STRUCTURAL INVESTIGATION OF NICKEL(II)-NICOTINAMIDE-SOLVENT INTERACTIONS IN SOLID COMPLEXES. CRYSTAL STRUCTURE OF [NI(H$_2$O)$_4$(NA)$_2$](NO$_3$)$_2$·2H$_2$O

Jóna Eugen[a]; Koman Marian[a]; Melník Milan[a]; Mroziński Jerzy[b]

[a] Department of Inorganic Chemistry, Slovak Technical University, Bratislava, Slovak Republic [b] Institute of Chemistry, Wroclaw University, Wroclaw, Poland

PLEASE SCROLL DOWN FOR ARTICLE

STRUCTURAL INVESTIGATION OF NICKEL(II)-NICOTINAMIDE-SOLVENT INTERACTIONS IN SOLID COMPLEXES. CRYSTAL STRUCTURE OF $[NI(H_2O)_4(NA)_2](NO_3)_2.2H_2O$.

JÓNA EUGEN[a], KOMAN MARIAN[a], MELNÍK MILAN[a]
and MROZIŃSKI JERZY[b],*

[a]*Department of Inorganic Chemistry, Slovak Technical University, 812 37 Bratislava, Slovak Republic,* [b]*Institute of Chemistry, Wroclaw University, 50–383 Wroclaw, Poland*

The crystal structure of $[Ni(H_2O)_4(NA)_2](NO_3)_2.2H_2O$ (NA=nicotinamide) has been determined. The complex cation has a monomeric *pseudo*-octahedral configuration about Ni(II). The basal plane contains four oxygen atoms of coordinated water molecules and axial positions are occupied by heterocyclic nitrogen atoms of the two nicotinamide ligands. The other two water molecules are not coordinated. Spectroscopic, magnetic and thermal data are in agreement with structural results. Trends of Ni—N and Ni—O interatomic distances in similar complexes are discussed.

INTRODUCTION

We have been studying antibacterial and antifungal activities of some Cu(II), Ni(II) and Fe(II) complexes. In this connection we have prepared and studied nickel(II) complexes with nicotinamide (NA). The biological activity of this ligand is well known. NA plays an important role in the metabolism of living cells. In order to be certain about the interactions between Ni(II) and NA the coordination of this ligand has been studied applying spectroscopic, magnetic and thermal methods.[1-5] Several complexes of NA contain solvent molecules. However, the nature of interactions with complex units is not well known. In order to clarify Ni(II)-NA-solvent interactions we focused our attention on halogen and thiocyanate complexes.[6]

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* Author for correspondence.

In this paper our investigation is extended to Ni(II) complexes with oxo-anions. Thermal, magnetic and spectroscopic properties of $Ni(NA)_2(NO_3)_2.6H_2O$ are correlated with X-ray structural data. The results are compared with those found for similar halogen complexes.

EXPERIMENTAL

Syntheses

Solid $Ni(NO_3)_2.6H_2O$ was dissolved with stirring in EtOH and then an ethanolic solution of nicotinamide in a 4 : 1 molar ratio to Ni was added. After 2 – 3 days, blue crystals separated. For $Ni(NA)_4(NO_3)_2.6H_2O$ (**III**), calcd.: 10.97% Ni; 26.91% C; 4.52% H and 15.71% N; found: 11.08% Ni; 27.08% C; 4.43% H and 15.73% N.

Magnetic Measurements

Magnetic susceptibilities of polycrystalline samples were measured by the Faraday method over the temperature range 77–300 K using a sensitive Cahn RG-HV electrobalance. The applied magnetic field was 6.25 kOe and $Hg[Co(NCS)_4]$ was employed as calibrant.[7] Corrections for diamagnetism of constituent atoms was calculated using Pascal's constants.[8] Magnetism of samples was found to be field-independent. Effective magnetic moments were calculated from the relation $\mu_{eff} = (\chi_M^{corr}.T)^{1/2}$.

