, 2-, and 3-D metal-organic networks. This interest is connected with the design and synthesis of supramolecular coordination polymeric open-framework materials with porous and other properties. A wide range of these frameworks have been generated with carboxylic acids because carboxylate can act as a bridging ligand, leading to various polynuclear complexes ranging from discrete molecules to 3-D networks [1–4]. The field of metal carboxylates has also become one of the intense research activities due to their specific network topologies, physico-chemical properties, and potential application as functional materials [1–8].

The present study deals with the synthesis and characterization of new metal complexes with cyclopentane-1,2,3,4-tetracarboxylic acid (CPTCA). The CPTCA and its compounds find applications in different fields of human life; in washing powders and detergents as active builders since the sodium salt also causes easy removal of dirt and impurities from fibers, with application as phosphate-free detergent

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components [9–12]. The acid improves the adhesion of dental materials and is used as a polymerizable conditioner for adhesive bonding to dentin and enamel [13]. Cyclopentane-1,2,3,4-tetracarboxylic acid and its alkali metal salts inhibit the transformation of amorphous calcium phosphate to hydroxyapatite and are therefore effective anticalculus agents, used in toothpaste and mouthwash solution [14, 15]. There is not much information about metal complexes with CPTCA.

This work was conducted to obtain complexes of d-block metal ions such as Ni(II), Co(II), Cu(II), and Zn(II), and sodium with cyclopentane-1,2,3,4-tetracarboxylic acid in the solid state, and to examine some of their physico-chemical properties including thermal stability in air, IR spectral characterization, X-ray powder investigations, and magnetic behavior at room temperature.

2. Experimental

2.1. *Materials*

All chemical reagents and solvents were of analytical grade, purchased commercially, and used without purification.

Complexes of Ni(II) and Co(II) were prepared by adding a hot aqueous solution of CPTCA to freshly precipitated hydroxides. Solutions were heated on a water bath to reduce volume. The solid products were isolated by evaporating the remaining solvent at room temperature for several days and dried at 25°C. The Cu(II) and Zn(II) cyclopentane-1,2,3,4-tetracarboxylates (CPTCs) were obtained by adding a hot solution of acid to metal acetates. Solid compounds were precipitated after adding 5% $NH_{3(aq)}$ until a pH of ~4.8 was reached. Mixtures were heated in a water bath at 80°C for 40 h. The precipitates were filtered off, washed with hot water to remove ammonium, and dried at room temperature to constant masses. Sodium CPTC was prepared by the addition of an equivalent amount of acid to NaOH and crystallizing. The polycrystalline product isolated was washed with cold water and dried at room temperature. During recrystallization from aqueous solution, a small amount of single crystals was obtained.

2.2. *Measurements*

Carbon and hydrogen content in complexes were determined by elemental analysis using a CHN 2400 Perkin-Elmer analyzer. The metal contents were calculated from TG curves. Chemical analysis confirms the composition (table 1).

The FTIR spectra of complexes were recorded from 4000 to 400 cm^{-1} using a FTIR 1725 × Perkin-Elmer spectrometer as KBr discs. Some of the results are presented in table 2.

The X-ray powder diffraction patterns were collected on a HZG 4 diffractometer using Ni-filtered Cu-Kα radiation. Measurements were made within the range of $2\theta = 5$–$70°$.

The thermal stability and decomposition of complexes were studied in air using a Setsys 16/18 TG, DTA instrument (table 3; Supplementary material). Samples ranging between 7.12 and 8.00 mg were heated in Al_2O_3 crucible to 850°C at a heating rate of 10°C min^{-1} in dynamic air atmosphere (75 mL min^{-1}).

Table 1. Characterization data of Na, Ni(II), Co(II), Cu(II), and Zn(II) CPTCs.

	Elemental analysis (%)							
	M		C		H			
Complex	Calcd	Found	Calcd	Found	Calcd	Found	Color	Magnetic moment μ_{eff} (μB)
$Na_3HL^a \cdot 7H_2O$	15.75	15.94	24.65	24.90	4.79	4.84	White	–
$Ni_2L \cdot 6H_2O$	25.11	24.20	23.10	22.94	3.85	4.01	Green	3.69
$Co_2L \cdot 5H_2O$	26.20	26.35	24.01	24.17	3.56	4.02	Dark violet	5.2
$Cu_2L \cdot 4H_2O$	28.82	28.50	24.49	24.57	3.17	3.28	Blue	2.25
$Zn_2L \cdot 3H_2O$	30.64	31.17	25.30	24.65	2.81	2.84	White	Diamagnetic

$L = C_5H_6(COO)_4$.
[a]One carboxylic group is protonated.

