ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2019, Vol. 45, No. 7, pp. 478–483. © Pleiades Publishing, Ltd., 2019.
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Synthesis and Crystal and Molecular Structures of Nickel(II) and Copper(II) 1,5-Napthalenedisulfonate Complexes with Nicotinamide

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Received August 24, 2018; revised January 29, 2019; accepted February 11, 2019

Abstract—Coordination compounds of nickel(II) and copper(II) 1,5-naphthalenedisulfonates with nicotinamides, $[Ni(L)_2(H_2O)_4](Nds) \cdot 3H_2O$ (**I**) and $[Cu(L)_2(H_2O)_4](Nds)$ (**II**) (L = nicotinamide, $NC_5H_4C(O)NH_2$, Nds^2 = doubly deprotonated 1,5-naphthaledisulfonate anion, $C_{10}H_6(SO_3)_2^{2-}$), were synthesized and studied by IR and diffuse reflectance spectroscopy. The crystal structures of **I** and **II** were determined by X-ray diffraction (CIF files CCDC nos. 1863367 (**I**) and 1863368 (**II**)). In both structures, the Ni and Cu atoms are coordinated by two nitrogen atoms of two monodentate L ligands and by four oxygen atoms of water molecules. The coordination polyhedron of Ni in **I** is a slightly distorted octahedron and that of Cu in **II** is a tetragonal (4 + 2) bipyramid extended due to the Jahn–Teller effect, with the $O(H_2O)$ atoms in the axial positions. The $[M(L)_2(H_2O)_4]^{2+}$ complex cations, the Nds^{2-} anions, and water molecules of crystallization in **II** are combined by a branched network of hydrogen bonds.

Keywords: synthesis, crystal structure, X-ray diffraction, nickel and copper complex with nicotinamide, 1,5-naphthalenedisulfonate anions

DOI: 10.1134/S1070328419070066

INTRODUCTION

The structure of 3*d* metal complexes with nicotinamide largely depends on the anion of the salt taken for the synthesis. Indeed, even at the same M : L ratio of 1 : 2, copper(II) complexes with the formate anion $Cu(L)_2(HCOO)_2 \cdot H_2O$ [1] are monomeric and contain monodentate anions and tetragonal pyramidal copper environment; complexes with the valerate anion $[Cu(L)_2(C_4H_9COO)_2]$ [2] are monomeric, but contain bidentate pseudo-bis-chelating anions and tetragonal pyramidal chelate units; and complexes with the phthalate anion $[Cu(L)_2(\mu\text{-Pht})(H_2O)] \cdot 0.5H_2O$ [3] have a chain structure with bridging anions, with the coordination polyhedron being an extended tetragonal bipyramid. Cobalt(II) acetate $[Co(L)_2(H_2O)_4]\text{-}(CH_3COO)_2 \cdot 2H_2O$ [4] and phthalate $[Co(L)_2(H_2O)_4][Pht] \cdot 2H_2O$ [5] complexes have the cation-anion nature and outer-sphere anions, with the coordination polyhedron being a slightly distorted octahedron; complexes with the valerate ion $[Co_2(L)_4(C_4H_9COO)_4(H_2O)]$ [6] are octahedra (dimers) containing both monodentate and bidentate anions; and complexes with the succinate ion $Co(L)_2(C_4H_4O_4)(H_2O)_4$ [7] are chain structures with bridging anions. Nicotinamide complexes with sulfonic acid anions are less studied than carboxylate compounds. The compounds $[Co(H_2O)_5(L)](Nds) \cdot H_2O$ [8] and $[Cu(L)_2(H_2O)_4][Cu(L)_2(H_2O)_2(Nds)_2] \cdot 4H_2O$ [9] were obtained by the reaction of the corresponding metal salt, nicotinamide, and sodium naphthalene-1,5-disulfonate (1 : 2 : 1 molar ratio) in an aqueous solution and were structurally studied. The cobalt atom in $[Co(H_2O)_5(L)](Nds) \cdot H_2O$ is coordinated by five water molecules and one nicotinamide ligand via the pyridine nitrogen atom, while the anion occurs in the outer sphere. In $[Cu(L)_2(H_2O)_4]\text{-}[Cu(L)_2(H_2O)_2(Nds)_2] \cdot 4H_2O$, the complex anion is formed by two nicotinamide molecules, two water molecules, and two naphthalene-1,5-disulfonate anions coordinated to copper(II). It is of interest to study the products of reaction of pre-synthesized 3*d* metal naphthalene-1,5-disulfonates with nicotinamide.