Spectroscopic Measurements

Electronic absorption spectra of solid nicotinamide complexes were measured at room temperature using the diffuse reflectance technique. Ground samples were mixed with magnesium(II) oxide and spectra recorded with a Beckman UV 5240 spectrophotometer in the range 2000–350 nm. Infrared spectra were measured from 4000 to 250 cm^{-1} with a Philips PU 9800 FTIR spectrophotometer in nujol mulls.

Thermal Measurements

TG, DTG and DTA curves were measured on a OD 102 Derivatograph (MOM Budapest). For thermal decomposition, a sample mass of 100 mg was used and the rate of temperature increase was 5°C min^{-1}.

X-ray Measurements

The crystal structure of $Ni(NA)_2(NO_3)_2.6H$ O (III) was determined by single crystal X-ray diffraction. All data were collected at room temperature with a Syntex $P2_1$ diffractometer. Intensities were corrected for Lorentz polarization factors. The structure was solved using the Patterson function to locate the nickel atom while successive difference Fourier maps and least-squares refinement were used for location of the remaining non-hydrogen atoms.[9] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms, except those in water molecules, were placed in calculated positions. Hydrogen atoms of water molecules were refined isotropically. Atomic scattering factors were taken from International Tables for X-ray Crystallography.[10]

RESULTS AND DISCUSSION

Thermal, Magnetic and Spectroscopic Properties

The nicotinamide complexes with Ni(II) were obtained as yellow crystalline chloride (I) and bromide (II) salts, whereas the nitrate (III) is a crystalline product of bluish colour. Bis(nicotinamide)nickel(II) nitrate is a hexahydrate. Thermal decomposition proved that the (III) undergoes endothermic dehydration reactions in the 100 to 200°C temperature range with loss of two and then four moles of water. Further heating causes decomposition of NO_3^- groups.

Values of molar susceptibilities corrected for diamagnetism, corresponding magnetic moments and other constants calculated for the complexes are given in Table I. Magnetic susceptibilities obey the Curie-Weiss law. Magnetic moments are slightly dependent on temperature (Figure 1). Effective magnetic moments gradually increased with lowering temperature (Table I). Halide complexes display similar behaviour.

TABLE I   Magnetic parameters of nickel(II) complexes with nicotinamide

Complex	μ_{eff}	Diamagnetic correction	TIP(Ni)	Weiss(K) constant θ (K)	Curie constant C
	(μ_B)	$\times 10^6$ $(cm^3 mol^{-1})$	$\times 10^6$ $(cm^3 mol^{-1})$		$(cm^3 mol^{-1})$
$Ni(NA)_2Cl_2$ (I)	3.24	−179	+250	24.2	1.20
$Ni(NA)_2Br$ (II)	3.29	−199	+260	18.5	1.27
$NI(NA)_2(NO_3)_2. 6H_2O$ (III)	2.83	−244	+210	23.7	0.93
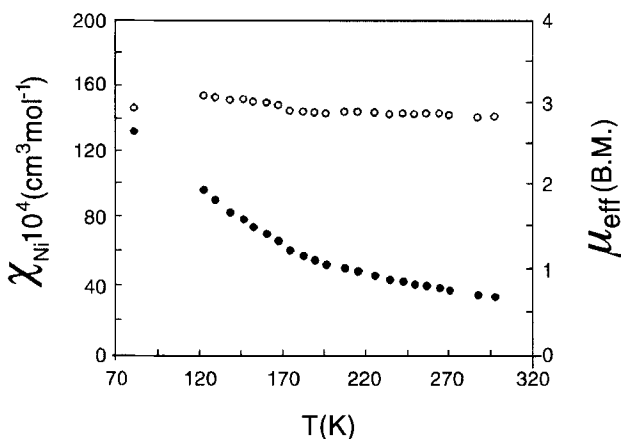
FIGURE 1   Dependence of effective magnetic moment of $[Ni(H_2O)_4(NA)_2](NO_3)_2 \cdot 2H_2O$ on temperature.