Table 2. Characteristic IR bands (cm^{-1}) of CPTCA and its metal complexes.

Complex	ν_{OH}[b]	$\nu_{as(COO^-)}$	$\nu_{s(COO^-)}$	ν_{M-O}	$\nu_{C=O}$
$Na_3HL^a \cdot 7H_2O$	3425	1581	1408	460	1682
$Ni_2L \cdot 6H_2O$	3430	1558	1407	–	–
$Co_2L \cdot 5H_2O$	3425	1559	1402	–	–
$Cu_2L \cdot 4H_2O$	3431	1592, 1554	1459	411	–
$Zn_2L \cdot 3H_2O$	3554, 3338	1544	1414	454	–
H_4L	3181	–	–	–	1736, 1718, 1681

$L = C_5H_6(COO)_4$.
[a]One carboxylic group is protonated.
[b]Maxima.

Table 3. Temperature of the dehydration and decomposition of CPTCs.

		Mass loss (%)				Mass loss (%)			Mass loss (%)	
Compound $L = C_6H_6O_4$	ΔT_1 (°C)	Calcd	Found	nH_2O	ΔT_2 (°C)	Calcd[b]	Found	ΔT_3 (°C)	Calcd	Found
$Na_3HL^a \cdot 7H_2O$	42–118	20.55	20.63	5	239–337	–	34.60	450–517	63.25	63.70
	138–220	28.77	28.31	2	338–447	–	49.75			
$Ni_2L \cdot 6H_2O$	40–259	23.10	22.81	6	–	–	–	306–435	68.04	69.20
$Co_2L \cdot 5H_2O$	40–176	20.00	19.90	5	–	–	–	349–452	66.68	66.50
$Cu_2L \cdot 4H_2O$	41–143	10.20	10.51	2.5	–	–	–	195–312	63.92	64.30
	153–187	16.32	16.29	1.5						
$Zn_2L \cdot 3H_2O$	35–117	8.43	8.05	2	–	–	–	395–501	61.85	61.20
	118–172	12.65	12.95	1						

$L = C_5H_6(COO)_4$.
[a]One carboxylic group is protonated.
[b]Unidentified, intermediate products of sodium salt decomposition.
ΔT_1 – temperature of dehydration process, ΔT_2 – temperature of sodium salt decomposition. ΔT_3 – temperature of decomposition of anhydrous complex of transition metal to oxides and intermediate product of sodium to carbonate.

The TG-FTIR coupled measurements have been carried out using a Netzsch TG 209 apparatus coupled with a Bruker FTIR IFS66 spectrophotometer identifying the gas-phase products of decomposition (Supplementary material). Samples (about 5.65–8.35 mg) were heated in ceramic crucibles up to 950°C at a heating rate of 15°C min^{-1} in flowing argon atmosphere.

Magnetic moments were determined at room temperature using the Gouy method. Magnetic susceptibility measurements were made using a magnetic susceptibility balance MSB–MKI, Sherwood Scientific Ltd., Cambridge. The correction for diamagnetism of the constituent atoms was calculated by the use of Pascal's constants. The effective magnetic moments were calculated from the equation $\mu_{\text{eff}} = 2.828(\chi_{\text{cor}}T)^{1/2}$. The results are presented in table 1.

Single-crystal diffraction data were measured at room temperature in the $\omega/2\theta$ mode on an Oxford Diffraction Xcalibur diffractometer using graphite-monochromated Mo-Kα radiation. The crystallographic data and refinement procedure details are given in table 4. All data were corrected for Lorentz, polarization, and absorption effects. The structures were solved by direct methods (program SHELXS-97 [16, 17]) and refined by full-matrix least-squares for all F^2 data using the SHELXL-97 [18] programs. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogens were included in calculated positions with the isotropic thermal parameters proportional to those of the connected carbon or oxygen. Selected bonding parameters are listed in tables 5 and 6.

