

Synthesis, Structures, and Magnetic Properties of Dinuclear Nickel(II) Complexes Containing *N,N,N',N'*-Tetrakis[(1-methyl-2-benzimidazolyl)methyl]-2-hydroxy-1,3-diaminopropane and a Thiocyanate Ion

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Three dinuclear nickel(II) complexes, $[\text{Ni}_2(\text{L-Me})(\text{NCS})(\text{H}_2\text{O})_3](\text{PF}_6)_2$ (**1**), $[\text{Ni}_2(\text{L-Me})(\text{NCS})_2(\text{CH}_3\text{OH})(\text{H}_2\text{O})]\text{PF}_6$ (**2**), and $[\text{Ni}_2(\text{L-Me})(\text{NCS})_2(\text{H}_2\text{O})_2]\text{NCS}$ (**3**) containing HL-Me (HL-Me = *N,N,N',N'*-tetrakis[(1-methyl-2-benzimidazolyl)methyl]-2-hydroxy-1,3-diaminopropane) have been synthesized and characterized by their IR and UV-Vis spectra and magnetic susceptibilities. The crystal structures of the complexes **1**, **2**, and **3**, from which **1**, **2**, and **3**, respectively, are derived, were determined by X-ray crystallography. These complexes are dimeric and only an alkoxo of L-Me⁻ bridges two octahedral Ni(II) ions. While **2** and **3** have symmetrical conformations of L-Me⁻, that of **1** is unsymmetrical. Magnetic susceptibility measurements from liquid helium temperature to room temperature showed a weak ferromagnetic exchange coupling between the two nickel(II) ions ($2J = 7.8 \text{ cm}^{-1}$, $H = -2JS_1 \cdot S_2$) for **1**. On the other hand, antiferromagnetic interactions were observed for **2** and **3** ($2J = -29.2$ and -27.8 cm^{-1} , respectively).

Key Words: Dinuclear nickel(II) complexes; Magnetic susceptibilities; Crystal structures

Introduction

Some dinuclear nickel(II) complexes such as $[\text{Ni}_2(\text{L-Et})(\text{OAc})(\text{CH}_3\text{OH})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O} \cdot \text{CH}_3\text{OH}$,

$[\text{Ni}_2(\text{L-Et})(\text{OOC-O-CH}_3)(\text{CH}_3\text{OH})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O} \cdot \text{CH}_3\text{OH}$, and $[\text{Ni}_2(\text{L-Et})(\mu-1,3-\text{N}_3)(\text{N}_3)(\text{H}_2\text{O})] \cdot [\text{Ni}_2(\text{L-Et})(\mu-1,3-\text{N}_3)(\text{N}_3)(\text{CH}_3\text{OH})](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ containing L-Et (HL-Et = *N,N,N',N'*-tetrakis[(1-ethyl-2-benzimidazolyl)methyl]-2-hydroxy-1,3-diaminopropane) have been synthesized, and their structure-magnetism relationship has been investigated [1]. The two nickel(II) ions in these complexes are bridged by an alkoxo of L-Et⁻ and by an acetato, a monomethylcarbonato, or an azido. However, dinu-

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clear nickel(II) complexes bridged by only an alkoxo group of L-Et⁻ have not been reported so far. In connection with these studies, in this study, we report the preparation, structures, and magnetic properties of three types of dinuclear nickel(II) complexes containing a thiocyanate ion and L-Me⁻ similar to L-Et⁻. Additionally, we describe the correlations between the magnetic behavior and the structural parameters.

Experimental

1. Ligand synthesis

The ligand HL-Me was synthesized according to the method described in the literatures [2, 3].

2. Preparation of $[\text{Ni}_2(\text{L-Me})(\text{NCS})(\text{H}_2\text{O})_3](\text{PF}_6)_2$ (1) and $[\text{Ni}_2(\text{L-Me})(\text{NCS})(\text{CH}_3\text{OH})_2(\text{H}_2\text{O})](\text{PF}_6)_2$ (1')

