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Synthesis and Crystal Structure of Nickel(II) Complex Based on 2-Trifluoroacetylcycloalkanone Benzoylhydrazones

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Abstract—The reaction of ethanol solutions of benzoylhydrazones of 2-trifluoroacetylcycloalkanones (H_2L) with a solution of nickel(II) acetate in aqueous ammonia in 1 : 1 ratio gave complexes $NiL \cdot NH_3$ with square structure. The composition and structure of the complexes were determined by elemental analysis, IR and ^1H NMR spectroscopy, and X-ray diffraction analysis.

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INTRODUCTION

Transition metal complexes with fluorinated derivatives of β-dicarbonyl compounds represent a promising line of research. The interest in these compounds is caused by the fact that these ligands are potentially multifunctional and polydentate [1–5] and may serve for elucidating the factors determining the mode of condensation of the acylhydrazones of fluorinated β-diketones and the type of ligand coordination in the complexes [6–8].

The purpose of this work was to prepare complexes $NiL^n \cdot NH_3$ (**I–III**, $n = 1–3$, respectively, where H_2L^n are the products of condensation of trifluoroacylcycloalkanones with benzoylhydrazine) and to study them by spectral methods and X-ray diffraction.

EXPERIMENTAL

Synthesis of $NiL^1 \cdot NH_3$ (I). A solution of nickel(II) acetate (0.37 g, 0.0015 mol) in aqueous ammonia was added with stirring to a hot solution of 2-trifluoroacetylcyclopentanone benzoylhydrazone (0.45 g, 0.0015 mol) (H_2L^1) in ethanol (25 mL). After 3 days, the crystals of the complex that formed were washed with water and ethanol and dried in a vacuum desiccator. The yield of $C_{14}H_{14}N_3O_2F_3Ni$ was 0.39 g (70%).

Nickel(II) complexes with a coordinated ammonia molecule in the fourth coordination site of the Ni(II) square were synthesized in a similar way. The results of elemental analysis, the yields, and the melting points of nickel(II) complexes are summarized in Table 1.

The X-ray diffraction study of $NiL^2 \cdot NH_3$ was performed on a CAD-4 automated diffractometer

Table 1. Results of elemental analysis, yields, and melting points of Ni(II) complexes with 2-trifluoroacetylcycloalkanone benzoylhydrazones

Compound	Molecular formula	T_{mp}, °C	Yield, %	Found/calculated, %		
				C	H	N
$NiL^1 \cdot NH_3$	$C_{14}H_{14}N_3O_2F_3Ni$	234	70	15.39/15.78	44.96/45.20	3.67/3.79
$NiL^2 \cdot NH_3$	$C_{15}H_{16}N_3O_2F_3Ni$	245	76	15.07/15.20	46.15/46.67	3.82/3.92
$NiL^3 \cdot NH_3$	$C_{16}H_{18}N_3O_2F_3Ni$	269	81	14.51/14.67	47.83/48.04	3.96/4.03

(λ MoK_α radiation, graphite monochromator, ω-scan mode, $2\theta_{max} = 50°$. The crystals of $C_{15}H_{16}N_3O_2F_3Ni$ (**II**) are triclinic ($M = 387.03$, $F(000) = 398$): $a = 7.787(10)$, $b = 10.428(2)$, $c = 11.178(2)$ Å, $\alpha = 108.58(2)°$, $\beta = 90.14(2)°$, $\gamma = 110.57(2)°$, $V = 798.98(2)$ Å^3, ρ(calcd.) = 1.609 g/cm^3, $Z = 2$, space group $P\bar{1}$.

