



A Bridged High-Spin Complex Bis-[Ni(II)(*rac*-5,5,7,12,12,14-hexamethyl- 1,4,8,11-tetraazacyclotetradecane)]-2,5- pyridinedicarboxylate Diperchlorate Monohydrate

ELENA V. BASIUK^{1*}, VLADIMIR V. BASIUK², JACOBO GOMEZ-LARA¹
and RUBEN ALFREDO TOSCANO¹

¹Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior C. U. A.
Postal 70-213, 04510 México, D.F., México;

²Instituto de Ciencias Nucleares, Universidad Nacional Autónoma de México, Circuito Exterior C.
U. A. Postal 70-543, 04510 México, D. F., Mexico

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Abstract. A bridged high-spin complex, bis-[Ni(II)(*rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)]-2,5-pyridinedicarboxylate diperchlorate monohydrate has been obtained by reaction of [Ni(II)(*rac*-5,5,7, 12,12,14-hexamethyl-1,4,8,11- tetraazacyclotetradecane)](ClO₄)₂ and 2,5-pyridinedicarboxylic acid in aqueous alkaline (NH₄OH) medium. C₃₉H₇₇Cl₂N₉Ni₂O₁₃, chemical formula weight 1068.42, orthorhombic, *P*2₁2₁2₁, *a* = 11.423(3) Å, *b* = 14.770(6) Å, *c* = 31.608(7) Å, $\alpha = \beta = \gamma = 90.00^\circ$, *V* = 5333(3) Å³, *Z* = 4, *D*_{calc} = 1.331 g cm⁻³, $\mu_{\text{calc}} = 0.869 \text{ mm}^{-1}$, *F*(000) = 2272, *T* = 293(2), *R* = 0.0870 for 2686 observed reflections [*I* > 2σ(*I*)]. The complex includes two folded [Ni(*rac*-Me₆[14]aneN₄)]²⁺ units having opposite diastereomeric configuration. They are bridged through a dianion of 2,5-pyridinedicarboxylic acid, with one Ni-atom coordinated to the O-atom of the 2-carboxylic group and the pyridine N-atom (forming a 5-membered chelate ring), and with the second Ni-atom coordinated to both O-atoms of the 5-carboxylic group (forming a 4-membered chelate ring). Hydrogen bonding involving macrocyclic NH groups, both 2- and 5-carboxylic groups, perchlorate anions and water molecules gives rise to the formation of an infinite supramolecular network in the title compound's crystals.

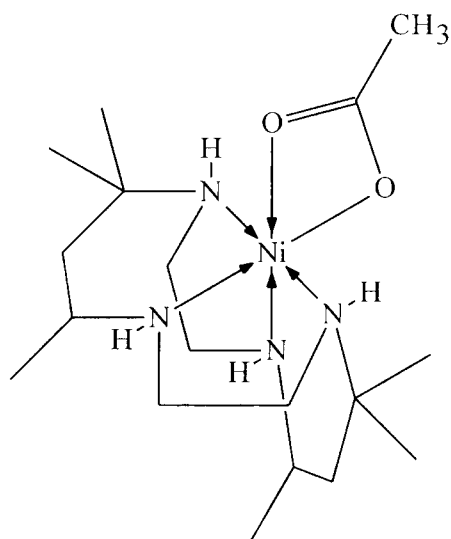
Key words: [Ni(*rac*-Me₆[14]aneN₄)], 2,5-pyridinedicarboxylate, preparation, crystal structure

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* Author for correspondence.

1. Introduction

Hexacoordinated octahedral high-spin complexes of nickel(II) are widely studied due to their structural features, magnetic and other physical properties (see, for example, recent works [1–10]). Especially interesting, from our point of view, and evidently less studied (although known for more than three decades) are tetraazamacrocyclic ‘Curtis-type’ Ni(II) complexes, where nitrogen donor atoms occupy four coordination sites, and the remaining two donor atoms are O-atoms of carboxylic acids [11–13]. In turn, the most elegant example is a complex with a commonly known saturated ligand *rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (*rac*-Me₆[14]aneN₄) and acetic acid, where the macrocyclic unit adopts a folded conformation in this way, allowing two carboxylic O-atoms to occupy two neighboring coordination sites and thus to form a four-membered chelate ring [13]:



