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Binuclear Nickel(II) Complexes of Schiff Bases Derived from Salicylaldehydes and 1,*n*-Diamino-*n*′-hydroxyalkanes (*n*,*n*′=3,2; 4,2; and 5,3) Having an Endogenous Alkoxo Bridge and a Pyrazolato Exogenous Bridge

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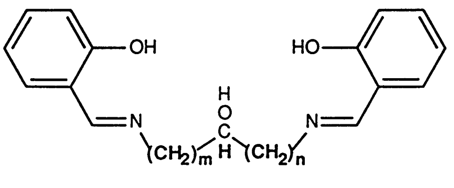
μ-Alkoxo-μ-pyrazolato-bridged binuclear nickel(II) complexes with 1,3-bis(salicylideneamino)-2-propanol (H_3L_a), 1,4-bis(salicylideneamino)-2-butanol (H_3L_b), and 1,5-bis(salicylideneamino)-3-pentanol (H_3L_c), $Ni_2(L_a)(pz)$, $Ni_2(L_b)(pz)$, and $Ni_2(L_c)(pz)$ (pz=pyrazolate anion), have been prepared and characterized by elemental analyses, infrared and electronic spectra, and magnetic susceptibilities. The molecular structures of these complexes were determined by the single-crystal X-ray structure analyses. The planarities of the molecules were discussed in relation to the variation of the chain lengths of the Schiff bases.

Although a large number of alkoxo-bridged binuclear copper(II) complexes have been extensively studied,[1–4] relatively few binuclear nickel(II) complexes with alkoxo-oxygen bridges have been reported; $[Ni_2(bdhe)_2](ClO_4)_2$ (where bdhe represents the anion of *N,N*-bis(2-diethylaminoethyl)-2-hydroxyethylamine)[5] and $[Ni_2(eia)_2]$ (where eia represents the anion of 1-hydroxy-4-methyl-3-azahept-3-en-6-one)[6] are few examples of such compounds for which structures have been reported. Recently, the Schiff bases of salicylaldehyde and 1,3-diamino-2-propanol, 1,4-diamino-2-butanol, or 1,5-diamino-3-pentanol have been shown to hold two metal atoms in close proximity and usefulness of the binucleating ligands has been recognized. Mazurek, Nishida, Sinn, Hendrickson, and co-workers recently reported the structures and magnetic properties of several unsymmetric doubly bridged binuclear copper(II) complexes using these binucleating ligands.[7–15] These complexes incorporate 1,3-diamino-2-propanol, 1,4-diamino-2-butanol, and 1,5-diamino-3-pentanol moieties where the two copper(II) ions are bridged by the deproptonated alkoxide oxygen atom and by another bridging ligand X^- such as pyrazolate anion. On the other hand, the corresponding nickel(II) complexes are less well studied and the only previous report of 1,3-bis(salicylideneamino)-2-propanolate and 1,5-bis(salicylideneamino)-3-pentanolate derivatives describes the electrochemical properties.[9] The authors stated that they could not grow the crystals of the nickel(II) complexes that are suitable for single-crystal X-ray diffraction studies. We have therefore made a detailed structural study of this series of alkoxo-bridged nickel(II) complexes. In this paper, we describe the preparation and structural characterization of three alkoxo-bridged derivatives of nickel(II) containing a pyrazolate exogenous bridge, $Ni_2(L_a)(pz)$, $Ni_2(L_b)(pz)$, and $Ni_2(L_c)(pz)$ (H_3L_a=1,3-bis(salicylideneamino)-2-propanol, H_3L_b=1,4-bis(salicylideneamino)-2-butanol, H_3L_c=1,5-bis(salicylideneamino)-3-pentanol; Hpz=pyrazole).



H_3L_a : m=1, n=1

H_3L_b : m=2, n=1

H_3L_c : m=2, n=2

Experimental

Ligand Synthesis. 1,3-Diamino-2-propanol was obtained from Tokyo Kasei Kogyo Co., Ltd. 1,4-Diamino-2-butanol dihydrochloride and 1,5-diamino-3-pentanol dihydrochloride were synthesized according to the method reported by Murase et al.[16,17] The free 1,4-diamino-2-butanol and 1,5-diamino-3-pentanol were obtained as sticky oils by passing the hydrochloride solutions through ion-exchange resins (Dowex 1X8, OH form) and evaporating the elutes to dryness under reduced pressure.

1,4-Bis(salicylideneamino)-2-butanol, H_3L_b. 1,4-Diamino-2-butanol (1.86 g, 0.018 mol) was dissolved in ethanol (15 ml) and added to a solution of salicylaldehyde (4.36 g, 0.036 mol) in ethanol (10 ml). The soltuion was refluxed for 2 h and then allowed to stand overnight. The resulting yellow crystals were filtered, washed with ethanol, and dried in vacuo over P_2O_5 (yield 3.31 g). Recrystallization from hot methanol gave yellow needlelike crystals. Anal. Calcd for $C_{18}H_{20}N_2O_3$: C, 69.21; H, 6.45; N, 8.97%. Found: C, 69.17; H, 6.42; N, 8.99%.

