

Synthesis, Crystal Structure and Spectroscopic Properties of a Dinuclear Nickel(II) Complex Bridged by an Alkoxide and a μ -Pyrazolate Ligand

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A nickel(II) complex, $[\text{Ni}_2(\text{L})(3,5\text{-prz})]$, ($\text{L} = 1,3\text{-bis}(2\text{-hydroxy-5-bromosalicylidene amino})\text{propan-2-ol}$; $3,5\text{-prz} = 3,5\text{-dimethylpyrazolate}$), was synthesized and characterized by means of elemental analysis, infrared and electronic spectra. The crystal structure of the complex has been determined by X-ray diffraction. The nickel(II) ions are bridged by the alkoxo group of the ligand and the N atoms of the μ -pyrazolate group. Each nickel ion is coordinated by two O atoms and two N atoms, forming a square with *trans*- N_2O_2 geometry.

Key words: Dinuclear Nickel(II) Complex, Crystal Structure, Schiff Base Complex, Infrared and Electronic Spectra

Introduction

Schiff base ligands which are able to form binuclear transition metal complexes have been of interest for many years [1–7], partly because of the relation between structures and magnetic exchange effects in homo- and hetero-binuclear metal complexes [8, 9] and partly because of the use of such complexes to mimic aspects of bimetallic biosites in various proteins and enzymes [10, 11]. The complexes thus play an important role in developing the coordination chemistry related to catalysis and enzymatic reactions, magnetism and molecular architectures [12–15]. Although a large number of unsymmetric doubly-bridged binuclear copper(II) complexes have been extensively studied [16–22], relatively few structures of unsymmetric doubly bridged binuclear nickel(II) complexes have been reported [23–25]. In the course of our studies on transition metal Schiff base complexes [26–29], we have therefore synthesized and characterized a binuclear

nickel(II) complex bridged by a μ -pyrazolate ligand and the alkoxide group of a new pentadentate Schiff-base ligand.

Experimental Section

Materials and reagents

All starting materials were of reagent grade as purchased from Aldrich Company and were used without further purification.

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Even small amounts of material should be handled with caution.

Preparation of ligand

The Schiff base ligand was prepared by reaction of 1,3-diaminopropan-2-ol with 5-bromosalicylaldehyde (1:2 mol ratio) in methanol. The yellow Schiff base precipitated from solution on cooling.

Preparation of the title complex

The complex was obtained when a solution of the ligand (1 mmol) in methanol (50 ml) was added dropwise to a stirred mixture containing 3,5-dimethylpyrazole (1 mmol) and nickel(II) perchlorate hexahydrate (2 mmol) in methanol (25 ml). Triethylamine (3 mmol) was added to the solution. The mixture was stirred and thin green crystals collected and washed with methanol. Recrystallization from acetone

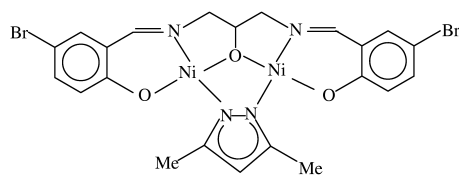


Fig. 1. Structural diagram of the compound.

Table 1. Summary of crystallographic data for complex.

Empirical formula	C ₂₂ H ₂₀ Ni ₂ Br ₂ N ₄ O ₃
Formula weight (g.mol ⁻¹)	665.60
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions	<i>a</i> [Å] = 10.7184(8) <i>b</i> [Å] = 7.3371(4) <i>c</i> [Å] = 29.183(4) β [Å] = 96.648(8)
<i>V</i> [Å ³]	2279.6(4)
<i>Z</i>	4
<i>D</i> _{calc} (g.cm ⁻³)	1.939
μ [mm ⁻¹]	6.44
Data collection	
Diffractometer	Enraf-Nonius CAD-4
Radiation type	Cu-K α , λ = 1.5418 Å
Temperature (K)	293
Index ranges	$-1 \leq h \leq 13$, $-1 \leq k \leq 9$, $-36 \leq l \leq 36$
Reflections collected	6724
Independent reflections	3436
Solution and refinement:	
Refinement method	full-matrix, least-squares on <i>F</i>
Goodness-of-fit on <i>F</i>	1.04
Final <i>R</i> indices	
[<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> = 0.0362, <i>wR</i> = 0.0438
Largest diff peak, hole	0.58 and -0.57 e.Å ⁻³

afforded single crystals suitable for X-ray structure determination. UV/vis (C₃H₆O): λ_{\max} (lg ϵ) = 330 nm (2.06), 420 nm (1.99). – IR (Pellet): ν = 1636 cm⁻¹ (CH=N). – C₂₂H₂₀Ni₂Br₂N₄O₃ (665.6): calcd. C 39.70, H 3.03, N 8.42; found C 40.03, H 3.08, N 8.66.

