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The Crystal Structure of $[Ni(H_2O)_6][C_6H_5SO_3]_2$: a Comparison of Hexaaqua Divalent Layered Ions

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Abstract

The title compound was prepared by slow evaporation of an acetonitrile solution of $(NEt_4)_2[Ni(SC_6H_5)_4]$ containing NO under unintentionally aerobic conditions and its structure determined by single-crystal X-ray diffractometry. It crystallizes in the monoclinic system, space group $P2_1/n$ with a = 6.976(1), b = 6.301(1), c = 22.384(4) Å, V = 981.9(3) Å^3, Z = 2. The ions pack in layers with hydrophilic and hydrophobic regions held together by strong hydrogen bonds between the oxygen atoms of the sulfonate anion and the hydrogen atoms of the coordinated water molecules at O–H...O distances averaging 1.83 Å. The relationship of this structure to others containing divalent metal ions in layered ionic structures and the significance of the hydrophilic and hydrophobic layering is discussed.

Introduction

Compounds of the general formula $[M(H_2O)_6]A_2$, with M = a divalent metal ion and A = a monovalent anion have been studied [1]. The structures of three salts with A = $C_6H_5SO_3$, $[Mg(H_2O)_6][C_6H_5SO_3]_2$, $[Cu(II)(H_2O)_6][C_6H_5SO_3]_2$ and $[Zn(H_2O)_6][C_6H_5SO_3]_2$, [2, 3] have been reported. We here report the structure of a fourth member of the series, $[Ni(H_2O)_6][C_6H_5SO_3]_2$.

Of particular interest concerning these salts is the crystal lattice in which the ions pack, specifically the layers of hydrophilic and hydrophobic regions which exist. Recent studies of transition-metal complexes which exhibit this layering highlight the unusual thermodynamic properties of such compounds, specifically the possibility of using these layered structures for thermal energy storage. Compounds of this type which contain long alkyl chains also undergo solid–solid state phase transformations [1a]. Although it is unknown whether the title structure undergoes phase transformations of this kind, it does have potential heat storage capabilities derived from the hydrogen-bonded interactions between the inorganic nickel regions and the organic benzenesulfonate regions.

Further motivation for reporting our structure is its relevance to the previously reported Mg [3, 4], Cu(II) [2] and Zn [3] structures. The present Ni structure is isomorphous with the Zn and Mg structures; however, the Cu(II) structure distorts from the monoclinic symmetry due to Jahn–Teller effects. Although the nickel structure distorts somewhat from a perfect octahedral arrangement around the metal, the distortions are considerably smaller than those in the Cu(II) structure. Also, our structure is the only study of a hexaaqua, divalent metal benzenesulfonate salt to be done with modern crystallographic methods. We have located all hydrogen atoms, which the previously reported isomorphous structures were unable to provide. The earlier studies produced poor results with R = 27% for the isomorphous magnesium structure and R = 30% for zinc.

Experimental

Preparation

The title compound was prepared while attempting to react $(NEt_4)_2[Ni(SC_6H_5)_4]$ [5] with NO. Crystals of the title compound were obtained by slow evaporation of an acetonitrile solution of the reaction mixture under unintentionally aerobic conditions.

X-ray Crystallography

Geometric and intensity data for $[Ni(H_2O)_6][C_6H_5SO_3]_2$ were taken with a Nicolet R3m automated diffractometer using standard procedures. Pertinent crystallographic data and unit-cell parameters are given in Table 1. The crystal was indexed on 25 intense reflections in the range $20 \leqslant 2\theta \leqslant 26°$ and the crystal system was found to be monoclinic. The lattice dimensions were verified by axial photography. Least-squares analysis was used to refine the unit-cell dimensions and orientation matrix. The symmetry operations of the acceptor for the hydro-

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TABLE 1. Crystal data for $[Ni(H_2O)_6][C_6H_5SO_3]_2$

Formula	$[Ni(H_2O)_6][C_6H_5SO_3]_2$
Formula weight	480.91
Space group	$P2_1/n$
Crystal system	monoclinic
Systematic absences	$0k0, k = 2n + 1$ $h0l, h + l = 2n + 1$
a (Å)	6.976(1)
b (Å)	6.301(1)
c (Å)	22.384(4)
β (°)	93.66(2)
V (Å^3)	981.9(3)
Z	2
D_{calc} (g cm^{-3})	2.08
Crystal size (mm)	0.35 × 0.17 × 0.10
μ(Mo Kα) (cm^{-1})	12.50
Diffractometer	Nicolet R3m
Radiation monochromated incident beam (λ (Å))	λ (Mo Kα), 0.71073
Orientation reflections: no., range (2θ) (°)	25, $20 \leqslant 2\theta \leqslant 25$
Temperature (°C)	23 ± 1
Scan method	Wyckoff
Data collection range, 2θ (°)	$4 \leqslant 2\theta \leqslant 48$
No. unique data, total with $F_o \geqslant 3\sigma(F_o)$	1069, 679
R (merge)	0.0544
No. parameters refined	169
Transmission factors, max., min.	0.54, 0.35
R^a	0.0473
$R_w{}^b$	0.0467
Quality-of-fit indicator^c	1.077
Largest shift/e.s.d., final cycle	0.015
Largest peak (e Å^{-3})	0.38