The other Schiff base ligands were prepared in a similar way.[7]

Preparation of Complexes. $Ni_2(L_b)(pz)$. Nickel(II) perchlorate hexahydrate (146 mg, 0.4 mmol) was added to a stirred solution of a mixture of 1,4-bis(salicylideneamino)-2-butanol (63 mg, 0.2 mmol) and pyrazole (21 mg, 0.3 mmol) in methanol (4 ml) to give a yellow-green solution. The addition of potassium hydroxide (45 mg, 0.8 mmol) in methanol (3

Table 1. Crystal Data and Data Collection Details

Complexes	$[Ni_2(L_a)(pz)]$	$[Ni_2(L_b)(pz)]$	$[Ni_2(L_c)(pz)]$
Formula	$Ni_2O_3N_4C_{20}H_{18}$	$Ni_2O_3N_4C_{21}H_{20}$	$Ni_2O_3N_4C_{22}H_{22}$
F.W.	479.8	493.8	507.8
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1$
a/Å	12.426(1)	24.692(5)	12.087(2)
b/Å	13.934(3)	16.158(6)	7.328(2)
c/Å	11.023(2)	9.971(3)	11.722(3)
β/°	102.55(1)	97.77(2)	90.03(2)
V/Å^3	1862.9	3941.3	1038.3
Z	4	8	2
D_c/g cm^{-3}	1.71	1.67	1.62
D_m/g cm^{-3}	1.72	1.67	1.63
F(000)	984	2032	524
μ(Mo $K\alpha$)/cm^{-1}	20.6	19.5	18.5
Crystal dimensions (mm)	0.23X0.40X0.55	0.10X0.50X0.50	0.10X0.15X0.63
2θ range/°	1.0—50.0	0.0—46.0	1.0—66.0
Total no. of observed reflections	3611	6075	4332
No. of unique reflections with $I>3\sigma(I)$	2354	2462	2136
Final no. of variables	262	541	279
Final rediduals			
R	0.036	0.060	0.043
R_w	0.040	0.065	0.044
Largest peak in final diff fourier (e/Å^3)	0.40	0.59	0.80

ml) gave a brown precipitate, which was filtered after 0.5 h, washed with methanol, and dried in vacuo over P_2O_5. Yield of crude complex was 165 mg. The infrared spectra of the crude samples show a broad band around 1100 cm^{-1}, suggesting that they are contaminated by small amounts of perchlorate ion derived from the metal source. The contaminant was removed by recrystallization from *N,N*-dimethylformamide (DMF). The recrystallization afforded single crystals suitable for X-ray crystallographic measurement. Anal. Calcd for $C_{21}H_{20}N_4Ni_2O_3$: C, 51.08; H, 4.08; N, 11.35%. Found: C, 51.06; H, 4.08; N, 11.44%.

$Ni_2(L_a)(pz)$. This complex was prepared in the same way as that of $Ni_2(L_b)(pz)$ except for using 1,3-bis(salicylideneamino)-2-propanol instead of 1,4-bis(salicylideneamino)-2-butanol.[9] The product was recrystallized from DMF. Anal. Calcd for $C_{20}H_{18}N_4Ni_2O_3$: C, 50.07; H, 3.78; N, 11.68%. Found: C, 50.14; H, 3.78; N, 11.73%.

$Ni_2(Lc)(pz)$. This complex was prepared in the similar way as that for $Ni_2(L_b)(pz)$ except for using 1,5-bis(salicylideneamino)-3-pentanol instead of 1,4-bis(salicylideneamino)-2-butanol.[9] The product was recrystallized from DMF. Anal. Calcd for $C_{22}H_{22}N_4Ni_2O_3$: C, 52.03; H, 4.37; N, 11.03%. Found: C, 51.98; H, 4.38; N, 11.09%.

Measurements. Carbon, hydrogen, and nitrogen analyses were carried out at the Service Center of Elemental Analysis, Kyushu University. Infrared spectra were measured with a JASCO Diffraction Grating Infrared Spectrophotometer Model IRA-1 in the region 4000—650 cm^{-1} on a KBr disk. Electronic spectra were measured with a Shimadzu UV-vis-NIR Recording Spectrophotometer Model UV-3100. Magnetic susceptibilities were measured by the Faraday method at room temperature. The susceptibilities were corrected for the diamagnetism of the constituent atoms by the use of Pascal's constants.[18] Effective magnetic moments were calculated from the equation, $\mu_{eff}=2.828\sqrt{\chi_A T}$, where χ_A is the atomic magnetic susceptibility.