Here we describe the synthesis, crystal and molecular structures, and the IR and diffuse reflectance spectra of nickel(II) and copper(II) 1,5-naphthalenedisulfonate complexes with nicotinamide, $[Ni(L)_2(H_2O)_4](Nds) \cdot 3H_2O$ (**I**) and $[Cu(L)_2(H_2O)_4](Nds)$ (**II**).

EXPERIMENTAL

Reagent grade nicotinamide was used. The initial nickel(II) and copper(II) 1,5-naphthalenedisulfonates were prepared by exchange reactions of nickel(II) and copper(II) nitrates with disodium 1,5-naphthalenedisulfonate in aqueous solutions.

Synthesis of I and II. Nicotinamide (1.22 g, 0.01 mol) was dissolved in water (40 mL), and a solution of nickel(II) or copper(II) 1,5-naphthalenedisulfonate (0.005 mol) was added in portions with continuous stirring. This resulted immediate formation of a green-blue precipitate (for nickel(II)) or a blue precipitate (for copper(II)); the precipitates were stirred for 15 min, separated from the mother liquor on a Schott filter, washed with water, and dried in air to a constant weight. The yield was 3.0 g (84%) for **I** and 2.9 g (87%) for **II**.

For $C_{22}H_{32}N_4O_{15}S_2Ni$ (**I**)					
Anal. calcd., %	C, 36.92	H, 4.48	N, 7.83	S, 8.95	Ni, 8.25
Found, %	C, 36.78	H, 4.41	N, 7.71	S, 8.69	Ni, 8.29
For $C_{22}H_{26}N_4O_{12}S_2Cu$ (**II**)					
Anal. calcd., %	C, 39.64	H, 3.90	N, 8.41	S, 9.61	Cu, 9.61
Found, %	C, 39.57	H, 3.67	N, 8.75	S, 9.43	Cu, 9.37

The crystals of **I** and **II** suitable for investigation were obtained by recrystallization of powdered products from water.

Elemental analysis for metal and sulfur was carried out by inductively coupled plasma atomic emission spectrometry on a Perkin-Elmer Optima 8000 instrument; carbon, hydrogen, and nitrogen were quantified on a LECO Tru Spec CHN analyzer.

IR spectra were measured on a Perkin-Elmer SPECTRUM BX II FT-IR SYSTEM instrument in the 4000–400 cm^{-1} range (KBr pellets).

Diffuse reflectance spectra were recorded on a Lambda-9 spectrophotometer (Perkin-Elmer) with MgO as the reference ($\beta_{MgO} = 100\%$).

X-ray diffraction of I and II. The structure was solved by the direct method and refined by least squares method in the full-matrix anisotropic approximation for all non-hydrogen atoms. The hydrogen atoms of water molecules and NH_2 groups were located from difference Fourier maps. The positions of other H atoms were calculated geometrically and included in the refinement according to the riding model. Crystallographic data and X-ray experiment details are summarized in Table 1. Selected interatomic distances and bond angles for structures **I** and **II** are given in Table 2 and the geometric parameters of hydrogen bonds are given in Table 3.

The atom coordinates and other structure parameters are deposited with the Cambridge Crystallographic Data Centre (nos. 1863367 (**I**), 1863368 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

