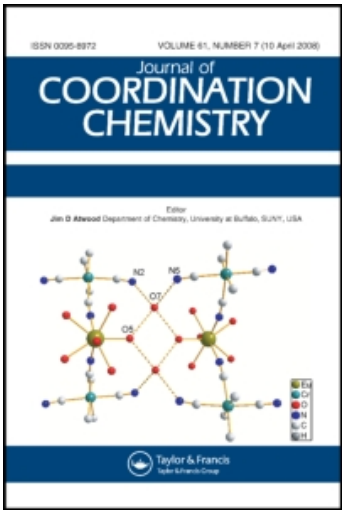

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Synthesis and Characterization of A Nickel(II) Complex With Bis(Benzimidazol-2-Ylmethyl) (2-Hydroxyethyl)Amine

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SYNTHESIS AND CHARACTERIZATION OF A NICKEL(II) COMPLEX WITH BIS(BENZIMIDAZOL-2-YLMETHYL) (2-HYDROXYETHYL)AMINE

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This paper reports the synthesis, crystal structure and properties of two new mononuclear nickel(II) complexes, $[NiL(phen)][ClO_4]_2$ (**1**) and $[NiL(bpy)][ClO_4]_2$ (**2**), where **L** is bis(benzimidazol-2-ylmetheyl)(2-hydroxyethyl)amine and phen and bpy are 1,10-phenanthroline and 2,2′-bipyridine, respectively. The crystal structure of **1** · 2EtOH has been determined by single-crystal X-ray analysis. It crystallizes in the monoclinic system, space group $C2/c$, $a = 24.279(2)$, $b = 20.864(2)$, $c = 17.635(1)$ Å, $\beta = 121.730(2)^\circ$, $Z = 8$, $R_1 = 0.064$, $wR_2 = 0.167$. The Ni(II) ion in **1** · 2EtOH is coordinated to three nitrogen atoms and one oxygen atom of the ligand L and two nitrogen atoms of phen to form a distorted octahedron. Spectroscopic properties of **1** and **2** are reported.

Keywords: Nickel(II) complex; Crystal structure; 1,10-phenanthroline; 2,2′-bipyridine; Spectroscopy

INTRODUCTION

The investigation of the catalytic functions of nickel in biological systems has become a rapidly developing research area. To date nickel has been identified as an integral component of a number of enzymes such as urease, carbon monoxide dehydrogenase (and CO dehydrogenase/acetyl-coenzyme A synthase), methyl-S-coenzyme M reductase, and one

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class of superoxide dismutase [1–4]. Polydentate ligands are widely used in biomimetic chemistry as well as the design of functional molecular materials. In a previous paper, the polydentate ligand bis(benzimidazol-2-ylmetheyl) (2-hydroxyethyl) amine was employed to synthesize a binuclear iron(III) complex as a model of the oxidized form of purple acid phosphatase [5]. In the course of our efforts to synthesize model complexes of nickel-containing enzymes using the same ligand, two mononuclear nickel(II) complexes with bidentate ligands 1,10-phenanthroline and 2,2′-bipyridine were obtained.

EXPERIMENTAL

Starting Materials

Bis(benzimidazol-2-ylmethyl)(2-hydroxyethyl)amine (L) was synthesized by published procedures [6]. All other chemicals used in the work were of reagent grade and used as commercially obtained.

Synthesis of [NiL(phen)][ClO_4]$_2$ (1)

Reaction of $Ni(ClO_4)_2 \cdot 6H_2O$, bis(benzimidozol-2-ylmethyl)(2-hydroxyethyl)amine (L), and 1,10 phenanthroline at 1 : 1 : 1 mol ratio (0.2 mmol) in ethanol (30 cm^3) for 30 mins at room temperature afforded a blue powder **1** (yield 80%). *Anal*. found: C, 47.35; H, 3.78; N, 12.55. Calcd. for $C_{30}H_{26}Cl_2N_7NiO_9$ (**1**): C, 47.49; H, 3.43; N, 12.93. Blue crystals (**1** · 2EtOH) suitable for single-crystal X-ray structure analysis were obtained by diffusion.

Synthesis of [NiL(bpy)][ClO_4]$_2$ (2)

The synthetic method for **2** is similar to that of **1** except that 1,10-phenanthroline was replaced by 2,2′-bipyridine. *Anal*. found: C, 45.97; H, 3.90; N, 12.80. Calcd. for $C_{28}H_{26}Cl_2N_7NiO_9$ (**2**): C, 45.78; H, 3.54; N, 13.35.

Physical Measurements

Infrared spectra of KBr pellets of complexes were recorded on a Shimadzu IR-408 spectrophotometer in the range $4000 \sim 600\,cm^{-1}$. Electronic spectra in CH_3CN were recorded on a Shimadzu UV-2401 PC recording spectrophotometer in the range $200 \sim 1000$ nm.

