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^{1}H NMR Spectra and Crystal Structure of the Nickel(II) Complex with Ethyl 5,5-Dimethyl-2,4-Dioxohexanoate Aroylhydrazones

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Abstract—Nickel(II) complexes $NiL^n \cdot NH_3$ (n = 1–5) with the products of condensation of ethyl 5,5-dimethyl-2,4-dioxohexanoate with aromatic acid hydrazides (H_2L^1–H_2L^5) were synthesized. The complexes were studied by elemental analysis and IR and ^{1}H NMR spectroscopy. The structure of the complex $NiL^1 \cdot NH_3$ was determined by X-ray diffraction (CIF file CCDC no. 1057268).

Keywords: benzoylhydrazone, β-diketone, ketoaldehydes, ketoesters, prototropy, acylhydrazines

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INTRODUCTION

Derivatives of acylhydrazones of 1,3-dicarbonyl compounds such as ketoaldehydes and ketoesters have proved themselves as promising compounds for investigation of prototropic, ring–chain, and ring–ring equilibria [1–5]. Therefore, acylhydrazines were chosen as nucleophiles in the present study. The Ni(II) complexes $NiL^n \cdot NH_3$ (n = 1–5) were synthesized from ethyl 5,5-dimethyl-2,4-dioxohexanoate benzoylhydrazones (H_2L^1–H_2L^5). All of the synthesized compounds were diamagnetic, readily soluble in chloroform and benzene, partly soluble in ethanol, and almost insoluble in water. The IR and ^{1}H NMR spectroscopy data attested to a square structure, similar to that of nickel(II) complexes of a similar composition with the condensation products of β-diketones.

EXPERIMENTAL

The complexes $NiL^1 \cdot NH_3$–$NiL^5 \cdot NH_3$ (**I–V**) were prepared by the reaction of ethanol solutions of the ligands with metal acetate solutions in aqueous ammonia [1, 2, 6, 7].

Synthesis of $NiL^1 \cdot NH_3$. A hot solution of nickel(II) acetate (1.25 g, 0.005 mol) in concentrated aqueous ammonia (15 mL) was gradually added to a solution of H_2L^1 (1.59 g, 0.005 mol) (prepared by procedures reported in [1, 6]) in 25 mL of ethanol. After 5–10 min, red crystals precipitated from the red solution thus obtained. The crystals were filtered off, repeatedly washed with water and ethanol, and dried in a vacuum desiccator over P_2O_5. The yield of $NiL^1 \cdot NH_3$ was 1.35 g (69%).

The yields, melting points, and elemental analysis data of the complexes are summarized in Table 1.

The monoclinic single crystals of $C_{17}H_{23}N_3O_4Ni$ suitable for X-ray diffraction were obtained by recrystallization of $NiL^1 \cdot NH_3$ from an ethanol–chloroform (1 : 1) mixture.

X-ray diffraction analysis was carried out on an Xcalibur automated diffractometer (CuK_α radiation, $\lambda = 1.54$ Å, graphite monochromator, ω-scan mode, $2\theta_{max} = 50°$). The structure of the complex was solved by the direct method. The solution and refinement (least-squares method in the anisotropic approximation to $R = 0.054$ and $R_w = 0.118$) were performed using 2568 independent reflections with $F^2 > 2\sigma$.

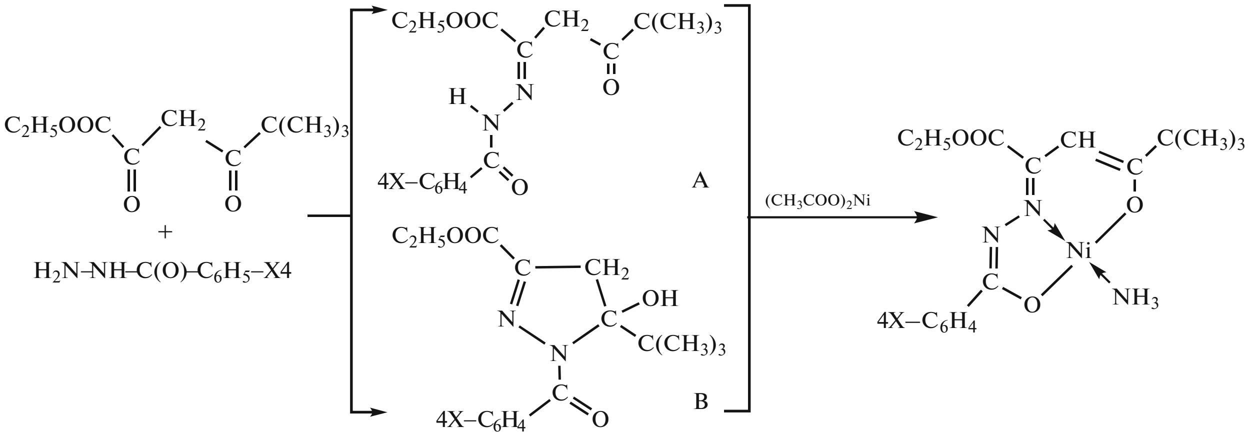
The main crystallographic data and structure refinement details for $NiL^1 \cdot NH_3$ are summarized in Table 2. The atom coordinates and other parameters of the crystals of **I** are deposited with the Cambridge Crystallographic Data Centre (CCDC no. 1057268; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

