A Novel Polymer of a Binuclear Nickel(II) Complex Bridged By 1,3-Diaminopropane: Structure and Magnetism

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A novel polymer of a binuclear nickel(II) complex of $[Ni_2L(\mu\text{-}H_2N\text{-}(CH_2)_3\text{-}NH_2)_2 \cdot (H_2O)_2]_n \cdot (ClO_4)_n \cdot (H_2O)_n$ (where L = [2 + 2] condensation of 2,6-diformyl-4-methylphenol with 1,3-diaminopropane) has been synthesized and characterized. The crystal structure of the compound has been solved. The compound crystallizes in the monoclinic system, space group $P2_1/a$, with formula weight = 901.004, $a = 13.918(2)$ Å, $b = 18.111(3)$ Å, $c = 16.079(2)$ Å, $\beta = 103.46(3)°$, and $Z = 4$. The interesting feature of this compound is the bridging behavior of 1,3-diaminopropane in an end-to-end fashion. Nickel atoms are placed in a distorted octahedral environment. The magnetic properties of the compound have been studied by means of susceptibility measurement vs temperature, which reveals a moderately strong intramolecular antiferromagnetic coupling (*J*) of -30 ± 4 cm^{-1} and a weak intermolecular ferromagnetic coupling (*zJ'*) of 2 ± 1 cm^{-1}.

Introduction

Complexes of ligands which bind two or more metal centers in close proximity are important as potential catalysts,[1] as models for a number of metalloproteins,[2] and because of the opportunity they provide for the investigation of magnetic interactions. The study of macrocyclic ligands and their complexes has for many years been a very active area of research interest which continues to expand.[3] The structural and magnetic properties of binuclear and polymetallic nickel-(II) complexes with various bridging ligands have received considerable attention in the past three decades. Though a large number of bimolecular and polymeric nickel(II) complexes with different bridging ligands have been reported in the literature, no specific magneto−structural correlation has evolved as yet. A few interesting trends have, however, emerged. For example, monodimensional nickel(II) complexes with various bridging ligands such as carboxylato derivatives,[4] oxalato derivatives,[5] nitrido,[6] halides,[7] cyanide,[8] and thiocyanato[9] ligands have been synthesized and well characterized by both X-ray crystallography and susceptibility measurements, most of which reveal the presence of antiferromagnetic coupling. Despite such general observations, a few coupled Ni(II) systems have been found to give rise to ferromagnetic coupling.[10−12] As is well-known, the azido ligand stabilizes either end-on or end-to-end coordination modes when it links two nickel(II) centers, giving ferro-[13−16] or antiferromagnetic[17−20] interactions, respectively, subject to certain restrictions on bond angles, torsion angles, and Ni−N bond distances.[21] Antiferromagnetic behavior has also been observed for the phenoxide-bridged macrocyclic binuclear nickel(II) complexes derived from [2 + 2] condensation of 2,6-diformyl-4-methylphenol with 1,3-diaminopropane or its 2-hydroxy derivative.[22−24] Though in the case of planar dihydroxo-bridged copper(II) complexes a linear relationship

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exists between the value of J and the Cu−O−Cu bridge angle,[25] a similar magneto−structural correlation has not been found in nickel(II) complexes because a large number of structural parameters seem to affect the superexchange mechanism in these systems. Furthermore, nickel(II) is known to have a large single-ion zero-field splitting, which tends to complicate the χ vs T curves.

Recently we have drawn our attention to the study of interactions between the paramagnetic metal ions in coupled systems, including polymeric and linear chains, especially the study of strong interactions between metal ions relatively far away from each other through the extended bridging ligand.[26] Here, we report the interesting crystal structure and magnetic properties of a new polymer of a binuclear nickel(II) complex of formula $[Ni_2L(\mu\text{-}H_2N\text{-}(CH_2)_3NH_2)_2\cdot(H_2O)_2]_n\cdot(ClO_4)_n\cdot(H_2O)_n$ (L = [2 + 2] condensation of 2,6-diformyl-4-methylphenol with 1,3-diaminopropane) where the diaminopropane ligand bridged in an end-to-end fashion (similar to azide ion bridges in binuclear nickel(II) complexes) is described. We have also made an attempt to compare the magnetic susceptibility of this polymeric binuclear nickel(II) complex with magnetic susceptibilities observed in other octahedrally coordinated binuclear nickel(II) systems to determine the influence of some structural parameters on the strength of the exchange coupling. To the best of our knowledge this is the first report of 1,3-diaminopropane acting as a bridging ligand with nickel(II) atoms providing an opportunity to study the magnetic exchange interactions.