X-ray Crystallography

A blue crystal of **1** · 2EtOH with approximate dimensions $0.30 \times 0.20 \times 0.10$ mm was mounted on a computer-controlled BRUKER SMART 1000 CCD diffractometer equipped with graphite-monochromatized MoKα radiation ($\lambda = 0.71073$ Å). Cell parameters were determined by a least-squares calculation based on the setting angles of 25 reflections with θ angles ranging from 2.28 to 26.42° at 293(2) K. A total of 7701 independent reflections was collected, of which 5566 were considered as obserced [$I > 2\sigma(I)$] and used for the structure determination. A SADABS absorption correction was applied. The structure was solved by direct methods (SHELXL-97 and SHELXS-97) [7] and refined by full-matrix least-squares on F^2. The largest peak and hole on the final difference-Fourier map had the values 0.447 and -0.772 e Å^{-3}, respectively. Crystallographic data and final atomic coordinates are listed in Tables I and II respectively.

RESULT AND DISCUSSION

Crystal Structure

The structure of **1** · 2EtOH has been determined by single-crystal X-ray diffraction and an ORTEP drawing is shown in Fig. 1 with the atom

TABLE I Crystallographic Data for **1**·2EtOH

Empirical formula	$C_{34}H_{38}Cl_2N_7NiO_{11}$
Fw	850.33
Temperature (K)	293(2)
Crystal system	Monoclinic
Space group	$C2/c$
a (Å)	24.2792(17)
b (Å)	20.8643(17)
c (Å)	17.6346(14)
β (°)	121.730(2)
V (Å^3)	7597.9(10)
Z	8
ρ_{calcd} (g cm^{-3})	1.488
λ(MoKα) (Å)	0.71073
μ(MoKα) (mm^{-1})	0.720
F(000)	3536
R_1[a]	0.064
WR_2[b]	0.167
S	1.017

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; [b] $wR_2 = (\sum[w(F_o^2 - F_c^2)^2]/\sum(F_o^2)^2)^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (0.1160P)^2 + 7.4872P]$, $P = (F_o^2 + 2F_c^2)/3$.

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\AA^2 \times 10^3$) for **1**·2EtOH

	x/*a*	*y*/*b*	*z*/*c*	*U*(*eq*)
Ni (1)	−2172 (1)	10663 (1)	3605 (1)	40 (1)
Cl (1)	−251 (1)	7997 (1)	3977 (1)	78 (1)
Cl (2)	0	10464 (1)	2500	72 (1)
Cl (3)	5000	10338 (1)	7500	104 (1)
O (1)	−2620 (2)	10165 (2)	2379 (2)	54 (1)
O (2)	−806 (4)	7786 (6)	3869 (7)	236 (5)
O (3)	−270 (4)	8698 (3)	3842 (5)	178 (3)
O (4)	297 (3)	7866 (4)	4771 (4)	166 (3)
O (5)	−152 (3)	7760 (3)	3306 (3)	125 (2)
O (6)	542 (2)	10872 (3)	2731 (3)	108 (1)
O (7)	133 (2)	10085 (2)	3240 (3)	107 (1)
O (8)	4717 (3)	9953 (4)	6719 (5)	171 (3)
O (9)	4496 (3)	10727 (4)	7429 (5)	166 (3)
O (10)	3778 (2)	10405 (2)	8279 (4)	119 (2)
O (11)	454 (2)	11891 (2)	4150 (3)	99 (1)
N (1)	−1505 (2)	9076 (2)	5191 (2)	66 (1)
N (2)	−2139 (2)	9824 (1)	4248 (2)	48 (1)
N (3)	−971 (2)	11831 (2)	3241 (2)	56 (1)
N (4)	−1835 (1)	11401 (1)	3168 (2)	44 (1)
N (5)	−1314 (2)	10228 (1)	3735 (2)	48 (1)
N (6)	−3020 (1)	11081 (1)	3354 (2)	43 (1)
N (7)	−1848 (1)	11105 (1)	4864 (2)	45 (1)
C (1)	−1064 (2)	9721 (2)	4428 (3)	64 (1)
C (2)	−1574 (2)	9533 (2)	4607 (3)	51 (1)
C (3)	−841 (2)	10749 (2)	3945 (3)	53 (1)
C (4)	−1214 (2)	11334 (2)	3452 (2)	47 (1)
C (5)	−1540 (2)	9976 (2)	2818 (3)	64 (1)
C (6)	−2193 (2)	9688 (2)	2378 (3)	69 (1)
C (7)	−2346 (2)	11389 (2)	4879 (2)	42 (1)
C (8)	−2965 (2)	11391 (2)	4073 (2)	41 (1)
C (11)	−2455 (2)	9554 (2)	4643 (2)	48 (1)
C (12)	−2054 (2)	9092 (2)	5247 (3)	63 (1)
C (13)	−2242 (3)	8742 (3)	5746 (4)	93 (2)
C (14)	−2836 (3)	8877 (3)	5613 (4)	101 (2)
C (15)	−3237 (3)	9341 (3)	5022 (4)	80 (1)
C (16)	−3058 (2)	9685 (2)	4515 (3)	59 (1)
C (21)	−2007 (2)	11997 (2)	2736 (2)	44 (1)
C (22)	−1463 (2)	12269 (2)	2789 (3)	52 (1)
C (23)	−1492 (3)	12859 (2)	2398 (3)	71 (1)
C (24)	−2082 (3)	13157 (2)	1950 (3)	73 (1)
C (25)	−2629 (2)	12891 (2)	1884 (3)	66 (1)
C (26)	−2608 (2)	12306 (2)	2274 (2)	51 (1)
C (31)	−3591 (2)	11082 (2)	2598 (3)	54 (1)
C (32)	−4137 (2)	11382 (2)	2504 (3)	65 (1)
C (33)	−4087 (2)	11693 (2)	3214 (3)	66 (1)
C (34)	−3490 (2)	11704 (2)	4034 (3)	51 (1)
C (35)	−3397 (2)	11998 (2)	4828 (3)	64 (1)
C (36)	−2824 (2)	11977 (2)	5587 (3)	65 (1)
C (37)	−2272 (2)	11672 (2)	5655 (3)	52 (1)
C (38)	−1664 (2)	11641 (2)	6431 (3)	61 (1)
C (39)	−1163 (2)	11351 (3)	6427 (3)	69 (1)
C (40)	−1281 (2)	11088 (2)	5622 (3)	57 (1)
C (41)	4540 (9)	10924 (9)	9676 (11)	273 (9)
C (42)	4048 (8)	10681 (10)	9089 (11)	298 (12)
C (43)	578 (11)	12966 (6)	4000 (13)	271 (10)
C (44)	708 (5)	12405 (4)	3913 (7)	142 (3)

