The Synthesis and Crystal Structure of a Dinuclear μ-Pyrazolato-N,N'-Bridged Dinickel(II) Complex of 1,3-Bis(2-hydroxy-4-methoxybenzylideneamino)propan-2-ol

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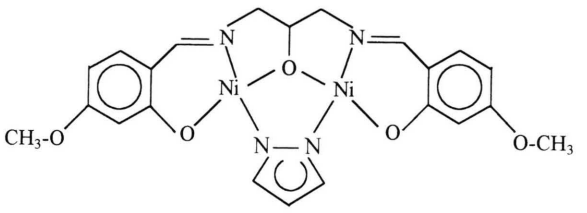
Dinuclear Nickel(II) Complex, Binucleating Ligand

The asymmetric unit of crystal of the title compound, $[Ni_2(L)(C_3H_3N_2)]$ (L = 1,3-Bis(2-hydroxy-4-methoxybenzylideneamino)propan-2-ol, $C_3H_3N_2$ = pyrazolate) contains two independent dinickel(II) complexes. In both molecules, the nickel(II) ions are bridged by the alkoxo group of the ligand and the N atoms of the pyrazolate group. Each nickel(II) ion is coordinated by two N and two O atoms, forming a square with trans-N_2O_2 geometry.

Introduction

There is much current interest in binucleating ligands and their transition-metal complexes due to the use of such complexes for bioinorganic modeling studies [1, 2] and attempts to establish magnetostructural correlations [3 - 6]. In comparison to doubly hetero-bridged dinuclear copper(II) complexes [7-10], relatively few structures of doubly hetero-bridged dinuclear nickel(II) complexes have been reported [11 - 13]. In this study, we have synthesized a μ-pyrazolato-N,N'-bridged dinickel(II) complex of 1,3-bis(2-hydroxy-4-methoxy-benzylideneamino)propan-2-ol and determined the crystal structure of the compound.



Experimental Section

The Schiff base ligand was synthesized by reaction of 1,3-diaminopropan-2-ol and 2-hydroxy-4-methoxy-benzaldehyde in 1:2 molar ratio at room temperature. The product was isolated as pale yellow crystals. The dinuclear complex was obtained when a sample of the Schiff base ligand (0.1 mmol) in methanol (50 ml) was added dropwise to a stirred mixture containing pyrazole (0.1 mmol) and nickel(II) perchlorate hexahydrate (0.2 mmol) in methanol (25 ml). Triethylamine (0.3 mmol) was added to the solution. The solution was allowed to evaporate at room temperature to give dark-red prisms, which were collected and washed with ethanol. *Caution:* Perchlorate salts are potentially explosive and should be handled in small quantities.

X-ray data collection was carried out on an Enraf-Nonius CAD-4 diffractometer [14] using a single crystal with dimensions $0.25\times0.15\times0.05$ mm with graphite monochromatized Mo-K_α radiation (λ = 0.71073 Å). Data reduction and corrections for absorption and decomposition were achieved using the Nonius Diffractometer Control Software [14]. The structure was solved by SHELXS-97 [15] and refined with SHELXL-97 [16]. The positions of the H atoms bonded to C atoms were calculated (C-H distance 0.96 Å) and refined using a riding model. H atom displacement parameters were restricted to be 1.2 U_{eq} of the parent atom. The crystal structure of the title compound is illustrated in Fig. 1 [17], experimental conditions are summarized in Table 1, and selected bond distances and bond angles are listed in Table 2. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-169131 [18].

Results

The title compound contains two independent binuclear molecules in the asymmetric unit in which

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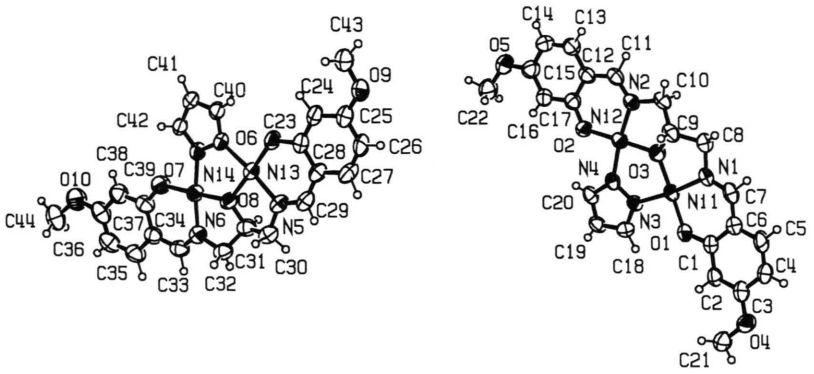

Fig. 1. View of the molecules (numbering of atoms corresponds to Table 2). Displacement ellipsoids are plotted at the 50% probability level and H atoms are presented as spheres of arbitrary radii.

