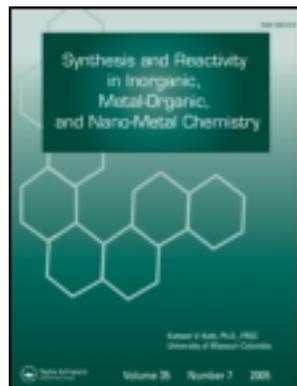


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Synthesis and 1-D Double Line Supramolecular Structure of a Ni(II) Complex with N-alkylated Dien

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A novel N-alkylated diethylenetriamine ligand $L \cdot 3HCl$ ($L=N$, N'-bis(4-methoxybenzyl)-diethylenetriamine) and its mononuclear Ni(II) complex $[Ni(L)phenCl]ClO_4$ (**1**) (phen = o-phenanthroline) were synthesized and spectroscopically characterized. X-ray analysis indicates that octahedral geometry of the Ni(II) center is finished by three N atoms of dien moiety of the ligand in meridional fashion, two N atoms of phen and one Cl anion. Along the a axis, the neighboring molecules are connected via hydrogen bonds involving ClO_4^- anions and N-H groups of the ligands, thus forming a 1-D linear structure which is further connected to the other symmetry-related line via $\pi \cdots \pi$ stacking interactions of phen rings. The steric effect related to the molecular structure of L has been discussed.

Keywords 1-D double line supramolecular structure, N-alkylated diethylenetriamine, Ni(II) complex, steric effect

INTRODUCTION

Great efforts have been devoted to the research of transition metal coordination compounds of dien(diethylene triamine) (Hynes et al., 1996; Mukherjee et al., 1994). Dien ligand has three coordination atoms which often coordinate metal center in facial or meridional fashion, thus forming stable tridentate chelate structure. There exist a wide range of applications of the transition metal coordination compounds of dien in the template synthesis of new compounds, preparation of low dimensional materials (Zheng et al., 1999). N-alkylation of dien can modify the structures and properties of the

corresponding complexes, due to the steric hindrance and electronic effect induced by the modification. Herein, we synthesized a novel derivative of dien ligand $L \cdot 3HCl$ ($L=N$, N'-bis(4-methoxybenzyl)-diethylenetriamine) and its mixed ligand complex $[Ni(L)phenCl]ClO_4$ (**1**) (phen = o-phenanthroline).

The self-assembly of supramolecular coordination assemblies has also caused extensive interest in recent years (Xie et al., 2003; Munakata et al., 1996; Dai et al., 1997). The amine groups in L and the ClO_4^- counteranions can act as donors and acceptors of hydrogen bonding, while the ring of phen can be involved in $\pi \cdots \pi$ stacking interactions. Thus, in the crystal structure of complex **1**, a double line 1-D supramolecular structure is formed by multiple hydrogen bonds and $\pi \cdots \pi$ stacking interactions. The steric hindrance concerning the modification of dien is discussed.

EXPERIMENTAL

Materials and Physical Measurements

All of the solvents and raw materials were analytical grade and used as received without further purification.

I.R. spectra were recorded on a Bruker Vector-22 spectrometer (KBr Disc.). The 1H NMR measurements were carried out on a Bruker 300 ultrashield NMR spectrometer in D_2O (99.85%). Elemental analyses (C, H and N) were performed on Elementar Vario EL-III elemental analyzer. Electronic spectra were measured by a UV-2401PC spectrophotometer in DMSO.

Preparation of $L \cdot 3HCl$ ($L=N$, N'-bis(4-methoxybenzyl)-diethylenetriamine)

To the methanol solution of 4-methoxy-phenylaldehyde (10.0 g, 0.073 mol) was added diethylenetriamine (3.8 g, 0.037 mol). After stirring for one day, KBH_4 (4.6 g) was added in small portions to the yellow-orange solution. The solution gradually faded to nearly colorless. Two hours later, the pH of the solution was adjusted to about 5 with

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hydrochloric acid, and then to about 9 with NaOH. After filtration, the resulting solution was concentrated in vacuo. The residue was extracted with water and CH_2Cl_2 . The CH_2Cl_2 layers were collected and dried overnight with Na_2SO_4 . After filtration, the resulting solution was concentrated in vacuo to give light yellow oily residue. Upon adding hydrochloric acid, a white solid precipitated, which was collected, washed with cold ethanol and dried. Yield: 10.1 g, 60.7%. Anal. Calc. for: $\text{C}_{20}\text{H}_{32}\text{N}_3\text{O}_2\text{Cl}_3$, C, 53.0; H, 7.1; N, 9.3%. Found: C, 52.7; H, 7.1; N, 9.6%. I.R. (KBr Disc, cm^{-1}): 2935(s), 2725(br, s), 2556(m), 2426(s), 1615(s), 1585(m), 1518(vs), 1451(m), 1303(m), 1254(vs), 1185(m), 1033(s), 972(w), 818(s), 757(w), 561(w), 532(w). ^1H NMR. (D_2O): 4.25 (4H, s, Ar- CH_2 -), 3.38–3.45 (8H, d, NH-(CH_2) $_2$ -NH), 7.05–7.45(8H, m, Ar-H), 3.85 (6H, s, - OCH_3).