Experimental Section

Caution! Perchlorate complexes of metal ions are potentially explosive. Only a small amount of material should be prepared, and it should be handled with caution.

Synthesis of the New Complex. A mixture of 2,6-diformyl-4-methylphenol (2 mmol, 0.328 g), NaOH (2 mmol, 0.080 g) and water (5 mL) was ground to a paste in a mortar. This was slowly added with stirring to boiling water (50 mL). When a clear yellow solution was obtained, a second solution of $Ni(ClO_4)_2\cdot6H_2O$ (2.5 mmol, 0.9143g) and 1,3-diaminopropane (5 mmol, 0.42 mL) in water (50 mL) was added to the first solution and boiled. The resulting deep green solution was allowed to concentrate on a hot plate. When the volume of the solution had been reduced to 25 mL, it was filtered hot. The filtrate was allowed to cool at room temperature, and green microcrystals were obtained and vacuum-dried (yield: quantitative).

Physical Measurement. The magnetic susceptibility of a finely powdered sample was measured by using a Métronique MSO3 SQUID magnetometer in the temperature range 220−2 K with applied field of 1 T. The contribution of the sample holder was determined separately in the same temperature ranges and fields. Diamagnetic corrections were estimated from Pascal's constants. The IR spectrum was recorded on a Bruker IFS66V FTIR spectrometer as KBr pellets in the 4000−400 cm^{-1} region.

Crystal Data Collection and Refinement. Green crystals of $[Ni_2L(\mu\text{-}H_2N(CH_2)_3NH_2)_2\cdot(H_2O)_2]_n\cdot(ClO_4)_n\cdot(H_2O)_n$ suitable for X-ray diffraction studies were obtained by slow evaporation of an aqueous solution of the complex. The diffraction intensities of an approximately $0.3 \times 0.2 \times 0.2$ mm crystal were collected using an Enraf-Nonius CAD4 single-crystal diffractometer with Mo Kα radiation (0.710 73 Å). The cell parameters were obtained by the method of short vectors followed by least-squares refinement of 25 randomly chosen higher

Table 1. Crystal Data and Structure Refinement for **1**

empirical formula	$C_{27}H_{48}Cl_2N_6Ni_2O_{16}$
fw	901.004
temp	293(2) K
wavelength (λ)	0.710 73 Å
cryst syst	monoclinic
space group	$P2_1/a$ (No.14)
unit cell dimens	$a = 13.918(2)$ Å, $b = 18.111(3)$ Å,
	$c = 16.079(2)$ Å
	$\alpha = 90°, \beta = 103.46(3)°, \gamma = 90°$
vol	3941.6(10) Å^3
Z	4
density (calcd)	1.518 g cm^{-3}
abs coeff (μ)	11.63 cm^{-1}
$R(F_0)$	R1 = 0.0474, wR2 = 0.1093
$R_w(F_0^2)$	R1 = 0.1051, wR2 = 0.1342

angle reflections. The stability of the crystal during data collection was checked by monitoring the intensities of two standard reflections after every 1 h of data collection. No significant variation of intensity could be noted. The intensity data were corrected for Lorentz, polarization, decay, and absorption (ψ-scan) effects using the computer program MolEn.[27] A total of 6909 reflections were collected in the range $2° > 2\theta < 50°$ of which 3990 reflections with $I > 2\sigma(I)$ were used for the structure determination. The structure was solved by direct methods using the computer program SHELXS-86[28] and refined using the program SHELXL-93.[29] All hydrogen atoms could be located in the Fourier map. The structure was refined by a full-matrix least-squares technique to find the results $R(F) = 0.0474$ and $R_w(I) = 0.1093$, respectively, using the weighting scheme