Table 1. Crystallographic data for the investigated compound.

Sum formula	$C_{22}H_{22}N_4O_5Ni_2$
f_w (g·mol^{-1})	539.90
Space group	$P2_1/c$
a = 30.001(6) Å	α = 90.00°
b = 13.468(2) Å	β = 92.13(1)°
c = 10.708(2) Å	γ = 90.00°
Vol [Å^3]	4323.6(13)
Z	8
D_{calc} (g·cm^{-3})	1.659
μ [cm^{-1}]	17.91
F(000)	2223
Index ranges	$-36 \leq h \leq 36$, $-16 \leq k \leq 0$, $-13 \leq l \leq 2$
Reflections collected	10022
Independent reflections	8480 [R(int) = 0.0455]
Data / restraints / params	8480 / 0 / 718
Goodness-of-fit on F 2	0.985
Final R indices [$I > 2\sigma(I)$]	R = 0.0403, wR = 0.0974
Largest diff. peak and hole	0.441 and –0.390 e·Å^{-3}

two nickel atoms are linked by the alkoxide O atom of the binucleating ligand and the N atoms of the pyrazole group. The coordination geometry of the nickel(II) centers is square-planar and each nickel(II) ion is surrounded by two N and two O atoms. The dihedral angles between the two coordination planes for the two molecules are 1.8(1)° and 2.2(1)°, indicating that the molecules are approximately planar. The sum of the bond angles around the bridging oxygen atoms O3 and O8 are 355.2° and 354.6°, respectively, showing that the bonds around these oxygen atoms are essentially planar. The remaining five-membered rings are not planar, as seen from the torsion angles N2-C10-C9-O3 of 35.4(6)° and N6-C32-C31-O8 of 37.8(7)°. The six membered rings are each planar to within 0.008 Å.

Table 2. Atomic coordinates ($\times$ 10^4) and equivalent isotropic displacement parameters (Å^2 $\times$ 10^3). Equivalent isotropic U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)
Ni(1)	–473(1)	1146(1)	3182(1)	46(1)
Ni(2)	447(1)	1281(1)	4843(1)	48(1)
N(1)	–970(2)	1273(3)	4132(4)	48(1)
N(2)	346(2)	1454(3)	6507(4)	46(1)
N(3)	76(1)	1036(3)	2404(4)	45(1)
N(4)	470(1)	1117(3)	3097(4)	46(1)
O(1)	–772(1)	1037(3)	1683(3)	55(1)
O(2)	1051(1)	1241(3)	4986(3)	58(1)
O(3)	–158(1)	1238(3)	4659(3)	57(1)
O(4)	–1978(1)	1246(4)	–1263(4)	75(1)
O(5)	2491(2)	1261(4)	6951(4)	79(1)
C(1)	–1206(2)	1118(4)	1483(5)	48(1)
C(2)	–1364(2)	1129(5)	231(6)	52(2)
C(3)	–1808(2)	1218(5)	–66(6)	61(2)
C(4)	–2115(2)	1274(6)	882(7)	72(2)
C(5)	–1970(2)	1277(6)	2086(7)	70(2)
C(6)	–1511(2)	1202(4)	2445(6)	54(1)
C(7)	–1379(2)	1268(5)	3713(6)	57(2)
C(8)	–860(2)	1328(5)	5478(6)	53(2)
C(9)	–387(2)	1696(5)	5647(6)	59(2)
C(10)	–127(2)	1458(4)	6817(6)	52(2)
C(11)	649(2)	1531(4)	7402(6)	53(2)
C(12)	1114(2)	1456(4)	7221(5)	54(2)
C(13)	1421(2)	1525(5)	8259(6)	62(2)
C(14)	1868(3)	1443(5)	8157(6)	69(2)
C(15)	2042(2)	1311(5)	6974(6)	66(2)
C(16)	1759(2)	1263(5)	5931(6)	59(2)
C(17)	1290(2)	1320(4)	6025(5)	53(1)
C(18)	177(2)	868(4)	1216(5)	51(2)
C(19)	637(2)	825(5)	1136(6)	57(2)
C(20)	797(2)	995(4)	2303(6)	51(2)
C(21)	–1673(2)	1178(7)	–2235(7)	73(2)
C(22)	2691(3)	1246(7)	5770(8)	83(2)

The intramolecular Ni(1)···Ni(2) and Ni(3)···Ni(4) distances are 3.233(2) and 3.235(2) Å, respec-

Table 2 (continued).

