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$[(C_6H_{10})(NH_3)_2][Ni(H_2O)_4C_6H_2(COO)_4]\cdot 4H_2O$ − A Coordination Polymer with the Chain-like Polyanion $\{Ni(H_2O)_4[C_6H_2(COO)_4]^{2-}\}_n$

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Abstract. Triclinic single crystals of $[(C_6H_{10})(NH_3)_2]$-$[Ni(H_2O)_4C_6H_2(COO)_4]\cdot 4H_2O$ have been prepared in aqueous solution at 55 °C. Space group $P\bar{1}$ (Nr. 2), a = 691.23(6), b = 924.84(5), c = 1082.43(7) pm, α = 74.208(6)°, β = 75.558(7)°, γ = 68.251(6)°, V = 0.60985(7) nm^3, Z = 1. The Nickel(II) species, located on a crystallographic inversion centre, is coordinated in a *trans*-octahedral fashion by two oxygen atoms stemming from the centrosymmetric pyromellitate anions and four from water molecules (Ni−O 205.82(12) − 208.11(13) pm). The connection between Ni^{2+} and $[C_6H_2(COO)_4)]^{4-}$ leads to infinite chain-like polyanions extending parallel to $[10\bar{1}]$ with $\{Ni(H_2O)_4[C_6H_2(COO)_4]^{2-}\}_n$ composition. $[(C_6H_{10})(NH_3)_2]^{2+}$-cations are accomodated between the chains, compensating for the negative charge of the polyanions. Thermogravimetric analysis in air showed that the loss of water of crystallisation occurs in two steps between 102 and 206 °C, corresponding to the loss of 6 and 2 water molecules per formula unit, respectively. The dehydrated sample was stable between 206 and 353 °C. Further decomposition yielded nickel(II) oxide (NiO).

Keywords: Nickel; Benzene-1,2,4,5-tetracarboxylic acid; *trans*-cyclohexylamine; Coordination polymer

Multi-dentate complexing agents are very well suited to form one-, two- and three-dimensional coordination polymers, if they are linked to suitable metal cations. These coordination polymers attract great interest due to their enormous structural variety and the various concomitant properties. A rational approach in synthesis requires systematic structural studies in order to shed light on the structure-governing principles. To this end we have employed anions of benzene carboxylic acids such as the tetraanion of pyromellitic acid (benzene-1,2,4,5-tetracarboxylic acid), which are capable of forming one-, two- or three-dimensionally infinite connections between cations and anions. Thus we have obtained chain structures, layered compounds, and three-dimensional frameworks as well [1−20]. Particularly appealing are three-dimensional framework structures with voids like those found in zeolites and molecular sieves [14]. In order to control the structural features it is possible to use template molecules such as amines. Thus, e.g., the characteristic feature in $\{Cu_2[Cu(H_2O)_4][(CH_2)_4(NH_3)_2]$-$[C_6H_2(COO)_4]_2\}\cdot 4H_2O$ [20] is a three-dimensional framework with negative excess charge and channel-like voids, which accomodate water molecules and $[(CH_2)_4(NH_3)_2]^{2+}$-cations. Here we report on the use of pyromellitate tetraanions, with *trans*-cyclohexyldiammonium cations as template agents, yielding $[(C_6H_{10})(NH_3)_2][Ni(H_2O)_4C_6H_2(COO)_4]\cdot 4H_2O$, which is characterised by infinite chain-like polyanions of $\{Ni(H_2O)_4[C_6H_2(COO)_4]^{2-}\}_n$ composition.

Experimental Section

Single crystals of $[(C_6H_{10})(NH_3)_2][Ni(H_2O)_4C_6H_2(COO)_4]\cdot 4H_2O$ were obtained by crystallization in aqueous solution at 55 °C. 5 ml 0.1 M $Ni(NO_3)_2$-solution, 5 ml 0.2 M *trans*-1,4-Diaminocyclohexane-solution and 5 ml 0.05 M $Na_4C_6H_2(COO)_4$-solution were combined. A temporarily occurring precipitate could be resolved by addition of 2N HNO_3. Afterwards 0.2 g urea was added. Sparingly soluble, light-green column-shaped crystals appeared after two days.