Electronic absorption spectra of the complexes (Table II) are characterised by three broad bands corresponding to $^3A_{2g} \to\ ^3T_{2g}(F)$ (v_1), $^3A_{2g} \to\ ^3T_{1g}(F)$ (v_2) and $^3A_{2g} \to\ ^3T_{1g}(P)$ (v_3) transitions in O_h symmetry.

Infrared data are summarised in Table III. The presence of water molecules in (III) is revealed by a broad band at 3447 cm^{-1} assigned to $v(OH)$. This does not occur in (I) and (II). The $v(CO)$ and $\delta(NH)$ frequencies observed for free NA are almost identical with those obtained for NA bonded in its complexes. However, some differences are observed in the 3500-3100 cm^{-1} region for $v(NH_2)$ bands and ring vibrations at about 1600 and 650 cm^{-1}. The IR spectrum of a benzene solution of NA[12] gives a $v_{as}(NH_2)$ band at about 3510 cm^{-1} while that of solid NA is at about 3357 cm^{-1}. This lowering of the band frequency by 160 cm^{-1} has been explained by the existence of hydrogen bonds in solid nicotinamide.[4] Consequently, the occurrence of the respective bands in the region 3354–3303 cm^{-1} is indicative of the presence of hydrogen bonds in the complexes.

TABLE II   Reflectance spectra details for Ni(II) complexes with nicotinamide

Complex	Maxima of absorption bands (cm^{-1})			D_q (cm^{-1})	B (cm^{-1})	β
	$v1$	$v2$	$v3$			
$Ni(NA)_2Cl_2$ (I)	8440	14080 12350sh	24500 22450sh	844	890	0.86
$Ni(NA)_2Br_2$ (II)	8150	13790 11700sh	23700	813	875	0.85
$Ni(NA)_2(NO_3)_2 6 H_2O$ (III)	10100	16400	27000	1010	869	0.87

TABLE III   Characteristic vibrations in the infrared spectra of Ni(II) complexes with nicotinamide (cm^{-1})

Vibrations	NA	$Ni(NA)_2Cl_2$	$Ni(NA)_2Br_2$	$Ni(NA)_2(NO_3)_2 \cdot 6H_2O$
$\nu(OH)$				3447
$\nu_{as}(NH_2)$	3357	3303	3328	3354
$\nu_s(N H_2)$	3150	3265	3214	3150
		3194		
$\nu(CO)$	1679	1667	1655	1684
$\delta(NH)$	1617	1624	1614	1618
$\nu(ring)$	1598	1605	1603	1608
	1580	1580	1570	1579
	1462	1462	1462	1466
$\nu_1(NO_3)$				1059
$\nu_2(NO_3)$				825
$\nu_3(NO_3)$				1365
$\nu_4(NO_3)$				701
$\gamma(CCC)$	644	654	648	650
	621	627	627	
$\rho r(H_2O)$				567
$\rho w(H_2O)$				517
$\nu(Ni—O)$				364
$\nu(Ni—N_{ring})$		282	272	282
Others in the	251	247	253	241
region of	237	230	237	229
$300\text{-}200\ cm^{-1}$	206	203	203	206

Ring vibrations of coordinated NA at about 1600 and 640 cm-¹ are shifted to higher frequencies (Table III). The latter shift and occurrence of bands in the region 300–200 cm^{-1} indicate[2,12] that NA is coordinated through the nitrogen atom of its heterocyclic ring.

Free nitrate anions show simple bands $\nu_1–\nu_4$.[11,14] Upon coordination of NO_3^-, ν_4 near 700 cm^{-1} splits into two bands and the magnitude of splitting is expected to be larger for bidentate than for unidentate ligands. Simple bands $\nu_1 - \nu_4$ in the spectrum of (III) (Table III) are assigned to ionic nitrate groups.