Sodium hydroxide (0.015g, 0.38mmol), sodium thiocyanate (0.025g, 0.30mmol), and nickel(II) nitrate hexahydrate (0.18g, 0.60mmol) were successfully added to a methanol solution (300cm³) of HL-Me (0.20g, 0.30mmol). The reaction mixture was stirred at room temperature (r. t.) for 2h. A methanol solution of potassium hexafluorophosphate (0.11g, 6.0mmol) was added to the clear solution obtained. The resulting solution was allowed to stand for several days at r. t. for the deposition of blue-green crystals, referred to as 1'. The crystal of 1' is stable in the methanol solution. Complex 1', however, readily changes to 1 by filtration in air. We attempted an analogous preparation several times by using other nickel(II) salts. However, we could not obtain a better crystal than 1'. Therefore, we used 1' for the X-ray work. Analytical and spectral data for 1. Found: C, 40.59; H, 4.28; N, 12.97%. Calcd for C₄₀H₄₇N₁₁O₄SP₂F₁₂Ni₂: C, 40.53; H, 4.00; N, 13.00%. IR (KBr method): 2070cm⁻¹ ($\nu_{\text{C=N}}$ for NCS⁻). UV (solid): λ_{max} = 916, 653, 411nm.

3. Preparation of $[\text{Ni}_2(\text{L-Me})(\text{NCS})_2(\text{CH}_3\text{OH})(\text{H}_2\text{O})]\text{PF}_6$ (2) and $[\text{Ni}_2(\text{L-Me})(\text{NCS})_2(\text{CH}_3\text{OH})_2]\text{PF}_6$ (2')

These were prepared analogously [HL-Me (0.20g, 0.30mmol), NaOH (0.015g, 0.38mmol), NaSCN (0.050g, 0.60mmol), Ni(NO₃)₂ · 6H₂O (0.18g, 0.60mmol)]. Complex 2' changes to 2 by filtration in air. Analytical and spectral data for 2. Found: C, 46.10; H, 4.47; N, 15.22%. Calcd for C₄₂H₄₇N₁₂O₃S₂PF₆Ni₂: C, 46.09;

H, 4.34; N, 15.36%. IR (KBr method): 2064cm⁻¹ ($\nu_{\text{C=N}}$ for NCS⁻). UV (solid): λ_{max} = 1009, 639, 401nm.

4. Preparation of $[\text{Ni}_2(\text{L-Me})(\text{NCS})_2(\text{H}_2\text{O})_2]\text{NCS}$ (3) and $[\text{Ni}_2(\text{L-Me})(\text{NCS})_2(\text{CH}_3\text{OH})_2]\text{NCS}$ (3')

These were prepared analogously [HL-Me (0.20g, 0.30mmol), NaOH (0.015g, 0.38mmol), NaSCN (0.070g, 0.90mmol), Ni(NO₃)₂ · 6H₂O (0.18g, 0.60mmol)] by using ethanol (100cm³). A crude complex was recrystallized from methanol. Complex 3' changes to 3 by filtration in air. Analytical and spectral data for 3. Found: C, 51.06; H, 4.82; N, 17.90%. Calcd for C₄₂H₄₅N₁₃O₃S₃Ni₂: C, 50.77; H, 4.57; N, 18.33%. IR (KBr method): 2065cm⁻¹ ($\nu_{\text{C=N}}$ for NCS⁻). UV (solid): λ_{max} = 1030, 639, 401nm.

1 and 3 are free from methanol, while 2 contains methanol. They were confirmed by using gas chromatography for each *N,N*-dimethylformamide solution containing water of 1, 2, and 3.

5. X-ray Structure Analysis for 1', 2', and 3'

X-ray diffraction data of 1', 2', and 3' were collected on a Rigaku RAXIS-RAPID imaging plate diffractometer with graphite monochromated Mo-K α at 23 ± 1°C for 1' and 2' and at -150 ± 1°C for 3'. For the data collection, each crystal of these compounds was sealed in a capillary tube. The crystal structures were solved by the Patterson method [4, 5] and expanded using Fourier techniques [5]. The nonhydrogen atoms were refined anisotropically using full-matrix least-squares techniques. The hydrogen atoms were fixed at their standard position and their thermal parameters were not refined. All calculations were performed using the teXsan crystallographic software package [6]. The accuracy of the structure analysis for 1' is unsatisfactory. High quality intensity data were not achieved because of the poor quality of the crystal.