[a] $R = \|F_o| - |F_c\|/|\Sigma F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/[\Sigma(|F_o|) + g(|F_o|^2)]$. [c] Quality-of-fit $= [\Sigma w(|F_o| - |F_c|)_2/(N_o - N_p)]^{1/2}$.

TABLE 2. Atomic coordinates (×10^4) and isotropic coordinates (Å × 10^4) for $[Ni(H_2O)_6][C_6H_5SO_3]_2$

	x	y	z	U^a
Ni	5000	5000	5000	30.3(3)
S	9793(2)	1143(2)	3954.9(6)	34.8(4)
O(1)	9776(5)	3429(6)	4032(2)	47(1)
O(2)	11466(5)	163(6)	4255(2)	45(1)
O(3)	8005(5)	178(6)	4124(2)	47(1)
O(4)	4905(5)	2151(6)	4577(2)	48(1)
O(5)	7018(6)	6086(6)	4448(2)	54(2)
O(6)	2822(6)	6064(6)	4426(2)	53(2)
C(1)	9376(8)	2198(11)	2766(3)	53(2)
C(2)	9507(10)	1736(12)	2163(3)	67(3)
C(3)	10145(9)	−174(14)	1983(3)	68(3)
C(4)	10699(10)	−1687(13)	2400(3)	61(3)
C(5)	10588(9)	−1299(10)	2998(3)	48(2)
C(6)	9933(7)	660(8)	3179(2)	38(2)

[a] Starred items: equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 3. Bond lengths (Å) and angles (°) for $[Ni(H_2O)_6]$-$[C_6H_5SO_3]_2$

Ni–O(4)	2.029(4)	Ni–O(5)	2.049(4)
Ni–O(6)	2.040(4)	Ni–O(4A)	2.029(4)
Ni–O(5A)	2.048(4)	Ni–O(6A)	2.039(4)
S–O(1)	1.451(4)	S–O(2)	1.447(4)
S–O(3)	1.459(4)	S–C(6)	1.771(6)
C(1)–C(2)	1.388(10)	C(1)–C(6)	1.379(8)
C(2)–C(3)	1.354(11)	C(3)–C(4)	1.372(11)
C(4)–C(5)	1.367(9)	C(5)–C(6)	1.386(8)
O(2y)–H(6ax)	1.818	O(1)–H(5b)	1.813
O(3x)–H(4bx)	1.802	O(2z)–H(6a)	1.818
O(4)–Ni–O(5)	91.0(2)	O(4)–Ni–O(6)	89.8(2)
O(5)–Ni–O(6)	91.3(2)	O(4)–Ni–O(4A)	180.0(1)
O(5)–Ni–O(4A)	89.0(2)	O(6)–Ni–O(4A)	90.2(2)
O(4)–Ni–O(5A)	89.0(2)	O(5)–Ni–O(5A)	180.0(1)
O(6)–Ni–O(5A)	88.7(2)	O(4A)–Ni–O(5A)	91.0(2)
O(4)–Ni–O(6A)	90.2(2)	O(5)–Ni–O(6A)	88.7(2)
O(6)–Ni–O(6A)	180.0(1)	O(4A)–Ni–O(6A)	89.8(2)
O(5A)–Ni–O(6A)	91.3(2)	O(1)–S–O(2)	112.4(2)
O(1)–S–O(3)	111.7(2)	O(2)–S–O(3)	112.3(2)
O(1)–S–C(6)	106.7(2)	O(2)–S–C(6)	106.8(2)
O(3)–S–C(6)	106.5(2)	C(2)–C(1)–C(6)	118.1(6)
C(1)–C(2)–C(3)	121.3(7)	C(2)–C(3)–C(4)	119.9(6)
C(3)–C(4)–C(5)	120.7(7)	C(4)–C(5)–C(6)	119.1(6)
S–C(6)–C(1)	120.4(4)	S–C(6)–C(5)	118.7(4)
C(1)–C(6)–C(5)	120.9(5)		

gen bonds are as follows: for x, $(1 - x)$ $(1 - y)$ $(1 - z)$; for y, $(-1 + x)$ $(-1 + y)$ $(1 - z)$; for z, $(-1 + x)(1 - y)(1 - z)$.

