The Synthesis, Crystal Structure and Spectroscopic Properties of a Dinuclear μ–Pyrazolato–*N,N'*–Bridged Dinickel(II) Complex of 1,3–Bis(salicylideneamino)propan–2–ol

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The title compound [Ni_2(L)(3,5 prz)], prz = pyrazolate with the formally pentadentate ligand L = 1,3-bis(salicylideneamino)propan-2-olate, was synthesized and identified using elemental analysis and IR spectroscopy. It crystallizes in the monoclinic space group $P2_1/c$ with cell parameters $a = 29.873(4)$, $b = 11.131(2)$, $c = 13.166(3)$ Å, $\beta = 107.770(10)^\circ$, $V = 4169.0(13)$ Å^3, $Z = 4$, $D_{\mathrm{cal}} = 1.618$ Mg/m^3. The nickel ions are bridged by the alkoxo group of the ligand and the N atoms of the μ-pyrazolate group. Each nickel(II) ion is coordinated by two N atoms and two O atoms, forming a square with *trans*-N_2O_2 geometry. The Ni$^{\cdots}$Ni distance and the Ni−O−Ni angle are 3.371(1) Å and 126.4(1)°, respectively.

Key words: Crystal Structure, Dinuclear Complex, Ni(II) Ion, Schiff Base

Introduction

Dinucleating Schiff base ligands can give homo and hetero polynuclear complexes with many transition metal ions, and their complexes have been of interest for many years [1 – 6]. This is partly because of the relation between structures and magnetic exchange effects in homo- and hetero-binuclear metal complexes of those ligands [7, 8], and partly because of the use of such complexes to mimic aspects of dimetallic biosites in various proteins and enzymes [9, 10]. The complexes play an important role in developing the coordination chemistry related to catalysis and enzymatic reactions, magnetism and molecular architectures [11 – 14], and provide structural models for dinuclear sites in several proteins involved in oxygen storage of hemerytherin and oxygen activation of methanemonooxygenase [15 – 18]. Especially, dinuclear nickel(II) complexes play an important role in the structure and catalytic function of the active site of the nickel-containing enzyme urease [19, 20]. The biophysical and biochemical properties of nickel-containing urease from microbial organisms and plants have been extensively reviewed and dinuclear nickel(II) complexes have been reported as models for the nickel site of urease [21 – 31].

Although a large number of unsymmetric doubly-bridged dinuclear copper(II) complexes have been reported [32 – 38], relatively few structures of unsymmetric doubly-bridged nickel(II) complexes are known [39 – 41]. In the course of our studies on transition metal Schiff base complexes [32, 42 – 46], we have therefore synthesized and characterized a dinuclear nickel(II) complex bridged by the alkoxide groups of a pentadentate Schiff-base ligand and a μ-pyrazolate anion (μ-prz).

Experimantal Section

Synthesis

All starting materials were of reagent grade and were used without further purification as purchased from the Aldrich Company. The Schiff base ligand was prepared by reaction of 1,3-diaminopropan-2-ol with salicylaldehyde (1:2 mol ratio) in methanol. The yellow Schiff base precipitated from solution on cooling. The dinuclear Ni(II) complex was obtained when a sample 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 suitable for X-ray struc-

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Table 1. Crystallographic data for the investigated complex.

Sum Formula	$C_{22}H_{22}N_4Ni_2O_3$
Formula weight (g·mol^{-1})	507.86
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimension (Å, °)	$a = 29.873(4)$
	$b = 11.131(2)$
	$c = 13.166(3)$
	β=107.77(1)°
Volume (Å^3)	4169 (1)
Z	4
Calculated density (Mg·m^{-3})	1.618
Absorption coefficient (mm^{-1})	1.839
$F(000)$	2096
θ Range for data collection	$2.41° \leq \theta \leq 30.20°$
Index ranges	$-41 \leq h \leq 39$,
	$0 \leq k \leq 15$, $0 \leq l \leq 18$
Reflections collected	5793
Independent reflections	5746 [$R(int) = 0.013$]
Data / restraints / parameters	5793 / 0 / 280
Goodness-of-fit on F^2	1.028
Final R indices [$I > 2\sigma(I)$]	$R = 0.0261$, $wR = 0.0698$
Final R indices (all data)	$R = 0.0263$, $wR = 0.0701$
Largest diff. peak and hole	0.318 and -0.363 e·Å^{-3}