X-Ray Crystal Structure Analysis. Diffraction data were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo $K\alpha$ radiation at 25±1 °C. Crystal data and details of the data collection are given in Table 1. Lattice constants were determined by least-squares refinement based on 25 reflections with $20\leqslant 2\theta\leqslant 30°$. The intensity data were corrected for Lorentz-polarization effects, but not for absorption. The structures were solved by the direct methods. Refinements were carried out by the full-matrix least-squares methods. Hydrogen atoms were not included in the calculations for the data of $Ni_2(L_b)(pz)$ but were inserted in their calculated positions and fixed at their positions for the data of $Ni_2(L_a)(pz)$ and $Ni_2(L_c)(pz)$. The final discrepancy factors, $R=\sum||F_o|-|F_c||/\sum|F_o|$ and $R_w=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}$, are listed in Table 1. The weighting scheme, $w=1/[\sigma^2(|F_o|)+(0.02|F_o|)^2+1.0]$, was employed. All the calculations were carried out on the Micro-VAXII computer using the Enraf-Nonius SDP program package.[19] Atomic coordinates and thermal parameters of non-hydrogen atoms are listed in Table 2. The anisotropic thermal parameters of non-hydrogen atoms, and the F_o-F_c tables are deposited as a Document No. 8977 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

The infrared spectra of the free Schiff base ligands show a broad band at 3250—3420 cm^{-1} which is likely to be a superposition of bands from the alcohol-OH and phenol-OH. The ν(OH) band is absent in the infrared spectra of the nickel(II) complexes. This indicates that the alcoholic and phenolic protons are lost upon complexation. The ν(C=N) band (ca. 1630 cm^{-1}) of the free ligands are shifted to a little lower frequencies (ca. 1620 cm^{-1}) upon complexation, suggesting that the imino nitrogen is coodinated to the nickel ion.[20] This information and the elemental analyses led to the proposition

Table 2. Fractional Positional Parameters and Thermal Parameters of Non-Hydrogen Atoms with Their Estimated Standard Deviations in Parentheses

