## COORDINATION COMPOUNDS

# Supramolecular Pseudometallacycles in a Nickel Compound with 4,4-Diaminodiphenylmethane: Synthesis and Structure of {Ni[(CH<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>)<sub>2</sub>]<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>}

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Abstract—The  $[Ni(DDM)_2(NO_3)_2(H_2O)_2]$  complex (DDM is 4,4-diaminodiphenylmethane  $[CH_2(C_6H_4NH_2)_2])$ 

is synthesized, and its structure is determined. The crystals are triclinic, space group  $P_1$ , a = 5.846(1) Å, b = 9.450(2) Å, c = 13.390(3) Å,  $\alpha = 105.63(3)^\circ$ ,  $\beta = 98.13(3)^\circ$ ,  $\gamma = 105.84(3)^\circ$ , V = 666.6(2) Å<sup>3</sup>,  $\rho_{calcd} = 1.553$  g/cm<sup>3</sup>, Z = 2. The Ni(II) ion (in the inversion center) is bound to a distorted octahedral array formed by the nitrogen atoms of the primary amino groups of the DDM molecules and the oxygen atoms of the monodentate nitrato groups and water molecules (Ni(1)–N(3) 2.119(2) Å, Ni(1)–O(1) 2.122(2) Å, Ni(1)–O(w) 2.047(2) Å, angles at the Ni atoms vary in the 85.08(9)°–94.92(9)° interval). The structure contains supramolecular metallacycles formed by the O(w)–H···N(2) hydrogen bonds between the coordinated H<sub>2</sub>O molecules and the terminal amino

groups of DDM. The metallacycles are joined by the Ni<sup>2+</sup> ions into infinite chains running in the [111] direction. **DOI:** 10.1134/S0036023608110089

Increased interest in the design and assembly of supramolecular architectures is due to their new unusual topology and a possibility of wide practical use [1–4]. Inorganic–organic hybrid coordination polymers are synthesized using polyfunctional organic ligands in order to bind transition metal ions due to the selfassembly resulting in compounds of various architectures. This requires careful choice of multidentate ligands to efficiently assist the formation of the corresponding polymeric structures. Pyrazine and bipyridine and their analogues are usually used as bridging ligands, whereas various amines (aromatic and aliphatic) are used more rarely. For example, coordination polymers of silver based on aminomethylpyridines [5, 6] and di- and triaminocyclohexane [7] are known. We recently synthesized and structurally characterized the coordination polymer of silver  $\{Ag[(CH_{2}(C_{6}H_{4}NH_{2})_{2}]_{2}(CH_{3}C_{6}H_{4}NH_{2})V_{2}\}NO_{3}$ [8] with the 4,4-diaminodiphenylmethane bridging ligand.

In the design of coordination polymers and supramolecular assemblies of bivalent metal compounds, the Co(II), Zn(II), and Cd(II) derivatives are used most actively, whereas Ni(II) is less often applied [9, 10].

As a rule, an octahedral environment is formed around the Ni<sup>2+</sup> ion. Four or two coordination sites should be blocked to obtain its coordination polymers (1D chains and 2D layers, respectively) involving ditopic nitrogen-containing ligands. Chelating or strongly coordinating monodentate ligands are used for this purpose [10–14]. This work is aimed at synthesizing and studying the structure of the coordination nickel polymer with the nonrigid ditopic nitrogen-containing ligand 4,4-diaminodiphenylmethane  $CH_2(C_6H_4NH_2)_2$  (DDM).

#### **EXPERIMENTAL**

**Synthesis.** To synthesize  $[Ni(DDM)_2(NO_3)_2(H_2O)_2]$ (I),  $Ni(NO_3)_2 \cdot 6H_2O$  (pure for analysis) and DDM (Merck) were used. Acetonitrile was purified by distillation over  $P_2O_5$ , and dimethylformamide (DMF) was distilled under reduced pressure in the presence of CaH<sub>2</sub>.