Atom	*x*	*y*	*z*	U(eq)
Ni(3)	4483(1)	8858(1)	1900(1)	51(1)
Ni(4)	5404(1)	8742(1)	430(1)	53(1)
N(5)	3987(2)	8685(3)	843(5)	56(1)
N(6)	5307(2)	8538(3)	–1265(5)	57(1)
N(7)	5034(2)	8976(3)	2792(4)	50(1)
N(8)	5421(2)	8912(4)	2168(4)	53(1)
O(6)	4182(1)	8982(3)	3333(4)	60(1)
O(7)	6008(1)	8793(3)	429(4)	67(1)
O(8)	4797(1)	8777(3)	489(3)	64(1)
O(9)	2960(1)	8796(4)	6017(4)	77(1)
O(10)	7440(2)	8817(4)	–1043(4)	93(2)
C(23)	3750(2)	8865(4)	3453(6)	55(2)
C(24)	3589(2)	8905(5)	4666(6)	60(2)
C(25)	3142(2)	8771(5)	4875(6)	63(2)
C(26)	2850(2)	8602(6)	3877(8)	77(2)
C(27)	2989(2)	8567(5)	2695(7)	74(2)
C(28)	3447(2)	8690(4)	2441(6)	57(2)
C(29)	3584(2)	8622(5)	1197(7)	63(2)
C(30)	4096(2)	8638(5)	–484(6)	63(2)
C(31)	4569(2)	8298(5)	–534(6)	62(2)
C(32)	4827(2)	8548(5)	–1660(6)	62(2)
C(33)	5616(3)	8436(4)	–2050(6)	62(2)
C(34)	6089(2)	8513(4)	–1780(6)	59(2)
C(35)	6383(3)	8401(5)	–2753(6)	73(2)
C(36)	6834(3)	8506(6)	–2547(7)	81(2)
C(37)	6999(3)	8716(5)	–1351(7)	76(2)
C(38)	6714(2)	8788(6)	–375(6)	69(2)
C(39)	6256(2)	8698(5)	–545(6)	61(2)
C(40)	5140(2)	9123(4)	4004(6)	54(2)
C(41)	5597(2)	9174(5)	4186(6)	61(2)
C(42)	5758(2)	9021(5)	3015(6)	55(2)
C(43)	3230(2)	9039(6)	7063(7)	86(2)
C(44)	7746(3)	8882(7)	–2011(10)	95(3)

tively. These distances are close to values of other doubly hetero-bridged dinuclear nickel(II) complexes [11, 13]. The Ni(1)-O(3)-Ni(2) and Ni(3)-O(8)-Ni(4) angles are 125.6(2)° and 125.5(2)°, respectively. The title compound is diamagnetic which is consistent with the planar geometry around the Ni(II) ions.

Table 3. Selected bond lengths [Å] and angles [°] characterizing the inner coordination sphere of the copper(II) centre (see Fig. 1 for labelling scheme adopted).

Ni1-O1	1.816(4)	Ni1-O3	1.817(4)
Ni1-N1	1.845(4)	Ni1-N3	1.880(4)
Ni2-O2	1.812(4)	Ni2-O3	1.819(4)
Ni2-N2	1.834(4)	Ni2-N4	1.886(4)
Ni3-O8	1.814(4)	Ni3-O6	1.816(4)
Ni3-N5	1.849(5)	Ni3-N7	1.886(5)
Ni4-O7	1.811(4)	Ni4-O8	1.824(4)
Ni4-N6	1.848(5)	Ni4-N8	1.874(5)
O1-Ni1-O3	178.1(2)	O1-Ni1-N1	96.5(2)
O3-Ni1-N1	85.4(2)	O1-Ni1-N3	90.8(2)
O3-Ni1-N3	87.4(2)	N1-Ni1-N3	172.7(2)
O2-Ni2-O3	176.2(2)	O2-Ni2-N2	97.1(2)
O3-Ni2-N2	84.7(2)	O2-Ni2-N4	90.5(2)
O3-Ni2-N4	87.8(2)	N2-Ni2-N4	172.5(2)
Ni1-O3-Ni2	125.6(2)	Ni3-O8-Ni4	125.5(2)
O8-Ni3-O6	177.6(2)	O8-Ni3-N5	85.1(2)
O6-Ni3-N5	96.6(2)	O8-Ni3-N7	87.3(2)
O6-Ni3-N7	91.1(2)	N5-Ni3-N7	172.2(2)
O7-Ni4-O8	175.8(2)	O7-Ni4-N6	97.3(2)
O8-Ni4-N6	85.2(2)	O7-Ni4-N8	90.3(2)
O8-Ni4-N8	87.3(2)	N6-Ni4-N8	172.3(2)

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