Preparation of $[\text{Ni}(\text{L})\text{phenCl}]\text{ClO}_4$ (**1**)

To the methanol solution of $\text{L} \cdot 3\text{HCl}$ (0.181 g, 0.40 mmol) was added $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.146(g), 0.40 mmol) with continuous stirring, followed by addition of aqueous solution of NaOH (4N, 0.30 ml). After refluxing for 1 hour, phen

TABLE 1
Crystallographic data for **1**

Empirical formula	$\text{C}_{32}\text{H}_{37}\text{Cl}_2\text{N}_5\text{NiO}_6$
Formula weight	717.28
Temperature	291(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, P2 (1)/c
Unit cell dimensions	a = 8.9670(18) Å, $\alpha = 90^\circ$ b = 15.274(3) Å, $\beta = 92.22(3)^\circ$ c = 24.161(5) Å, $\gamma = 90^\circ$
Volume	3306.6(12) Å ³
Z, Calculated density	4, 1.441 $\text{Mg} \cdot \text{m}^{-3}$
Absorption coefficient	0.800 mm^{-1}
F(000)	1496
Crystal size	0.22 × 0.20 × 0.20 mm
θ range for data collection	1.58° to 24.00°
Index ranges	0 ≤ h ≤ 10, -17 ≤ k ≤ 17, -27 ≤ l ≤ 27
Reflections collected/unique	7680/4472 [R(int) = 0.0972]
Completeness to $2\theta = 24.00$	88.6%
Max. and min. transmission	0.8564 and 0.8437
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	4472/0/428
Goodness-of-fit on F ²	1.005
Final R indices [$I > 2\sigma(I)$]	$R_1^a = 0.0685$, $wR_2^b = 0.1709$
R indices (all data)	$R_1^a = 0.0967$, $wR_2^b = 0.1844$
Extinction coefficient	0.0037(7)
Largest diff. peak and hole	0.620 and -0.697 $\text{e} \cdot \text{Å}^{-3}$

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|; ^b wR_2 = \sum ||F_o| - |F_c|| w^{1/2} / \sum |F_o| w^{1/2}.$$

(0.079 g, 0.40 mmol) was added. Two hours later, the residue was filtered off. The resulting light green solution was concentrated in vacuo and left undisturbed at room temperature for two weeks, yielding light green crystals suitable for X-ray diffraction analysis. Yield: 0.120 g, 41.8%. Anal. Calc. for $\text{C}_{32}\text{H}_{37}\text{Cl}_2\text{N}_5\text{NiO}_6$: C, 53.6; H, 5.2; N, 9.8%. Found: C, 53.9; H, 5.0; N, 9.6%. I.R. (KBr Disc, cm^{-1}): 3441(m), 3284(m), 2927(m), 2360(w), 1611(m), 1584(w), 1512(s), 1445(m), 1426(s), 1336(w), 1304(w), 1247(s), 1208(w), 1177(m), 1140(w), 1099(s), 1026(s), 996(w), 958(s), 919(w), 878(w), 840(s), 813(m), 754(w), 725(m), 622(s), 522(w), 424(w).

Crystallographic Data Collection and Refinement of the Structure

Single crystal of **1** was mounted on a glass-fiber. All measurements were made on a Rigaku RAXIS-IV image plate area detector with graphite monochromated Mo- $\text{K}\alpha$ radiation. The data were collected at 18 °C and corrected for Lorentz and polarization effects. The correction for secondary extinction was applied. The structure was solved by direct methods, and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on observed reflections ($I > 2.00\sigma(I)$) and variable parameters. All calculations were performed using SHELX-97 software package (Sheldrick, 1997). Crystallographic data for **1** are listed in Table 1. Selected bond lengths and angles for **1** are listed in Table 2.