The structural units of the crystals of **I** and **II** are the $[M(L)_2(H_2O)_4]^{2+}$ complex cations (M = Ni in **I**, Cu in **II**) and the Nds^{2-} anions (in **I**, also crystal water molecules); L is the nicotinamide $NC_5H_4C(O)NH_2$, Nds^{2-} is the doubly deprotonated 1,5-naphthalenedisulfonate anion $C_{10}H_6(SO_3)_2^{2-}$. In centrosymmetric complex anions of both structures, the Ni and Cu atoms are coordinated by two nitrogen atoms of two monodentate L ligands and four oxygen atoms of water molecules. The coordination polyhedron of Ni in **I** is a slightly distorted octahedron and that of Cu in **II** is the tetragonal (4 + 2) bipyramid extended due to the Jahn–Teller effect, with the $O(H_2O)$ atoms in the axial positions. The bond lengths are as follows: Ni–O, 2.054 and 2.060; Ni–N, 2.123 Å in **I**; $Cu–O(1)_{eq.}$, 1.966; $Cu–O(2)_{ax.}$, 2.405; Cu–N, 2.007 Å in **II**. The bond angles at the metal atoms in **I** are 86.95°–93.05°; in **II**, they are 87.87°–92.13°.

The $[M(L)_2(H_2O)_4]^{2+}$ complex cations, the Nds^{2-} anions, and water molecules of crystallization in **II** are combined by a branched network of hydrogen bonds: H···O, 1.70–2.32; 1.81–2.50; O···O, 2.643–2.800, 2.610–2.826; N···O, 2.973 and 3.056, 2.753–3.190 Å; OHO angles, 146°–168°, 153°–172°; NHO angles, 163° and 172°, 115°–160° in **I** and **II**, respectively. The packing of structural units in the crystal of **I** and **II** is shown in Fig. 1.

The key absorption bands in the IR spectra of nicotinamide and the complexes (Table 4) were assigned resorting to published data [1–12]. Owing to hydrogen bonds, the free nicotinamide molecules are associated in the solid state, which results in some frequency changes in the IR spectra. This has a more pronounced effect on the spectra of crystalline amines, whereas for spectra of their metal complexes in the solid state in the absence of coordination through the amino group nitrogen, this effect is insignificant, which was confirmed by numerous spectral and X-ray diffraction data [12]. For more correct interpretation of the shifts of nicotinamide absorption bands upon complexation, its IR spectra were used (KBr pellets and mineral oil mulls).

The IR spectrum of the copper(II) complex has more bands in the ν(NH) absorption range than the spectrum of the nickel(II) complex, but the intensity of these bands is somewhat lower. This can be attributed to the presence of outer-sphere water in the nickel(II) complex, which is involved in hydrogen bonding and thus leads to broadening of the bands

Table 1. Crystallographic characteristics and X-ray experiment and structure refinement details for **I** and **II**

Parameter	Value	
	I	**II**
M	715.33	666.14
T, K	293(2)	
System; space group	Triclinic; $P\bar{1}$	Triclinic; $P\bar{1}$
a, Å	8.5346(10)	6.8642(10)
b, Å	9.571(2)	9.941(2)
c, Å	9.856(2)	11.195(3)
α, deg	62.608(10)	80.73(2)
β, deg	74.97(2)	75.82(2)
γ, deg	68.01(2)	86.584(10)
V, Å^3	659.1(2)	730.8(3
Z; ρ(calcd.), g/cm^3	1; 1.678	1; 1.625
μ, mm^{-1}	3.299	3.004
$F(000)$	343	372
Crystal size, mm	0.25 × 0.15 × 0.07	0.15 × 0.15 × 0.08
Diffractometer	CAD4 Enraf-Nonius	
Scan mode	ω	
Radiation; λ, Å	CuK_α; 1.5418	
θ_{min}–θ_{max}, deg	4.9–64.9	4.1–64.9
Ranges of indices:	$-10 \le h \le 10$,	$-8 \le h \le 8$,
	$-11 \le k \le 11$,	$-11 \le k \le 11$,
	$-11 \le l \le 11$	$-13 \le l \le 13$
Number of reflections:		
measured	4207	3763
unique	2174	2076
R_{int}	0.024	0.017
Completeness on θ, %	97.0	83.9
T_{max}, T_{min}	0.794, 0.580	0.786, 0.669
Refinement method	Full-matrix least-squares on F^2	
Number of refined parameters	204	230
GOOF (F^2)	1.072	1.089
R ($I > 2\sigma(I)$)	$R_1 = 0.042$, $wR_2 = 0.115$	$R_1 = 0.0588$, $wR_2 = 0.1596$
R (for all reflections)	$R_1 = 0.046$, $wR_2 = 0.119$	$R_1 = 0.0631$, $wR_2 = 0.1648$
Residual electron density (max/min), e/Å^3	0.349/–0.551	0.358/–0.682

[13]. For this reason, it is also impossible to distinguish bands typical of the C–H bonds of the aromatic rings in the spectrum of the nickel(II) complex. The δ(NH$_2$) frequencies in the spectra of complexes are intermediate between those in the spectra of the ligand in KBr pellets and in mineral oil. The described behavior of the bands involving N–H bonds implies the absence of bonding through the amine nitrogen.