Our work is focused on the synthesis of new crystalline materials having extended supramolecular structures, by combining polyazamacrocyclic cations with anions of polyfunctional aromatic acids capable of forming multiple hydrogen bonds [14–16]. The ability of the square-planar $\text{Ni}(\text{rac-Me}_6[14]\text{aneN}_4)^{2+}$ macrocyclic cation to adopt octahedral coordination seemed very attractive for us, since in the case of using additional polyfunctional carboxylic ligands one could expect the formation of bridged or polymeric assemblies in the solid phase, which will most likely exhibit interesting supramolecular features. Besides that, the resulting high-spin complexes would have paramagnetic properties and, probably, non-linear optical properties due to chirality of the ligand *rac*-Me₆[14]aneN₄ and its metal complexes. In the present paper we describe the preparation, X-ray crystal structure determination and some spectral properties of one such compound, a bridged high-spin complex bis-[Ni(II)(*rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-

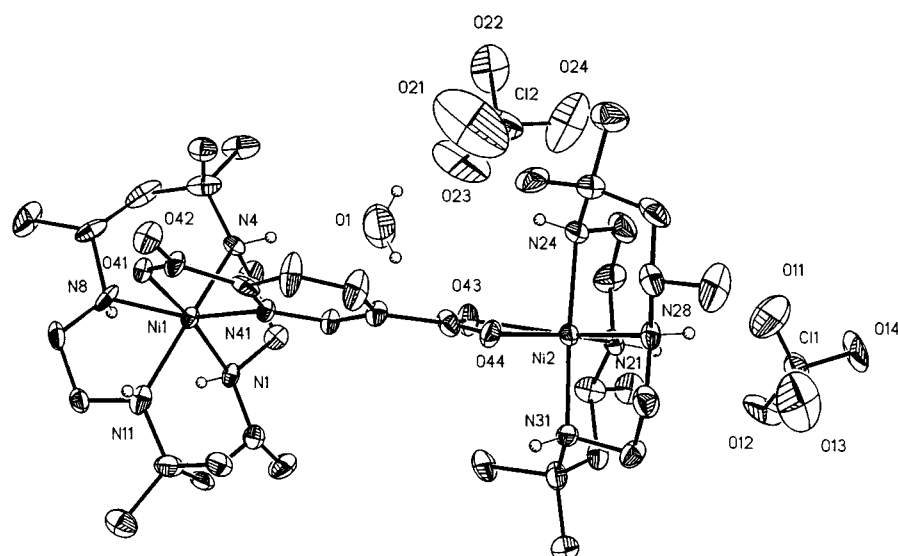


Figure 1. Drawing of the bridged high-spin complex bis-[Ni(II)(*rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)]-2,5-pyridinedicarboxylate diperchlorate monohydrate with atomic labelling. Thermal ellipsoids are drawn at the 30% probability level. H-atoms are represented by spheres of arbitrary size.

tetraazacyclotetradecane)]-2,5-pyridinedicarboxylate diperchlorate monohydrate (Figure 1).

2. Experimental

2,5-Pyridinedicarboxylic acid from Aldrich was used without any further purification. [Ni(*rac*-Me₆[14]aneN₄)](ClO₄)₂ was synthesized by complexation of the free ligand with Ni(II) acetate in methanol followed by addition of perchloric acid [11]. The title complex was synthesized as follows. [Ni(*rac*-Me₆[14]aneN₄)](ClO₄)₂ (0.54 g, 1 mmol) was dissolved in 50 mL of water. 0.16 g (1 mmol) of 2,5-pyridinedicarboxylic acid was dissolved in another 50 mL of water, with addition of NH₄OH until total dissolution of the acid. The two solutions were then combined, and final pH was adjusted to ca. 12 by adding NH₄OH. The color first turned blue, then brownish-green. The solution was heated under stirring during 1 h; the solvent was evaporated by half. After one week of standing at ambient temperature, violet-blue crystals of the product could be filtered off (0.38 g, 72% yield). *Anal. Calcd.* (%) for C₃₉H₇₇Cl₂N₉Ni₂O₁₃ (1068.42): C = 43.84, H = 7.26, N = 11.80. *Found* (Gailbraith): C = 43.83, H = 7.51, N = 11.73.