Dimethylformamide was added dropwise with stirring to a mixture of nickel nitrate (0.40 g, 1.37 mmol) and 4,4-diaminodiphenylmethane (0.82 g, 4.13 mmol) in MeCN (10 mL) until the salt dissolved completely, and the solution was kept for several days. The crystals that precipitated (dark green in bulk) were separated from the mother liquor, washed with a minimal amount of MeCN, and dried in air at room temperature. The yield was 73%. The crystals were examined using elemental analysis, NMR, IR spectroscopy, and X-ray diffraction.

For  $C_{13}H_{16}N_3Ni_{0.5}O_4$  anal. calcd. (%): N, 13.65; C, 50.71; H, 5.20.

Found (%): N, 13.21; C, 51.01; H, 5.08.

When the synthesis was carried out with an equimolar ratio of the reactants, the composition of the isolated crystals did not differ from the above composition (according to the elemental analysis data).

**IR** absorption spectra were recorded as Nujol mulls on a Specord 75 IR spectrophotometer in the range 4000-400 cm<sup>-1</sup>.

**X-ray diffraction analysis.** An experimental material for the crystals of compound I was obtained on an Enraf-Nonius CAD-4 automated diffractometer. Absorption correction was applied empirically according to the North–Phillips algorithm using two  $\Psi$  scan curves. The structure was solved by the heavy-atom method and refined by the least-squares method in the full-matrix anisotropic approximation for all nonhydrogen atoms. Hydrogen atoms were introduced in geometrically calculated positions and refined as riding on their bond atoms with fixed isotropic temperature parameter ( $U_{iso} = 0.08 \text{ Å}^2$ ). The H atoms of the water molecules were found from a difference Fourier synthesis. All calculations were performed using the SHELXS86 and SHELXL93 program packages.

The crystallographic data and selected experimental details for structure I are given in Table 1. The coordinates of atoms and their temperature factors are presented in Table 2. Selected bond lengths and bond angles are listed in Table 3. The hydrogen bond geometry is given in Table 4.

#### **RESULTS AND DISCUSSION**

The IR spectrum of compound I shows five bands at 3377–3165 cm<sup>-1</sup>, i.e., in the region where bands of symmetric and asymmetric stretching vibrations of the  $NH_2$  groups appear. The spectrum of compound I is more complicated than that of free DDM due to such factors as the presence of water molecules in the complex, the nonequivalent character of the amino groups of the ditopic ligand, and, most likely, hydrogen bonding. A significant difference between the spectra of the complex and free DDM is observed in the long-wavelength region as well. It is known [15] that primary amines should produce absorption at longer wavelengths caused by external bending vibrations of the NH<sub>2</sub> groups. Although this phenomenon is poorly studied, most primary amines give rise to a broad band at 650–900 cm<sup>-1</sup>, which is attributed to this type of vibrations. The spectrum of free DDM also shows a broad strong band at 620 cm<sup>-1</sup>, which can be attributed to  $\delta(NH_2)$ . This band is strongly shifted to the high-frequency region (by  $\sim 200 \text{ cm}^{-1}$ ), which is probably due to the nonequivalence of the NH<sub>2</sub> groups. The three strongest bands at 1427, 1301, and 1040  $\text{cm}^{-1}$  (the latter is split into two components) correspond to, respectively,  $v_{as}(NO_2)$ ,  $v_s(NO_2)$ , and v(NO) of the monodentate NO<sub>3</sub> groups. This assignment agrees entirely with the results of the detailed study of the nickel complexes with differently bound nitrate groups [16], including the value  $\Delta = v_{as} - v_s$ , which is, as a rule, significantly higher

Table 1.	Crystallograp	hic data	and	selected	experimental
details fo	or structure I				