$$R(F) = \sum ||F_o| - |F_c||/\sum F_o$$

$$R_w(I) = [\sum [w[|F_o|^2 - |F_c|^2]]^2/\sum (w|F_o|^2)]^{1/2}$$

where

$$w = 1/[\sigma^2(F_o^2) + (0.066P)^2 + 2.6P]$$

$$P = (Max(F_o^2, 0) + 2F_c^2)/3$$

The final difference map was featureless. A summary of the crystal and diffraction data is given in Table 1 and atomic coordinates are given in Table 2.

Results and Discussion

IR Spectra. The interest of the IR spectra of the titled compound lies mainly in the bands due to coordinated water, an amino group, and the formation of a macrocycle. The formation of a macrocycle is confirmed by the absence of carbonyl stretching frequency from the reactant and the presence of a strong band in the 1634 cm^{-1} region due to the imine (−CH=N) stretching frequency. A broad signal centered at around 3500 cm^{-1} has been observed. Apparently it corresponds to the stretching vibration for the mixed form of coordinated and uncoordinated water and a primary amine group. The stretching frequency at around 2925 cm^{-1} corresponds to an aliphatic C−C stretch. The feature at 1553 cm^{-1} corresponds to an aromatic C−O stretch.

Crystal Structure. The structure consists of a polymeric chain of dimers intramolecularly bridged by a phenoxide oxygen atom and intermolecularly bridged by 1,3-diaminopropane. The

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Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for **1**[a]

atom	x	y	z	U(eq)
Ni(1)	814(1)	5577(1)	−101(1)	40(1)
Ni(2)	4015(1)	5179(1)	5281(1)	47(1)
Cl(1)	444(1)	3927(1)	3626(1)	88(1)
Cl(2)	5028(1)	4433(1)	−1520(1)	73(1)
O(1)	320(2)	4541(2)	−499(2)	42(1)
O(2)	−263(2)	6019(2)	−1235(2)	55(1)
O(3)	5009(2)	5674(2)	4715(2)	48(1)
O(4)	4963(2)	5544(2)	6527(2)	61(1)
O(5)	−271(4)	3452(4)	3745(6)	185(3)
O(6)	1218(6)	3506(5)	3573(8)	246(5)
O(7)	157(5)	4408(3)	2933(3)	139(2)
O(8)	700(11)	4346(5)	4334(4)	299(7)
O(9)	4463(5)	3893(3)	−1263(5)	157(3)
O(10)	4434(4)	5041(3)	−1838(3)	123(2)
O(11)	5453(5)	4177(4)	−2185(4)	144(2)
O(12)	5798(4)	4658(4)	−843(4)	155(3)
O(13)	5656(5)	2526(3)	1525(4)	147(2)
O(14)	7476(7)	2209(6)	2563(8)	327(8)
O(15)	9741(6)	1326(3)	612(4)	171(3)
O(16)	9625(6)	1991(3)	2913(4)	166(3)
N(1)	1834(3)	5529(2)	−826(2)	46(1)
N(2)	1017(3)	6636(2)	295(2)	45(1)
N(3)	1796(3)	5090(2)	953(2)	47(1)
N(4)	3202(3)	4787(2)	4088(2)	51(1)
N(5)	3287(3)	6146(3)	5298(2)	61(1)
N(6)	3249(3)	4538(3)	5951(2)	56(1)
C(1)	717(3)	4052(3)	−921(3)	41(1)
C(2)	334(3)	3330(3)	−1063(3)	44(1)
C(3)	770(4)	2820(3)	−1526(3)	51(1)
C(4)	1582(4)	2986(3)	−1841(3)	53(1)
C(5)	1952(4)	3691(3)	−1693(3)	50(1)
C(6)	1550(4)	4233(3)	−1248(3)	48(1)
C(7)	2029(5)	2430(3)	−2342(4)	71(2)
C(8)	2036(4)	4950(3)	−1201(3)	49(1)
C(9)	2431(5)	6187(3)	−914(4)	72(2)
C(10)	2588(7)	6709(5)	−154(8)	133(4)
C(11)	1747(4)	7091(3)	10(4)	65(2)
C(12)	1964(4)	5422(3)	1813(3)	49(1)
C(13)	2481(4)	4909(3)	2525(3)	48(1)
C(14)	2769(5)	5297(4)	3397(3)	60(2)
C(15)	5067(4)	6368(3)	4494(3)	49(1)
C(16)	5804(4)	6616(3)	4072(3)	54(1)
C(17)	5824(5)	7354(4)	3837(4)	67(2)
C(18)	5174(5)	7879(3)	3989(4)	67(2)
C(19)	4483(5)	7638(4)	4402(4)	70(2)
C(20)	4383(4)	6907(3)	4656(3)	55(1)
C(21)	5220(7)	8680(4)	3691(5)	93(2)
C(22)	3563(4)	6759(4)	5053(3)	61(2)
C(23)	2403(6)	6162(5)	5674(5)	81(2)
C(24)	2492(6)	5660(5)	6428(5)	93(3)
C(25)	2391(4)	4862(4)	6219(4)	73(2)
C(26)	489(4)	6965(3)	740(3)	50(1)
C(27)	3454(4)	3855(4)	6127(3)	66(2)