Elemental analysis: $C_{16}H_{34}N_2NiO_{16}$ (569.19) C 33.63 (calc. 33.77), H 6.02 (6.09), N 4.92 (4.90) %

Characteristic *IR* absorption bands occur at 2944 and 2869 cm^{-1} (C-H), 1564 and 1528 cm^{-1} (C-O), and 1372 cm^{-1} (N-C).

Thermal analysis: This was carried out in air using a Netzsch STA-429 device, revealing that water of crystallizationwas evolved endothermically in two steps between 102 and 206 °C. The first step corresponds to a loss of $6H_2O$ per formula unit, the further $2H_2O$ were released in the second step. The dehydrated sample was stable up to approx. 320 °C. Several exothermic decomposition steps followed, essentially complete at 420 °C yielding NiO, which was identified by X-ray powder diffraction.

X-ray diffraction intensities up to θ_{max} = 25° have been collected at room temperature using a Siemens P4 four-circle diffractometer with graphite-monochromatized MoK_α-radiation, λ = 71.07 pm. A numerical absorption correction has been applied. The phase problem was solved by direct methods. Difference Fourier-maps revealed positions of hydrogen atoms, which were included in the final cycles of refinement with isotropic displacement parameters. Crystallographic data are given in Table 1. Further details concerning the crystal structure analysis have been deposited with

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Table 1 Crystallographic Data for $[(C_6H_{10})(NH_3)_2][Ni(H_2O)_4\text{-}C_6H_2(COO)_4]\cdot 4H_2O$

Formula	$C_{16}H_{34}N_2NiO_{16}$
Crystal system	triclinic
Space group	$P\bar{1}$ (no.2)
Unit cell dimensions	a = 691.23(6) pm b = 924.84(5) pm c = 1082.43(7) pm α = 74.208(6)° β = 75.558(7)° γ = 68.251(6)°
Unit cell volume	0.60985(7) nm^3
Formulas in unit cell	1
Formula weight	569.16 g/mol
Density (calc.)	1.550 g/cm^3
Absorption coefficient	0.875 mm^{-1}
Absorption correction	face-indexed numerical
min./max. transmission	0.90/0.94
Temperature	293(2) K
Crystal size	0.08 mm x 0.12 mm x 0.70 mm
F (000)	1392
Limiting indices	$-1 \le h \le 8$, $-10 \le k \le 10$, $-12 \le l \le 12$
Reflections collected	2710
Independent reflections	2129 (R_{int} = 0.0144)
Structure solution	Direct methods
Structure refinement	Full-matrix-LS on $\lvert F\rvert^2$
Refined parameters	216
Extinction parameter	0.0027(11)
Residuals (all data)	R_1 = 0.0284 wR_2 = 0.0545
Max. features in last difference Fourier synthesis	+261/−203 e/nm^3
Program	SHELXTL [23]

Cambridge Crystallographic Data Centre, The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK, Fax +(1223)336-033, e-mail data_request@ccdc.cam.ac.uk, www.ccdc.cam.ac.uk/data_request.cif under CCDC 640703.