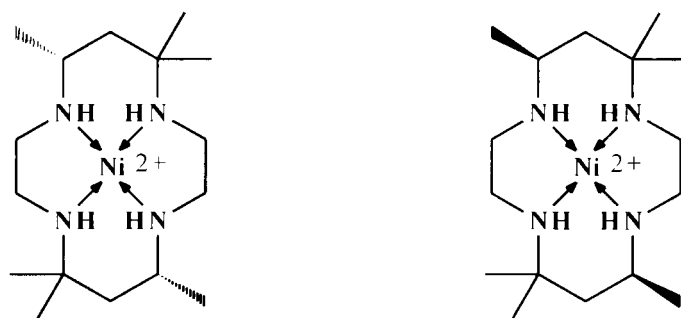
Infrared spectra were measured on a Nicolet Magna 750 FT-IR spectrometer. Most intense bands, cm⁻¹: 624, 835, 979, 1092, 1170, 1363, 1390, 1458, 1609, 1633, 2971, 3257, 3411 (diffuse). UV-Vis spectra were recorded on a Shimadzu

U-160 spectrophotometer. Wavelengths, nm (ϵ): 210 (76 200), 229 (26 800), 269 (8390), 365 (134), 448 (73), 568 (30).

Crystal data and summary of intensity data collection and structure refinement are presented in Table I.

3. Results and Discussion

The X-ray data (atomic coordinates and equivalent isotropic displacement parameters for non-H atoms) obtained for the title complex are listed in Table II (for atomic labelling, see the ORTEP diagram in Figure 1). According to them, the complex includes two folded $[\text{Ni}(\text{rac-Me}_6[14]\text{aneN}_4)]^{2+}$ units having opposite diastereomeric configurations of the macrocyclic ligand.



They are bridged through a dianion of 2,5-pyridinedicarboxylic acid, the left one being coordinated to an O-atom of the 2-carboxylic group and the pyridine N-atom (forming a five-membered chelate ring), and the right one is coordinated to both O-atoms of the 5-carboxylic group (forming a four-membered chelate ring). (Since we can derive the structure from a single crystal analysis only, and are unable to analyze all the bulk material, it remains unclear whether the optical configuration is the same for the entire product (this fact is especially important for the synthesis of materials for non-linear optics)). In both cationic units, the less-crowded side of the macrocycle (that with the two asymmetric C—H groups) is directed towards the 2,5-pyridinedicarboxylic dianion; or, in other words, the asymmetric C—CH₃ groups are directed outwards from the bridging dianion. The NH-groups neighboring them are directed towards the same side; and those NH-groups which are neighboring to the geminal CH₃-groups are directed towards the 2,5-pyridinedicarboxylic dianion.

The two octahedral coordination spheres thus have noticeable differences, and we analyzed their geometries by comparing corresponding bond distances and angles (Table II) to those reported for the $[\text{Ni}(\text{rac-Me}_6[14]\text{aneN}_4)\text{OAc}]^+$ cation [13], the closest analogue of the title compound. The macrocyclic units are folded about N(4)—Ni(1)—N(11) and N(24)—Ni(2)—N(31) (168° and 176°, respectively). The coordination octahedra are distorted: the only angles, formed by Ni-

Table I. Crystal data and summary of intensity data collection and structure refinement