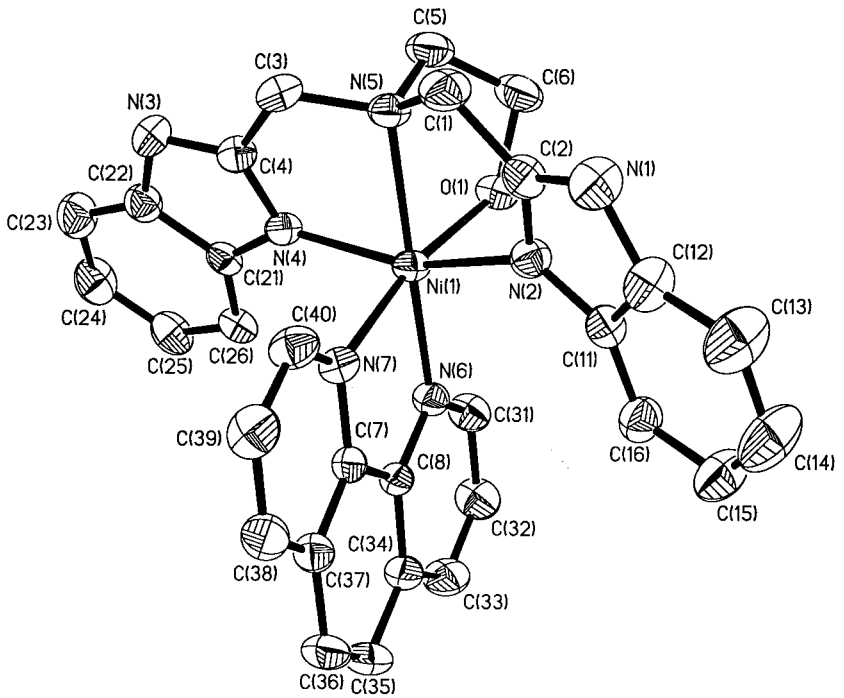

FIGURE 1 ORTEP drawing of **1**·2EtOH, showing the atom numbering scheme.

numbering scheme. Selected bond lengths and angles are listed in Table III. The Ni(II) ion in the complex is coordinated to one oxygen and three nitrogen atoms of the ligand, and two nitrogen atoms of phenanthroline to form a distorted octahedron. The distance between Ni and O(1) is 2.112 Å. The Ni-N bond lengths are 2.05 to 2.17 Å with an average value of 2.10 Å. Hydrogen bonds have been found between the ethanol molecule and the ligand, as well as the ethanol molecule and the perchlorate ion.