RESULTS AND DISCUSSION

Spectroscopic Characterization of **1**

The medium band in the IR spectrum at 3284 cm^{-1} is related to $\nu(\text{NH})$ of the ligand, and two strong bands at 1099 cm^{-1} and 622 cm^{-1} are characteristic of uncoordinated ClO_4^- . Upon coordination, two obvious absorption bands for free phen at 1421 cm^{-1} and 853 cm^{-1} are each shifted upfield and downfield, i.e., to 1426 cm^{-1} and 840 cm^{-1} ,

TABLE 2
Selected bond lengths (Å) and bond angles (°) for **1**

Ni(1)-N(4)	2.069(5)	Ni(1)-N(2)	2.080(4)
Ni(1)-N(1)	2.122(4)	Ni(1)-N(5)	2.135(5)
Ni(1)-N(3)	2.183(5)	Ni(1)-Cl(1)	2.447(2)
N(4)-Ni(1)-N(2)	173.3(2)	N(4)-Ni(1)-N(1)	97.4(2)
N(2)-Ni(1)-N(1)	78.5(2)	N(2)-Ni(1)-N(5)	93.9(2)
N(4)-Ni(1)-N(5)	81.6(2)	N(2)-Ni(1)-Cl(1)	91.7(1)
N(1)-Ni(1)-N(5)	100.5(2)	N(1)-Ni(1)-Cl(1)	169.0(1)
N(4)-Ni(1)-N(3)	82.1(2)	N(5)-Ni(1)-Cl(1)	85.1(2)
N(2)-Ni(1)-N(3)	103.1(2)	N(3)-Ni(1)-Cl(1)	86.0(1)
N(1)-Ni(1)-N(3)	91.2(2)	N(5)-Ni(1)-N(3)	161.0(2)
N(4)-Ni(1)-Cl(1)	92.8(2)		

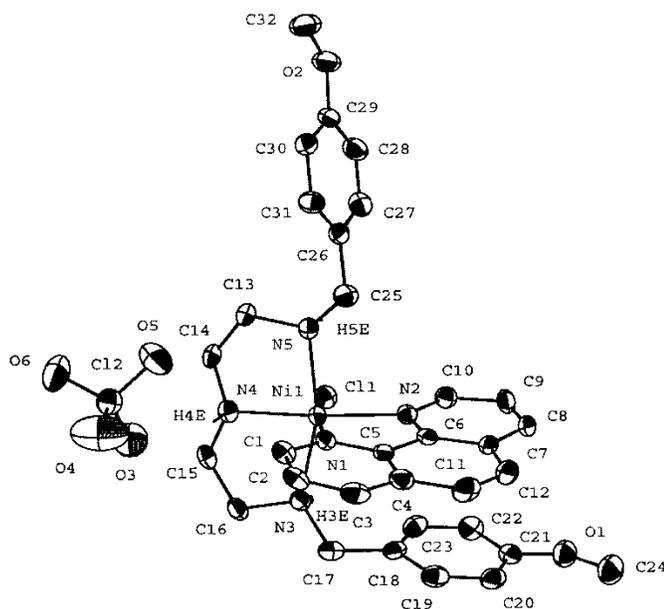


FIG. 1. ORTEP view of complex **1** at the 30% probability level.

respectively. For dien, there exist several rotation isomers, e.g., cis, trans, gauche(λ), gauche(δ); however, upon coordination, gauche isomers are most commonly observed (Kazuo, 1986). In contrast to free L, the appearance of one weak band of **1** at 919 cm^{-1} suggests that, when coordinated, two ethylenediamine moieties of L are both in gauche geometry (vide infra) (Kazuo, 1986).

In the electronic spectra of **1**, two weak bands located at 565 nm and 818 nm may be assigned to two d-d transitions of the octahedrally coordinated Ni(II) complex, ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, but, the third d-d transition for ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ is overlapped by other strong bands of higher energy.

Description of the Structure

X-ray diffraction analysis indicates that **1** consists of one $[\text{Ni}(\text{L}_4)\text{phenCl}]^+$ cation and one ClO_4^- anion (Figure 1). The Ni(II) center is situated in distorted octahedral coordination environment, which is composed of three N atoms of

dien moiety of the ligand in meridional fashion, two N atoms of phen and one Cl^- anion. The distortion can be evidenced by the relative small trans angles (about between $161 \sim 173^\circ$), very large variation of cis angles (about from 78° to 97°) and Ni(1)-N distances (from 2.08 to 2.18 Å) (Table 2). In **1**, two long Ni(1)-N bonds and one short Ni(1)-N bond are each corresponding to two terminal NH groups and one middle NH group of L. The difference of Ni(1)-N distances may be derived from the large steric hindrance of benzyl group, which may also cause three N atoms of dien moiety of L to coordinate to Ni(II) in meridional fashion in **1**. In contrast, the introduction of methyl group to the middle NH group of dien may favor three N atoms of dien in facial configuration as in $[\text{Ni}(\text{medien})(\text{NCS})(\mu\text{-SCN})]_n$ (medien = N-(2-aminoethyl)-N-methyl-1, 2-ethanediamine) (Nayak et al., 1998). The two bite angles of dien for Ni(II) center ($\text{N}(4)\text{-Ni}(1)\text{-N}(3) = 82.1(2)^\circ$, $\text{N}(4)\text{-Ni}(1)\text{-N}(5) = 81.6(2)^\circ$) are smaller than 90° is the result of steric constraints imposed by ethylene bridges, while that its trans angle is smaller than 180° is caused by steric constraint imposed by tridentate coordination mode of dien (Johns and Malik, 2002). Selected torsion angles of **1** are listed in Table 3.