Compound	C ₃₉ H ₇₇ Cl ₂ N ₉ Ni ₂ O ₁₃
Color/shape	Light-violet prism
Formula weight	1068.42
Crystal system	Orthorhombic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁
Temp., °C	20(2)
Cell constants	
<i>a</i> , Å	11.423(3)
<i>b</i> , Å	14.770(6)
<i>c</i> , Å	31.608(7)
α, deg	90.00
β, deg	90.00
γ, deg	90.00
Cell volume, Å ³	5333(3)
Formula units/unit cell	4
<i>D</i> _{calc} , g cm ⁻³	1.331
<i>μ</i> _{calc} , mm ⁻¹	0.869
<i>F</i> (000)	2272
Diffractometer, scan	Siemens P4/PC, <i>θ</i> /2 <i>θ</i>
Radiation, graphite monochromator	Mo <i>K</i> _α (λ = 0.71073)
Max. crystal dimensions, mm ⁻³	0.56 × 0.20 × 0.08
Standard reflections	3 every 97 reflections (−2−11, −101, −21−1)
Reflections measured	5524
2 <i>θ</i> range, deg	3 < 2 <i>θ</i> < 51
Index ranges	0 ≤ <i>h</i> ≤ 13, 0 ≤ <i>k</i> ≤ 17, 0 ≤ <i>l</i> ≤ 38
Decay, %	10
Refinement	Full-matrix least-squares on <i>F</i> ² , SHELXL-97
Data/restraints/parameters	5524/42/610
H-atoms	Mixed
Weights	$w = 1/\sigma^2(F_o^2) + (0.0985P)^2 + 4.4744P$ where $P = (F_o^2 + 2F_c^2)/3$
GOF	1.021
Final <i>R</i> ₁ and <i>wR</i> ₂	0.0870 and 0.1899 (observed) 0.1979 and 0.2656 (all)

Table II. Atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for non-H atoms. U_{eq} defined as one third of the trace of the orthogonalized U_{ij} tensor; s.o.f., site occupancy factor

	x	y	z	U_{eq}	s.o.f.
Ni(1)	0.4942(2)	0.90126(13)	0.21513(6)	0.0292(5)	
N(1)	0.5014(15)	0.7709(8)	0.1868(4)	0.033(3)	
C(2)	0.4007(18)	0.7653(11)	0.1563(6)	0.040(4)	
C(3)	0.294(2)	0.8071(13)	0.1759(7)	0.055(6)	
N(4)	0.3206(11)	0.9045(9)	0.1878(4)	0.030(3)	
C(5)	0.2220(19)	0.9491(13)	0.2103(9)	0.058(6)	
C(6)	0.206(2)	0.9102(13)	0.2528(7)	0.063(7)	
C(7)	0.3133(17)	0.9196(13)	0.2860(7)	0.054(5)	
N(8)	0.4184(16)	0.8649(9)	0.2735(4)	0.045(4)	
C(9)	0.514(2)	0.8673(12)	0.3039(5)	0.047(5)	
C(10)	0.6211(18)	0.8252(11)	0.2864(5)	0.044(5)	
N(11)	0.6545(17)	0.8683(9)	0.2445(5)	0.046(4)	
C(12)	0.7547(19)	0.8196(14)	0.2241(7)	0.054(5)	
C(13)	0.7079(18)	0.7293(12)	0.2028(6)	0.045(5)	
C(14)	0.6153(19)	0.7397(12)	0.1691(6)	0.041(4)	
C(15)	0.250(2)	1.0523(13)	0.2108(8)	0.055(6)	
C(16)	0.102(2)	0.9339(15)	0.1863(9)	0.076(8)	
C(17)	0.266(3)	0.8960(19)	0.3311(7)	0.084(9)	
C(18)	0.8035(17)	0.8847(14)	0.1907(6)	0.049(5)	
C(19)	0.857(2)	0.7938(15)	0.2527(8)	0.062(6)	
C(20)	0.598(3)	0.6454(14)	0.1480(7)	0.069(7)	
Ni(2)	0.6039(2)	1.00334(15)	-0.03167(6)	0.0335(5)	
N(21)	0.5241(13)	0.9078(11)	-0.0703(4)	0.042(4)	
C(22)	0.394(2)	0.9312(16)	-0.0694(9)	0.070(7)	
C(23)	0.379(3)	1.0338(16)	-0.0710(7)	0.071(8)	
N(24)	0.4442(14)	1.0795(9)	-0.0354(5)	0.045(4)	
C(25)	0.446(2)	1.1779(15)	-0.0380(7)	0.061(6)	
C(26)	0.535(2)	1.2089(14)	-0.0736(7)	0.070(9)	
C(27)	0.664(2)	1.1885(13)	-0.0694(6)	0.052(6)	
N(28)	0.6856(15)	1.0909(10)	-0.0759(4)	0.040(4)	
C(29)	0.806(2)	1.0674(13)	-0.0712(7)	0.059(6)	
C(30)	0.826(2)	0.9669(12)	-0.0702(6)	0.050(6)	
N(31)	0.7574(13)	0.9290(9)	-0.0322(5)	0.040(4)	
C(32)	0.759(2)	0.8290(15)	-0.0313(7)	0.056(5)	
C(33)	0.676(2)	0.7889(12)	-0.0643(6)	0.053(6)	
C(34)	0.5433(19)	0.8087(13)	-0.0607(8)	0.054(6)	
C(35)	0.482(2)	1.2183(13)	0.0030(7)	0.066(7)	
C(36)	0.329(2)	1.221(2)	-0.0502(9)	0.090(10)	