6. Crystallography for 1', 2', and 3'

Crystal data for 1': C₄₂H₅₂N₁₁O₄SP₂F₁₂Ni₂, Fw = 1213.32, monoclinic, space group *P*2₁/*n*, *a* = 19.9105(5), *b* = 13.5292(3), *c* = 23.5874(5) Å, β = 100.7644(8)°, *Z* = 4, *D*_c = 1.291 g cm⁻³, μ = 7.67 cm⁻¹, *R* = 0.0889 for 8200 reflections with *I* > 3 σ (*I*), and GOF = 1.796 for 567 parameters. For 2': C₄₃H₄₉N₁₂O₃S₂PF₆Ni₂, Fw = 1108.42, triclinic, space group *P* $\bar{1}$, *a* = 11.2414(4), *b* = 13.4215(7), *c* = 16.3127(9) Å, α = 82.559(3), β = 87.905(3),

$\gamma = 88.206(2)^\circ$, $Z = 2$, $D_c = 1.510 \text{ g cm}^{-3}$, $\mu = 9.66 \text{ cm}^{-1}$, $R = 0.075$ for 8771 reflections with $I > 3\sigma(I)$, and $\text{GOF} = 1.42$ for 572 parameters. For $3'$: $\text{C}_{44}\text{H}_{49}\text{N}_{13}\text{O}_3\text{S}_3\text{Ni}_2$, $F_w = 1021.54$, triclinic, space group $P\bar{1}$, $a = 11.1123(7)$, $b = 13.3572(7)$, $c = 15.951(1) \text{ \AA}$, $\alpha = 81.188(3)$, $\beta = 85.464(4)$, $\gamma = 87.411(1)^\circ$, $Z = 2$, $D_c = 1.455 \text{ g cm}^{-3}$, $\mu = 9.98 \text{ cm}^{-1}$, $R = 0.090$ for 13213 reflections with $I > 3\sigma(I)$, and $\text{GOF} = 1.04$ for 586 parameters.

7. Measurements

The infrared and visible absorption spectra and the magnetic susceptibilities were measured as described in the previous paper [1a].

Results and Discussion

ORTEP of the complex cation of $1'$ and the atom labeling scheme are shown in Fig. 1. Selected bond lengths and angles are given in Table 1. In the cation of $1'$, the two nickel(II) ions are bridged by only an alkoxo group of L-Me^- , although an azido and an alkoxo of L-Et^- in the corresponding azido-containing complex $[\text{Ni}_2(\text{L-Et})(\mu\text{-}1,3\text{-N}_3)(\text{N}_3)(\text{H}_2\text{O})] \cdot [\text{Ni}_2(\text{L-Et})(\mu\text{-}1,3\text{-N}_3)(\text{N}_3)(\text{CH}_3\text{OH})](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ link two nickel(II) atoms. Further, the characteristic feature observed

in this structure is the conformation of L-Me^- . The $\text{Ni}_2(\text{L-Me}^-)$ or $\text{Ni}_2(\text{L-Et}^-)$ moiety of some dinuclear nickel(II) complexes such as $[\text{Ni}_2(\text{L-Et})(\text{OAc})(\text{CH}_3\text{OH})_2]^{2+}$ [1a], $[\text{Ni}_2(\text{L-Et})(\text{OOC-O-CH}_3)(\text{CH}_3\text{OH})_2]^{2+}$ [1b], and complex $2'$ described below are symmetrical and have an approximate mirror plane through the oxygen atom of the alkoxo group and the carbon atom of the methine group in L-Me^- or L-Et^- ; however, the conformation of L-Me^- in $1'$

Table 1 Selected bond distances (Å) and angles ($^\circ$) of $1'$

Bond distances			
Ni1-O1	2.02(1)	Ni1-O2	2.18(2)
Ni1-O3	2.07(2)	Ni1-N1	2.10(2)
Ni1-N3	2.08(2)	Ni1-N5	2.16(2)
Ni2-O1	2.03(1)	Ni2-O4	2.21(2)
Ni2-N6	2.08(2)	Ni2-N8	2.06(2)
Ni2-N10	2.16(2)	Ni2-N11	2.07(2)
Bond angles			
Ni1-O1-Ni2	138.2(7)	O1-Ni1-O2	178.0(6)
O1-Ni1-O3	89.7(6)	O1-Ni1-N1	95.0(6)
O1-Ni1-N3	93.9(6)	O1-Ni1-N5	85.4(6)
O1-Ni2-O4	87.8(6)	O1-Ni2-N6	160.8(6)
O1-Ni2-N8	96.5(6)	O1-Ni2-N10	82.2(6)
O1-Ni2-N11	98.6(6)		