3. Results and discussion

Cyclopentane-1,2,3,4-tetracarboxylates of Ni(II), Co(II), Cu(II), Zn(II), and Na were obtained as solid, hydrated products. The studied complexes of d-block metal have a general formula $M_2C_5H_6(COO)_4 \cdot nH_2O$, where $n = 6$ for Ni(II), $n = 5$ for Co(II), $n = 4$ for Cu(II), and $n = 3$ for Zn(II). X-ray powder diffractions showed that the complexes of Ni(II) and Co(II) are amorphous. The remaining compounds were obtained as polycrystalline substances, which crystallize in a low-symmetry system. Sodium CPTC was found to be $Na_3C_5H_6COOH(COO)_3 \cdot 7H_2O$ for polycrystalline compound and $C_5H_6(COONa)_3COOH \cdot 8H_2O$ for the single crystal. The analytical and physical properties of these compounds are listed in table 1.

3.1. *Infrared spectroscopy*

The IR spectrum of CPTCA exhibits two strong characteristic bands, which can be assigned to $\nu_{(OH)}$ of hydroxyl and $\nu_{(OC)}$ of carbonyl. The first band is broad at 3181 cm^{-1}; low frequency, broad band, and strong absorption indicate that in the acid-strong intramolecular hydrogen bonds are present [19, 20]. The second band is sharp and split into three submaxima (1736, 1718, and 1681 cm^{-1}) suggesting that the carboxylic groups have different characters. The low frequencies of $\nu_{(OC)}$ confirm the presence of intramolecular hydrogen bonds.

The –COOH present in the acid spectrum completely disappears in the spectra of the d-block metal complexes and two bands arising from asymmetric and symmetric vibrations of the COO^- occur at 1592–1544 and 1459–1402 cm^{-1}, respectively. In the sodium salt, bands arising from asymmetric and symmetric vibrations of COO^- group appear at 1581 and 1408 cm^{-1}, respectively, and the band at 1682 cm^{-1} is observed, which indicates that some carboxylic groups remain protonated. The presence of one protonated carboxylic group was confirmed by an X-ray single crystal analysis. The magnitude of separation $\Delta\nu = \nu_{\text{as}(COO^-)} - \nu_{\text{s}(COO^-)}$ and the direction of the shifts of these bands in relation to the respective frequencies in the spectrum of the sodium salt of the acid are of spectroscopic criteria to determine the mode of carboxylate binding [20, 21]. For CPTC complexes of d-block metals, it is not possible to determine the coordination mode of COO^- groups based only on IR data because one deprotonated group in the sodium salt is not coordinated to metal ions.

Cyclopentane-1,2,3,4-tetracarboxylate complexes are hydrates, and the presence of water molecules in all the investigated complexes is confirmed by a broad band in the region 3800–2500 cm^{-1} with strong maxima listed in table 2. This band was assigned to the OH-stretching mode of water molecules [19–21].

3.2. *Magnetic moments*

Divalent Ni cation ($3d^8$) should exhibit a magnetic moment for two unpaired electrons (octahedral normal range is 2.8–3.2 μB and tetrahedral normal range is 3.4–4.0 μB) whereas square-planar complexes would be diamagnetic [20, 22]. The observed magnetic moment of the Ni(II) complex of CPTC is 3.69 μB. This value is characteristic for tetrahedral geometry. The magnetic susceptibility measurement for Co(II) complex is 5.2 μB, suggesting an approximate high-spin octahedral geometry of ligands around cobalt (normal range for octahedral Co(II) complexes is 4.3–5.2 μB [20, 22]). The room temperature magnetic moments for the Cu(II) complexes (2.25 μB) is indicative of one unpaired electron per Cu(II) ion, $\mu_{\text{eff}} = 1.8–2.2$ μB, slightly higher than the spin-only value, which indicates the absence of any magnetic exchange interaction between Cu(II) ions [20, 22]. The Zn(II) complex is diamagnetic as expected for d^{10} configuration.