Table II. Continued.

C(37)	0.737(3)	1.2481(13)	-0.1004(8)	0.095(12)	
C(38)	0.719(2)	0.8020(16)	0.0153(7)	0.072(8)	
C(39)	0.880(2)	0.7880(15)	-0.0374(7)	0.064(6)	
C(40)	0.480(2)	0.7483(14)	-0.0943(7)	0.064(6)	
N(41)	0.5579(12)	0.9876(9)	0.1646(4)	0.030(3)	
C(42)	0.5896(18)	1.0717(10)	0.1783(6)	0.040(5)	
C(43)	0.628(2)	1.1380(13)	0.1503(6)	0.064(8)	
C(44)	0.640(3)	1.1218(12)	0.1098(6)	0.069(8)	
C(45)	0.605(2)	1.0363(10)	0.0942(5)	0.037(4)	
C(46)	0.5636(16)	0.973 1(9)	0.1223(5)	0.032(4)	
C(47)	0.5643(17)	1.0896(12)	0.2232(5)	0.039(4)	
O(41)	0.5163(12)	1.0276(7)	0.2450(3)	0.034(3)	
O(42)	0.5883(14)	1.1660(7)	0.2390(4)	0.050(4)	
C(48)	0.602(2)	1.0173(12)	0.0478(5)	0.046(5)	
O(43)	0.5349(12)	0.9593(8)	0.0319(4)	0.048(3)	
O(44)	0.6694(12)	1.0651(9)	0.0241(4)	0.044(3)	
O(1)	0.315(2)	0.9568(17)	0.0895(6)	0.131(9)	
Cl(1)	0.6192(8)	0.9576(4)	-0.18619(19)	0.080(2)	
O(11)	0.566(3)	1.024(3)	-0.1639(8)	0.201(17)	
O(12)	0.628(4)	0.865(3)	-0.1724(16)	0.102(15)	0.50
O(13)	0.739(5)	1.007(5)	-0.1769(18)	0.17(2)	0.50
O(14)	0.580(6)	0.965(3)	-0.2274(10)	0.108(15)	0.50
O(12B)	0.494(8)	0.939(5)	-0.192(2)	0.20(2)	0.50
O(13B)	0.653(5)	0.967(4)	-0.2261(17)	0.102(17)	0.50
O(14B)	0.679(5)	0.904(4)	-0.1625(19)	0.129(19)	0.50
Cl(2)	0.1000(9)	1.0061(6)	0.0080(4)	0.123(3)	
O(21)	0.176(4)	1.070(3)	0.0309(18)	0.31(3)	
O(22)	-0.013(3)	1.035(4)	0.0137(15)	0.141(17)	0.50
O(23)	0.106(8)	0.926(2)	0.030(3)	0.19(2)	0.50
O(24)	0.098(4)	1.016(6)	-0.0408(16)	0.20(2)	0.50
O(22B)	-0.024(10)	1.011(7)	0.044(3)	0.26(3)	0.50
O(23B)	0.064(8)	1.081(6)	-0.018(3)	0.22(3)	0.50
O(24B)	0.183(7)	0.946(5)	0.007(2)	0.15(2)	0.50

atoms and two neighboring donor atoms, approaching 90° are N(4)—Ni(1)—N(41) and N(31)—Ni(2)—N(21). The angles N(1)-Ni(1)-N(8) and N(21)—Ni(2)—N(28) are 99° and 103°, respectively; that is, the Ni(1) macrocyclic unit is a little more folded than the Ni(2) unit and the acetate analogue (103° [13]). Most of the bonds between Ni and the donor O- and N-atoms (as well as corresponding