Atom	x	y	z	B_{eq}/Å^2 a)
(1) $Ni_2(L_a)(pz)$				
Ni1	0.17507(5)	0.11382(5)	0.44721(5)	2.84(1)
Ni2	−0.00993(5)	0.10768(5)	0.61468(5)	2.76(1)
O1	0.3168(3)	0.1005(3)	0.4305(3)	3.80(8)
O2	0.0331(3)	0.1194(3)	0.4669(3)	3.75(8)
O3	−0.0504(3)	0.0878(3)	0.7630(3)	3.53(8)
N1	0.1158(3)	0.1478(3)	0.2840(4)	2.88(9)
N2	−0.1489(3)	0.1371(3)	0.5227(4)	2.88(9)
N3	0.2181(3)	0.0899(3)	0.6196(4)	3.01(9)
N4	0.1398(3)	0.0900(3)	0.6908(4)	2.97(9)
C1	0.3548(4)	0.1222(4)	0.3311(5)	3.5(1)
C2	0.4682(5)	0.1094(5)	0.3374(5)	4.4(1)
C3	0.5139(5)	0.1337(5)	0.2388(6)	4.9(1)
C4	0.4485(5)	0.1680(5)	0.1279(5)	4.7(1)
C5	0.3380(5)	0.1799(4)	0.1170(5)	4.1(1)
C6	0.2878(4)	0.1563(4)	0.2181(5)	3.4(1)
C7	0.1707(4)	0.1674(4)	0.2002(5)	3.2(1)
C8	−0.0060(5)	0.1547(4)	0.2550(5)	3.4(1)
C9	−0.0383(4)	0.1774(4)	0.3767(5)	3.4(1)
C10	−0.1541(4)	0.1521(4)	0.3875(4)	3.0(1)
C11	−0.2384(4)	0.1441(4)	0.5642(5)	3.3(1)
C12	−0.2439(4)	0.1264(4)	0.6917(5)	3.5(1)
C13	−0.3469(5)	0.1378(5)	0.7247(6)	4.5(1)
C14	−0.3577(5)	0.1238(5)	0.8445(6)	5.0(1)
C15	−0.2657(5)	0.0970(5)	0.9351(5)	4.7(1)
C16	−0.1636(5)	0.0844(4)	0.9064(5)	4.0(1)
C17	−0.1503(4)	0.0993(4)	0.7831(5)	3.3(1)
C18	0.3168(4)	0.0774(4)	0.6955(5)	3.7(1)
C19	0.3053(5)	0.0699(4)	0.8164(5)	3.8(1)
C20	0.1941(5)	0.0784(4)	0.8093(5)	3.6(1)
(2) $Ni_2(L_b)(pz)$				
Ni1	0.62337(8)	0.1380(1)	0.8805(2)	4.45(4)
Ni2	0.51568(8)	0.1111(1)	1.0348(2)	4.41(4)
Ni3	1.16108(9)	0.0223(1)	0.9155(2)	5.02(5)
Ni4	1.06707(8)	−0.0620(1)	1.0735(2)	5.06(5)
O1	0.6973(4)	0.1310(7)	0.8847(9)	5.1(3)
O2	0.5470(4)	0.1441(6)	0.8849(9)	5.0(2)
O3	0.4923(4)	0.0884(7)	1.195(1)	5.6(3)
O4	1.2113(5)	0.1038(7)	0.912(1)	6.3(3)
O5	1.1050(4)	−0.0555(6)	0.9258(9)	5.4(3)
O6	1.0391(4)	−0.0704(8)	1.234(1)	6.5(3)
N1	0.6110(5)	0.1696(8)	0.699(1)	4.9(3)
N2	0.4451(5)	0.1006(8)	0.933(1)	4.9(3)
N3	0.6316(4)	0.1128(8)	1.065(1)	4.7(3)
N4	0.5889(5)	0.1088(7)	1.130(1)	4.6(3)
N5	1.1702(5)	−0.0180(9)	0.745(1)	5.8(3)
N6	1.0089(5)	−0.1256(7)	0.977(1)	5.4(3)
N7	1.1529(5)	0.0538(8)	1.093(1)	4.4(3)
N8	1.1187(5)	0.0149(8)	1.163(1)	4.9(3)
C1	0.7263(6)	0.1509(9)	0.792(1)	4.5(4)
C2	0.7847(7)	0.143(1)	0.818(2)	5.9(4)
C3	0.8177(7)	0.164(1)	0.722(2)	6.4(5)
C4	0.7965(8)	0.193(1)	0.593(2)	6.3(5)
C5	0.7374(7)	0.199(1)	0.563(2)	5.5(4)
C6	0.7042(6)	0.179(1)	0.659(1)	4.5(4)
C7	0.6456(7)	0.185(1)	0.619(2)	5.1(4)
C8	0.5505(6)	0.178(1)	0.651(1)	5.9(4)
C9	0.5248(7)	0.202(1)	0.773(2)	6.7(5)
C10	0.4635(7)	0.195(1)	0.749(2)	6.5(5)
C11	0.4445(7)	0.108(1)	0.780(1)	6.1(4)
C12	0.3997(6)	0.0840(9)	0.981(1)	4.7(4)
C13	0.3945(6)	0.0738(9)	1.120(1)	4.4(4)
C14	0.3435(6)	0.059(1)	1.156(1)	4.8(4)
C15	0.3349(7)	0.045(1)	1.288(2)	6.0(5)
C16	0.3823(7)	0.049(1)	1.392(2)	6.1(5)
C17	0.4340(6)	0.064(1)	1.357(1)	5.5(4)
C18	0.4433(7)	0.0774(9)	1.220(1)	4.7(4)
C19	0.6791(6)	0.100(1)	1.157(2)	5.8(4)
C20	0.6606(7)	0.088(1)	1.284(1)	5.3(4)
C21	0.6039(6)	0.094(1)	1.265(1)	4.8(4)
C22	1.2395(7)	0.123(1)	0.815(1)	5.5(4)
C23	1.2726(7)	0.196(1)	0.836(2)	6.4(5)
C24	1.3053(7)	0.218(1)	0.736(2)	7.2(5)
C25	1.3071(7)	0.170(1)	0.616(2)	7.9(5)
C26	1.2709(7)	0.101(1)	0.595(2)	6.8(5)
C27	1.2378(6)	0.079(1)	0.693(1)	5.3(4)
C28	1.2025(6)	0.009(1)	0.665(2)	5.8(4)
C29	1.130(1)	−0.090(1)	0.702(2)	11.4(8)
C30	1.108(1)	−0.114(2)	0.822(3)	13.7(9)
C31	1.065(1)	−0.175(1)	0.800(2)	10.7(7)
C32	1.0117(7)	−0.137(1)	0.828(2)	6.5(5)
C33	0.9674(6)	−0.152(1)	1.020(2)	5.6(4)
C34	0.9571(7)	−0.147(1)	1.161(2)	5.2(4)
C35	0.9087(6)	−0.182(1)	1.197(2)	5.5(4)
C36	0.8967(8)	−0.182(1)	1.331(2)	7.1(5)
C37	0.9360(8)	−0.141(1)	1.431(2)	6.9(5)
C38	0.9835(8)	−0.106(1)	1.397(2)	6.5(5)
C39	0.9956(6)	−0.107(1)	1.262(2)	5.4(4)
C40	1.1827(6)	0.113(1)	1.176(1)	5.4(4)
C41	1.1635(6)	0.105(1)	1.302(2)	5.7(4)
C42	1.1236(7)	0.045(1)	1.293(1)	6.0(4)
(3) $Ni_2(L_c)(pz)$				
Ni1	0.88609(7)	0.333	0.29901(7)	3.02(1)
Ni2	0.70666(7)	0.3336(3)	0.49860(6)	2.79(1)
O1	0.9486(4)	0.1666(9)	0.1988(5)	4.5(1)
O2	0.8132(4)	0.4595(7)	0.4135(4)	3.2(1)
O3	0.6105(5)	0.1750(8)	0.5723(4)	4.3(1)
N1	1.0080(5)	0.484(1)	0.3025(6)	3.9(1)
N2	0.7255(5)	0.4820(9)	0.6252(5)	3.4(1)
N3	0.7589(5)	0.1855(9)	0.2843(5)	3.0(1)
N4	0.6816(5)	0.1849(9)	0.3680(5)	2.8(1)
C1	1.0399(6)	0.186(1)	0.1389(7)	3.9(2)
C2	1.0671(7)	0.047(2)	0.0604(7)	4.7(2)
C3	1.1609(7)	0.062(2)	−0.0060(7)	5.2(2)
C4	1.2302(7)	0.210(2)	0.0044(7)	5.8(2)
C5	1.2059(6)	0.346(2)	0.0817(7)	5.0(2)
C6	1.1105(5)	0.338(2)	0.1504(6)	3.9(1)
C7	1.0909(7)	0.477(1)	0.2338(7)	4.2(2)
C8	1.0031(8)	0.641(1)	0.3831(9)	5.8(2)
C9	0.898(1)	0.750(1)	0.361(1)	6.4(3)
C10	0.7902(8)	0.649(1)	0.3888(7)	4.2(2)
C11	0.7292(9)	0.735(1)	0.4882(9)	5.2(2)
C12	0.7701(9)	0.665(1)	0.6021(7)	5.2(2)
C13	0.6935(7)	0.447(1)	0.7284(7)	3.7(2)
C14	0.6365(6)	0.285(1)	0.7631(6)	3.2(2)
C15	0.6104(6)	0.258(1)	0.8802(6)	3.6(2)
C16	0.5452(7)	0.119(1)	0.9156(6)	4.0(2)
C17	0.5032(7)	−0.003(1)	0.8361(8)	4.8(2)
C18	0.5266(7)	0.016(1)	0.7208(7)	4.0(2)
C19	0.5937(6)	0.162(1)	0.6824(6)	3.5(2)
C20	0.7243(7)	0.072(1)	0.2023(6)	3.8(2)
C21	0.6236(6)	−0.003(1)	0.2323(6)	3.6(2)
C22	0.6002(6)	0.071(1)	0.3382(6)	3.0(1)