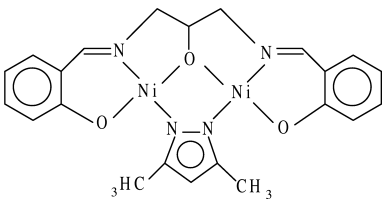

Fig. 1. Formula of the investigated compound.

ture determination collected and washed with methanol. The formula of the complex is given in Fig. 1.

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Even small amounts of material should be handled with caution. M. p. > 310 °C (decomposition), yield 45% (0.382 g). [$C_{22}H_{22}N_4Ni_2O_3$] (507.86): calcd. C 52.03, H 4.36, N 11.03, Ni 23.12; found C 51.98, H 4.42, N 11.15, Ni 23.20.

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 acetone solutions in the 900–200 nm range were recorded on a Perkin-Elmer Lambda 2.

Crystal structure determination

A crystal of dimension $0.07 \times 0.15 \times 0.45$ mm^3 was mounted on an Enraf-Nonius CAD-4 diffractometer [47] equipped with a graphite monochromatized Mo-K$_\alpha$ radiation source ($\lambda = 0.71073$ Å). Precise unit cell dimensions were determined by least-squares refinement on the setting angles of 25 reflections ($2.41° \leq \theta \leq 30.20°$) carefully centered on the diffractometer. Three standard reflections ($\bar{1}$ 1 2, $\bar{2}$ 2 2, 8 2 7) were measured every 7200 s and the orientation of the crystal was checked after every 600 reflections. A total of 5750 reflections were recorded, in the range $h_{\min} = -41$, $h_{\max} = 39$, $k_{\min} = 0$, $k_{\max} = 15$, $l_{\min} = 0$, $l_{\max} = 18$. An absorption correction based on the ψ-scan method was applied. The collected intensity data were corrected for Lorentz polarization effect.

Table 2. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) of the non-hydrogen atoms.

Atom	x	y	z	$^*U_{(eq)}$
C1	0.35428(5)	0.10791(14)	0.61624(13)	0.0346(3)
C2	0.39950(6)	0.11781(14)	0.68164(14)	0.0389(3)
C3	0.43437(7)	0.09926(17)	0.63520(15)	0.0499(5)
C4	0.42469(7)	0.06416(17)	0.52731(14)	0.0492(5)
C5	0.37903(6)	0.05291(18)	0.46210(15)	0.0473(4)
C6	0.34228(5)	0.07118(14)	0.50908(13)	0.0369(3)
C7	0.29678(6)	0.05533(19)	0.43747(18)	0.0541(5)
C8	0.21426(6)	0.04069(19)	0.38605(15)	0.0459(4)
C9	0.17684(7)	0.04828(19)	0.43118(14)	0.0481(4)
C10	0.12824(6)	0.04351(18)	0.37776(13)	0.0441(4)
C11	0.05736(5)	0.08382(16)	0.41283(13)	0.0378(3)
C12	0.02812(5)	0.13464(15)	0.46964(13)	0.0372(3)
C13	−0.02033(7)	0.14402(17)	0.41949(17)	0.0507(5)
C14	−0.05113(8)	0.19604(18)	0.46298(19)	0.0568(5)
C15	−0.03436(6)	0.23109(16)	0.57123(15)	0.0444(4)
C16	0.01232(5)	0.21952(15)	0.62578(13)	0.0366(3)
C17	0.04223(5)	0.16333(13)	0.57462(13)	0.0320(3)
C18	0.18448(6)	0.26973(17)	0.79509(14)	0.0431(4)
C19	0.22973(7)	0.29882(19)	0.85562(14)	0.0487(4)
C20	0.26126(6)	0.24991(17)	0.80979(14)	0.0428(4)
C21	0.14004(8)	0.3002(2)	0.81482(18)	0.0574(5)
C22	0.31291(7)	0.25645(19)	0.85083(17)	0.0546(5)
N1	0.25909(5)	0.06409(13)	0.46268(11)	0.0374(3)
N2	0.10107(5)	0.08446(13)	0.44510(10)	0.0361(3)
N3	0.18811(5)	0.20608(11)	0.71010(10)	0.0321(2)
N4	0.23608(5)	0.19456(11)	0.72053(9)	0.0300(2)
O1	0.32015(4)	0.12320(10)	0.66204(10)	0.0384(2)
O2	0.18957(4)	0.09548(9)	0.53277(8)	0.0298(2)
O3	0.08860(4)	0.15716(10)	0.63311(9)	0.0383(2)
Ni1	0.253822(6)	0.120521(17)	0.600073(13)	0.02861(6)
Ni2	0.140186(7)	0.140417(17)	0.585013(14)	0.03106(6)