angles) in the former are close to those for the acetate complex. The mean Ni—N distance is 2.12 Å, which is typical of octahedral triplet ground-state Ni(II) coordinated to secondary amino groups [13]. Only Ni(2)—O(43) is slightly longer (by ca. 0.1 Å) than the other Ni—O bonds, probably due to steric hindrance between the macrocyclic units. The C—O distances, as well as the O—C—O angles for both carboxylic groups are also approximately the same, despite different ways of coordination. The sharpest angle, as could be expected, is O(44)—Ni(2)—O(43), ca. 60°, i.e. insignificantly (by 2°) sharper than in the acetate analogue. In the other Ni-carboxylate fragment (five-membered chelate ring), the corresponding angle O(41)—Ni(1)—N(41) is 77°.

The 2,5-pyridinedicarboxylate anion is not planar, as can be seen from the torsion angles presented in Table II. The angles closest to 0° or 180° are N(41)—C(42)—C(47)—O(41) and N(41)—C(42)—C(47)—O(42), respectively. The 2-carboxylic group is less turned around the C(42)—C(47) bond than the 5-carboxylic group around the C(45)—C(48) bond, which is natural since in the former case the more planar conformation is stabilized by participation of the pyridine nucleus's atom N(41) in the five-membered chelate ring formation.

One of the aspects of primary interest for us is a possibility of the formation of developed supramolecular networks by combining polyazamacrocyclic compounds with aromatic acids [14–16]. A basis for such networks is hydrogen bonds. In the present case we also attempted to analyze possible H-bonds, although the quality of the grown crystals and the subsequent crystal structure refinement (Table I) was not very good. The possible H-bonds are listed in Table III, and can be classified as follows:

- (1) between macrocyclic NH-groups and carboxylate O-atoms: N(1)—H(1)···O(42) and N(8)—H(8)···O(42);
- (2) between macrocyclic NH-groups and water molecules: N(4)—H(4)···O(1);
- (3) between macrocyclic NH-groups and perchlorate anions: N(11)—H(11)···O(13B), N(11)—H(11)···O(13), N(21)—H(21)···O(14B), N(21)—H(21)···O(11), N(28)—H(28)···O(11) and N(31)—H(31)···O(22);
- (4) between water molecules and carboxylic O-atoms: O(1)—H(1A)···O(43);
- (5) between water molecules and perchlorate anions: O(1)—H(1B)···O(21), O(1)—H(1B)···O(24B) and O(1)—H(1)···O(23).

These hydrogen bonding patterns involving macrocyclic NH-groups, both 2- and 5-carboxylic groups, perchlorate anions and water molecules give rise to the formation of an infinite supramolecular network in the title compound's crystals, which can be seen in Figure 2 showing the packing diagram for the complex.

Based on the results obtained, we suggest that combining Ni(II)-tetraazamacrocyclic cations, capable of forming folded high-spin octahedral forms, with aromatic dicarboxylic acids, capable of bridging such macrocyclic units, can be used in crystal engineering for the synthesis of novel materials with developed supramolecular networks and, probably, interesting optical and magnetic properties.

Table III. Selected bond distances (Å), bond angles (°) and torsion angles (°) in the macrocyclic cations