The ν(C=O) frequency (amide **I**) in the spectra of both complexes barely differs from that in the spectrum of free nicotinamide, which implies the absence of bonding through the carbonyl oxygen. The absorption bands of the pyridine ring behave in different ways. The band at 1580 cm^{-1} shifts slightly, but somewhat decreases in intensity for both complexes. Conversely, the band in the 1020–1030 cm^{-1} range increases in intensity, especially for the copper(II) complex, for which this band also shifts to higher frequency by 24 cm^{-1} with respect to that for the free ligand. The 965 cm^{-1} band observed for the nickel(II) complex does not shift, but decreases in intensity, while that for the copper(II) complexes shifts by 24 cm^{-1} to lower frequency without a change in intensity. These changes in the frequency relationships and band intensities of pyridine ring vibrations may be indicative of symmetry changes in the pyridine ring upon coordination to the metals.

The absorption bands of the 1,5-naphthalenedisulfonate anion were assigned resorting to published data [14–19]. The C–H stretching vibrations in the spectrum of the Cu(II) complex give rise to one weak band at 2928 cm^{-1}. As noted above, for Ni(II) complex this band cannot be identified due to superimposition of water absorption bands. The naphthalene rings give rise to quite a number of bands, the most intense of which are at about 615 cm^{-1}. The SO_3^- group is manifested as a number of bands: $\nu_s(SO_3^-)$ accounts for

Table 2. Selected bond lengths (Å) and bond angles (deg) in structures of **I** and **II**

Bond	*d*, Å	
	I (M = Ni)	**II** (M = Cu)
M(1)–O(1)	2.060(3)	1.966(3)
M(1) –N(1)	2.123(4)	2.007(2)
M(1)–O(2)	2.054(4)	2.405(3)
S(1)–O(6)	1.450(3)	1.437(3)
S(1)–O(5)	1.442(3)	1.444(3)
S(1)–O(4)	1.465(3)	1.446(3)
S(1)–C(7)	1.769(5)	1.776(3)
N(1)–C(1)	1.347(5)	1.337(4)
N(1)–C(5)	1.335(6)	1.339(4)
N(2)–C(6)	1.331(6)	1.339(4)
C(6)–O(3)	1.227(6)	1.309(4)
Angle	ω, deg	ω, deg
O(1)Cu(1)N(1)	90.72(14)	90.85(11)
N(1)Cu(1)O(2)	86.95(15)	87.87(10)
O(1)Cu(1)O(2)	88.45(16)	92.05(12)

Table 3. Geometric parameters of hydrogen bonds (Å, deg) for compounds **I** and **II***

D–H···A	Distance, Å			DHA angle, deg
	D–H	H···A	D···A	
		I		
O(1)–H(1*W*)···O(4)	1.01(8)	1.81(8)	2.802(5)	168(6)
O(7)–H(7*W*)···O(6)	1.10(11)	1.81(10)	2.797(6)	147(8)
O(7)–H(7*AW*)···O(3)	0.68(11)	2.32(11)	2.907(7)	146(12)
O(2)–H(2*W*)···O(3)$^{\#1}$	0.96(8)	1.70(8)	2.643(5)	167(6)
O(2)–H(2*AW*)···O(4)$^{\#1}$	0.64(5)	2.18(5)	2.764(5)	152(6)
N(2)–H(2*A*)···O(7)$^{\#2}$	0.86	2.12	2.973(6)	172
N(2)–H(2*B*)···O(6)$^{\#3}$	0.86	2.22	3.053(6)	163
O(1)–H(1*AW*)···O(7)$^{\#4}$	0.75(7)	2.07(7)	2.800(6)	166(7)
		II		
O(2)–H(2O)···O(4)	0.81(5)	2.01(5)	2.753(4)	153(4)
N(2)–H(2*A*)···O(3)$^{\#3}$	0.86	2.13	2.753(4)	160
N(2)–H(2*B*)···O(4)$^{\#2}$	0.86	2.50	3.190(4)	138
N(2)–(H2*B*)···O(5)$^{\#1}$	0.86	2.61	3.083(4)	115
O(1)–H(O1)···O(5)$^{\#4}$	0.69(5)	2.01(5)	2.679(4)	164(5)
O(1)–H(*A*O1)···O(3)$^{\#5}$	0.82(5)	1.81(5)	2.610(3)	165(4)
O(2)–H(2*A*O)···O(6)$^{\#6}$	0.84(7)	1.99(7)	2.826(4)	172(6)