$^*U_{(eq)} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$.

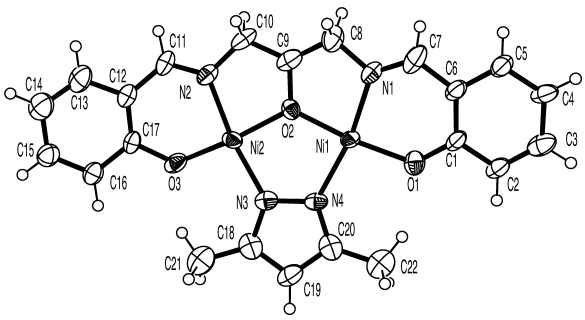

Fig. 2. The molecular structure of the compound. Displacement ellipsoids are plotted at the 50% probability level.

Table 3. Selected bond lengths (Å) and angles (°).

Ni1…Ni2	3.347(1)	N1−Ni1	1.966(2)
N2−Ni2	1.958(1)	N3−N4	1.403(2)
N3−Ni2	1.964(1)	N4−Ni1	1.997(1)
O1−Ni1	1.899(1)	O2−Ni1	1.873(1)
O2−Ni2	1.876(1)	O3−Ni2	1.846(1)
Ni1−O2−Ni2	126.4(1)	C17−O3−Ni2	128.4(1)
O2−Ni1−O1	171.8(1)	O2−Ni1−N1	82.8(1)
O1−Ni−1N1	92.0(1)	O2−Ni1−N4	87.4(1)
O1−Ni1−N4	98.5(1)	N1−Ni1−N4	167.9(1)
O3−Ni2−O2	170.1(1)	O3−Ni2−N2	91.9(1)
O2−Ni2−N2	83.1(1)	O3−Ni2−N3	98.4(1)
O2−Ni2−N3	87.3(1)	N2−Ni2−N3	168.7(1)

The structure was solved by direct methods using the program SHELXS-97 [48] in the WinGX package [49] and refined by the full-matrix least-squares method using SHELXL-97 [48]. The positions of the H atoms bonded to C atoms were calculated (C-H distance 0.96 Å), and refined using a riding model, with H atom displacement parameters restricted to $1.2U_{eq}$ of the parent atom. The crystal data, intensity data collection details and refinement parameters are summarized in Table 1. The final positional parameters are presented in Table 2. Fig. 1 shows the chemical diagram, and a perspective ORTEP drawing of the molecule is shown in Fig. 2 [50]. Selected bond lengths and angles are summarized in Table 3. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC–232690 [51].