[a] U(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

chain is isolated by ClO_4^- anions and water molecules which are found in the interchain space. There are two perchlorate anions and four water molecules present in each dimeric unit. Hydrogen bonds between the perchlorate group and water molecules and between water molecules are present. An ORTEP representation of one dimeric unit of the chain is shown in Figure 1, and selected interatomic distances and angles relevant to the nickel coordination sphere are given in Table 3.

The structure consists of crystallographically inequivalent nickel(II) dimers which are intermolecularly bridged by diaminopropane ligands in an end-to-end fashion. In each dimer nickel(II) centers are coordinated by two phenoxide oxygen atoms and two imino nitrogen atoms completing the NiN_2O_2 basal plane. Each of the nickel(II) atoms achieves a distorted
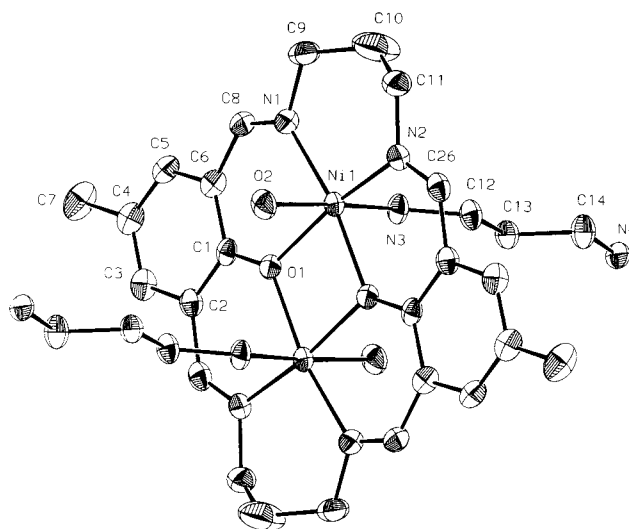
Figure 1. ORTEP representation (30% probability thermal ellipsoids) of the repeat unit of the polymeric complex $[Ni_2L(\mu\text{-}H_2N(CH_2)_3NH_2)_2 \cdot (H_2O)_2]_n \cdot (ClO_4)_n \cdot (H_2O)_n$.

Table 3. Selected Bond Distances (Å) and Angles (deg) for $[Ni_2L(\mu\text{-}H_2N\text{-}(CH_2)_3NH_2)_2 \cdot (H_2O)_2]_n \cdot (ClO_4)_n \cdot (H_2O)_n$[a]

Bond Distances					
Ni1−O1	2.050 (3)	Ni1−N2	2.020(4)	Ni2−O3	2.033(3)
Ni1−O1 #1	2.044(3)	Ni1−N3	2.108(3)	Ni2−N4	2.111(4)
Ni1−O2	2.221(3)	Ni1−Ni1 #1	3.156(1)	Ni2−Ni2 #2	3.148(1)
Ni1−N1	2.038(4)	Ni1−Ni2	8.79(4)	Ni2−O4	2.226(3)