FW	307.64
Crystal size, mm	$0.15 \times 0.23 \times 0.68$
Crystal system	Triclinic
Space group	$P\overline{1}$
Cell parameters:	
<i>a</i> , Å	5.846(1)
b, Å	9.450(2)
<i>c</i> , Å	13.390(3)
α, deg	105.63(3)
β, deg	98.13(3)
γ, deg	105.84(3)
<i>V</i> , Å <sup>3</sup>	666.6(2)
Ζ	2
$\rho_{calcd}$ , g/cm <sup>3</sup>	1.533
$\mu_{Mo}$ , mm <sup>-1</sup>	0.790
<i>F</i> (000)	322
<i>Т</i> , К	293
Radiation $(\lambda, A)$	Mo $K_{\alpha}$ (0.71073), graphite monochromator
Scan type	ω
$\theta$ range, deg	1.62-29.97
Index ranges	$-8 \le h \le 1, -13 \le k \le 13, \\ -18 \le l \le 18$
Total number of reflections	2855
Number of observed reflections with $I \ge 2\sigma(I)$	2215 [ $R(int) = 0.0185$ ]
Number of refined parameters	188
GOOF on $F^2$	0.452
$R\left[I \ge 2\sigma(I)\right]$	R1 = 0.0340, wR2 = 0.0930
Extinction coefficient	0.000(4)
Residual electron density (max/min), e/Å <sup>3</sup>	0.363/0.260

(by  $\sim 70 \text{ cm}^{-1}$ ) for the bidentate coordination. Note that the band at 1300 cm<sup>-1</sup>, unlike two other bands, almost coincides with that appeared in the IR spectrum of free DDM.

The structure of molecule **I** is shown in Fig. 1. The coordination polyhedron of the Ni atom (in the inversion center) is a distorted octahedron formed by the symmetrically bound nitrogen atoms of the primary amino groups of the monodentate DDM ligand and oxygen atoms of the nitrato groups and water molecules. The distances are Ni(1)–N(3), 2.119(2); Ni(1)–O(1), 2.122(2); and Ni(1)–O(w), 2.047(2) Å; and the angles at the Ni atom vary within 85.08(9)°– 94.92(9)°.

Note that the terminal nitrogen atoms of DDM participate in the O(w)-H···N(2) hydrogen bonds as proton

Atom	x	у	Z	$U_{\rm eq}, {\rm \AA}^2$
Ni(1)	0	0	0	0.027(1)
N(1)	0.2763(4)	0.0473(3)	-0.1706(2)	0.035(1)
N(2)	-0.8505(5)	-0.7172(3)	-0.6773(2)	0.045(1)
N(3)	0.0930(4)	-0.1948(2)	0.0180(2)	0.036(1)
O(1)	0.2922(4)	0.0336(3)	-0.0782(2)	0.043(1)
O(2)	0.4028(5)	-0.0069(3)	-0.2269(2)	0.059(1)
O(3)	0.1410(4)	0.1126(3)	-0.2022(2)	0.057(1)
O(w)	0.2593(3)	0.1294(2)	0.1381(1)	0.035(1)
C(1)	-0.3726(5)	-0.7574(3)	-0.4263(2)	0.033(1)
C(2)	-0.2137(5)	-0.4446(3)	-0.0916(2)	0.034(1)
C(3)	-0.1221(5)	-0.6177(3)	-0.2388(2)	0.030(1)
C(4)	-0.2834(5)	-0.5819(3)	-0.1764(2)	0.034(1)
C(5)	0.0205(5)	-0.3393(3)	-0.0682(2)	0.030(1)
C(6)	0.1116(5)	-0.5117(3)	-0.2125(2)	0.035(1)
C(7)	0.1827(5)	-0.3731(3)	-0.1283(2)	0.035(1)
C(8)	-0.6917(5)	-0.7307(3)	-0.5925(2)	0.035(1)
C(9)	-0.2028(5)	-0.7653(3)	-0.3333(2)	0.038(1)
C(10)	-0.6220(5)	-0.8350(3)	-0.4504(2)	0.040(1)
C(11)	-0.2855(5)	-0.6685(3)	-0.4887(2)	0.038(1)
C(12)	-0.4417(6)	-0.6546(3)	-0.5706(2)	0.041(1)
C(13)	-0.7796(5)	-0.8220(3)	-0.5327(2)	0.041(1)
H(2A)	-0.789	-0.660	-0.717	
H(2B)	-1.013	-0.766	-0.692	
H(3A)	0.033	-0.217	0.072	
H(3B)	0.257	-0.164	0.039	
H(2C)	-0.327	-0.423	-0.492	
H(4A)	-0.446	-0.654	-0.193	
H(6A)	0.227	-0.535	-0.253	
H(7A)	0.345	-0.301	-0.112	
H(9A)	-0.061	-0.784	-0.355	
H(9B)	-0.285	-0.851	-0.312	
H(10A)	-0.686	-0.899	-0.410	
H(11A)	-0.113	-0.615	-0.474	
H(12A)	-0.377	-0.593	-0.613	
H(13A)	-0.952	-0.877	-0.548	
H(1)	0.220	0.183	0.201	
H(2)	0.363	0.089	0.161	

