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Nickel(II) and Zinc(II) Complexes with Benzoylacetaldehyde Derivatives

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Abstract—Ni(II) and Zn(II) complexes, $[M(L^n)A]$ ($n = 1–3$, $A = NH_3$, Py), were prepared from the products of condensation of benzoylacetaldehyde with aromatic acid hydrazides (H_2L^1–H_2L^3). The obtained complexes were examined by elemental analysis and IR and ^1H NMR spectroscopy. The structure of $[Ni(L^2)Py]$ was determined by X-ray diffraction analysis (CIF file CCDC no. 1508698).

Keywords: ketoaldehyde, acylhydrazine, aroylhydrazone, five- and six-membered pseudo-aromatic metallocycle system, X-ray diffraction

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INTRODUCTION

Aroylhydrazone derivatives with 1,3-dicarbonyl compounds such as ketoaldehydes are of considerable interest as sources of potentially prototropic ring–chain equilibrium forms [1–3]. Therefore, aroylhydrazones were chosen as nucleophiles in this study. We synthesized the complexes $[M(L^n)NH_3]$ (M = Ni, Zn; $n = 1–3$) based on H_2L^1 = benzoylhydrazone, H_2L^2 = *para*-methylbenzoylhydrazone, and H_2L^3 = *ortho*-hydroxybenzoylhydrazone of benzoylacetic aldehyde, respectively. The obtained products are diamagnetic, soluble in chloroform, benzene, and pyridine, and virtually insoluble in water. The IR and ^1H NMR data attest to a square geometry of the complexes.

EXPERIMENTAL

The ligands H_2L^1–H_2L^3 used in the study were synthesized according to a known procedure [3, 4]. Commercial reagent grade nickel(II) and zinc(II) acetates and concentrated ammonia, analytical grade pyridine, and distilled high-purity grade solvents, EtOH and diethyl ether, were used in the work.

Synthesis of $[Ni(L^1)NH_3]$. A hot solution of nickel(II) acetate (1.25 g, 0.005 mol) in concentrated ammonia (15 mL) was gradually added to a solution of H_2L^1 (1.33 g, 0.005 mol) in EtOH (20 mL). After 5–10 min, a red polycrystalline solid precipitated; the precipitate was collected on a filter, washed with water and ethanol, and dried in a vacuum desiccator over P_2O_5. The yield of $[Ni(L^1)NH_3]$ was 1.23 g (86%).

The complexes $[Zn(L^1)NH_3]$, $[Ni(L^2)NH_3]$, and $[Ni(L^3)NH_3]$ were synthesized in a similar way. The ammonia complexes are readily soluble in organic solvents and insoluble in water.

Dissolution of $[Ni(L^1)NH_3]$ in the minimum amount of Py followed by precipitation with diethyl ether affords the complex $[Ni(L^1)Py]$ [4, 5]. The precipitated red solid was collected on a filter, washed with ethanol and diethyl ether, and dried in air. The yield of $[Ni(L^1)Py]$ was 0.66 g (74%).

The complexes $[Ni(L^2)Py]$ and $[Zn(L^2)Py]$ were synthesized in a similar way.

The results of elemental analysis and the yields of Ni(II) and Zn(II) compounds are summarized in Table 1.

Recrystallization of $[Ni(L^2)Py]$ from an ethanol–chloroform mixture (1 : 1) gave the single crystals of $C_{22}H_{19}N_3O_2Ni$ suitable for X-ray diffraction.

X-ray diffraction analysis of $[Ni(L^2)Py]$ was carried out on a Xcalibur automated diffractometer (CuK_α radiation, $\lambda = 1.54184$ Å, graphite monochromator, ω-scan mode, $2\theta_{max} = 75.9°$). The structure was solved by the direct method and refined by the least squares method in the anisotropic approximation for non-hydrogen atoms. The hydrogen atoms were located from electron density maps and refined in the isotropic approximation.