* Symmetry codes for equivalent atoms: $^{\#1}$ $-x, -y + 1, -z + 1$; $^{\#2}$ $-x - 1, -y + 2, -z + 1$; $^{\#3}$ $-x, -y + 2, -z + 1$; $^{\#4}$ $x + 1, y, z$ (**I**). $^{\#1}$ $-x, -y, -z$; $^{\#2}$ $-x + 1, -y - 1, -z - 1$; $^{\#3}$ $-x + 1, -y, -z + 1$; $^{\#4}$ $-x, -y, -z - 1$; $^{\#5}$ $-x + 1, -y, -z$; $^{\#6}$ $-x, -y - 1, -z$ (**II**).

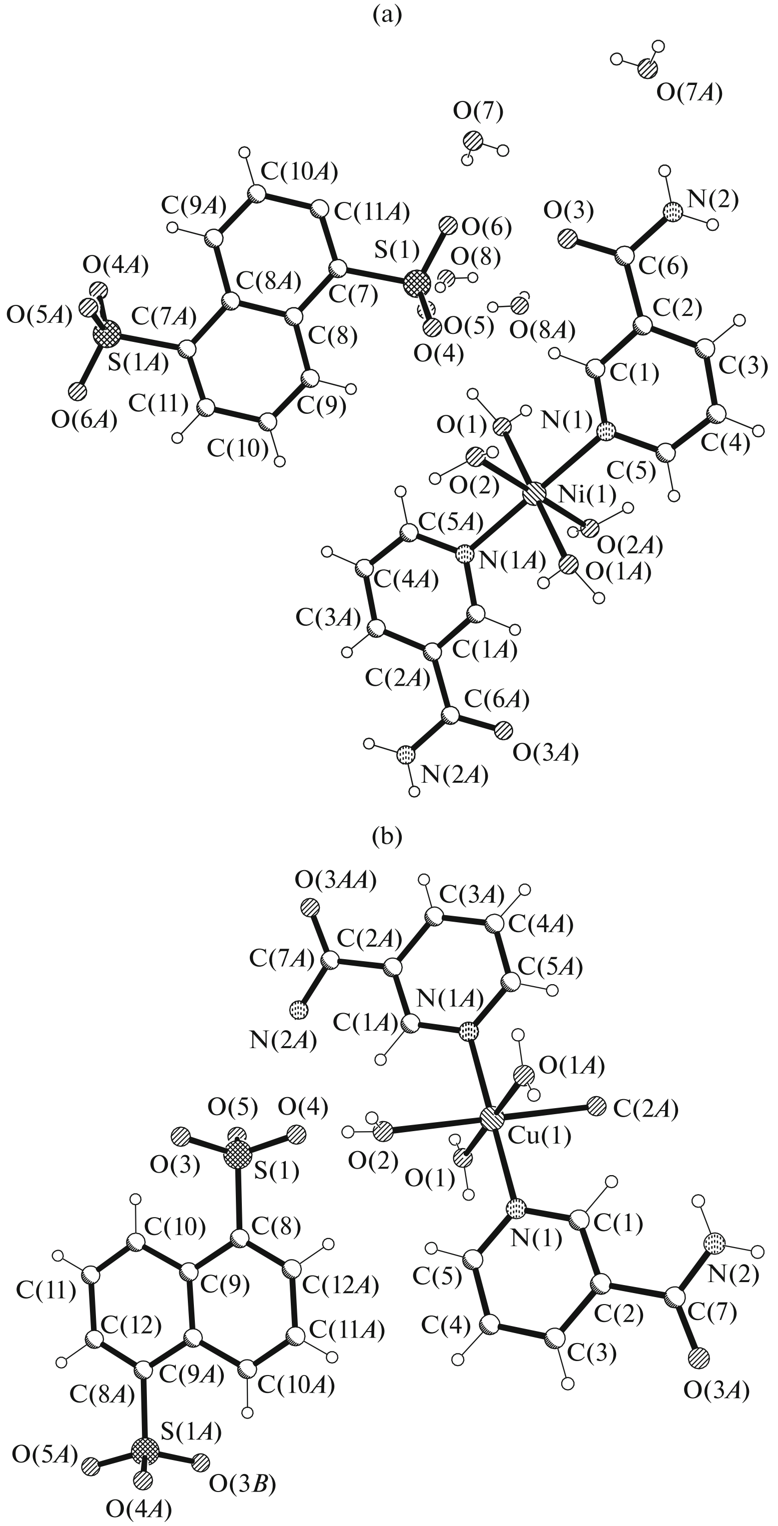

Fig. 1. Packing of structural units of (a) **I** and (b) **II** in the crystal.

very strong bands at about 1040 cm^{-1}, $\nu_{as}(SO_3^-)$ is manifested as single bands at about 1240 and 1160 cm^{-1}. Rather intense bands are present at about 1200 cm^{-1}: a single band for complex **I** and a doublet for **II**. The SO_3^- absorption bands at 1200 and 1040 cm^{-1} are the most intense in the IR spectra of both complexes.

Thus, the data of vibrational spectroscopy are consistent with X-ray diffraction data.

Table 4. Wave numbers (frequencies, cm^{-1}) of the absorption maxima in the IR spectra of nicotinamide and complexes **I** and **II**

Assignment	L (KBr pellets)	L (mineral oil suspensions)	[Ni(L)$_2$(H$_2$O)$_4$](Nds) · 3H$_2$O (**I**)	[Cu(L)$_2$(H$_2$O)$_4$](Nds) (**II**)