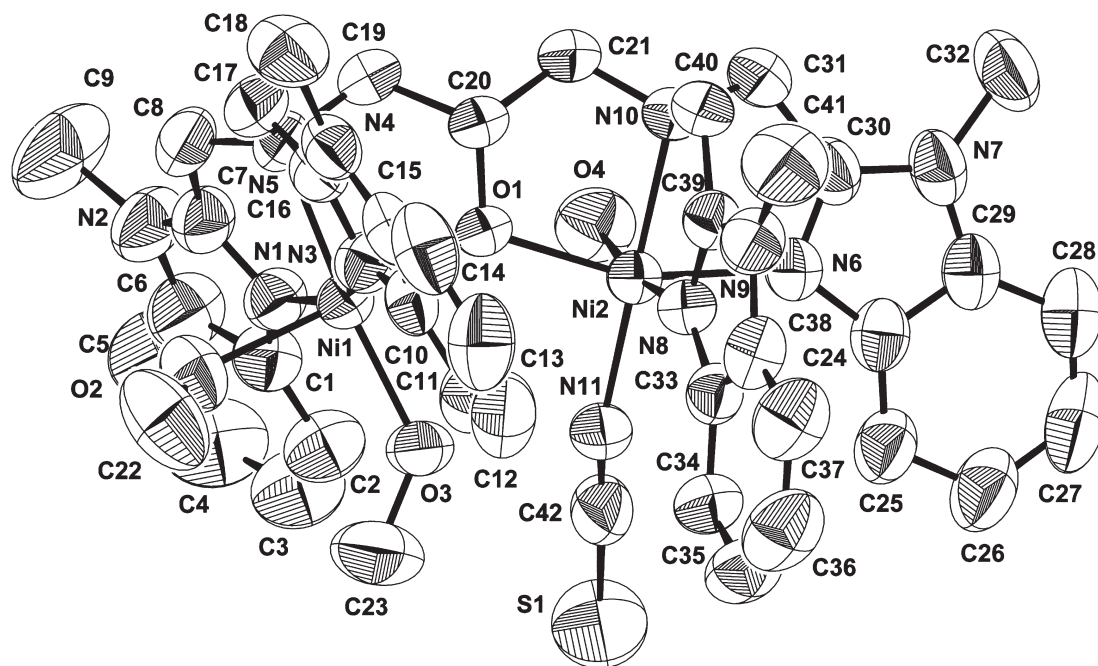


Fig. 1 An ORTEP drawing of $1'$ with 30% probability ellipsoids.

is unsymmetrical. In this regard, the O1-Ni1-N1 and N1-Ni1-N3 angles are $95.0(6)^\circ$ and $158.3(7)^\circ$, respectively, which are largely distinct from the corresponding angles of $[\text{Ni}_2(\text{L-Et})(\text{OAc})(\text{CH}_3\text{OH})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O} \cdot \text{CH}_3\text{OH}$ ($158.0(2)^\circ$ and $95.4(3)^\circ$ [1a], respectively) and $[\text{Ni}_2(\text{L-Et})(\text{OOC-O-CH}_3)(\text{CH}_3\text{OH})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O} \cdot \text{CH}_3\text{OH}$ ($158.7(5)^\circ$ and $88.7(5)^\circ$, respectively) [1b]. The Ni1-O1-Ni2 angle is $138.2(7)^\circ$; it is greater than those of $[\text{Ni}_2(\text{L-Et})(\text{OAc})(\text{CH}_3\text{OH})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O} \cdot \text{CH}_3\text{OH}$ [1a] and $[\text{Ni}_2(\text{L-Et})(\text{OOC-O-CH}_3)(\text{CH}_3\text{OH})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O} \cdot \text{CH}_3\text{OH}$ ($127.9(3)$ and $128.3(5)^\circ$, respectively) [1b]. The Ni1 \cdots Ni2 distance is $3.785(4)\text{\AA}$. The thiocyanate ion acts as a monodentate (-N) ligand showing the Ni2-N11-C42 angle of $161(1)^\circ$. The two planes [O1, O3, O2, N5] and [O1, N11, N6, N10] make an angle of 24.8° .