a) Anisotropicaly refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $4/3[a^2B(1,1)+b^2B(2,2)+c^2B(3,3)+ab(\cos\gamma)B(1,2)+ac(\cos\beta)B(1,3)+bc(\cos\alpha)B(2,3)]$.

that the μ-alkoxo-μ-pyrazolato binuclear nickel(II) complexes had been formed. Crystals suitable for single-crystal X-ray structure determination could be grown from DMF for all the three complexes.

The crystal structure of $\mathrm{Ni_2(L_a)(pz)}$ is illustrated in Fig. 1. Selected bond distances and angles are listed in Table 3. The two nickel ions, Ni1 and Ni2, are bridged by an alkoxo oxygen atom, O2, and two pyrazolate nitrogen atoms, N3 and N4. The Ni1–Ni2 separation is 3.245(1) Å and the Ni1–O2–Ni2 angle is 125.4(2)°. Each nickel ion is coordinated by two nitrogen atoms and two oxygen atoms forming a square plane. The Ni–O bond distances (1.819(4)—1.831(4) Å) are slightly shorter than the corresponding distances found in the related complex, $\mathrm{[Ni_2(eia)_2]}$, which also has an alkoxo-bridged structure (average 1.867(6) Å).6) The Ni–N distances (1.849(4)—1.887(4) Å) are comparable to those (1.811(5)—1.849(7) Å) of diamagnetic nickel(II) complexes with binuclear structures, $\mathrm{[Ni_2(eia)_2]}$6) and $\mathrm{[Ni_2(iaa_2en_2)]}$ ($\mathrm{H_4(iaa_2en_2)}$=5,14-dimethyl-9,18-diisopropyl-1,4,10,13-tetraazacyclooctadeca-5,8,14,17-tetraene-7,16-dione).21) These short distances are typical of low-spin nickel(II) complexes.22) The dihedral angle between the two coordination planes of the nickel ions is 179.1°, thereby the whole molecule is almost planar, as can be seen in Fig. 2.