The study is devoted to the structure and properties of complexes obtained from the products of condensation of ethyl 5,5-dimethyl-2,4-dioxohexanoate with *para*-substituted aromatic acid hydrazides. The reaction of nickel(II) acetate with an ethanol solution of ethyl 5,5-dimethyl-2,4-dioxohexanoate benzoylhydrazone (H_2L^1) in an equimolar ratio results in the precipitation of red crystals of compound **I**. The composition and structure of the complexes $NiL^n \cdot NH_3$ (n = 1–5) were established by elemental analysis (Table 1) and IR and ^{1}H NMR spectroscopy:

Table 1. Yields, melting points, and elemental analysis data of nickel(II) complexes with ethyl 5,5-dimethyl-2,4-dioxohexanoate aroylhydrazones

Compound	Molecular formula	Yield, %	T_m, °C	Content (found/calculated), %			
				Ni	C	H	N
$NiL^1 \cdot NH_3$	$C_{17}H_{23}N_3O_4Ni$	73	158	14.92/14.97	52.01/52.08	5.87/5.91	10.82/10.72
$NiL^2 \cdot NH_3$	$C_{18}H_{25}N_3O_4Ni$	63	165	14.41/14.45	53.20/53.24	6.17/6.20	10.43/10.35
$NiL^3 \cdot NH_3$	$C_{18}H_{25}N_3O_5Ni$	56	178	13.86/13.91	51.17/51.22	5.93/5.97	10.01/9.95
$NiL^4 \cdot NH_3$	$C_{17}H_{22}N_4O_6Ni$	54	182	13.39/13.43	46.67/46.72	5.01/5.07	12.89/12.82
$NiL^5 \cdot NH_3$	$C_{19}H_{28}N_4O_4Ni$	71	197	13.43/13.49	52.40/52.44	6.46/6.49	12.94/12.88



X = H ($NiL^1 \cdot NH_3$); CH_3 ($NiL^2 \cdot NH_3$); OCH_3 ($NiL^3 \cdot NH_3$); NO_2 ($NiL^4 \cdot NH_3$); $N(CH_3)_2$ ($NiL^5 \cdot NH_3$).

The IR spectra of $NiL^n \cdot NH_3$ (n = 1–5) exhibit absorption bands at 3375, 3337, 3280, and 3170 cm^{-1}, corresponding to symmetric and antisymmetric stretching vibrations of the coordinated ammonia molecule. The strong band at ~1730 cm^{-1} corresponds to the ester C=O-group stretching mode. In the IR spectra of the initial free ligands in the hydrazone form A, this band occurs at 1740–1750 cm^{-1} [8, 9]. The low-frequency shift of the ν(C=O) mode in the complexes relative to that of free ligands may indicate inclusion of the electron-withdrawing $COOC_2H_5$ group into the six-membered conjugation chain of the complex. Several strong and medium bands in the range of 1400–1620 cm^{-1} of the IR spectra of the complexes are attributable to the predominantly stretching and bending modes of the conjugation system formed by one-and-a-half bonds in the five- and six-membered metallacycles [10].

The conclusion about the planar structure of the complex with tridentate coordination of the ligand dianion $(L^n)^{2-}$ drawn from the IR data was confirmed by X-ray diffraction study of the grown single crystal of the complex $NiL^1 \cdot NH_3$.

The crystals of $C_{17}H_{23}N_3O_4Ni$ are monoclinic, a = 12.0019(5), b = 8.5823(4), c = 18.1664(6) Å, β = 92.161(4)°, V = 1869.87(13) Å^3, ρ(calcd.) = 1.659 g/cm^3, Z = 2, space group $P2_1/c$. The molecule of complex **I** contains virtually planar coupled five- and six-membered metallacycles (figure).