ORTEP of the complex cation of 2' and the atom labeling scheme are shown in Fig. 2. Selected bond lengths and angles are given in Table 2. Similar to 1', the two nickel(II) ions are bridged by only an alkoxo group of L-Me⁻. The Ni1-O1-Ni2 angle is $134.6(2)^\circ$, which is larger than the corresponding angles ($127.9(3)^\circ$ and $128.3(5)^\circ$) [1a, 1b] of $[\text{Ni}_2(\text{L-Et})(\text{OAc})(\text{CH}_3\text{OH})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O} \cdot \text{CH}_3\text{OH}$ and $[\text{Ni}_2(\text{L-Et})(\text{OOC-O-CH}_3)(\text{CH}_3\text{OH})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O} \cdot \text{CH}_3\text{OH}$, in which the conformation of L-Et⁻ is similar to that of

L-Me⁻ in 2'. The Ni1 \cdots Ni2 distance of $3.699(1)\text{\AA}$ is slightly greater than those of $[\text{Ni}_2(\text{L-Et})(\text{OAc})(\text{CH}_3\text{OH})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O} \cdot \text{CH}_3\text{OH}$ and $[\text{Ni}_2(\text{L-Et})(\text{OOC-O-CH}_3)(\text{CH}_3\text{OH})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O} \cdot \text{CH}_3\text{OH}$ ($3.521(2)$, $3.527(3)\text{\AA}$) [1a, 1b]. The two planes [O1, O2, N1, N5] and [O1, N12, N7, N11] make an angle of 23.8° , which is larger than the corresponding angles (10.9° and 10.8°) [1a, 1b] of $[\text{Ni}_2(\text{L-Et})(\text{OAc})(\text{CH}_3\text{OH})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O} \cdot \text{CH}_3\text{OH}$ and $[\text{Ni}_2(\text{L-Et})(\text{OOC-O-CH}_3)(\text{CH}_3\text{OH})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O} \cdot \text{CH}_3\text{OH}$.

Table 2 Selected bond distances (\AA) and angles ($^\circ$) of 2'

Bond distances			
Ni1-O1	2.011(5)	Ni1-O2	2.104(5)
Ni1-N1	2.092(6)	Ni1-N3	2.063(5)
Ni1-N5	2.143(5)	Ni1-N6	2.079(6)
Ni2-O1	1.999(4)	Ni2-O3	2.179(5)
Ni2-N7	2.076(6)	Ni2-N9	2.064(5)
Ni2-N11	2.191(6)	Ni2-N12	2.053(6)
Bond angles			
Ni1-O1-Ni2	134.6(2)	O1-Ni1-O2	96.5(2)
O1-Ni1-N1	162.7(2)	O1-Ni1-N3	89.2(2)
O1-Ni1-N5	82.2(2)	O1-Ni1-N6	91.3(2)
O1-Ni2-O3	79.4(2)	O1-Ni2-N7	156.6(2)
O1-Ni2-N9	97.5(2)	O1-Ni2-N11	83.0(2)
O1-Ni2-N12	100.4(2)		

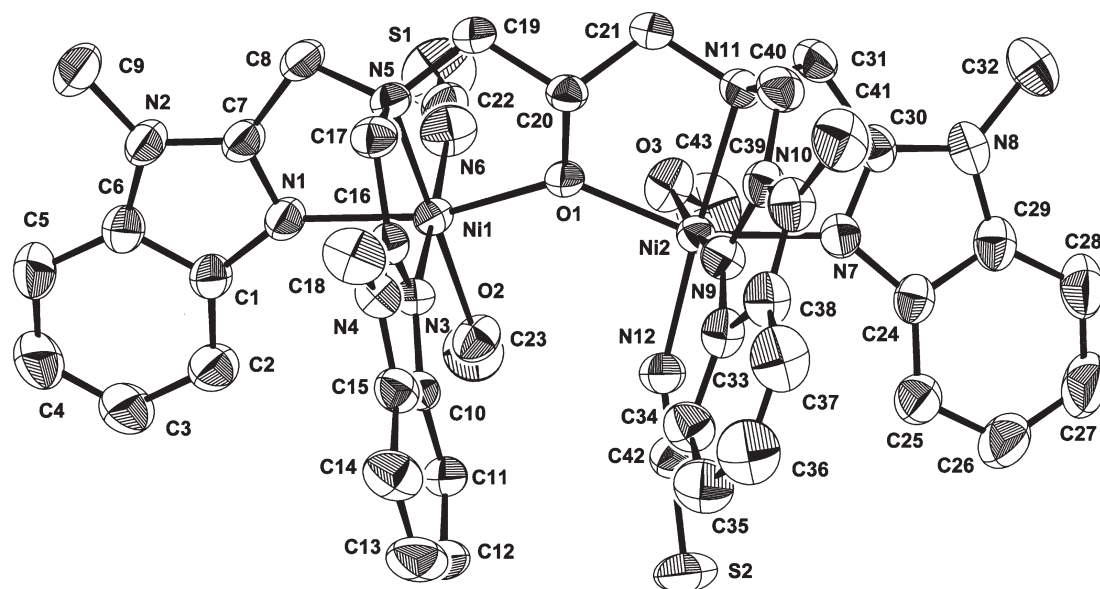


Fig. 2 ORTEP of 2' with 30% probability ellipsoids.