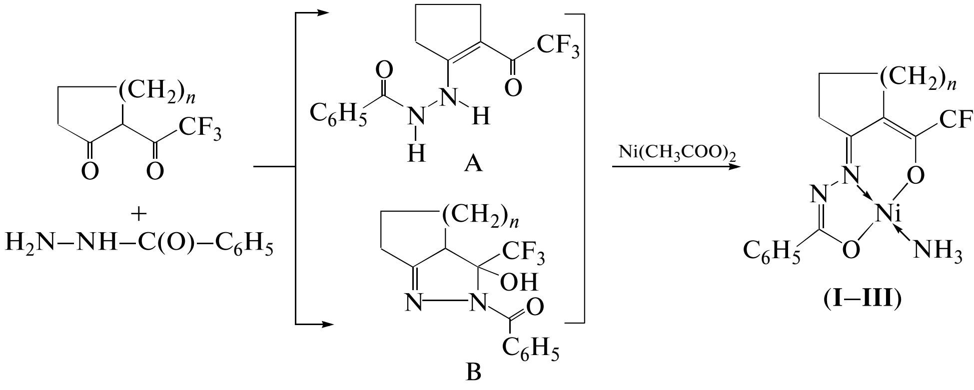
The θ scanning range was from 1.94° to 24.94°, the ranges of indexes were $0 \le h \le 8$, $-12 \le k \le 11$, $-13 \le l \le 13$, the crystal dimensions were $0.5 \times 0.4 \times 0.3$ mm.

The structure was solved by direct methods with a total number of measured reflections of 2634 (SHELXS-97) [9] and refined by the full-matrix least squares method in the anisotropic approximation for non-hydrogen atoms (SHELXL-97) [10] for 2557 independent reflections, $R_{int} = 0.0176$ with 220 refinement parameters, and GOOF = 1.092. The hydrogen atoms were located from the difference electron density maps and refined isotropically. The R factors were $R_1 = 0.1088$ and $wR_2 = 0.3795$ for the reflections with $I > 2\sigma(I)$. The residual electron density $\Delta\rho_{max}/\Delta\rho_{min} = 0.272/-0.822$ e/Å^{-3}. Selected geometric parameters are presented in Table 2. The atom coordinates and other parameters of the structure of **II** are deposited with the Cambridge Crystallographic Data Centre (no. 981752; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif) and are available from the authors.

RESULTS AND DISCUSSION

Previously [7, 8, 11], we studied the molecular and crystal structures of the benzoylhydrazone of trifluoroacetylacetone and its complex with the nickel(II) ions. As a continuation of these works, we synthesized several 2-trifluoroacetylcycloalkanone benzoylhydrazones (H_2L^1–H_2L^3). Earlier, it was found by X-ray diffraction that the size of cycloalkanones determines the ligand structure [8, 12, 13]. For example, 2-trifluoroacetylcyclopentanone benzoylhydrazone H_2L^1 has a ene-hydrazine structure (A), while expansion of the carbon ring by at least one CH_2 group results in the formation of 1-acyl-5-hydroxypyrazolines (B). More detailed and fine investigation of 2-trifluoroacetylcycloalkanone acyl- and heteroaroylhydrazones by ^{1}H and ^{13}C NMR spectroscopy in solutions was reported earlier [14, 15].

Irrespective of the structure of the initial ligands, they react with an equimolar amount of nickel(II) acetate in aqueous ammonia to give complexes with two nearly planar metal-containing rings:



H_2L^n, $n = 1, 2, 3$. $NiL^1 \cdot NH_3$ (**I**), $NiL^2 \cdot NH_3$ (**II**), $NiL^3 \cdot NH_3$ (**III**).

The IR spectra of complexes **I–III**, unlike the spectra of free ligands H_2L^n, do not exhibit the characteristic stretching bands at 1660–1680 and 3500 cm^{-1}. This attests to deprotonation and ring–chain rearrangement of ligands upon complexation of H_2L^2 and H_2L^3.

The ^{1}H NMR data and diamagnetism of the compounds indicate a square coordination sphere of the central complexing ion.

As an example, consider the ^{1}H NMR spectrum of $NiL^1 \cdot NH_3$ (**I**) in a $CDCl_3$ solution. The spectrum exhibits multiplet signals for the protons of the β-diketone cyclopentanone ring at $\delta = 1.62$ ppm and for the protons of the benzohydrazide phenyl ring at $\delta = 7.31$, 7.68 ppm. The proton signals of the coordinated ammonia molecule occur at $\delta = 2.51$ ppm and have a somewhat lower integrated intensity, which is in our opinion caused by partial replacement of the ammonia molecules in the nickel coordination environment by the solvent molecules. The ^{1}H NMR spectra of $NiL^2 \cdot NH_3$ and $NiL^3 \cdot NH_3$ largely coincide with the spectrum of $NiL^1 \cdot NH_3$. The minor difference in the spectra is in higher integrated intensity of the proton signals in the high-field region caused by the increase in the number of CH_2 units in the cycloalkane ring.