3.3. *Thermal studies*

The thermal stabilities were investigated by thermogravimetric analysis. The thermal decomposition curves for Co(II) and sodium complexes, as examples, are represented graphically in Supplementary material and all data of CPTC decompositions are listed in table 3. The complexes are stable to 35°C but dehydrate in the range of 35–259°C in one or two steps losing the water of crystallization and forming anhydrous compounds. This process is accompanied by an endothermic effect in the DTA curves. The dehydration processes are confirmed by a FTIR analysis of the gaseous product of the thermal decomposition of CPTCs complexes. The characteristic stretching and deformation vibration bands of water molecules appear at 40–270°C in the wavenumber ranges of 3950–3500 and 2000–1350 cm^{-1} [23–27], respectively (Supplementary material). The anhydrous compounds are stable at 195–395°C. Further heating causes their decomposition (except sodium salt) to the corresponding oxides. The decomposition of the organic ligand is connected with a strong exothermic effect in the DTA curve. The beginning of the decomposition process is connected with the release of carbon dioxide; bands characteristic of CO_2 appear at 230–400°C in the wavenumber ranges of 2350–2250 and 750–600 cm^{-1}, due to valence and deformation vibrations [23–27], respectively. For all complexes at higher temperature bands, the characteristic of water and carbon oxides are also observed. The characteristic double peaks for CO, 2176 and 2095 cm^{-1}, and water bands appear at 238–433°C. The FTIR spectra of the gas-phase products of Co(II) and Zn(II) CPTCs indicate that the decomposition of these complexes are also connected with the release of hydrocarbons (e.g. methane) and some carboxylic acids. Bands from 3150 to 2850 cm^{-1} and 1050 to 850 cm^{-1} are characteristic for stretching [ν(CH)] and skeleton [γ(C–C)], appearing at 433 and 442°C for Co(II) and Cu(II), respectively. In the same temperature, at 1750 cm^{-1} for Co(II) and 1740 cm^{-1} for Zn(II), the stretching band of C=O is observed, which indicates the presence of carboxylic acid in evolved gases. Anhydrous CPTC of sodium decomposes to carbonate with unidentified, intermediate formations. The first stage is connected with the release of CO_2 at 384°C. Next, decomposition shows FTIR spectra characteristic for CO_2, CO, water, hydrocarbons, and carboxylic acid in evolved gases. The final step from 450 to 517°C corresponds to the decomposition of unstable products and CO_2, CO, water, and hydrocarbons are released. The final product for this decomposition is sodium carbonate. The decomposition scheme for complexes can be presented as follows:

$$\mathrm{Na_3HL\cdot 7H_2O} \xrightarrow{\text{Endo}} \mathrm{Na_3HL\cdot 2H_2O} \xrightarrow{\text{Endo}} \mathrm{Na_3HL} \xrightarrow{\text{Exo}} \mathrm{X_1} \xrightarrow{\text{Exo}} \mathrm{X_2} \xrightarrow{\text{Exo}} \mathrm{Na_2CO_3}$$

$$\mathrm{Co_2L\cdot 5H_2O} \xrightarrow{\text{Endo}} \mathrm{Co_2L} \xrightarrow{\text{Exo}} \mathrm{CoO}$$

$$\mathrm{Ni_2L\cdot 6H_2O} \xrightarrow{\text{Endo}} \mathrm{Ni_2L} \xrightarrow{\text{Exo}} \mathrm{NiO}$$

$$\mathrm{Zn_2L\cdot 3H_2O} \xrightarrow{\text{Endo}} \mathrm{Zn_2L\cdot H_2O} \xrightarrow{\text{Endo}} \mathrm{Zn_2L} \xrightarrow{\text{Exo}} \mathrm{ZnO}$$

$$\mathrm{Cu_2L\cdot 4H_2O} \xrightarrow{\text{Endo}} \mathrm{Cu_2L\cdot 1.5H_2O} \xrightarrow{\text{Endo}} \mathrm{Cu_2L} \xrightarrow{\text{Exo}} \mathrm{CuO}$$