Ni(1)—O(41)	2.107(10)
Ni(1)—N(8)	2.108(13)
Ni(1)—N(11)	2.110(18)
Ni(1)—N(1)	2.126(12)
Ni(1)—N(4)	2.164(13)
Ni(1)—N(41)	2.170(13)
Ni(2)—N(3 1)	2.069(14)
Ni(2)—N(21)	2.077(14)
Ni(2)—N(28)	2.121(14)
Ni(2)—O(44)	2.123(12)
Ni(2)—N(24)	2.146(15)
Ni(2)—O(43)	2.255(13)
C(47)—O(42)	1.264(19)
C(47)—O(41)	1.27(2)
C(48)—O(43)	1.25(2)
C(48)—O(44)	1.29(2)
O(41)—Ni(1)—N(8)	83.3(5)
O(41)—Ni(1)—N(11)	84.4(5)
N(8)—Ni(1)—N(11)	85.0(7)
O(41)—Ni(1)—N(1)	170.7(6)
N(8)—Ni(1)—N(1)	98.9(5)
N(11)—Ni(1)—N(1)	86.7(6)
O(41)—Ni(1)—N(4)	105.6(5)
N(8)—Ni(1)—N(4)	88.8(6)
N(11)—Ni(1)—N(4)	167.5(6)
N(1)—Ni(1)—N(4)	83.5(6)
O(41)—Ni(1)—N(41)	76.7(4)
N(8)—Ni(1)—N(41)	158.8(5)
N(11)—Ni(1)—N(41)	99.7(6)
N(1)—Ni(1)—N(41)	102.1(5)
N(4)—Ni(1)—N(41)	90.0(5)
N(31)—Ni(2)—N(21)	90.4(6)
N(31)—Ni(2)—N(28)	86.9(6)
N(21)—Ni(2)—N(28)	102.6(6)
N(31)—Ni(2)—O(44)	86.3(5)
N(21)—Ni(2)—O(44)	159.4(5)
N(28)—Ni(2)—O(44)	97.5(5)
N(31)—Ni(2)—N(24)	176.4(6)
N(21)—Ni(2)—N(24)	87.2(6)

Table III. Continued

N(28)—Ni(2)—N(24)	91.0(6)
O(44)—Ni(2)—N(24)	96.9(6)
N(31)—Ni(2)—O(43)	98.6(6)
N(21)—Ni(2)—O(43)	100.1(5)
N(28)—Ni(2)—O(43)	156.6(5)
O(44)—Ni(2)—O(43)	60.4(4)
N(24)—Ni(2)—O(43)	84.5(6)
O(42)—C(47)—O(41)	121.6(14)
O(43)—C(48)—O(44)	120.6(15)
N(41)—C(42)—C(47)—O(41)	0(3)
C(43)—C(42)—C(47)—O(41)	172(2)
N(41)—C(42)—C(47)—O(42)	-178.7(17)
C(43)—C(42)—C(47)—O(42)	-7(3)
C(46)—C(45)—C(48)—O(43)	21(3)
C(44)—C(45)—C(48)—O(43)	-154(2)
C(46)—C(45)—C(48)—O(44)	-160.7(19)
C(44)—C(45)—C(48)—O(44)	24(3)

Table IV. Distances (Å) and angles (°) for possible hydrogen bonds.

D—H...A	D—H	H—A	D—A	Angle D—H—A
N(1)—H(1)...O(42)	0.90	2.11	2.991(18)	164.6 ^a
N(4)—H(4)...O(1)	0.90	2.35	3.20(2)	156.9
N(8)—H(8)...O(42)	0.90	2.12	2.965(18)	156.7 ^a
N(11)—H(11)...O(13B)	0.90	2.56	3.41(6)	156.1 ^b
N(11)—H(11)...O(13)	0.90	2.63	3.33(5)	134.6 ^b
N(21)—H(21)...O(14B)	0.90	2.55	3.41(6)	158.7
N(21)—H(21)...O(11)	0.90	2.65	3.45(3)	149.9
N(28)—H(28)...O(11)	0.90	2.36	3.25(3)	168.4
N(31)—H(31)...O(22)	0.90	2.62	3.38(5)	142.1 ^c
O(1)—H(1A)...O(43)	0.85	2.29	3.10(3)	160.5
O(1)—H(1B)...O(21)	0.85	2.15	2.95(5)	156.8
O(1)—H(1B)...O(24B)	0.85	2.49	3.00(7)	119.6
O(1)—H(1B)...O(23)	0.85	2.51	3.07(7)	124.3

^a $(-x + 1, y - 1/2, -z + 1/2)$; ^b $(-x + 3/2, -y + 2, z + 1/2)$; ^c $(x + 1, y, z)$.