The intensity data, gathered by the Wyckoff technique, were reduced by routine procedures. Calculations were carried out using a Data General S-30 computer with SHELXTL (5.1) computer programs. Empirical absorption corrections were applied, based on 216 scans of six reflections. After equivalent data had been merged, there remained 1069 data with $F_o \geqslant 3\sigma(F_o)$ that were used in the development and refinement of the structure.

The structure was solved intuitively. All non-hydrogen atoms were anisotropically refined and all hydrogen atoms were found and isotropically refined. In the final cycle, 169 parameters were refined giving a data:parameter ratio of 1069:169 and residuals of R = 0.0473 and R_w = 0.0467. Atomic coordinates and isotropic thermal parameters are presented in Table 2. Bond lengths and angles are presented in Table 3. A comparison of the intraion distances and angles for $[Mg(H_2O)_6][C_6H_5SO_3]_2$, $[Cu(II)(H_2O)_6][C_6H_5SO_3]_2$, $[Zn(H_2O)_6][C_6H_5SO_3]_2$ and $[Ni(H_2O)_6][C_6H_5SO_3]_2$ is given in Table 4 (see also 'Supplementary Material'). A labeling diagram is shown in Fig. 1 and a packing diagram is shown in Fig. 2.

TABLE 4. Comparison of pertinent bond distances and angles $[M(H_2O)_6][C_6H_5SO_3]_2$

	Mg [3]	Ni	Cu [2]	Zn [3]
Average M–O (Å)[a]	2.04	2.039(4)	2.261(4) (eq.) 1.971(3) (ax.)	2.08
Metal radii[b] (Å) [5]	0.86	0.83	0.87	0.88
Average hydrogen bonded O...O (Å)	2.77	2.757(3)	2.805	2.77
Average S–O (Å)	1.42	1.452(4)	1.459(3)	1.39
Average O–S–O (°)	c	112.1(1)	112.15(2)	c

[a]M = divalent metal. [b]Radii for six-coordinated 2^+ metal ions. [c]These values are as expected for structures isomorphous with the title ion.

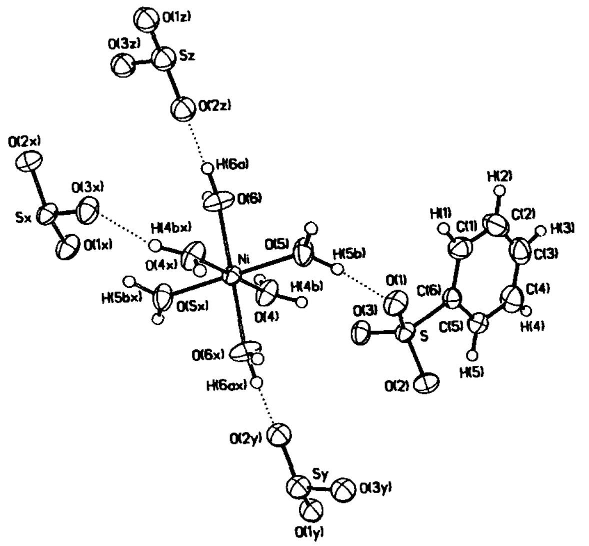

Fig. 1. An ORTEP drawing of $[Ni(H_2O)_6][C_6H_5SO_3]_2$ including generated hydrogen-bonded interactions.

Results

Interest in hexaaqua divalent metal benzenesulfonate ions centers around the layered packing arrangements which these ions adopt. The lattice systems for the title compound and other divalent benzenesulfonate ions are affected more by ion–ion interactions than by intraionic forces. Strong hydrogen bonding between the sulfonate oxygen atoms and the water hydrogen atoms links the ions in a tight lattice arrangement of alternating hydrophilic and hydrophobic regions. The strong hydrogen bonding between the coordinated water molecules and the sulfonate regions in the Ni structure affects the packing arrangement by rotating the hydrophobic phenyl rings out of the way of the hydrogen bonding. This results in the characteristic separation into the hydrophilic and hydrophobic regions.

The hydrophobic phenyl rings twist out of the way of the hydrogen bonding at interplanar angles of 41.6°. Ring structures are usually considered to