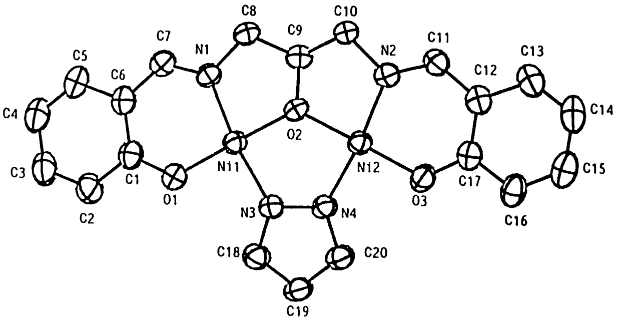


Fig. 1. A perspective view of $\mathrm{Ni_2(L_a)(pz)}$.

Table 3. Selected Interatomic Distances (*l*/Å), Bond Angles (*φ*/°), and Dihedral Angles (*τ*/°)

Complex	$\mathrm{Ni_2(L_a)(pz)}$	$\mathrm{Ni_2(L_b)(pz)}$		$\mathrm{Ni_2(L_c)(pz)}$
		Molecule A	Molecule B	
Distances (*l*/Å)				
Ni1–Ni2	3.245(1)	3.277(3)	3.274(3)	3.193(1)
Ni1–O1	1.819(4)	1.825(10)	1.813(12)	1.854(6)
Ni1–O2	1.825(4)	1.895(10)	1.883(11)	1.854(5)
Ni1–N1	1.851(4)	1.863(11)	1.865(13)	1.846(7)
Ni1–N3	1.887(4)	1.870(11)	1.876(12)	1.888(6)
Ni2–O2	1.827(4)	1.853(10)	1.853(11)	1.874(5)
Ni2–O3	1.831(4)	1.804(10)	1.830(11)	1.857(6)
Ni2–N2	1.849(4)	1.903(11)	1.914(12)	1.854(6)
Ni2–N4	1.883(4)	1.924(11)	1.914(12)	1.903(6)
N3–N4	1.376(6)	1.310(17)	1.329(17)	1.357(8)
Angles (*φ*/°)				
Ni1–O2–Ni2	125.4(2)	122.0(5)	122.4(5)	117.9(3)
Ni1–N3–N4	119.5(3)	120.5(8)	122.0(9)	119.9(5)
Ni2–N4–N3	119.9(3)	121.5(8)	119.2(9)	118.1(5)
O2–Ni1–N1	85.0(2)	88.6(5)	89.9(5)	93.7(3)
O2–Ni1–O1	176.5(2)	177.3(4)	174.9(5)	168.9(2)
O2–Ni1–N3	87.6(2)	88.0(4)	87.5(5)	87.9(2)
N1–Ni1–O1	96.8(2)	94.1(5)	93.9(5)	94.7(3)
N1–Ni1–N3	171.4(2)	175.4(6)	175.3(6)	175.6(3)
O1–Ni1–N3	90.9(2)	89.4(5)	89.0(5)	84.2(3)
O2–Ni2–N2	84.9(2)	92.6(5)	93.3(5)	93.1(3)
O2–Ni2–O3	176.3(2)	171.8(4)	171.9(5)	170.7(3)
O2–Ni2–N4	87.5(2)	86.3(5)	87.7(5)	87.9(2)
N2–Ni2–O3	96.8(2)	94.3(5)	93.0(5)	94.1(3)
N2–Ni2–N4	171.1(2)	173.1(5)	171.9(5)	177.8(3)
O3–Ni2–N4	91.1(2)	87.3(5)	86.9(5)	85.2(3)
Dihedral angles between the coordination planes (*τ*/°)				
	179.1	167.5	167.0	147.2

The crystal structure of $\mathrm{Ni_2(L_b)(pz)}$ comprises two crystallographically independent binuclear molecules; they are represented as A and B. Their structures are essentially the same as that of $\mathrm{Ni_2(L_a)(pz)}$, having the alkoxide and pyrazolate double-bridged structure. A perspective view of A is illustrated in Fig. 3. The Ni1–Ni2 separation is 3.277(3) Å and the Ni1–O2–Ni2 angle is 122.0(5)°. The Ni–O and Ni–N distances are comparable with the distances observed for $\mathrm{Ni_2(L_a)(pz)}$. The dihedral angle between the two coordination planes is 167.5° and a slight twist is observed in the backbone atoms, C9, C10, and C11 (Fig. 4). This twist may be due to the presence of a six-membered chelate ring in the

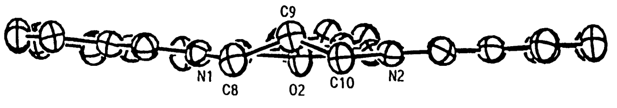


Fig. 2. Another view of $\mathrm{Ni_2(L_a)(pz)}$.