Physical measurements

Elemental (C, H, N) analyses were carried out by standard methods at TUBITAK Research Center (Ankara, Turkey). IR spectra were measured with a Perkin-Elmer Bx FT-IR instrument with the samples as KBr pellets in the 4000–400 cm⁻¹ range. Electronic spectra in the 900–200 nm range were recorded on a Perkin-Elmer Lambda 2 instrument for acetone solutions.

X-ray structure determination

X-ray data collection was carried out on an Enraf-Nonius CAD-4 diffractometer [30] using a single crystal with dimensions 0.07 × 0.12 × 0.45 mm with graphite monochromatized Cu-K α radiation (λ = 1.5418 Å) by using the scan technique. 4649 reflections were measured in the range $0^\circ \leq \theta \leq 74.33^\circ$. A total of 3436 reflections were classified as observed applying the condition *I* > 3σ(*I*). Data reduction was achieved using the RC93 program [31]. Data corrections for absorption and decomposition were applied using the Nonius Diffractometer Control Software [30]. The structure was solved by SIR92 [32] and refined with CRYSTALS [33]. The H atom

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å² × 10³). Equivalent isotropic *U*(eq) is defined as one third of the trace of the orthogonalized *U*_{ij} tensor.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
Ni(1)	4654(1)	−57(1)	2059(1)	399
Ni(2)	3475(1)	−10(1)	3029(1)	402
Br(1)	2148(1)	1229(1)	5413(1)	670
Br(2)	8650(1)	1097(1)	199(1)	717
O(1)	4565(2)	360(3)	1440(1)	528
O(2)	2184(1)	569(3)	3363(1)	527
O(3)	4779(1)	−468(3)	2687(1)	423
N(1)	6410(2)	−73(3)	2147(1)	423
N(2)	4710(2)	212(3)	3530(1)	447
N(3)	2850(2)	−265(3)	2051(1)	423
N(4)	2388(2)	−447(3)	2475(1)	407
C(1)	6928(3)	−361(4)	2633(1)	476
C(2)	5923(3)	336(4)	2903(1)	443
C(3)	5991(3)	−136(4)	3404(1)	475
C(4)	4567(3)	549(5)	3949(1)	481
C(5)	3367(3)	770(4)	4114(1)	458
C(6)	3326(3)	971(5)	4590(1)	503
C(7)	2193(3)	1077(4)	4766(1)	496
C(8)	1074(3)	1050(5)	4475(1)	537
C(9)	1097(3)	870(5)	4008(1)	536
C(10)	2239(3)	719(4)	3809(1)	442
C(11)	7163(3)	113(4)	1839(1)	473
C(12)	6777(3)	414(4)	1361(1)	478
C(13)	7720(3)	602(5)	1061(1)	525
C(14)	7392(3)	908(4)	601(1)	537
C(15)	6123(4)	1054(5)	423(1)	598
C(16)	5208(3)	877(5)	711(1)	576
C(17)	5494(3)	528(4)	1186(1)	472
C(18)	1190(2)	−1028(4)	2398(1)	448
C(19)	861(3)	−1209(4)	1929(1)	508
C(20)	1920(3)	−716(4)	1719(1)	487
C(21)	1999(4)	−660(6)	1211(1)	679
C(22)	368(3)	−1411(5)	2765(1)	550

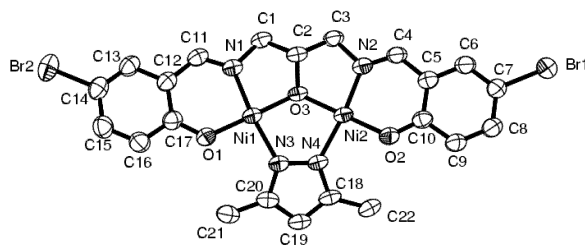


Fig. 2. View of the molecule (numbering of atoms corresponds to Table 2). Displacement ellipsoids are plotted at the 50% probability level.

parameters were not refined. The crystallographic data, conditions used for the intensity data collection and some features of the structure refinement are listed in Table 1. The final positional parameters are presented in Table 2. A perspective drawing of the molecule is shown in Fig. 2 [34].