ν(OH)			3442 sh	3576 m, 3418 m
ν(NH)	3376 s, 3300 m, 3170 s	3350 s, 3145 s	3367 s, 3224 s	3325 m, 3269 w, 3216 m, 3192 w
ν(C–H)$_{\text{arom.}}$	3090 w, 3035 w, 2970 w, 2960 w, 2910 w, 2890 w, 2820 w			2928 w
ν(C=O)	1687 s	1665 s	1666 vs	1663 vs
δ(NH$_2$)	1627 m	1610 m	1619 m	1623 m
Naphthalene ring bands			1619 s, 1503 m, 1430 s, 799 w, 789 w, 650 m, 615 s, 568 w, 520 m	1623 s, 1500 m, 1444 m, 794 w, 769 s, 656 m, 613 s, 572 m, 530 m
Pyridine ring ν	1580 s, 1030 m, 1005 m	1585 s, 1560 m, 1020 m, 965 m	1581 m, 1028 s, 966 w	1578 m, 1044 vs, 941 m
$\nu_{as}\left(\mathrm{SO}_3^-\right)$			1236 sh, 1214 vs, 1190 vs, 1159 s	1238 m, 1205 vs, 1161 s
$\nu_{s}\left(\mathrm{SO}_3^-\right)$			1040 vs	1044 vs

The diffuse reflectance data for the complexes (cm^{-1}): 15450 ($^3A_{2g} \to I_{1g}$), 9850 ($^3A_{2g} \to I_{2g}$), and 1455 for **I** and **II**, respectively, are consistent with their octahedral structure [20].

ACKNOWLEDGMENTS

X-ray diffraction analysis was performed at the Center for Collective Use of Physical Investigation Methods, Kurnakov Institute of General and Inorganic Chemistry, RAS.

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Translated by Z. Svitanko