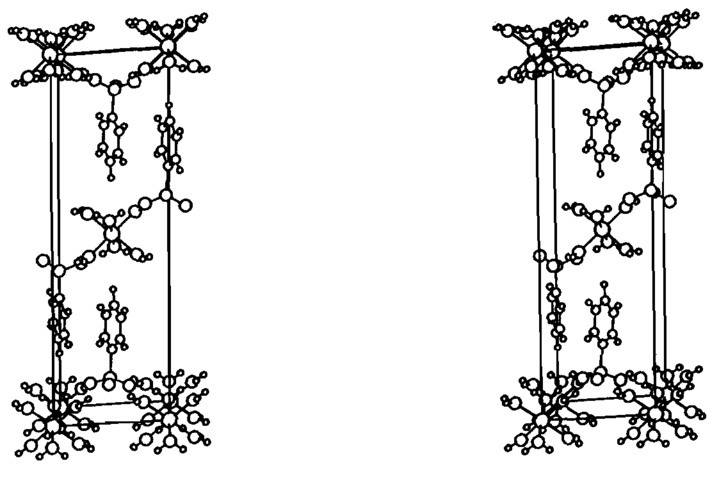

Fig. 2. A packing diagram of $[Ni(H_2O)_6][C_6H_5SO_3]_2$ viewed along the *a* axis.

be mutually repulsive because of π-bonding orbitals, but this is not always the case. The planes of the rings in the title structure are 3.5 Å apart. A recent study of a dibenzyl bipyridal Mo structure, in which the ring ligands stack close to each other in spite of the availability of a less-constrained configuration [6], illustrates the tendency for ring structures not to absolutely repel each other but to stack as they do in the Ni salt.

Because in the previously reported analog structures hydrogen atoms were not located, we here report the non-bonded O...O distances for our structure so that a valid comparison can be made with the Mg, Zn and Cu(II) structures: O(5)...O(1) = 2.758, O(4)...O(3) = 2.744, O(6*x*)...O(2*y*) = 2.769 Å. The average oxygen–oxygen non-bonded distances in the Zn and Mg structures range from 2.72 to 2.86 Å, with an average value of 2.77 Å. The oxygen–oxygen non-bonded distances in the Zn and Mg salts range from 2.72 to 2.86 Å. The Cu(II) salt has average non-bonded oxygen distances of 2.75 Å and extremes of 2.73 and 2.84 Å [3]. The average O–H...O distance in $[Ni(H_2O)_6][C_6H_5SO_3]_2$ is 1.83(4) Å with a range from 1.802(4) to 1.84(4) Å.

The ion-lattice environment and the structure of the benzenesulfonate anion do not differ significantly for the different metals, except in the case of Cu(II) which distorts due to Jahn–Teller effects. The sulfonate group bond angles and distances in our structure are similar to those of the other metal systems (see Table 4); S–O bond distances are 1.454(3) and 1.461(3) Å, and the O–S–O angles are 112.2(2) and 111.4(2)°. The Zn structure does show a slight shortening of the S–O bond; however, the Mg structure does not. The electron environment of the Cu(II) metal does distort the cation in that structure to produce average axial bonds equal to 2.261(4) Å and average equatorial bonds equal to 1.971(3) Å [2, 3].

In each of the four structures, the metal ion is surrounded by six water molecules. Distortions from lattice isomorphism occur in the Cu(II) structure due to Jahn–Teller effects; as predicted, the Cu(II) structure adopts an axially distorted octahedral structure. The Cu(II) structure has an average Cu–O distance of 2.051(3) and extremes of 1.961(3) and 2.264(3) Å [2]. The nickel structure is slightly distorted with an average nickel–oxygen bond length of 2.039(4) Å and extremes of 2.029(4) and 2.049(4) Å. The slight distortions in the Ni structure here are most likely caused by differences in the hydrogen bonding environment of the coordinated water molecules and the sulfonate oxygen atoms. The oxygen atoms of water molecules involved in shorter hydrogen bonds have longer Ni–O bonds [O(2*y*)...H(6a*x*) = 1.818 and Ni–O(6*x*) = 2.040(4), O(1)...H(5*x*) = 1.813 and Ni–O(5) = 2.049]. The Mg and Zn structures show no significant distortions from octahedral symmetry. The average metal–oxygen distance for the magnesium structure is 2.04 Å; that for the zinc structure is 2.08 Å [3]. The ion radii for these four metal ions do not parallel the metal–oxygen distances. An inverse relation actually exists between the size of the ion and the metal–oxygen distance. The ion radii are as follows: Mg = 0.86, Ni = 0.83, Cu(II) = 0.87, Zn = 0.88 Å [7].

Differences in the hydrogen bonding distances in the Ni structure, although small (1.802 versus 1.842 Å), illustrate the distortions which lead to the interesting packing arrangement for this salt. Deviations in the octahedral symmetry of the water molecules around the metal are not caused by Jahn–Teller distortions in the Ni structure, but can be better attributed to the total ionic environment of the salt. Interactions between the sulfonate ions and the phenyl rings, as well as backbonding through the phenyl rings affect the strength of attraction between the sulfonate oxygens and the water hydrogens. This in turn affects the strength of nickel–oxygen interactions and, therefore, the bond length between the atoms.

Supplementary Material

Tables of anisotropic thermal parameters and structure factors are available from the authors on request.

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