Spectroscopic Properties

IR spectra of both **1** and **2** are similar and show strong absorption of $\nu_{(ClO_4)}$ at 1080–1150 cm^{-1}. The ν(NH) of the ligand (L) is observed at *ca* 3500 and the $\nu_{(C=N)}$ bands of ligand L and bidentates 1,10-phenanthroline and 2,2′-bipyridine are observed at 1580–1620 cm^{-1} [8].

Electronic spectra of both complexes in CH_3CN show very strong absorptions at *ca* 300, 325 and 347 nm, which can be assigned to charge-transfer

TABLE III Selected bond lengths (Å) and angles (°) for 1 · 2EtOH.

Ni (1)–N (6)	2.059 (3)	Ni (1)–N (2)	2.063 (3)
Ni (1)–N (4)	2.073 (3)	Ni (1)–O (1)	2.112 (3)
Ni (1)–N (7)	2.136 (3)	Ni (1)–N (5)	2.171 (3)
O (1)–C (6)	1.437 (5)	N (1)–C (2)	1.348 (5)
N (1)–C (12)	1.388 (6)	N (2)–C (2)	1.318 (5)
N (2)–C (11)	1.398 (5)	N (3)–C (4)	1.339 (5)
N (3)–C (22)	1.376 (5)	N (4)–C (4)	1.323 (5)
N (4)–C (21)	1.402 (4)	N (5)–C (3)	1.480 (5)
N (5)–C (1)	1.484 (5)	N (5)–C (5)	1.502 (5)
N (6)–C (31)	1.325 (5)	N (6)–C (8)	1.365 (4)
N (7)–C (40)	1.322 (5)	N (7)–C (7)	1.359 (4)
C (1)–C (2)	1.483 (6)	C (3)–C (4)	1.496 (5)
C (5)–C (6)	1.479 (7)		
N (6)–Ni (1)–N (2)	102.91 (12)	N (6)–Ni (1)–N (4)	98.67 (11)
N (2)–Ni (1)–N (4)	157.67 (12)	N (6)–Ni (1)–O (1)	94.02 (11)
N (2)–Ni (1)–O (1)	89.78 (13)	N (4)–Ni (1)–O (1)	94.38 (13)
N (6)–Ni (1)–N (7)	79.68 (11)	N (2)–Ni (1)–N (7)	84.73 (12)
N (4)–Ni (1)–N (7)	93.64 (11)	O (1)–Ni (1)–N (7)	170.47 (13)
N (6)–Ni (1)–N (5)	174.56 (11)	N (2)–Ni (1)–N (5)	80.18 (12)
N (4)–Ni (1)–N (5)	78.77 (11)	O (1)–Ni (1)–N (5)	81.45 (12)
N (7)–Ni (1)–N (5)	105.19 (11)	C (6)–O (1)–Ni (1)	111.0 (3)
C (2)–N (2)–Ni (5)	112.6 (2)	C (11)–N (2)–Ni (1)	138.0 (2)
C (4)–N (4)–Ni (1)	112.0 (2)	C (21)–N (4)–Ni (1)	142.9 (2)
C (3)–N (5)–Ni (1)	107.2 (2)	C (1)–N (5)–Ni (1)	109.9 (2)
C (5)–N (5)–Ni (1)	104.2 (2)	C (31)–N (6)–Ni (1)	128.0 (3)
C (8)–N (6)–Ni (1)	113.7 (2)	C (40)–N (7)–Ni (1)	131.2 (3)
C (7)–N (7)–Ni (1)	111.3 (2)		

transitions of the ligand. In the visible region, two strong bands can be observed at *ca* 560 and 880 nm for **1** and **2**. They can be assigned to the spin-allowed *d–d* transition bands of Ni(II) (d^8) $\nu_3(^3T_{1g}(P) \leftarrow {}^3A_{2g})$, and $\nu_2(^3T_{1g}(F) \leftarrow {}^3A_{2g})$, respectively. The electronic spectrum of Ni(II) (d^8) has generally three spin-allowed transitions in an octahedral crystal field. The spin-allowed band $\nu_1(^3T_{2g}(P) \leftarrow {}^3A_{2g})$ in the near-infrared region was not observed in the scan range (200–1000 nm). The ligand-field constants Dq, B′ and β were calculated from Lever's transition energy ratio [9] by using observed bands ν_3 and ν_2. The calculated Dq is 1136 cm^{-1}, greater than for $[Ni(II)(H_2O)_6]^{2-}$ (850 cm^{-1}); B′ is 812 cm^{-1}. Compared with the free Ni(II) ion (1041 cm^{-1}), the calculated value of $\beta = B_{complex}/B_{free\ ion} = 0.78$, shows covalent bonding of Ni(II) in the complex.

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Supplementary Material

Full lists of crystallographic data are available from the author upon request.

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