ORTEP of the complex cation of 3' and the atom labeling scheme are shown in Fig. 3. Selected bond lengths and angles are given in Table 3. The structure of complex 3' consists of dinuclear cations $[\text{Ni}_2(\text{L-Me})(\text{NCS})_2(\text{CH}_3\text{OH})_2]^+$ separated by NCS^- anions (Fig. 3). The cations of 3' and 2' have extremely similar structures. The Ni1-O1-Ni2 angle is $135.09(8)^\circ$, which is similar to that of 2'. The Ni1 \cdots Ni2 distance of $3.730(1)\text{\AA}$ is slightly greater than that of 2'. The two planes $[\text{O1}, \text{O2}, \text{N1}, \text{N5}]$ and $[\text{O1}, \text{N12}, \text{N7}, \text{N11}]$ make an angle of 20.96° , which is smaller than the corresponding angle (23.8°) of 2'.

One or two methanol molecules in 1', 2', and 3' are substituted by water molecules in 1, 2, and 3, respectively. It is known that the substitution of one or two monodentate ligands in similar complexes does not lead to any significant structural variation. For example, the structures of the two complexes $[\text{Ni}_2(\text{L-Et})(\text{OAc})(\text{CH}_3\text{OH})_2]^{2+}$ and $[\text{Ni}_2(\text{L-Et})(\text{OAc})(\text{ur})(\text{H}_2\text{O})]^{2+}$ (ur = urea) have rather similar overall geometries and dimensions involving the ligands and the

nickel centers [1c]. Accordingly, it is estimated that the structures of 1, 2, and 3 are analogous to those of 1', 2', and 3', respectively.

The $\nu_{\text{C=N}}$ stretches based on NCS^- in the IR spectra of 1, 2, and 3 are observed in the range of $2064\text{--}2070\text{cm}^{-1}$. It is hitherto known that a mono-

Table 3 Selected bond distances (\AA) and angles ($^\circ$) of 3'

Bond distances			
Ni1-O1	2.018(2)	Ni1-O2	2.093(2)
Ni1-N1	2.091(2)	Ni1-N3	2.069(2)
Ni1-N5	2.147(2)	Ni1-N6	2.077(3)
Ni2-O1	2.018(2)	Ni2-O3	2.128(2)
Ni2-N7	2.071(2)	Ni2-N9	2.068(2)
Ni2-N11	2.197(2)	Ni2-N12	2.050(2)
Bond angles			
Ni1-O1-Ni2	135.09(8)	O1-Ni1-O2	96.11(7)
O1-Ni1-N1	163.35(7)	O1-Ni1-N3	89.26(8)
O1-Ni1-N5	82.90(7)	O1-Ni1-N6	90.46(8)
O1-Ni2-O3	79.29(7)	O1-Ni2-N7	157.05(8)
O1-Ni2-N9	98.11(8)	O1-Ni2-N11	82.63(7)
O1-Ni2-N12	99.80(8)		