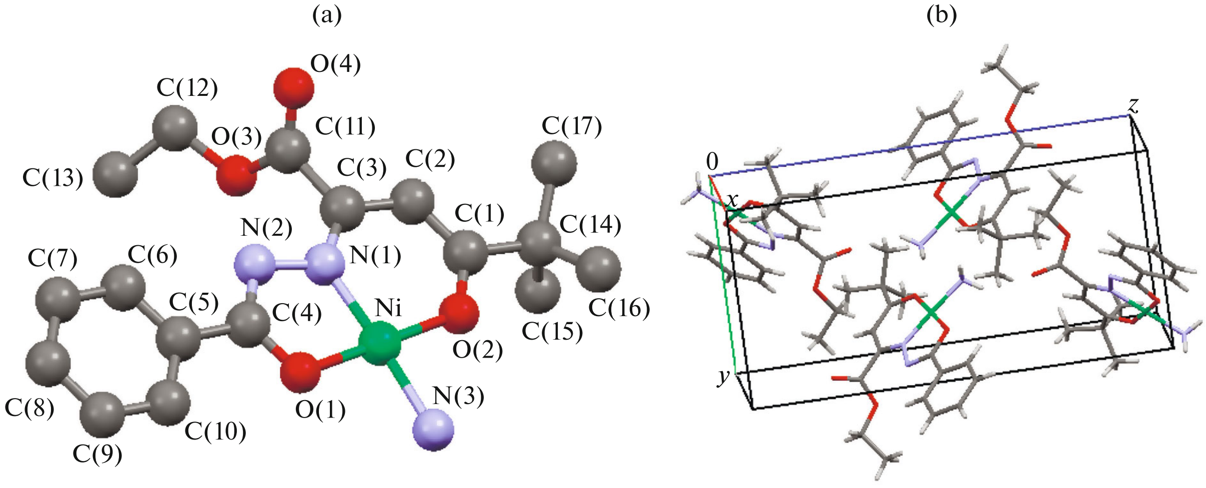
The doubly deprotonated residue of H_2L^1 is coordinated to nickel via two oxygen atoms and the hydrazone nitrogen atom. The fourth site in the planar square of the *trans*-N_2O_2 coordination unit is occupied by the ammonia nitrogen atom. The Ni–O(1) (1.852(2) Å) and Ni–O(2) (1.835(2) Å) bond lengths in the crystal of this complex are close to analogous values in the nickel complexes of the same type with the $[N_2O_2]$ coordination unit. The Ni–N(1) bond (1.818(8) Å) is markedly shorter than the analogous values, and the Ni–N(3) bond length (1.933(3) Å) agrees with the literature data [6, 11, 12].

The central nickel atom slightly deviates from the mean plane through the coordinated O(1), O(2), N(1), and N(3) atoms. The nearly planar coupled five- and six-membered metallacycles are not strictly coplanar. The dihedral angle between the ring planes differs somewhat from these angles in analogous complexes. This distortion of the coplanar arrangement of the two rings is attributable, in our opinion, to the presence of two bulky groups, C_2H_5COOC and $(CH_3)_3C$, in the β-diketone moiety of the ligand L^1.

The ^{1}H NMR spectrum (in CCl_4–DMSO-d_6) of the complex $NiL^1 \cdot NH_3$ with substituted β-ketoester aroylhydrazone resembles the spectra of nickel complexes with various acyl- and aroylhydrazones of β-diketones, β-ketoaldehydes, and β-ketoesters [12]. The spectrum exhibits signals for the ethoxycarbonyl C_2H_5COOC protons and for other terminal protons. The triplet from three CH_3-group protons was detected at δ 1.36 ppm. The CH_2 protons give rise to a quadruplet at δ 4.28 ppm, with a 3 : 2 integrated intensity ratio and spin–spin coupling constant $J_{AB} = 7$ Hz. The single vinylic proton resonates at δ 5.03 ppm, and the nine protons of the *tert*-C_4H_9 butyl groups are responsible for an intense singlet at δ 1.00 ppm. The multiplets centered at δ 7.14 and 7.67 ppm are due to the aromatic protons (5H) of the hydrazone moiety. The signal pattern is somewhat complicated because the signals overlap. The proton signal of the coordinated ammonia molecule was detected at δ 2.07 ppm.

Table 2. Main crystallographic data and structure refinement details for $NiL^1 \cdot NH_3$

Parameter	Value
M	392.09
Temperature, K	293
Crystal system	Monoclinic
Space group	$P2_1/c$
a, Å	11.9969(8)
b, Å	8.5818(4)
c, Å	18.1740(13)
β, deg	92.209(6)
V, Å^3	1869.7(2)
Z	4
ρ(calcd.), g/cm^3	1.206
μ, mm^{-1}	1.72
Crystal size, mm	0.2 × 0.3 × 0.7
θ Range, deg	3.7–76.0
h, k, l range	$-4 \le h \le 10$, $-10 \le k \le 9$, $-22 \le l \le 21$
Measured reflections	6954
Unique reflections	3768
R_{int}	0.054
Reflections with $I > 2\sigma(I)$	2568
Number of refined parameters	243
GOOF (F^2)	1.00
R_1, wR_2 ($I > 2\sigma(I)$)	0.048, 0.120
R_1, wR_2 (all reflections)	0.047, 0.118
$\Delta\rho_{max}/\Delta\rho_{min}$, e/Å^3	0.29/–0.27



(a) Crystal structure of $NiL^1 \cdot NH_3$ and (b) packing of molecules in the crystal.

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