Results and Discussion

X-ray crystal structure

The title complex consists of dinuclear molecules in which two nickel atoms are linked by the alkoxide oxygen and μ-pyrazolate nitrogen atoms. Each nickel(II) ion is coordinated by two nitrogen and two oxygen atoms forming a coordination plane. The average distances Ni–N and Ni–O are 1.971(1) and 1.874(1) Å, respectively. These distances are comparable with the bond lengths reported for other nickel(II) complexes [52 – 56]. The Ni1–O2–Ni2 bridging angle is 126.4(1)° which is in the range of similar binuclear nickel(II) complexes [57, 58], but it is larger than the angle of a hydroxo bridge [25]. The distance between the two nickel(II) centres is 3.347(1) Å.

In the solid state, planar nickel(II) Schiff base complexes have been found to appear in a "stepped" centrosymmetric conformation [59, 60 – 62]. Due to the non-planarity of the chelate rings in solution, two chiral "umbrella" conformations are also possible. In the title compound, the atoms with the greatest deviation from the coordination planes Ni1, N1, O1, N4, O2 and Ni2, N2, O3, N3, O2 are O2 at 0.116(1) Å and O2 at 0.127(1) Å, respectively. The maximum deviation from the plane defined by atoms O1, C1-C7, N1, C8 and C9 is 0.095(2) Å for C9, and for C9, C10, N2, C11-C17 and O3 it is −0.169(2) Å for the C9. The deviation of C9 from the plane defined by atoms Ni1, O2, Ni2 and C9 is −0.013(1) Å. The maximum deviation from the same plane is 0.034(1) Å for O2. The dihedral angles between the Ni1, N1, O1 and Ni2, N2, O3 planes with respect to the NiONi plane are 6.9(1)° and 9.7(1)°. Another important feature is the geometry of the bridging O atom, O2. The bond angles around O2 of 117.1(1), 126.4(1) and 116.3(1)° indicate a pyramidal stereochemistry at this atom. The five-membered rings are not planar, as seen from the torsion angles N1–C8–C9–O2 of 10.3(2)°. The whole molecule is not planar since the two halves are folded with respect to one another. The least-squares planes through each half of the molecule are inclined at an angle of 10.9(1)°, forming a shallow umbrella form as reported in other planar monomeric nickel(II) structures [44, 63].

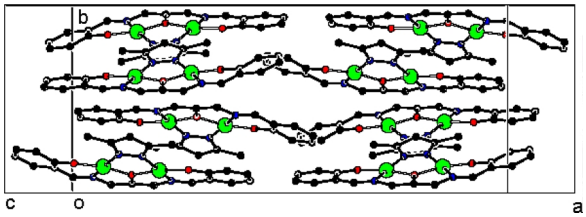

Fig. 3. Packing of the molecules viewed down the *c* axis.

The packing diagram for the complex is shown in Fig. 3 as a projection along the *c* axis. The molecules are stacked parallel to *b* with each Ni atom almost directly above the other. The closest intermolecular Ni···Ni distance is 3.865(1) Å, and there is an infinite Ni···Ni···Ni chain along the *b* axis.

Although some octahedral nickel(II) complexes exhibit a weak intramolecular antiferromagnetic or ferromagnetic interaction [64], the investigated compound is diamagnetic which is consistent with the planar geometry around the Ni(II) ions.

Spectroscopic properties

The IR spectra of the free Schiff base ligand show a broad band at 3250 – 3420 cm^{-1}, which is likely to be a superposition of ν(OH) bands from alcoholic and phenolic groups. The ν(OH) band is absent in the IR spec-

tra of the complex. This indicates that the alcoholic and phenolic protons are lost upon complexation. The ν(C=N) band (*ca.* 1634 cm^{-1}) of the free ligand is slightly shifted to lower frequencies (*ca.* 1625 cm^{-1}) upon complexation, suggesting that the imino nitrogen atoms are coordinated to the nickel ion [65] as confirmed by the structural work (above).

The electronic spectra of the complex show a strong band at 330 nm which is assigned to the intraligand charge transfer transitions ($\pi \rightarrow \pi^*$), a moderately intense peak at 420 nm which is due to ligand to metal charge transfer transitions and a weak band due to *d*-*d* transitions at around 550 – 650 nm. The spectrum is thus characteristic of diamagnetic square planar Ni(II) complexes [66].

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