Lattice water exhibits vibrational modes in the low frequency range that are due to rotational oscillations of the water molecule restricted by interactions with neighbouring atoms.[11] Coordinated water exhibits other modes and in particular Ni—OH_2 stretching vibrations are characteristic. Therefore, the broad bands at 567 and 517 cm^{-1} in the spectrum of (III) have been assigned to H_2O rocking and wagging modes (ρ_r, ρ_w) while a weak band at 364 cm^{-1} is the nickel-oxygen stretching vibration $\nu(Ni—O)$. The latter was observed at 327 cm^{-1} in the IR spectrum of $[Ni(H_2O)_4Cl_2].2H_2O$.[13] As expected, the bands do not occur in the IR spectrum of anhydrous $Ni(NA)_2(NO_3)_2$.

Crystal Structure

Structural data for nickel(II) compounds of the type $Ni(H_2O)_4L_n$ (n = 1 or 2) are summarised in Table IV and data for $[Ni(H_2O)_4(NA)_2](NO_3)_2.2H_2O$ **(III)** are given in Table V to Table VII. The compound consists of $[Ni(H_2O)_4(NA)_2]^{2+}$ cations, NO_3^- anions and H_2O molecules. All atoms are in general positions. The complex cation has a monomeric *pseudo*-octahedral configuration about Ni(II), as shown in Figure 2. The basal plane contains four oxygen atoms of coordinated water molecules (Ni—O_3 = 2.064(2), Ni—O_4 = 2.063(2), Ni—O_5 = 2.164(2), Ni—O_6 = 2.042(2)Å) whereas the axial positions are occupied by heterocyclic nitrogen atoms of two NA ligands (Ni—N_1 = 2.084(3), Ni—N_2 = 2.103(3) Å). The other two water molecules are not in the primary coordination sphere. Planes which define molecules of NA are nearly perpendicular to the equatorial plane formed by Ni, O(3), O(4), O(5) and O(6). Dihedral angles are 91.6(6)° and 90.5(7)°. One contact of the neighbouring molecule on respective $H_2O(6)$, while on the remaining three, $H_2O(3)$, $H_2O(4)$ and $H_2O(5)$, are three or even five such contacts.
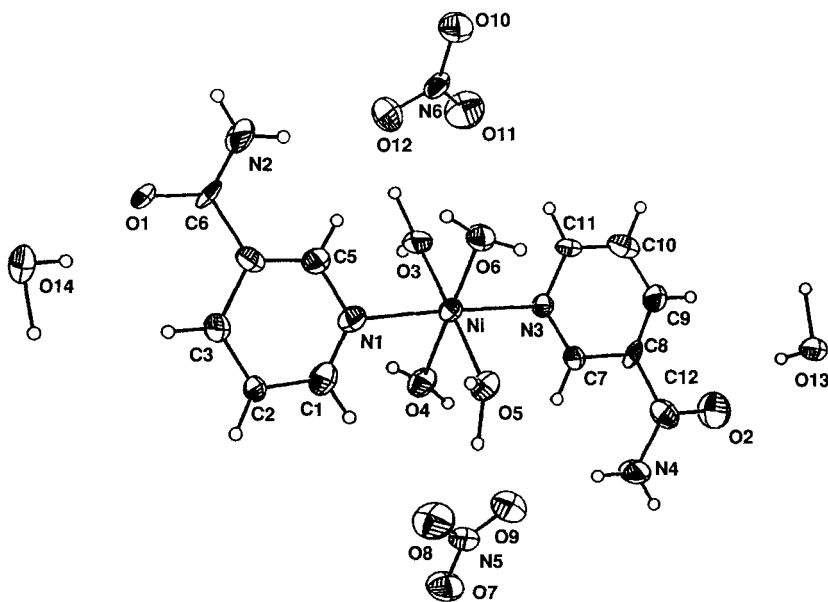
FIGURE 2   Structure of $[Ni(H_2O)_4(NA)_2](NO_3)_2 \cdot 2H_2O$ sharing the atom numbering scheme.