Bond Angles			
O1−Ni1−O2	87.73(13)	O3−Ni2−O4	87.07(12)
O1−Ni1−N1	90.58(14)	O3−Ni2−N5	91.1(2)
O1−Ni1−N2	168.56(15)	O3−Ni2−N6	168.3(14)
O1−Ni1−N3	88.57(14)	O3−Ni 2−N4	91.00(2)
O1−Ni1−O1 #1	79.15(14)	O3−Ni 2−O3 #2	79.3(2)
Ni1−O1−Ni1 #1	100.85(12)	Ni2−O3−Ni2 #2	100.7(12)
Ni1−N3−C12	121.0(3)	Ni2−N4−C14	121.2(2)

[a] Symmetry transformations used to generate equivalent atoms: #1 = −x, −y + 1, −z; #2 = −x + 1, −y + 1, −z + 1.

octahedral configuration through the axial coordinations of water and the diaminopropane ligand, which are *trans* to each other. The interesting feature of this structure is that the diaminopropane not only acts as an axial ligand but also bridges the two crystallographically inequivalent dimers. Each dimer has a centrosymmetric structure with a center of inversion at the middle of the Ni_2O_2 plane. The macrocyclic donor atoms (from two N and two O atoms, making it a N_2O_2 plane) form an exact plane within 0.027 Å from which the nickel atom is displaced above and below by 0.079 Å. The intradimer distance between two nickel atoms Ni1−Ni1' was found as 3.156(1) Å with a bridge angle (Ni1−O1−Ni1') of 100.9 (2)°. However, the distance between two nickel atoms Ni1−Ni2 bridged by diaminopropane was found equal to 8.79(2) Å, which is too long compared to the earlier reported octahedral nickel(II) complexes with various bridging ligands.[6,11] The long bond distance observed is due to the increased chain length of saturated diaminopropane. Moreover, the presence of perchlorate anion and water molecules which lie above and below the chain can also lead to the observed long distance between the nickel atoms. The bond distance involving axial ligands Ni−O and Ni−N are not equal. The Ni−O distance 2.225(4) Å of Ni−OH$_2$ is rather long compared to the range 2.04−2.16 reported for various *trans*-aqua octahedral nickel(II) complexes.[30] Similarly in Ni−NH$_2$−(CH$_2$)$_3$NH$_2$ the Ni−N bond distance of 2.12(4) Å is also long compared to the range 2.03− 2.08 reported for various nitrogen-containing ligands which are

axially coordinated to the octahedral nickel(II) atoms.[31] The bridging behavior of diaminopropane gives a chain of dimers that propagate in the *ac* diagonal plane, depicted in Figure 2.

Magnetic Susceptibility. Variable temperature magnetic susceptibility measurements were performed on a finely powdered sample of the title compound between the temperatures 226 and 2 K. There is no exact mathematical expression to evaluate the susceptibility of such a complicated $S = 1$ system. Thus, we have applied the Ginsberg et al.[10] dimer model to evaluate the susceptibility. This model takes into consideration intradimer exchange (J), zero-field splitting (D), and also an interdimer exchange interaction (zJ'). The spin Hamiltonian (eq 1) includes these terms, and the resulting susceptibility equation

$$\mathcal{H} = -2J\hat{s}_1 \cdot \hat{s}_2 - D(\hat{s}_1^2 + \hat{s}_2^2) - 2zJ'\hat{s}_i\langle\hat{s}_i\rangle - g_i\beta H\hat{s}_i \quad (1)$$

for χ (g, J, D, zJ') derived by Ginsberg et al. has been modified to account for monomeric impurity [ρ represents the fraction of a possible magnetically dilute mononuclear nickel(II) impurity] and temperature independent paramagnetism (N_α). The final equation used to fit the susceptibility is given in eq 2.