Table 2. Bond lengths and bond angles in the structure of NiL^2 · NH$_3$

Bond	d, Å	Bond	d, Å
Ni(1)–N(1)	1.790(16)	C(2)–C(3)	1.43(3)
Ni(1)–O(1)	1.798(13)	C(2)–C(7)	1.54(3)
Ni(1)–O(2)	1.831(13)	C(3)–C(4)	1.56(3)
Ni(1)–N(3)	1.951(18)	C(4)–C(5)	1.52(3)
F(1)–C(8)	1.30(3)	C(5)–C(6)	1.52(3)
F(2)–C(8)	1.27(3)	C(6)–C(7)	1.49(3)
F(3)–C(8)	1.31(3)	C(9)–C(10)	1.45(3)
O(1)–C(1)	1.30(2)	C(10)–C(15)	1.40(3)
O(2)–C(9)	1.30(2)	C(10)–C(11)	1.42(3)
N(1)–C(3)	1.35(2)	C(11)–C(12)	1.40(3)
N(1)–N(2)	1.40(2)	C(12)–C(13)	1.40(4)
N(2)–C(9)	1.35(2)	C(13)–C(14)	1.38(4)
C(1)–C(2)	1.38(3)	C(14)–C(15)	1.37(3)
C(1)–C(8)	1.52(3)		
Angle	ω, deg	Angle	ω, deg
N(1)Ni(1)O(1)	95.6(6)	N(1)Ni(1)O(2)	85.1(7)
O(1)Ni(1)O(2)	178.0(7)	N(1)Ni(1)N(3)	173.5(9)
O(1)Ni(1)N(3)	89.3(7)	O(2)Ni(1)N(3)	90.2(7)
C(1)O(1)Ni(1)	125.8(13)	C(9)O(2)Ni(1)	110.2(12)
C(3)N(1)N(2)	114.6(15)	C(3)N(1)Ni(1)	129.1(13)
N(2)N(1)Ni(1)	116.1(11)	C(9)N(2)N(1)	106.4(15)
O(1)C(1)C(2)	127.3(19)	O(1)C(1)C(8)	110.1(18)
C(2)C(1)C(8)	122.4(19)	C(1)C(2)C(3)	121.4(18)
C(1)C(2)C(7)	120.5(18)	C(3)C(2)C(7)	118.1(18)
N(1)C(3)C(2)	120.2(17)	N(1)C(3)C(4)	118.0(17)
C(2)C(3)C(4)	121.7(17)	C(5)C(4)C(3)	112.8(19)
C(6)C(5)C(4)	108(2)	C(7)C(6)C(5)	108(2)
C(6)C(7)C(2)	111.4(18)	F(2)C(8)F(1)	107(2)
F(2)C(8)F(3)	105(2)	F(1)C(8)F(3)	105(2)
F(2)C(8)C(1)	115(2)	F(1)C(8)C(1)	111.3(19)
F(3)C(8)C(1)	114(2)	O(2)C(9)N(2)	122.1(18)
O(2)C(9)C(10)	119.5(17)	N(2)C(9)C(10)	118.4(18)

According to the X-ray diffraction data, the molecule of NiL^2 · NH$_3$ in the crystal has a square structure with two nearly planar metal-containing rings (figure). The oxygen atoms bonded to nickel are in the *trans*-positions relative to each other. The bond lengths: Ni–O(1), 1.798; and Ni–O(2), 1.831 Å (Table 2) are close to the corresponding bond lengths in other nickel(II) complexes with the coordination sphere Ni[N$_2$,O$_2$] [4, 6, 7] but somewhat differ from the bond lengths: Ni–O(1), 1.833 Å [6, 16]; Ni–O(1), 1.840 Å [6, 12]; Ni–O(1), 1.85 Å [6, 11]; and Ni–O(2), 1.85 Å in the mononuclear complex Ni[H$_3$COOCC(NNCOC$_6$H$_5$)–CHCOC(CH$_3$)$_3$]PPh$_3$ with the coordination sphere Ni[NO$_2$P] [17]. The Ni–N(1) distance of 1.790 Å is much shorter than Ni–N(1) of 1.85 Å [11–13] or 1.90–1.99 Å [17] but virtually coincides with the Ni–N(1) bond length [6, 7, 11, 17].