Results and Discussion

The nickel cation occupies a crystallographic inversion centre of space group $P\bar{1}$ (Wyckoff-position 1a) and is coordinated octahedrally in a moderately distorted fashion. Water molecules (2 x O(w1), 2 x O(w2)) make up the equatorial plane. Oxygen atoms stemming from the pyromellitate tetra-anion (2 x O(3)) occupy apical positions. The Ni−O bond lengths differ over the range from 205.8(1) to 208.1(1) pm with no significant difference between those of the water molecules and those of the oxygen atoms of the carboxylate groups (Table 2). Their bond order (1.96) calculated by the method of *Brown* [21] is close to the expected value. The pyromellitate tetra-anion is disposed about an inversion centre as well and is essentially planar with respect to its carbon atoms. The largest deviation from a plane fitted to the carbon skeleton of the anion is 4.2 pm at C(6). The carboxylate groups are inclined to the plane of the C_6 ring by 51.4° (C(7), O(1), O(2)) and 50.9° (C(8), O(3), O(4), Fig. 1), respectively. The C-O bond lengths, ranging from 124.1(2) to 126.9(2) pm show no significant difference between those of the oxygen atoms bound to Ni^{2+} and the others (Table 2), indicating an essentially unperturbed delocalization of the π-electrons.

Table 2 Interatomic Distances /pm

The Ni^{2+} environment:					
Ni-O(w1)	205.96(14) (2x)	Ni-O(w2)	208.11(13) (2x)		
Ni-O(3)	205.82(12) (2x)				
Pyromellitate Anion:					
C(4)-C(5)	139.9(3)	C(4)-C(7)	151.1(2)	C(7)-O(2)	124.1(2)
C(4)-C(6)	139.4(3)	C(5)-C(8)	150.8(2)	C(8)-O(3)	126.9(2)
C(5)-C(6)	138.8(3)	C(7)-O(1)	126.7(2)	C(8)-O(4)	124.3(2)
trans-Cyclohexyldiammonium-cation:					
N-C(1)	149.4(3)	C(1)-C(3)	151.8(3)		
C(1)-C(2)	152.0(3)	C(2)-C(3)	153.1(3)		

Ni^{2+} and $[C_6H_2(COO)_4]^{4-}$ form infinite chain-like polyanions of $\{Ni(H_2O)_4[C_6H_2(COO)_4]^{2-}\}_n$ composition extending in the $[10\bar{1}]$ direction (Fig. 2). These chains are stacked in an ...AAA... sequence in the [010] direction. The linear charge density is 0.177 e/Å, expressed in a more convenient manner as length/unit charge, is 5.6 Å/unit charge. The negative charge is compensated for by $[(C_6H_{10})(NH_3)_2]^{2+}$-cations intercalated between neighbouring chains. The $[(C_6H_{10})(NH_3)_2]^{2+}$-cation adopts a chair conformation (Fig. 1) and is disposed about a crystallographic inversion centre, with approximate symmetry C_{2h}. The C−C bond lengths range from 151.8(3) pm to 153.1(3) pm and the C(1)−N bond is slightly shorter (149.4(3) pm).

A similar chain-like polycation $\{Mn(H_2O)_4(pyz)^{2+}\}_n$ is the dominant feature in $Mn(pyz)[C_6H_4(COO)_2]\cdot 4H_2O$ [22] with a higher charge density of 3.7 Å/unit charge. Chain-like polyanions $\{Co(H_2O)_4[C_6H_2(COO)_4]^{2-}\}_n$ occur as well in dicobaltpyromellitate-octadecahydrate ($Co_2[C_6H_2(COO)_4]\cdot 18H_2O$) [3, 10] with the same linear charge density as in $\{Ni(H_2O)_4[C_6H_2(COO)_4]^{2-}\}_n$. However, there, the negative charge is compensated for by $[Co(H_2O)_6]^{2+}$ octahedra between adjacent chains.