3.4. *Structure of sodium salt*

The complex of sodium with CPTCA was obtained as a powder of heptahydrated compound, $Na_3HL \cdot 7H_2O$, with a small amount of single crystals. X-ray diffraction studies show that octahydrated salt crystallizes in the triclinic system, in the $P\bar{1}$ space group (figure 1). In the structure there are three independent sodium ions. Each Na^+ is surrounded by six oxygens from carboxylates and/or water. The polyhedron of Na ions takes the form of significantly distorted octahedron. In Na(1) and Na(3) four oxygens of water and two oxygens of carboxylate coordinate. The Na(1)–O_{aqua} distances vary from 2.343(3)° to 2.728(3) Å while Na(1)–$O_{carboxyl}$ bond lengths are 2.359(3) Å and 2.361(3) Å (table 4). Angles range from 76.5(1)° to 101.6(1)°. The Na(3)–O_{aqua} distances are 2.387(3)–2.504(3) Å and Na(3)–$O_{carboxyl}$, bond lengths are 2.470(3) Å, and angles range from 76.1(1)° to 106.8(1)°. The Na(2) is coordinated only by water with Na(2)–O_{aqua} distances in the range 2.311(3)–2.555(3) Å. Na(1) is connected with Na(2) by three bridging waters O(1W), O(2W), and O(3W). Na(1) is also linked with two other Na(1) cations (with first by means of two CPTCs and the second via water O(1W) and O(1W)′). Such linked sodium centers form 2-D layers. Na(3) is also connected through water with other Na(3) to form infinite zigzag chains (Na(3)′μ_2O(8W)–O(8W)′Na(3)μ_2O(7W)–O(7W)′–Na(3)″). The chains formed by Na(3) and the layers formed by Na(1) and Na(2) are further connected by CPTCA to form a 3-D network. Water molecules are monodentate (O(4W), O(5W), and O6(W)); bidentate bridging (O(2W), O(3W), O7(W), and O(8W)); and tridentate bridging (O(1W)) ligands. The tridentate character of water molecules is rather rare but observed for sodium compounds [27, 28].

In CPTCA there are four carboxylic groups. After reaction with sodium hydroxide only three are deprotonated. The C–O distances in COO^- systems are in the range

Table 4. Crystal data and structure refinement.

Empirical formula	$C_9H_{23}Na_3O_{16}$
Formula weight	456.24
Crystal system	Triclinic
Space group	$P\bar{1}$
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Unit cell dimensions (Å, °)	
a	6.052(3)
b	11.181(5)
c	14.074(6)
α	75.53(4)
β	86.78(4)
γ	83.52(4)
Volume (Å^3), Z	915.9(7), 2
$F(000)$	476
Absorption coefficient (mm^{-1})	0.215
Calculated density (mg m^{-3})	1.654
Crystal size (mm^3)	0.48 × 0.24 × 0.20
θ range for data collection (°)	3.67–30.06
Limiting indices	$-8 \leq h \leq 8$, $-5 \leq k \leq 15$, $0 \leq l \leq 19$
Reflections collected	5547
Independent reflection	5346 [R(int) = 0.0556]
Goodness-of-fit on F^2	0.949
Final R indices $[I > 2\delta(I)]$	$R_1 = 0.0665$, $wR_2 = 0.1579$
R indices (all data)	$R_1 = 0.1370$, $wR_2 = 0.2024$
Largest difference peak and hole (e Å^{-3})	0.688 and −0.543

$R_1 = \Sigma(F_o - F_c)/\Sigma F_o$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Table 5. Selected bond lengths (Å) and angles (°).

Na(1)–O(3W)	2.343(3)		
Na(1)–O(6)$^{\mathrm{i}}$	2.359(3)	O(1W)–Na(1)$^{\mathrm{ii}}$	2.728(3)
Na(1)–O(6)	2.361(3)	O(7W)–Na(3)$^{\mathrm{iii}}$	2.458(3)
Na(1)–O(2W)	2.384(3)	O(8W)–Na(3)$^{\mathrm{v}}$	2.504(3)
Na(1)–O(1W)	2.411(3)		
Na(1)–O(1W)$^{\mathrm{ii}}$	2.728(3)	C(1C)–O(1)	1.215(4)
		C(1C)–O(2)	1.310(4)
Na(2)–O(4W)	2.311(4)	C(2C)–O(3)	1.250(4)
Na(2)–O(6W)	2.366(3)	C(2C)–O(4)	1.249(3)
Na(2)–O(3W)	2.376(3)	C(3C)–O(5)	1.278(4)
Na(2)–O(5W)	2.406(3)	C(3C)–O(6)	1.229(3)
Na(2)–O(2W)	2.420(3)	C(4C)–O(7)	1.244(4)
Na(2)–O(1W)$^{\mathrm{ii}}$	2.555(3)	C(4C)–O(8)	1.252(4)
Na(3)–O(7W)	2.387(3)	O(1)–C(1C)–O(2)	120.6(3)
Na(3)–O(8W)	2.424(3)	O(3)–C(2C)–O(4)	124.8(3)
Na(3)–O(7W)$^{\mathrm{iii}}$	2.458(3)	O(6)–C(3C)–O(5)	122.4(3)
Na(3)–O(1)$^{\mathrm{iv}}$	2.470(3)	O(7)–C(4C)–O(8)	125.1(3)
Na(3)–O(8)	2.470(3)		
Na(3)–O(8W)$^{\mathrm{v}}$	2.504(2)		