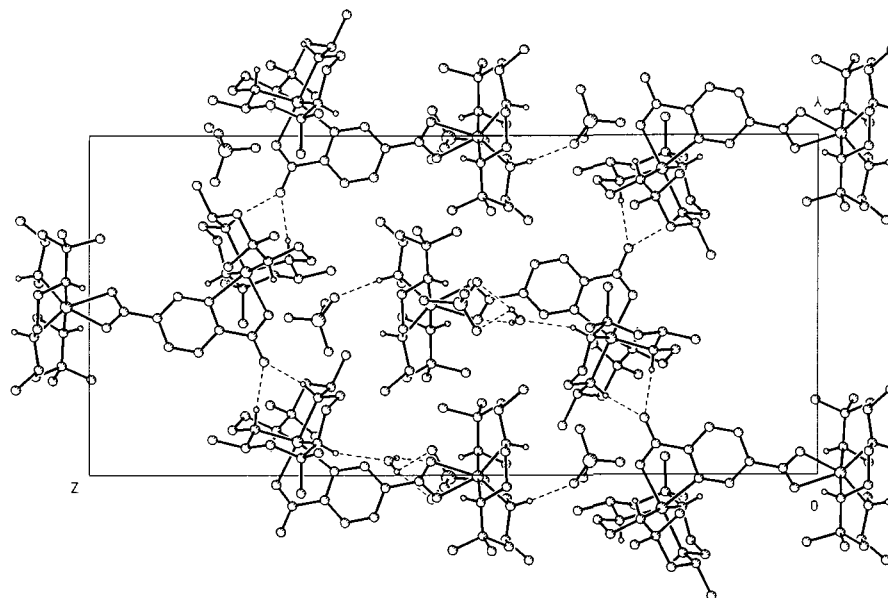


Figure 2. Packing diagram for the title complex. Hydrogen bonds are shown as dashed lines.

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References

1. A. Garoufis, S. Kasselouri, C. P. Raptopoulou, and A. Terzis: *Polyhedron* **18**, 585 (1998).
2. D. Black, A. J. Blake, K. P. Dancey, A. Harrison, M. McPartlin, S. Parsons, P. A. Tasker, G. Whittaker, and M. Schroder: *J. Chem. Soc. Dalton Trans.* 3953 (1998).
3. A. A. A. Emará: *Syn. Reactiv. Inorg. Metal. – Org. C* **29**, 87 (1999).
4. Y. X. Tong, M. L. Tong, X. L. Yu, and X. M. Chen: *Acta Crystallogr.* **C55**, 180 (1999).
5. K. S. Siddiqi and N. Nishat: *Syn. Reactiv. Inorg Metal. – Org. C* **29**, 297 (1999).
6. A. K. Barik, S. Paul, S. K. Kar, R. J. Butcher, and J. C. Bryan: *Polyhedron* **18**, 571 (1998).
7. A. Garoufis, S. Kasselouri, C. A. Mitsopoulou, J. Sletten, C. Papadimitriou, and N. Hadjiliadis: *Polyhedron* **18**, 39 (1998).
8. C. Bruckner, D. L. Caulder, and K. N. Raymond: *Inorg. Chem.* **37**, 6759 (1998).
9. A. Escuer, R. Vicente, M. S. El Fallah, S. B. Kumar, F. A. Mautner, and D. Gatteschi: *J. Chem. Soc. Dalton Trans.* 3905 (1998).
10. M. A. Ali, M. Nazimuddin, R. Shaha, R. J. Butcher, and J. C. Bryan: *Polyhedron* **17**, 3955 (1998).
11. N. F. Curtis: *J. Chem. Soc.* 2644 (1964).
12. N. F. Curtis: *J. Chem. Soc. (A)* 1584 (1968).
13. P. O. Whimp, M. F. Bailey, and N. F. Curtis: *J. Chem. Soc. (A)* 1956 (1970).
14. M. E. Sánchez-Vergara, J. Gómez-Lara, R. A. Toscano, and S. Hernández-Ortega: *J. Chem. Crystallogr.* **28**, 827 (1999).

15. J. Gómez-Lara, V. A. Basiuk, E. V. Basiuk, and S. Hernández-Ortega: *J. Chem. Cryst.* **29**, 469 (1999).
16. E. V. Basiuk, J. Gómez-Lara, V. A. Basiuk, and R. A. Toscano: *J. Chem. Cryst.* accepted (1999).