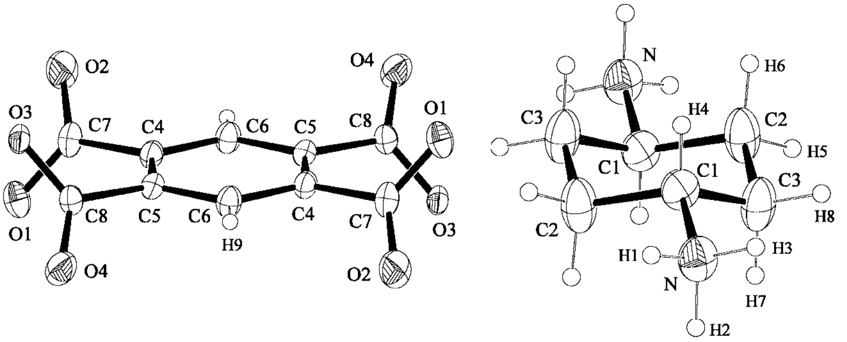

Fig. 1 The $[C_6H_2(COO)_4]^{4-}$ anion and the *trans*-cyclohexyldiammonium-cation. (50 % probability ellipsoids, arbitrary radii for hydrogen atoms.)

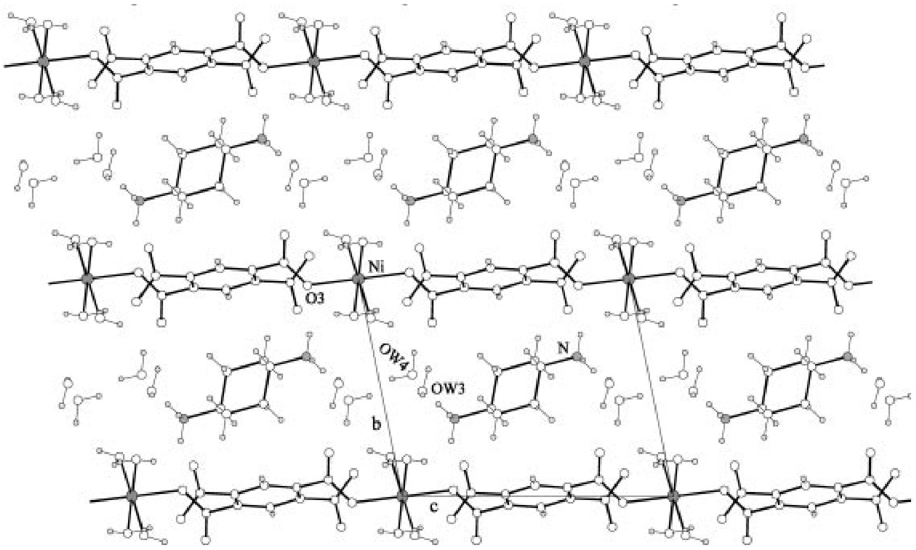

Fig. 2 The crystal structure of$[(C_6H_{10})(NH_3)_2][Ni(H_2O)_4C_6H_2(COO)_4]\cdot 4H_2O$ viewed from [100]. $[(C_6H_{10})(NH_3)_2]^{2+}$ cations and water molecules (O(w3) and O(w4)) are intercalated between neighbouring chains.

Table 3 Hydrogen-Bonds /pm

N···O Distances (pm)			
N-H(1)···O(w3)	291.1	N-H(3)···O(w2)	290.1
N-H(2)···O(w4)	284.2	N-H(3)···O(3)	289.1
O···O Distances (pm)			
O(w1)-H(11)···O(1)	282.4	O(w3)-H(32)···O(4)	273.5
O(w1)-H(12)···O(2)	263.8	O(w4)-H(41)···O(w3)	289.2
O(w2)-H(21)···O(4)	268.3	O(w4)-H(42)···O(1)	283.1
O(w2)-H(22)···O(1)	273.1		

The additional uncoordinated water molecules (O(w3) and O(w4)) stabilize the crystal structure by hydrogen-bonding. The NH_3^+-groups of the $[(C_6H_{10})(NH_3)_2]^{2+}$ cations act as proton donors for O(w2), O(w3), O(w4) and the carboxylate oxygen atom O(3). Those carboxylate oxygen atoms that are not bound to Ni^{2+} act as proton acceptors in hydrogen bonds. O(w3) and O(w4) are linked to each other by hydrogen bonding. The O···O distances range from 263.8 to 289.2 pm indicating hydrogen-bonds of high and medium strength (Tab. 3).

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