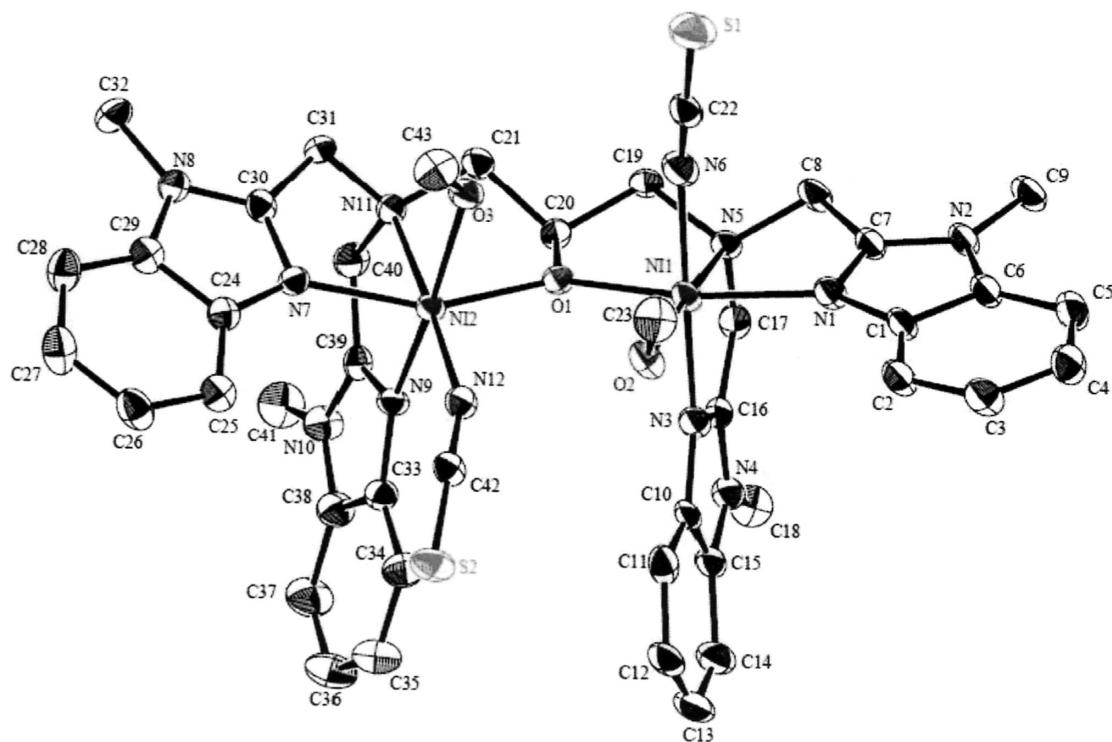


Fig. 3 ORTEP of 3' with 50% probability ellipsoids.

dentate end-on NCS^- has a $\nu_{\text{C=N}}$ stretch below 2100cm^{-1} [7, 8]. The three λ_{max} values of the d-d absorption bands of 1, 2, and 3 were observed in the ranges of 1030–916, 639–653, and 411–401nm, respectively, which are characteristic for octahedral nickel(II) complexes [9].

The magnetic moments (μ_{eff}) of 1, 2, and 3 at r. t. are 3.31, 3.09, and 3.11 BM/Ni, respectively (non-S. I. units employed: $\text{BM} = 9.27\text{JT}^{-1}$). The μ_{eff} value for 1 is approximately constant in the range of 300–70K; however, this value increases slightly below 60K, reaching a maximum at 10K (Fig. 4). This indicates a ferromagnetic interaction within the dinuclear complex of 1. The magnetic parameters g , $2J$, N_{α} , and p can be estimated from the best fit of χ_A (χ_A : magnetic susceptibility) to Eq.(1) [10] based on the isotropic Heisenberg model ($H = -2JS_1 \cdot S_2$, $S_1 = S_2 = 1$):

$$\chi_A = \frac{Ng^2\beta^2}{kT} \times \frac{[5 + \exp(4x)](1-p)}{5 + 3\exp(4x) + \exp(6x)} + \frac{(2Ng^2\beta^2)p}{3kT} + N_{\alpha} \quad (1)$$

where g , x , p , and N_{α} represent the g factor, $-J/kT$ (J is the exchange integral), the percentage of paramagnetic impurities, and T.I.P., respectively.

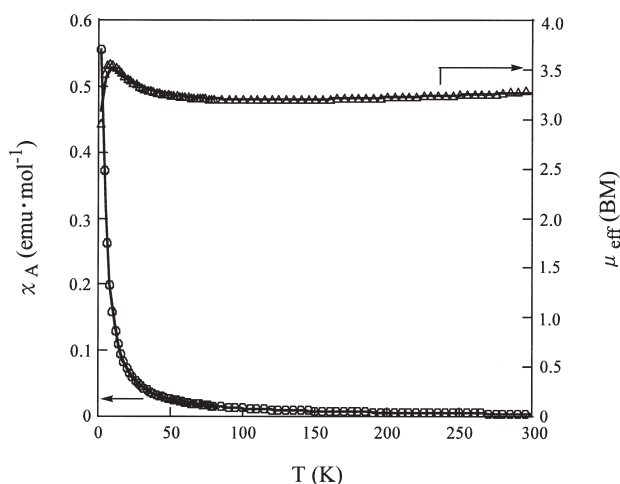


Fig. 4 Temperature dependence of the magnetic susceptibility and magnetic moment of 1. Magnetic susceptibility (○) and magnetic moment (△) as a function of temperature for 1. The solid lines are calculated from theory.