The nickel atom slightly deviates from the mean plane through the coordinated atoms of the six-membered metal ring (by –0.0546 Å) and from the mean plane of the five-membered metal ring (by –0.0046 Å) (Table 3). The five- and six-membered metal rings are almost coplanar; the dihedral angle between their planes is 3.62°. The bond lengths of NiL^2 · NH$_3$ alternate in both rings: C(1)–O(1), N(1)–N(2), C(2)–C(3), and C(9)–O(2) of 1.30, 1.40, 1.43, and 1.30 Å are single and C(9)–N(2), C(3)–N(1), C(1)–C(2) of 1.35, 1.35, and 1.38 Å are double bonds (Table 2).

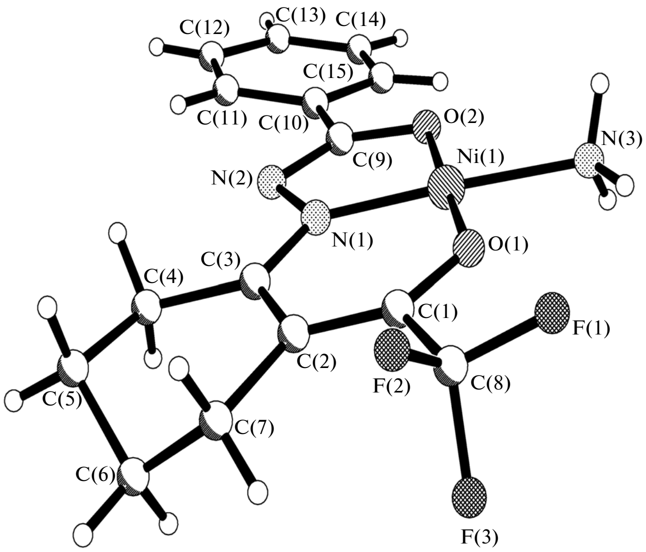
The dihedral angle between the nearly planar five-membered metal ring and the phenyl ring is 13.21°, which attests that spatial coplanarity of these planes is retained. The coplanarity of five- and six-membered metal rings and the aromatic ring, in our opinion, indicates that the metal rings are pseudo-aromatic to some extent [6, 7, 11, 16, 17]. This coplanarity of the phenyl ring with five-membered metal ring does not always hold; in some cases, these angles are as large as 52.5° [7, 11] or 50° [6, 7, 16–19].

In the NiL^2 · NH$_3$ molecule, two hydrogen atoms of the coordinated ammonia molecule are involved in intermolecular hydrogen bonds with F(3) atoms ($-x$, $-y + 2$, $-z + 1$) and O(2) ($-x$, $-y + 2$, $-z$). These H-bonds give rise to centrosymmetric dimers [16–18].

Table 3. Atom deviations from the mean planes in the structure of NiL^2 · NH$_3$

Atom and its deviation, Å						
C(2) –0.0070	C(3) 0.0071	C(4) –0.0034	C(7) 0.0033	C(1) 0.0056	C(5)* 0.2722	C(6)* –0.5787
C(10) –0.0190	C(11) –0.0010	C(12) 0.0163	C(13) –0.0115	C(14) –0.0087	C(15) 0.0239	
Ni –0.0546	O(1) 0.0305	N(1) 0.0466	C(1) 0.0240	C(2) –0.0519	C(3) 0.0054	
Ni –0.0046	O(2) 0.0146	N(1) –0.0032	N(2) 0.0130	C(9) –0.0198		

* Atoms not included in the calculation of this plane.



Crystal structure of the complex $NiL_2 \cdot NH_3$.

The H-bond parameters in the dimers are as follows: N(3)–H(3*A*) (0.89), H(3*A*)···F(3) (2.60), N(3)···F(3) (3.396 Å); N(3)H(3*A*)F(3), 149°; and N(3)–H(3*B*), 0.89; N(3)–H(3*B*) (0.89), H(3*B*)···O(2) (2.12), N(3)···O(2) (3.005 Å); N(3)H(3*B*)F(3) 170.52°.

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