$$\chi_M = \chi(g, J, D, zJ')(1 - \rho) + 2N\beta^2 g^2\rho/3kT + N_\alpha \quad (2)$$

$$\chi = Ng^2\beta^2/3k\left\{\frac{F_1(J, D, T)}{T - 4ZJ'F_1(J, D, T)} + \frac{2F'(J, D, T)}{1 - 4ZJ'F'(J, D, T)}\right\}$$

$$F_1(J, D, T) = \{1 + e^{4J/(kT)} + 4e^{4J/(kT)}e^{D/(kT)}\}/\{2 + e^{D/(kT)} + e^{J/(kT)}e^{-\delta/(kT)} + e^{J/(kT)}e^{\delta/(kT)} + 2e^{4J/(kT)} + 2e^{4J/(kT)}e^{D/(kT)}\}$$

$$F'(J, D, T) = \frac{1}{D}F_2(J, D, T) + \frac{3C_2^2}{3J - \delta}F_3(J, D, T) + \frac{3C_1^2}{3J + \delta}F_4(J, D, T)$$

$$F_2(J, D, T) = \{2e^{4J/(kT)}e^{D/(kT)} + e^{D/(kT)} - 1 - 2e^{4J/(kT)}\}/\{2 + e^{D(kT)} + e^{J/(kT)}e^{-\delta/(kT)} + e^{J/(kT)}e^{\delta/(kT)} + 2e^{4J/(kT)} + 2e^{4J/(kT)}e^{D/(kT)}\}$$

$$F_3(J, D, T) = \{e^{4J/(kT)} - e^{J/(kT)}e^{\delta/(kT)}\}/\{2 + e^{D/(kT)} + e^{J/(kT)}e^{-\delta/(kT)} + e^{J/(kT)}e^{\delta/(kT)} + 2e^{4J/(kT)} + 2e^{4J/(kT)}e^{D/(kT)}\}$$

$$F_4(J, D, T) = \{e^{4J/(kT)} - e^{J/(kT)}e^{-\delta/(kT)}\}/\{2 + e^{D/(kT)} + e^{J/(kT)}e^{-\delta/(kT)} + e^{J/(kT)}e^{\delta/(kT)} + 2e^{4J/(kT)} + 2e^{4J/(kT)}e^{D/(kT)}\}$$

$$\delta = [(3J + D)^2 - 8JD]^{1/2}$$

$$C_1 = 2\sqrt{2}D/[(9J - D + 3\delta)^2 + 8D^2]^{1/2}$$

$$C_2 = (9J - D + 3\delta)/[(9J - D + 3\delta)^2 + 8D^2]^{1/2}$$

A nonlinear least-squares fitting of the theoretical expression given in eq 2 to the experimental data by using a computer program SUSCEP.FOR[32] gives a moderately strong intramo-
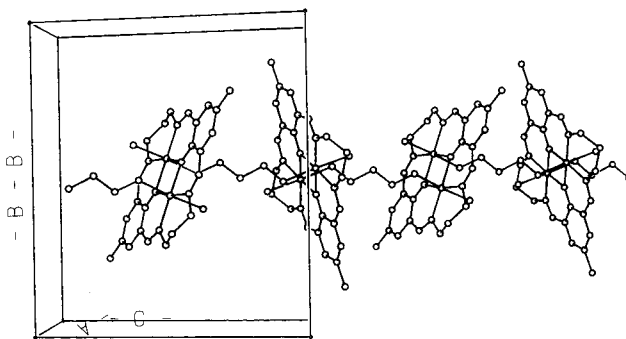
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Figure 2. Unit cell packing of the polymeric complex [Ni$_2$L(μ-H$_2$N(CH$_2$)$_3$NH$_2$)$_2$·(H$_2$O)$_2$]$_n$·(ClO$_4$)$_n$·(H$_2$O)$_n$. (For clarity the perchlorate ion and the uncoordinated water molecules have not been shown.)

lecular antiferromagnetic coupling (J) of -30 (± 4) cm^{-1}, the weak intermolecular ferromagnetic coupling (zJ') of 2.0 (± 1) cm^{-1}, a zero-field splitting parameter (D) of 1.3 (± 0.04), $g = 2.16$, $N_\alpha = 4.00 \times 10^{-4}$, and $\rho = 0.040$. The least-squares error (R) is 1.82×10^{-4}. Our results are compared with the earlier reported values for similar types of binuclear nickel(II) complexes; the comparison is given in Table 4.