Symmetry transformations used to generate equivalent atoms: (i) $-x, -y+1, -z+1$; (ii) $-x+1, -y+1, -z+1$; (iii) $-x-1, -y+2, -z$; (iv) $-x, -y+1, -z$; (v) $-x, -y+2, -z$.

Table 6. Hydrogen bond lengths (Å) and angles (°) for sodium CPTC.

D–H···A	D–H	H···A	D···A	∠DH···A
O(1W)–H(1W)···O(5)$^{\text{ii}}$	0.86	1.86	2.707(3)	167.6
O(1W)–H(2W)···O(4)$^{\text{i}}$	0.86	2.12	2.929(4)	156.5
O(2W)–H(3W)···O(4)	0.86	2.08	2.903(4)	162.1
O(2W)–H(4W)···O(5W)$^{\text{vi}}$	0.85	1.91	2.747(4)	166.3
O(3W)–H(5W)···O(8)$^{\text{i}}$	0.85	1.92	2.775(3)	173.7
O(3W)–H(6W)···O(7)$^{\text{ii}}$	0.85	2.05	2.752(4)	139.2
O(4W)–H(7W)···O(4)$^{\text{vii}}$	0.86	1.95	2.797(4)	170.4
O(4W)–H(8W)···O(2W)$^{\text{viii}}$	0.86	2.50	3.321(4)	160.3
O(5W)–H(9W)···O(8)$^{\text{ii}}$	0.85	2.03	2.849(3)	161.0
O(5W)–H(9W)···O(7)$^{\text{ii}}$	0.85	2.66	3.318(4)	135.1
O(5W)–H(10W)···O(3)$^{\text{viii}}$	0.85	1.88	2.726(3)	168.3
O(6W)–H(11W)···O(5W)$^{\text{vi}}$	0.85	2.61	3.305(4)	138.8
O(6W)–H(12W)···O(2)$^{\text{viii}}$	0.86	2.10	2.867(4)	148.2
O(7W)–H(13W)···O(7)$^{\text{vi}}$	0.85	1.94	2.745(3)	156.3
O(7W)–H(14W)···O(6W)$^{\text{i}}$	0.85	2.29	2.998(4)	140.8
O(7W)–H(14W)···O(1)$^{\text{ix}}$	0.85	2.56	3.037(3)	116.3
O(8W)–H(15W)···O(3)$^{\text{iv}}$	0.85	1.94	2.790(3)	176.8
O(8W)–H(16W)···O(1)$^{\text{x}}$	0.86	2.26	2.922(4)	134.4
O(2)–H(2)···O(5)	0.82	1.65	2.461(3)	167.3

Symmetry transformations used to generate equivalent atoms: (i) $-x, -y+1, -z+1$; (ii) $-x+1, y+1, -z+1$; (iii) $-x-1, -y+2, -z$; (iv) $-x, -y+1, -z$; (v) $-x, -y+2, -z$; (vi) $x-1, y, z$; (vii) $x+1, y, z$; (viii) $-x+1, -y, -z+1$; (ix) $x-1, y+1, z$; (x) $-x+1, -y+1, -z$.

1.229(3)–1.278(4) Å, confirming the deprotonation of carboxylic groups. The values of O–C–O angles are 122.4(3)°, 124.8(3)°, and 125.1(3)°. The last carboxylic group is protonated. The C–O lengths are 1.215(4) Å and 1.310(4) Å, and O–C–O angle is 120.6(3)°. Sodium ions are coordinated by one carboxylic and two carboxylate groups. Deprotonated carboxylic groups are monodentate while protonated is bidentate bridging.