Table 1. Yields and results of elemental analysis of Ni(II) and Zn(II) complexes

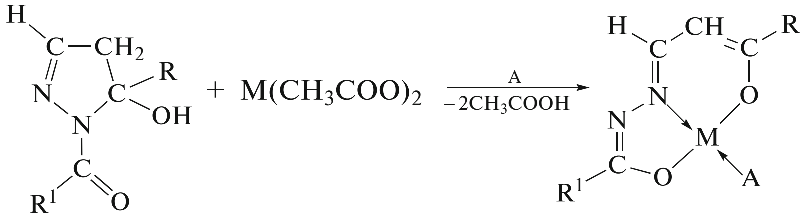
Compound	Molecular formula	Yield, %	T_m, °C	Found/calculated, %			
				M	C	H	N
$[Ni(L^1)NH_3]$	$C_{16}H_{15}N_3O_2Ni$	86	158	17.21/17.26	56.54/56.52	4.41/4.45	12.39/12.36
$[Ni(L^1)Py]$	$C_{21}H_{17}N_3O_2Ni$	74	166	14.56/14.60	62.69/62.73	4.23/4.26	10.48/10.45
$[Ni(L^2)NH_3]$	$C_{17}H_{17}N_3O_2Ni$	58	178	16.53/16.58	57.62/57.67	4.79/4.84	11.90/11.87
$[Ni(L^2)Py]$	$C_{22}H_{19}N_3O_2Ni$	56	182	14.07/14.11	63.46/63.50	4.56/4.60	10.13/10.10
$[Ni(L^3)NH_3]$	$C_{17}H_{17}N_3O_4Ni$	76	193	15.15/15.20	52.83/52.89	4.39/4.44	10.93/10.89
$[Zn(L^1)NH_3]$	$C_{16}H_{15}N_3O_2Zn$	63	172	18.82/18.86	55.38/55.43	4.31/4.36	12.14/12.12
$[Zn(L^2)Py]$	$C_{16}H_{15}N_3O_2Zn$	68	185	15.36/15.40	65.47/65.56	4.48/4.50	9.98/9.95

The atom coordinates and other $NiL^2 \cdot Py$ structural parameters are deposited with the Cambridge Crystallographic Data Centre (no. 1508698); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

Here we discuss the structure and properties of complex compounds based on the products of condensation of benzoylacetaldehyde with *para*- and *ortho*-substituted aromatic acid hydrazides.

The reaction between metal acetates dissolved in aqueous ammonia and ethanol solutions containing equimolar amounts of H_2L resulted in the synthesis of complexes $[M(L^n)A]$ (M^{2+} = Ni, Zn; *n* = 1–3; A = NH_3, Py) (**I**) [1–3]. On the basis of IR and ^{1}H NMR spectra, the complexes with square geometry were identified as structures **I** (Scheme 1).



(H_2L^n) (**I**)

$[Ni(L^1)NH_3]$, $[Ni(L^1)Py]$, $[Zn(L^1)NH_3]$: M = Ni(II), Zn(II); A = NH_3, Py
$R = R^1 = C_6H_5$
$[Ni(L^2)NH_3]$, $[Ni(L^2)Py]$, $[Zn(L^2)Py]$: $R = C_6H_5$, R^1 = 4-$CH_3C_6H_4$
$[Ni(L^3)NH_3]$: R = 4-$CH_3OC_6H_4$, R^1 = 2-OHC_6H_4

Scheme 1.

The composition and structure of the resulting complexes were determined relying on elemental analysis (Table 1), IR and ^{1}H NMR spectroscopy, and X-ray diffraction analysis of $[Ni(L^2)Py]$.

The IR spectra of complexes exhibit absorption bands at 3375–3380, 3320–3330, 3240–3250, and 3150 cm^{-1}, which are attributable to symmetrical and antisymmetrical stretching vibrations of the coordinated NH_3 molecule [1, 6]. The IR spectrum of $NiL^1 \cdot Py$ exhibits a band at about 1600 cm^{-1}, which was assigned to the Py ν(C=N), but no band above 1640 cm^{-1} corresponding to the carbonyl stretching vibrations. The medium and strong absorption bands detected in the ranges of 1580–1585, 1530–1540, 1470–1480, 1420–1430, and 1395–1400 cm^{-1} are caused by the stretching and bending modes of the conjugated system of bonds of the five- and six-membered metallocycles. The C–O stretching frequency decreases by 15–25 cm^{-1}, whereas the C=N frequency increases by 5–10 cm^{-1}, which indicates that the ligand is coordinated to the metal via oxygen atoms [7–9].