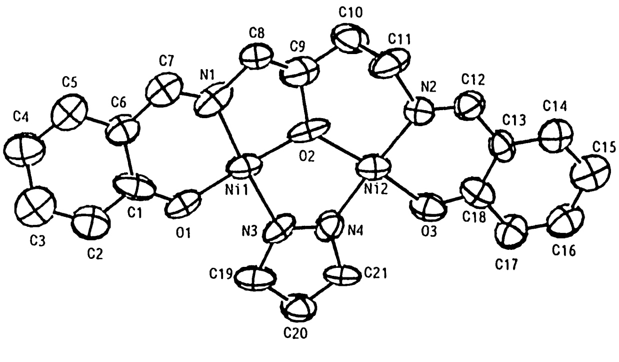


Fig. 3. A perspective view of $\mathrm{Ni_2(L_b)(pz)}$ (molecule A).

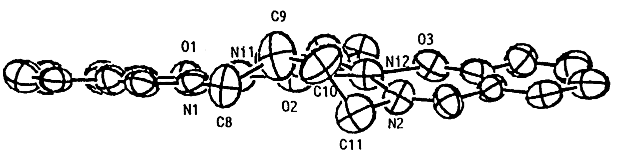


Fig. 4. Another view of $\mathrm{Ni_2(L_b)(pz)}$ (molecule A).

asymmetric backbone.

The crystal structure of Ni$_2$(L$_c$)(pz) is illustrated in Fig. 5. The binuclear structure is similar to those of Ni$_2$(L$_a$)(pz) and Ni$_2$(L$_b$)(pz). The Ni1–Ni2 separation is 3.193(1) Å and the Ni1–O2–Ni2 angle is 117.9(3)°. The Ni–O and Ni–N distances are comparable with those for Ni$_2$(L$_a$)(pz) and Ni$_2$(L$_b$)(pz). The dihedral angle between the coordination planes is 147.2°, showing a considerable bending of the two coodination planes. Thus, the molecule has a bent structure as shown in Fig. 6. This bending of the molecule is caused by the twisting of the Schiff-base backbone and leads to a smaller Ni–Ni separation and a smaller Ni–O–Ni angle. In Figs. 7 and 8, the dihedral angles between the two coordination planes, τ, for the nickel(II) complexes are plotted against the M–O–M angles (M=metal ion) and M–M separations, respectively, together with the data available in the literatures for the same type of copper(II) complexes.[8,14,15] Although no clear relationship is found for the plot of the τ value vs. the M–M

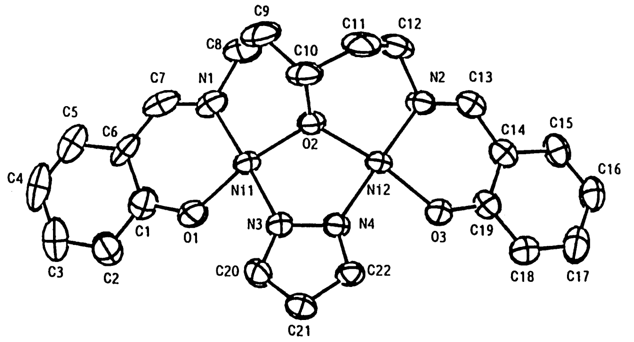


Fig. 5. A perspective view of Ni$_2$(L$_c$)(pz).

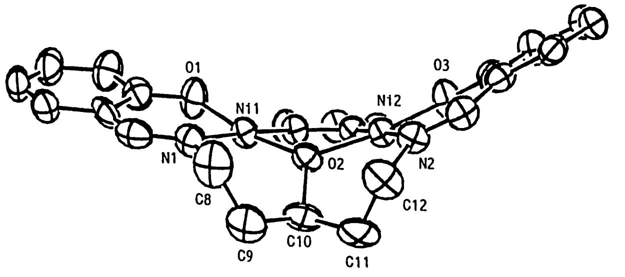


Fig. 6. Another view of Ni$_2$(L$_c$)(pz).

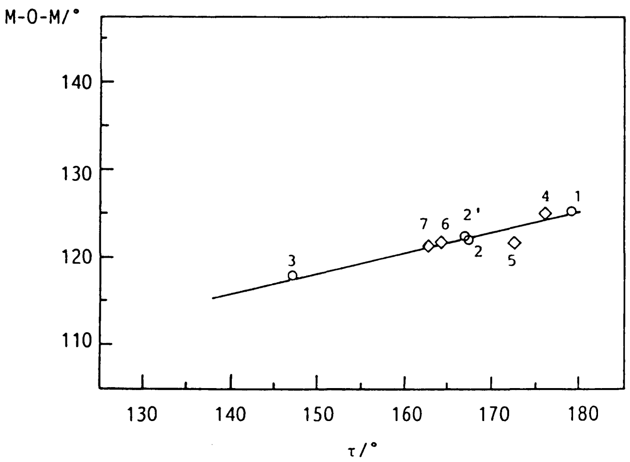


Fig. 7. A plot of the dihedral angle between the coordination planes, τ, vs. the M–O–M angle. 1; Ni$_2$(L$_a$)(pz), 2; Ni$_2$(L$_b$)(pz) (molecule A), 2′; Ni$_2$(L$_b$)(pz) (molecule B), 3; Ni$_2$(L$_c$)(pz), 4; Cu$_2$(L$_a$)(pz)·H$_2$O,[9] 5; Cu$_2$(L$_a$)(pz),[15] 6; Cu$_2$(L$_b$)(pz),[16] 7; Cu$_2$(L$_c$)(pz).[15]