A plot of effective magnetic moment versus temperature is given in Figure 3. The observed and calculated magnetic moment μ_{eff} decreases from a value of 4.64 μ_B at 226 K to a minimum of 2.12 μ_B at 2.42 K; however, before getting to the minimum moment at 2.42 K, there is a saddle point around 25 K. The increase in magnetic moment is noted contrary to the expectation that it should drop to a constant value at lower temperatures in the case of an antiferromagnetically coupled system. Sometimes such an increase could happen either due to a large contribution from a paramagnetic impurity fraction or due to a substantial contribution from ferromagnetic coupling. The first possibility can be ruled out because highly crystalline specimens with satisfactory analytical data were used for the magnetic susceptibility measurements. It seems that in the lower temperature regions there is a substantial contribution from ferromagnetic coupling; however, the origin of ferromagnetic coupling is not clear at this stage. One suggestion is that it may be due to a long-range interaction mediated through the crystal lattice as revealed by the molecular structure of the complex, which shows an extensive network of diaminopropane ligands bridging the two crystallographically inequivalent dimeric units. It is extremely gratifying to note the good agreement between calculated and experimental values as evidence for the above said proposition.

Magnetostructural Correlations. The exchange interactions between paramagnetic transition metal ions propagated through azido bridges are strongly dependent on the bridging mode of the N$_3^-$ ion. A reasonably good amount of work on Ni(II) complexes with various bridging modes (both end-on and end-to-end) of azide ions have been studied extensively by Escuer et al.[16,21,33,34] They have correlated the exchange coupling constant with structural parameters like Ni–N distance, Ni–N–N angle, and Ni–NNN–Ni torsion angle. But in the case of our system, the behavior of the Ni (μ-H$_2$N(CH$_2$)$_3$NH$_2$)Ni core is more difficult to predict. However, as can be seen in Table 4, the compounds studied earlier, viz., **2–4**, and the title compound **7** have a common characteristic Ni–Ni bond distance of $\sim$3.1 Å, a Ni–O–Ni bridge angle of 100 $\pm 1°$, and a common

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Table 4. Magnetic and Structural Parameters for Octahedrally Coordinated Binuclear and Polynuclear Ni(II) Complexes

no.	compd[a]	Ni−Ni (Å)	Ni−O−Ni (deg)	J (cm^{-1})	zJ' (cm^{-1})	g	D (cm^{-1})	ref
1	[Ni$_2$(tren)$_2$(N$_3$)$_2$](BPh$_4$)$_2$	5.220		−35.1	0.35	2.32	6.8	17
2	[Ni$_2$(H$_2$L1)(H$_2$O)$_2$Cl$_2$]·2H$_2$O	3.100	101.5	−27.0				23
3	[L'Ni$_4$(OH)(CH$_3$O·H·OCH$_3$)(N$_3$)$_2$(H$_2$O)$_2$]	3.058	99.9	−28.5				24
4	[Ni$_2$L''(NCS)$_2$(H$_2$O)$_2$]·2Me$_2$NCHO	3.105	99.2	−21.3	2.0	2.19	1.9	35
5	[Ni$_2$(Me$_2$Cyclen)$_2$Ox](ClO$_4$)$_2$·2H$_2$O	5.465		−34.0		2.30		36
	[Ni$_2$(Cyclen)$_2$Ox](NO$_3$)$_2$			−35.0		2.15		
6	[Ni$_2$L$_2$^{1}(H$_2$O)$_2$Ox][NO$_3$]$_2$·2H$_2$O			−25.5		2.10		37
7	[Ni$_2$L(μ-H$_2$N(CH$_2$)$_3$NH$_2$)$_2$·(H$_2$O)$_2$]$_n$·(ClO$_4$)$_n$·(H$_2$O)$_n$	3.156	100.8	−30	2.0	2.16	1.0	this work