The ^{1}H NMR spectral parameters of solutions of Ni(II) complexes in DMSO-d_6 are given in Table 2. In

Table 2. ^{1}H NMR spectral parameters of the Ni(II) and Zn(II) complexes in a DMSO-d_6 solution

Compound	δ, ppm				
	R proton signals	**H–C=N**	**–CH=**	R^1 proton signals	NH_3 or Py proton signals
[Ni(L^1)NH_3]	7.29 m; 7.66 m	5.95	5.86	7.29 m; 7.66 m	**
[Ni(L^1)Py]	7.34 m; 7.66 m	6.04	5.98	7.34 m; 7.66 m	7.74 m; 8.08 m; 8.95 m
[Zn(L^1)NH_3]	7.25 m; 7.72 m	6.38	5.32	7.25 m; 7.72 m; 7.95 m	1.75
[Ni(L^2)NH_3]	7.23 m; 7.69 m	6.35	5.34	7.23 m; 7.70 m; 7.93 m	1.77
[Ni(L^2)Py]	7.34 m; 7.66 m	6.04	5.98	7.34 m; 7.66 m	7.74 m; 8.08 m; 8.95 m
[Zn(L^2)Py]	7.32 m; 7.64 m	6.03	5.97	7.35 m; 7.67 m	7.75 m; 8.09 m; 8.94 m
[Ni(L^3)NH_3]	7.25 m; 7.48 m*	6.34	5.28	7.25 m; 7.48 m	1.86

* The proton signals of two aromatic rings overlap; centers of the signals are given.

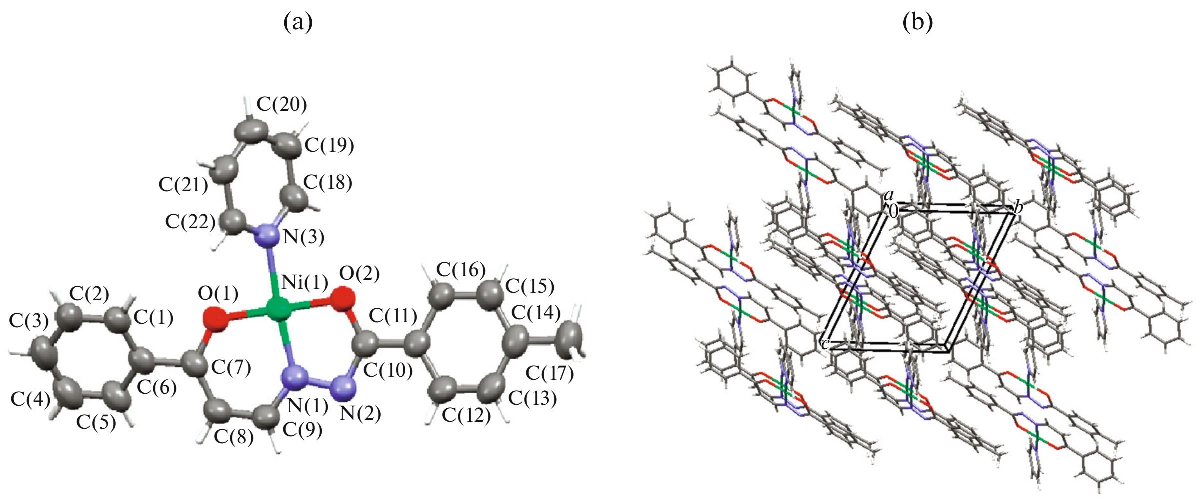
** Signals are not observed due to the exchange of coordinated ammonia between solvent molecules.

order to unambiguously confirm the square geometry of Ni(II) and Zn(II) complexes (evidenced by IR and ^{1}H NMR spectroscopy data), single crystals of NiL^2 · Py were grown via recrystallization from an EtOH–$CHCl_3$ mixture. The key crystallographic data and structure refinement details for NiL^2 · Py are summarized in Table 3.