**Table 2.** Atomic coordinates and temperature factors  $(U_{eq} = 1/3\Sigma U_{ij})$  for structure I

acceptors, resulting in the formation of the supramolecular rings. Each cycle includes two Ni<sup>2+</sup> ions, two DDM ligands, and two water molecules. The rings share the Ni<sup>2+</sup> ions to form infinite chains extended in the [111] direction (Fig. 2). The Ni…Ni distance in the ring is 13.5 Å. The aromatic rings in DDM are planar, and the dihedral angle between their planes is  $101.9^{\circ}$ . The monodentate planar nitrato groups NO<sub>3</sub> participate through the terminal oxygen atoms in hydrogen bonding with the H<sub>2</sub>O molecules and with the nitrogen atoms of DDM (Table 4) as proton acceptors to stabilize the structure.

Note that the involvement of the Ni<sup>2+</sup> ion in the coor-

dination of the water molecules and  $NO_3^-$  anions, along with the DDM molecules, results in the saturation of its coordination sphere and the formation of only supramolecular rings that form original chains. In the silver coordination polymer [8], rather rare octahedral coordination of Ag<sup>+</sup> ions due to the primary amino groups of the DDM ligands and *p*-toluidine is observed and the 2D polymer forms from conjugated manymembered metallacycles with the bridging DDM

ligands. The  $NO_3^-$  anion exists in the outer sphere.

It is likely that noncoordinating anions (for example,  $PF_6^-$ ,  $BF_4^-$  should be used in the presence of water molecules to obtain a coordination polymer of nickel with such a ditopic nitrogen-containing ligand as DDM.

In bivalent metal compounds, both coordination and hydrogen bonds are involved in the two- and threedimensional networks from metal-containing building blocks. Both types of bonding are pertinent since they exert directed effect. When metal centers are bound by rigid ligands (for instance, bipyridine and others), rigid networks are formed, whereas nonrigid supramolecular structures are formed when weaker hydrogen bonds are involved in binding. For example, in the  $[Cu(3,5-PDC)(H_2O)_2]$  compound (3,5-PDC) is pyridine-3,5dicarboxylate) [17] the supramolecular three-dimensional coordination polymer is formed due to joining the adjacent layers through the hydrogen bonds between the coordinated water molecules and bifunctional carboxylate groups. The  $[Co(3,5-PDC)(H_2O)_5]$ . 2H<sub>2</sub>O structure [18] is composed of discrete molecules in which the Co<sup>2+</sup> ion is coordinated to the vertices of an octahedron formed by five oxygen atoms of the water molecules and the nitrogen atom of the 3,5-PDC ligand, whereas the noncoordinated carboxy groups of 3,5-PDC are involved in intermolecular hydrogen bonding with the coordinated water molecules to form a supramolecular two-dimensional cyclic network. As an example we can present a silver compound  $[Ag_2(CF_3COO)_2(PIP)_4]$  (PIP is piperazine) [19] in which the Ag<sub>2</sub>(CF<sub>3</sub>COO)<sub>2</sub> dimers are linked by N-H...O hydrogen bonds to form a unique two-dimensional network consisting of the rhomboid supramolecular rings.