Two torsion angles of dien, $\text{N}(5)\text{-C}(13)\text{-C}(14)\text{-N}(4)$ ($53.5(7)^\circ$) and $\text{N}(4)\text{-C}(15)\text{-C}(16)\text{-N}(3)$ ($-58.1(6)^\circ$), indicate that two ethylenediamine groups are each in gauche(λ) and gauche(δ) geometries respectively, i.e., $\lambda\delta$ geometry, which is consistent with that of the reported Ni(II) complex of dien (Johns and Malik, 2002). It is interesting that there exists strong intramolecular $\pi \cdots \pi$ stacking interaction in edge to edge fashion between one phenyl ring of L and phen ring, the shortest distance between carbon atoms of them being about 3.38 Å.

Along the a axis, 1D supramolecular structure, consisting of symmetry related double lines, is constructed (Figure 2). In each line, the adjacent molecules are connected through hydrogen bonds forming between ClO_4^- anions and N-H groups of the ligands (Table 4). It is worth noting that, like intramolecular aromatic stacking interaction (vide supra), obvious $\pi \cdots \pi$ stacking interactions in edge to edge fashion also occur between phen rings from intermolecular double lines where the shortest distance between carbon atoms of phen rings is about 3.44 Å.

TABLE 3
Selected torsion angles ($^\circ$) for **1**

C(25)-N(5)-C(13)-C(14)	-169.5(5)	Ni(1)-N(5)-C(13)-C(14)	-32.9(6)
C(15)-N(4)-C(14)-C(13)	-170.8(5)	Ni(1)-N(4)-C(14)-C(13)	-47.4(6)
N(5)-C(13)-C(14)-N(4)	53.5(7)	C(14)-N(4)-C(15)-C(16)	169.6(5)
Ni(1)-N(4)-C(15)-C(16)	46.2(6)	C(17)-N(3)-C(16)-C(15)	178.1(5)
Ni(1)-N(3)-C(16)-C(15)	39.4(5)	N(4)-C(15)-C(16)-N(3)	-58.1(6)
C(16)-N(3)-C(17)-C(18)	169.5(5)	Ni(1)-N(3)-C(17)-C(18)	-62.3(6)
N(3)-C(17)-C(18)-C(19)	147.4(6)	N(3)-C(17)-C(18)-C(23)	-34.9(8)

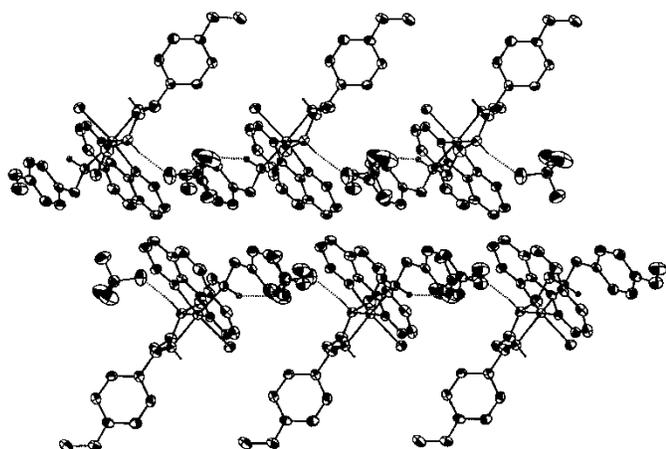


FIG. 2. View of 1-D supramolecular structure of **1** consisting of symmetry related double lines along the *a* axis.

TABLE 4
Hydrogen bond lengths (Å) and angles (°) for **1**

D-H	d(D-H)	d(H...A)	<DHA	d(D...A)	A (symmetry operations)
N4-H4E	0.85	2.32	149	3.07	O3
N3-H3E	0.93	2.60	148	3.41	O5 [x-1, y, z]

In conclusion, a novel derivative of dien and its mixed ligand mononuclear Ni(II) complex **1** were synthesized and characterized. Crystal structure research indicates that the Ni(II) center is coordinated by three dien N atoms of the ligand in meridional fashion, two phen N atoms and one Cl⁻ anion, thus forming distorted octahedral geometry. Along the *a* axis, 1D double line supramolecular structure is assembled via intermolecular hydrogen bonds and $\pi \cdots \pi$ stacking interactions. The steric effect concerning the molecular structure of **1** has also been discussed.

Supplementary Data

Crystal structure data of **1** have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number 244550. Copies of this information can be

obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

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