The doubly deprotonated residue of the H_2L^2 ligand is coordinated to Ni(II) via two oxygen atoms and a nitrogen atom of the hydrazone part of the molecule. The fourth coordination site in the square is occupied by the N atom of the Py donor molecule (Fig. 1a).

The bond lengths, Ni–O(1), 1.826(2); Ni–O(2), 1.835(2); Ni–N(1), 1.823(3); and Ni–N(3), 1.926(3) Å, in the crystal of [Ni(L^2)Py] are close to those found in the coordination polyhedra of Ni(II) complexes with the benzoylhydrazones of ethyl 5,5-dimethyl-2,4-dioxohexanoate [4, 5, 10, 11], methyl 5,5-dimethyl-2,4-dioxohexanoate [12–20], and trifluoroacetylacetone [7, 8, 12, 16–20]. The large difference between the O(1)NiN(1) (95.76(12)°) and N(1)NiO(2) (83.76(13)°) bond angles can be explained, in our opinion, by the presence and size of conjugated five- and six-membered metallocycles around the complexing ion, which is in line with reported data [8, 9, 14, 15, 17–20]. The atoms of the NiO_2N_2 polyhedron, NiO(1)O(2)N(1)N(3), occur in one plane to within ±0.02 Å. The coplanar five-membered (NiO(2)C(10)N(2)N(1)) and six-membered (NiO(1)C(7)C(8)C(9)N(1)) metallocycles are conjugated and are planar to within 0.003–0.022 Å.

The packing of the structural units in the crystal of NiL^2 · Py is shown in Fig. 1b. One of the hydrogen atoms of the coordinated pyridine molecule is involved in hydrogen bonds, that is, the C(18)–H(18)···O(2) intramolecular bond (C···O, 2.937(4) Å; C(18)H(18)O(2), 102°; C(18)–H(18), 0.93; and


(a)

(b)

Fig. 1. (a) Crystal structure of the complex compound [Ni(L^2)Py] and (b) molecular packing of the cell.

Table 3. Key crystallographic data and structure refinement parameters for [Ni(L^2)Py]

Parameter	Value
M	416.11
Temperature, K	293
System	Triclinic
Space group	$P\bar{1}$
a, Å	9.3151(9)
b, Å	10.5675(11)
c, Å	11.9266(7)
α, deg	112.030(7)
β, deg	92.227(6)
γ, deg	115.341(10)
V, Å^3	955.33(17)
Z	2
ρ(calcd.), g/cm^3	1.446
μ, mm^{-1}	1.649
Crystal size, mm	0.5 × 0.4 × 0.3
Scanning range on θ, deg	4.1–75.9
Range of indices h, k, l	$-11 \le h \le 11$, $-13 \le k \le 13$, $-14 \le l \le 8$
Number of collected reflections	6440
Number of unique reflections	3836
R_{int}	0.036
Number of reflections with $I > 2\sigma(I)$	2607
The number of refined parameters	255
GOOF (F^2)	0.975
R [$F^2 > 2\sigma(F^2)$], wR (F^2)	0.045, 0.106
S	0.98
$\Delta\rho_{min}/\Delta\rho_{max}$, e Å^{-3}	–0.24/0.33

H(18)···O(2), 2.60 Å) and C(18)–H(18)···N(2) intermolecular bond (C···N, 3.437(4) Å); the latter gives rise to a centrosymmetric dimer. The molecules are arranged according to a centered motif in such a way that the five- and six-membered metallocycles form pseudo-stacks with one another. The molecule has one more intramolecular hydrogen bond, C(22)–H(22)···O(1) (C···O, 2.861(3) Å; C(22)H(22)O(1), 104°; C(22)–H(22), 0.93; H(22)···O(1), 2.48 Å).

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