To take into account the intercluster exchange interactions for complex 1, a molecular field correction term is added to Eq.(1). The equation for the exchange-corrected susceptibility thus assumes the following form:

$$\chi_A' = \frac{\chi_A}{1 - (2zJ'/Ng^2\beta^2)\chi_A} \quad (2)$$

where χ_A is the susceptibility calculated from Eq.(1), J' is the intercluster-exchange constant, and z is the number of interacting nearest neighbors. Table 4 lists the magnetic parameters estimated from the least-squares fit of magnetic data for 1, and the value of $2zJ'$ is -0.36cm^{-1} . The χ_A vs. T (K) curve of 2 shows a peak near 40K and a decrease at a lower temperature (Fig. 5), indicating an antiferromagnetic interaction within the dinuclear complex of 2. A similar magnetic behavior was observed for complex 3 (Fig. 6). The magnetic parameters estimated from the best fit of the χ_A values to Eq. 1 for 2 and

Table 4 Magnetic parameters of 1, 2, and 3

Complex	g	$2J$ (cm^{-1})	N_{α} (emu mol^{-1})	p (%)
1	2.15	7.8	0.0001	0.10
2	2.06	-29.2	0.0002	0.11
3	1.98	-27.8	0.0001	0.16

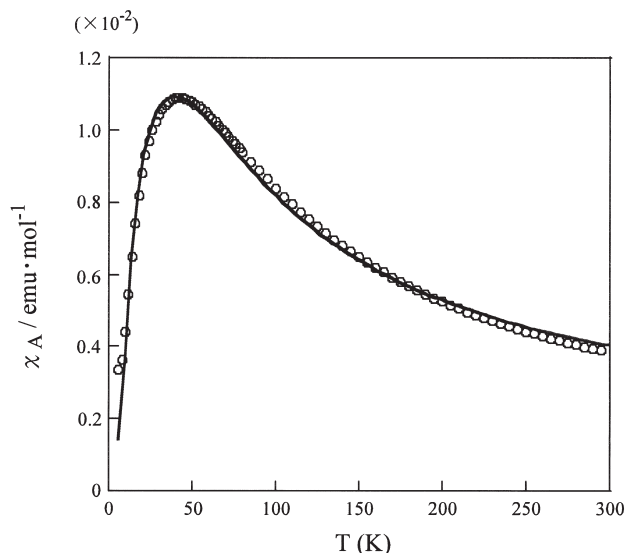


Fig. 5 Magnetic susceptibility (○) as a function of temperature for 2. The solid lines are calculated from theory.

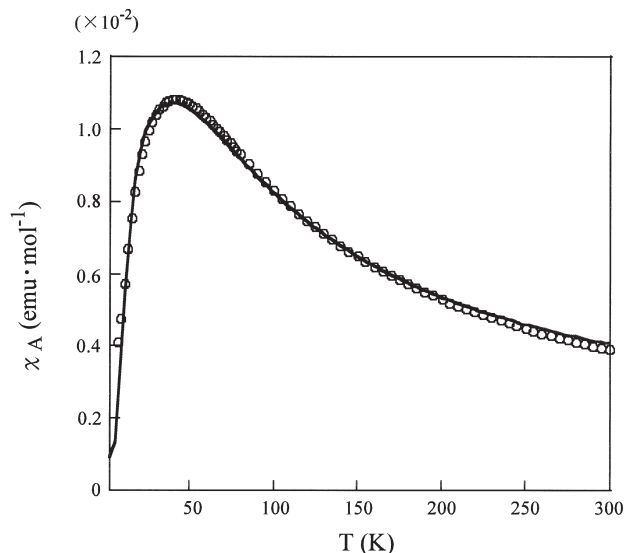


Fig. 6 Magnetic susceptibility (○) as a function of temperature for 3. The solid lines are calculated from theory.

3 are given in Table 4.

The difference in the magnetic properties of 1, 2, and 3 may be affected by the Ni(1)-O(1)-Ni(2) angles, which decrease in the order 1'(138.2(7)°) > 3' (135.09(8)°) > 2'(134.6(2)°). Further, the Ni...Ni distances may be correlated to the magnetic properties in these complexes (1'(3.785(4)) > 3'(3.730(1)) > 2'(3.69(9)) Å).

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