TABLE IV   Crystallographic data for mononuclear nickel(II) compounds of the type $[Ni(H_2O)_4L_n]X_m$[15]

Compound	Space group	Chromophore	M - L $[\AA]$
$Ni(H_2O)_4(C_4H_4NO)_2].2H_2O$	$Pnnm$	NiO_4N_2	H_2O_{eq} 2.087(5) N_{ax} 2.102(2)
$[Ni(H_2O)_4(sac)_2].2H_2O$	$P21/c$	NiO_4N_2	H_2O_{eq} 2.069(2) N_{ax} 2.154(1)
$[Ni(H_2O)_4(CN_5O_2)]$	$Cmca$	NiO_4N_2	H_2O_{eq} 2.125(5) N_{ax} 2.105(6)
$[Ni(H_2O)_4(NA)_2](NO_3)_2 \cdot 2H_2O$	Cc	NiO_4N_2	H_2O_{eq} 2.058(2) N_{eq} 2.084(3)
$[Ni(H_2O)_4(en)]SO_4.2H_2O$	$C\,2/c$	NiO_4N_2	H_2O_{eq} 2.063(2) N_{eq} 2.061(2) H_2O_{ax} 2.106(2)
$Ni(H_2O)_4(en)](NO_3)_2$	$P21/c$	NiO_4N_2	H_2O_{eq} 2.085(4) N_{eq}.066(6) H_2O_{ax} 2.090(4)
$[Ni(H_2O)_4(bipy)]SO_4.2H_2O$	$P1$	NiO_4N_2	H_2O_{eq} 2.051(2) N_{eq} 2.063(2) H_2O_{ax} 2.087(2)
β - $[Ni(H_2O)_4(edna)]$	$C\,2/c$	NiO_4N_2	H_2O_{eq} 2.072(2) N_{eq} 2.102(2) H_2O_{ax} 2.075(2)

TABLE V   Crystal data and structure refinement detail for $[Ni\,(H_2O)_4(NA)_2]\,(NO_3)_2 \cdot 2H_2O$

Empirical formula	$C_{12}H_{24}N_6NiO_{14}$
Formula weight	535.08
Temperature	293(2)K
Wavelength crystal	0.71073Å
Crystal system	Monoclinic
Space group	Cc
Unit cell dimensions	a = 15.896(3) Å
	b = 7.068(1) Å beta = 108.99 (3)°
	c = 20.174(4) Å
Volume	2143.2(7) Å^3
z	4
Density (calculated)	1.658 Mg/m^{-3}
Absorption coefficient	0.988 mm^{-1}
F (000)	1112
Crystal size	0.60 × 0.60 × 0.45 mm
Theta range for data collection	2.14 to 27.55 deg
Index ranges	$0<=h<=20,\ 0<=k<=9,\ -25<=l<=24$
Reflections collected	2570
Independent reflections	2550 [$R(int)$ = 0.0144]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2532 /2 / 298
Goodness-of-fit on F^2	1.050
Final R indices [$I>2sigma\ (I)$]	R = 0.0368, R_w = 0.1000

TABLE VI   Atomic coordinates ($\times 10)^4$ and equivalent isotropic displacement parameters ($\mathring{A}^2 \times 10)^3$ for [Ni(H$_2$O)$_4$(NA)$_2$] (NO$_3$)$_2$ · 2H$_2$O. U (*eq*) is defined as one third of the trace of the orthogonalized *U*ij tensor