[a] tren = 2,2′,2″-triaminotriethylamine; H$_2$L1 = [2 + 2] condensation of 2,6-diformyl-4-methylphenol with 1,3-diamino-2-hydroxypropane; L′ = [2 + 2] condensation of 2,6-diformyl-4-methylphenol with 2,6-bis(aminomethyl)-4-methylphenol; L″ = [2 + 2] condensation of 2,6-diformyl-4−methylphenol with 1,3-diaminopropane. N$_3$ = azide anion; Me$_2$cyclen = 1,7-dimethyl-1,4,7,10-tetraazacyclododecane; Cyclen = 1,4,7,10-tetraazacyclododecane; Ox = oxalate anion; L$_2$1 = 1,4,7-triazacyclononane; L = [2 + 2] condensation of 2,6-diformyl-4-methylphenol with 1,3-diaminopropane.
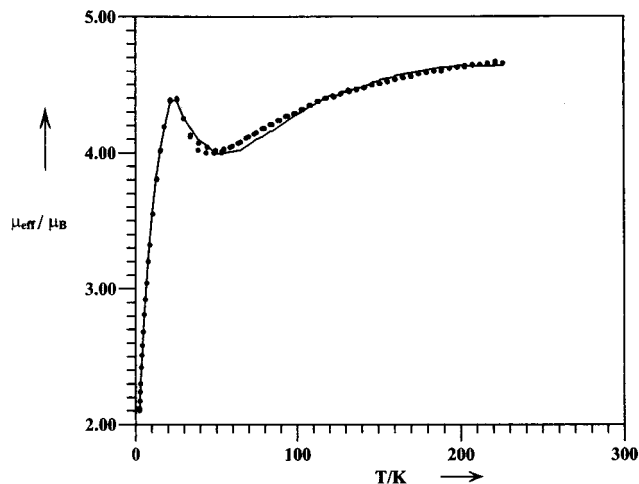

Figure 3. Temperature variation of the magnetic moment of the complex [Ni$_2$L(μ-H$_2$N(CH$_2$)$_3$NH$_2$)$_2$·(H$_2$O)$_2$]$_n$·(ClO$_4$)$_n$·(H$_2$O)$_n$ with dots representing the experimental data and the line representing the theoretical simulation using the expression in eq 2

least-squares plane around Ni(II), namely, N$_2$O$_2$; accordingly all are reported to be antiferromagnetic[23,24,35] to the extent of $-J \sim 25$ cm^{-1}. This, in essence, should explain the nature and magnitude of exchange coupling in the title compound with the superexchange pathway being dominated by the $d_{x^2-y^2}$ orbital and p$_x$ and p$_y$ orbitals of oxygen of the ^{3}A$_{1g}$ ground state of this nominally octahedral Ni(II) coordination, while the origin of ferromagnetism between the dimers should be through the d_{z^2} orbital. It is worth mentioning at this point that a similar chainlike dimer [Ni(N$_3$)$_2$(2,2-dimethylpropane-1,3-diamine)]$_n$ has been reported[38] where the dimers are linked by the bridging azides. Although in this compound a long-range magnetic ordering with a net magnetic moment (canting) has been reported, our compound shows no such property in view of the fact that variable temperature susceptibility could be fitted well with eq 2 with moderately strong antiferromagnetic coupling and weak interdimer ferromagnetic coupling. No evidence is available for canting.

In conclusion, we have synthesized a novel polymer of a binuclear nickel(II) complex intramoleculariy bridged by phenoxide oxygen and intermolecularly bridged by 1,3-diaminopropane, a rare bridging mode. This is the first report of 1,3-diaminopropane acting as a bridging ligand with nickel atoms. The distance between two dimers which are bridged by 1,3-diaminopropane is found to be 8.79 Å. This distance is somewhat longer than the earlier reported distances of binuclear nickel(II) systems. In addition to moderately strong intramolecular antiferromagnetic interaction, a weak ferromagnetic coupling was also observed. The present work has provided an additional bridging mode for inclusion in future considerations.

Supporting Information Available: Tables listing crystal data and details of the structure determination, atomic positional and thermal parameters, anisotropic thermal parameters, and full bond distances and bond angles (9 pages). Ordering information is given on any current masthead page.

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