In the crystal, besides strong coordination bonds, a system of hydrogen bonds occurs. Water molecules take part twice in hydrogen bonds as proton donors in O–H···O, except O(5W) and O(7W), which are three times proton donors. Besides water, the hydroxyl oxygen from the carboxylic group is also a proton donor. The water molecules O(2W), O(5W), and O(6W) are also involved in hydrogen bonds as proton acceptors. Parameters of hydrogen bond geometry are given in table 6.

4. Conclusions

New CPTCs of Co(II), Ni(II), Cu(II), Zn(II), and Na(I) have been synthesized and characterized by elemental analysis, thermal stability in air, IR spectra, X-ray powder analysis, and magnetic properties. The compounds are hydrates, stable at room temperature. When heated, CPTCs of d-block metal ions dehydrate to form anhydrous salts. Similar temperatures at the beginning of decomposition indicate similar dehydration energies. Anhydrous compounds decompose to the oxides. Sodium salt decomposes to carbonate through unstable intermediates. The FTIR spectra of the gas-phase products indicate that the decomposition is connected with the release of CO_2, H_2O,

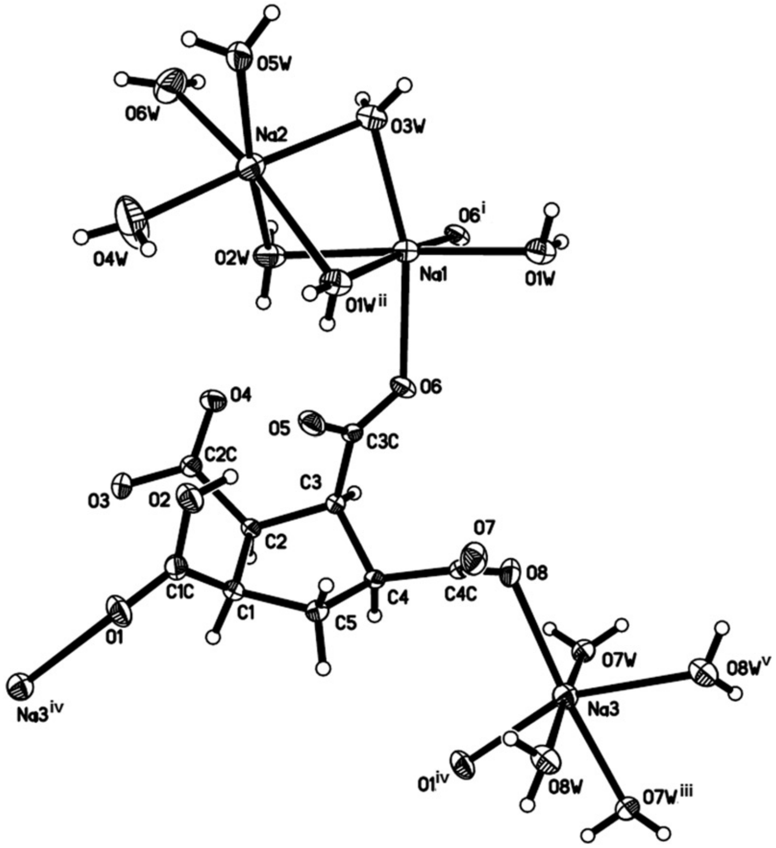

Figure 1. The molecular structure of the title complex with the atom labeling scheme. Symmetry transformations used to generate equivalent atoms: (i) $-x$, $-y+1$, $-z+1$; (ii) $-x+1$, $-y+1$, $-z+1$; (iii) $-x-1$, $-y+2$, $-z$; (iv) $-x$, $-y+1$, $-z$; (v) $-x$, $-y+2$, $-z$.

and CO. For Zn(II), Cu(II), and sodium salts, hydrocarbons and also some carboxylic acid are evolved.

The studies of coordination polymers containing carboxylates are mostly concentrated on d-block [29–32] and lanthanide [33–35] metal ions. Until recently, alkali and alkaline earth metal carboxylates were not only an underdeveloped area, but they also form interesting networks [32, 36–39]. In this article, we present a coordination polymer of sodium which forms a 3-D network. The sodium ions are coordinated to six oxygens from carboxylate groups and/or water. In coordination to Na the ligand uses two deprotonated and one protonated carboxylic groups.

Supplementary material

Supplementary data are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, on request quoting the deposition number 720 422 (Fax: +44-1223-336 033; Email: deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk).

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