In structure I, the DDM ligand plays a dual role: one  $NH_2$  group forms the donor-acceptor bond with the  $Ni^{2+}$  ion, whereas the second, noncoordinated  $NH_2$  group acts as a proton acceptor in the H-bond with the  $H_2O$  molecule that coordinates the adjacent Ni atom. As a result, the supramolecular rings producing unique

Bond	<i>d</i> , Å	Bond	<i>d</i> , Å
Ni(1)-O(w)	2.047(2)	C(2)–C(4)	1.388(4)
Ni(1)–N(3)	2.119(2)	C(2)–C(5)	1.389(4)
Ni(1)–O(1)	2.122(2)	C(3)–C(6)	1.386(4)
N(1)–O(3)	1.225(3)	C(3)–C(4)	1.395(4)
N(1)–O(2)	1.238(3)	C(3)–C(9)	1.513(3)
N(1)–O(1)	1.271(3)	C(5)–C(7)	1.375(4)
N(2)–C(8)	1.418(3)	C(6)–C(7)	1.390(4)
N(3)–C(5)	1.440(3)	C(8)–C(13)	1.378(4)
C(1)–C(10)	1.387(4)	C(8)–C(12)	1.389(4)
C(1)–C(11)	1.388(4)	C(10)–C(13)	1.388(4)
C(1)–C(9)	1.512(3)	C(11)–C(12)	1.383(4)
Angle	ω, deg	Angle	ω, deg
O(w)Ni(1)N(3)	86.81(8)	C(2)C(4)C(3)	121.4 (2)
O(w)Ni(1)N(3)	85.97 (8)	C(7)C(5)C(2)	119.7 (2)
N(3)Ni(1)O(1)	85.08(9)	C(7)C(5)N(3)	120.0(2)
O(3)N(1)O(2)	121.4(2)	C(2)C(5)N(3)	120.2(2)
O(3)N(1)O(1)	120.8(2)	C(3)C(6)C(7)	121.5(2)
O(2)N(1)O(1)	117.8(2)	C(5)C(7)C(6)	120.0(2)
C(5)N(3)Ni(1)	121.9(2)	C(13)C(8)C(12)	118.8(2)
N(1)O(1)Ni(1)	125.1(2)	C(13)C(8)N(2)	121.2(3)
C(10)C(1)C(11)	117.7(2)	C(12)C(8)N(2)	120.0(2)
C(10)C(1)C(9)	121.1(2)	C(1)C(9)C(3)	112.3(2)
C(11)C(1)C(9)	121.2(2)	C(1)C(10)C(13)	121.2(3)
C(4)C(2)C(5)	119.8(2)	C(12)C(11)C(1)	121.4(3)
C(6)C(3)C(4)	117.6(2)	C(11)C(12)C(8)	120.3(2)
C(6)C(3)C(9)	121.5 (2)	C(8)C(13)C(10)	120.6(3)
C(4)C(3)C(9)	120.9 (2)		

Table 3. Bond lengths (d) and bond angles ( $\omega$ ) in structure I

Table 4. Hydrogen bonding geometry in structure I

Bond A–H $\cdots$ B	Position of atom B	А…В	A–H	Н…В	Angle AHB, deg
O(w)-H(1)N(2)	1 + x, 1 + y, 1 + z	2.765(3)	0.95	1.82	179
O(w)–H(2)···O(2)	1-x, -y, -z	2.826(3)	0.86	1.97	175
N(2)- $H(2A)$ ···O( $W$ )	-1 + x, -1 + y, -1 + z	2.765(3)	0.90	2.49	98
N(2)–H(2B)····O(2)	-1 - x, -1 - y, -1 - z	3.361(4)	0.90	2.52	156
N(3)–H(3A)····O(3)	-x, -y, -z	3.010(3)	0.90	2.27	139
N(3)–H(3B)····O(2)	1 - x, -y, -z	3.446(4)	0.90	2.50	167







Fig. 2. Fragment of structure I: the chains of the supramolecular rings extended in the [111] direction.

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chains are formed from the  $[Ni(DDM)_2(H_2O)_2(NO_3)_2]$  building units.

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