Table 3. Selected bond lengths [Å] and angles [°] characterizing the inner coordination sphere of the nickel(II) centre (see Fig. 2 for labelling scheme adopted).

Ni1-Ni2	3.231(1)	Ni1-O1	1.824(2)
Ni1-O3	1.847(2)	Ni1-N1	1.869(2)
Ni1-N3	1.938(2)	Ni2-O2	1.831(2)
Ni2-N3	1.840(2)	Ni2-N2	1.861(3)
Ni2-N4	1.908(2)	N3-N4	1.391(4)
Ni1-O3-Ni2	122.5(1)	O1-Ni1-O3	178.8(1)
O1-Ni1-N1	94.3(1)	O3-Ni1-N1	84.6(1)
O1-Ni1-N3	93.6(1)	O3-Ni1-N3	87.5(1)
N1-Ni1-N3	171.3(1)	O2-Ni2-O3	177.0(1)
O2-Ni2-N2	94.3(1)	O3-Ni2-N2	85.8(1)
O2-Ni2-N4	93.7(1)	O3-Ni2-N4	86.3(1)
N2-Ni2-N4	171.5(1)		

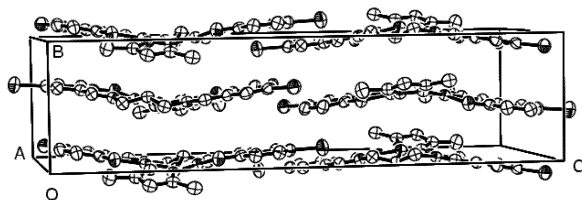


Fig. 3. View of the unit cell packing.

Selected bond lengths and angles are summarized in Table 3. Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre, CCDC-213734 [35].

Results and Discussion

X-ray crystal structure

The complex consists of binuclear molecules in which each nickel ion is surrounded by two O and two N atoms in a square planar coordination. The Ni-N and Ni-O bond lengths are comparable with the bond lengths reported in other nickel(II) complexes [36–40]. The distance between the two nickel(II) centers is 3.231(1) Å and the Ni-O-Ni bridging angle is 122.5(1)°, which is in the range of similar binuclear nickel(II) complexes [23, 24]. The dihedral angle formed by the two coordination planes is 24° (Fig. 3).

The mean deviation of the atoms from the Ni1, Ni2, O3, N3, N4 plane is 0.17 Å, the other five membered rings are not planar as seen *e.g.* in the values for the N1-C1-C2-O3 torsion angle of 47.6(3)°. The remaining six membered rings are planar. An important feature is the geometry of the bridging O atom, O3, the bond angles of which are 109.8(2), 122.5(1) and 110.4(2)° indicating a pyramidal stereochemistry.

Molecules are partially stacked along the b-axis in the crystal as illustrated in Fig. 3. The shortest intermolecular Ni...Niⁱ distance is 4.173 (1) Å (*i* = $-x + 1, y - 1/2, -z + 1/2$), and the Ni-Oⁱⁱ distance is 3.486 (2) Å (*ii* = $-x + 1, y + 1/2, -z + 1/2$).

Spectroscopic properties

The IR spectrum of the free Schiff base ligand shows a broad band at 3250–3420 cm⁻¹, which is likely to be a superposition of bands from alcohol-OH and phenol-OH groups. The ν(OH) band is absent in the IR spectrum of the complex. This indicates that the alcoholic and phenolic protons are lost upon complexation. The ν(C=N) band (*ca.* 1636 cm⁻¹) of the free ligand is shifted slightly to lower frequency (*ca.* 1628 cm⁻¹) upon complexation, suggesting that the imino nitrogen is coordinated to the nickel ion [41].

The electronic spectra of the complex show a strong band at 330 nm which is assigned to the intraligand charge transitions ($\pi \rightarrow \pi^*$), a moderately intense peak at 420 nm due to ligand to metal charge transitions and a weak band at around 550–650 nm, due to d-d transitions which are characteristic of diamagnetic square planar Ni(II) complexes [42].

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