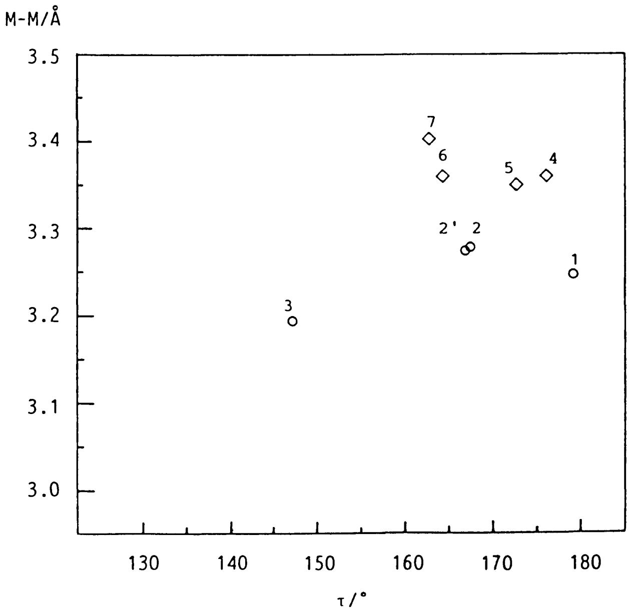


Fig. 8. A plot of the dihedral angle between the coordination planes, τ vs. the M–M separation.

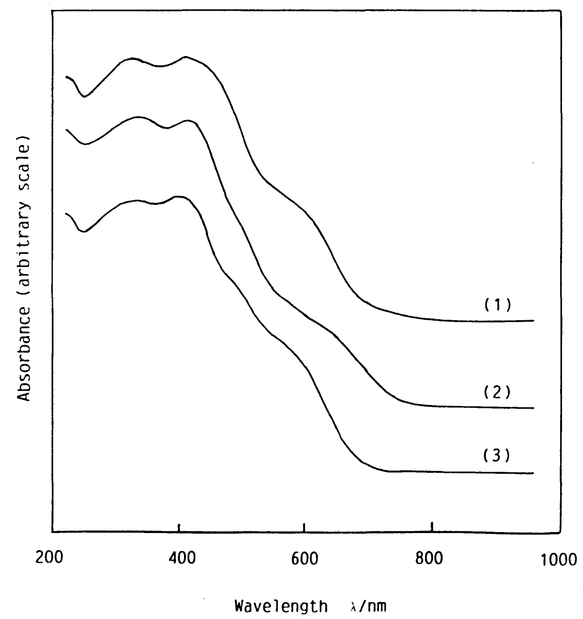


Fig. 9. Diffuse reflectance spectra of (1) Ni$_2$(L$_a$)(pz), (2) Ni$_2$(L$_b$)(pz), and (3) Ni$_2$(L$_c$)(pz).

Table 4. Electronic Spectral Data

Complex	Reflectance λ_{max}/nm	DMF solution λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})
$Ni_2(L_a)(pz)$	600sh[a)]460sh 411 332	411(2800) 334(5400)
$Ni_2(L_b)(pz)$	650sh 500sh 412 332	410(2520) 334(4080)
$Ni_2(L_c)(pz)$	580sh 490sh 403 331	380(3540) 344(3420)

a) sh=shoulder.

separation, the plot of the τ value against the M–O–M angle reveals a nearly linear correlation between them. This implies that the M–O–M angle is sensitive to the twisting of the molecule caused by inclusion of six-membered chelate ring in the Schiff base backbone.

The magnetic moments per nickel ion of $Ni_2(L_a)(pz)$, $Ni_2(L_b)(pz)$, and $Ni_2(L_c)(pz)$ are 0.37, 0.39, and 0.42 B.M., respectively, at room temperature, showing that these complexes are essentially diamagnetic, i.e., low-spin state.

The diffuse reflectance spectra of all the complexes are characterized by low-intensity absorptions of shoulders around 500 and 600 nm, which can be associated with d-d transitions from $^1A_{1g}$ to $^1B_{2g}$ and $^1A_{2g}$,[23,24)] respectively, and intense absorptions in the range 300—450 nm, which are clearly charge transfer transitions in origin (Fig. 9, Table 4). The electronic spectra in DMF are similar to those in the solid state; however, the lower energy shoulder bands in the diffused reflectance spectra could not be observed in the solution spectra, owing to the low solubility of the complexes.

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