	x/a	y/b	z/c	U(eq)
Ni	2510(1)	2503(1)	3(1)	24(1)
O5	3469(1)	4577(3)	155(1)	30(1)
O6	1556(1)	4560(3)	−258(1)	36(1)
Cl	3424(2)	2708(5)	1562(2)	41(1)
O2	3857(2)	2084(5)	−2763(1)	68(1)
O1	1163(2)	2735(5)	2766(1)	56(1)
C3	2791(2)	2832(5)	2477(2)	39(1)
C6	1105(2)	2831(5)	2147(2)	36(1)
N4	4703(2)	1946(6)	−1641(2)	66(1)
N2	354(2)	2875(7)	1675(2)	74(2)
C12	3900(2)	2157(5)	−2149(2)	38(1)
C4	1917(2)	2771(4)	1938(2)	33(1)
C10	1563(2)	2197(6)	−2224(2)	46(1)
O3	1570(1)	392(4)	−146(1)	39(1)
C11	1608(2)	2342(4)	−1568(2)	30(1)
N1	2653(2)	2576(3)	1067(1)	32(1)
C8	3074(2)	2259(4)	−1957(1)	28(1)
O4	3504(1)	490(3)	282(1)	34(1)
N3	2426(2)	2433(3)	−1059(1)	25(1)
C5	1906(2)	2611(4)	1259(2)	32(1)
C2	3557(2)	2808(5)	2292(2)	35(1)
C9	2296(2)	2099(5)	−2435(2)	36(1)
C7	3128(2)	2430(4)	−1251(2)	27(1)
O14	2056(2)	2450(3)	4111(1)	39(1)
O13	2974(2)	2531(3)	−4118(1)	39(1)
N6	−469(2)	2503(3)	−563(1)	29(1)
O12	−48(2)	2582(4)	69(1)	52(1)
O9	5125(2)	2415(5)	−23(2)	69(1)
O11	−229(2)	1447(4)	−952(1)	62(1)
O8	5226(2)	3512(5)	969(1)	57(1)
O10	−1181(1)	3399(4)	−811(1)	47(1)
N5	5527(2)	2573(4)	592(2)	39(1)
O7	6217(2)	1586(4)	833(2)	51(1)

TABLE VII   Selected bonds lengths [$\mathring{A}$] and angles [deg] for [Ni(H$_2$O)$_4$(NA)$_2$](NO$_3$)$_2$.2H$_2$O

Ni—O6	2.042(2)
Ni—O3	2.064(2)
Ni—O4	2.063(2)
Ni—O5	2.064(2)
Ni—N1	2.084(2)
Ni—N3	2.103(2)
O2—C12	1.219(2)
O1—C6	1.224(2)
C6—N2	1.263(2)
C6—C4	1.482(2)
N4—C12	1.360(2)
C12—C8	1.487(2)
N6—O11	1.229(2)
N6—O12	1.234(2)
N6—O10	1.250(2)

TABLE VII *(Continued)*

O9—N5	1.202(2)
O8—N5	1.218(2)
N5—O7	1.257(2)
O6—Ni—O3	92.09(9)
O6—Ni—C4	178.17(10)
O6—Ni—O4	89.71(10)
O6—Ni—O5	89.03(8)
O3—Ni—O5	178.94(10)
O4—Ni—O5	89.24(8)
O6—Ni—N1	94.07(9)
O3—Ni—N1	89.93(10)
O4—Ni—N1	85.33(10)
O5—Ni—N1	90.10(9)
O6—Ni—N3	87.60(9)
O3—Ni—N3	91.83(10)
O4—Ni—N3	92.94(10)
O5—Ni—N3	88.11(9)
N1—Ni—N3	177.53(12)
O1—C6—N2	120.6(3)
O1—C6—O4	120.3(2)
N2—C6—O4	118.9(3)
O2—C12—N4	119.4(4)
O2—C12—C8	120.2(3)
N4—C12—C8	120.0(3)
O11—N6—O12	120.6(3)
O11—N6—O10	118.7(3)
O12—N6—O10	120.5(3)
O9—N5—O8	120.7(3)
O9—N5—O7	116.8(4)
O8—N5—O7	122.1(3)

As can be see from Table IV, in the first four examples of $Ni(H_2O)_4L_n$ complexes, four water molecules build an equatorial plane about Ni(II), while axial positions are occupied by two N—unidentate ligands. On the other hand, when a bidentate N—donor ligand is present, the equatorial plane is built up by two water molecules and one N—bidentate ligand (en, edna, bipy) and the remaining two water molecules occupy axial positions. The average Ni—N(eq) value of 2.073 Å is somewhat shorter than Ni—N(ax), 2.111 Å. Similar trends can be seen for Ni—O$_2$H(eq) *vs* Ni—O$_2$H(ax) distances. A study of the biological activities of the compound is in progress. Supplementary Data Full lists of X-ray data are available from the authors.

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