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Oxamido-bridged heterobinuclear copper(II)–nickel(II) complex and homotrinuclear nickel(II) complex with 2D supramolecular structure: synthesis, crystal structure, magnetic and spectroscopic properties

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Abstract

The oxamido-bridged heterobinuclear copper(II)–nickel(II) complex, $[Cu(oxbe)Ni(phen)_2]ClO_4 \cdot 3H_2O$ (**1**) and homotrinuclear nickel(II) complex $\{[Ni(oxbe)]_2Ni(H_2O)_2\} \cdot 2.5DMF$ (**2**) have been synthesized and characterized by means of elemental analysis, IR, EPR, and electronic spectra and magnetic susceptibility, where H_3oxbe is dissymmetrical ligand *N*-benzoato-*N′*-(2-aminoethyl)oxamido, phen = 1,10-phenanthroline, DMF = dimethylformamide. Complex **1** has an extended oxamido-bridged structure consisting of planar copper(II) and octahedral nickel(II) ions. The χ_M and μ_{eff} versus T plots of **1** is typical of an antiferromagnetically coupled Cu(II)–Ni(II) pair with a spin-doublet ground state, and magnetic analysis leads to $J = -57.1$ cm^{-1}. The molecular structure of **2** is centrosymmetrical, with one octahedral nickel atom lying at an inversion center and two terminal Ni(II) atoms in approximately square planar environment. Through the hydrogen bonds and π–π stacking interactions, a 2D supramolecular structure is formed.

Keywords: Oxamido-bridged; Heterobinuclear complexes; Spin-doublet ground state; Homotrinuclear nickel(II) complexes; Supramolecular structures

1. Introduction

Molecular magnetism has a rapid development in the last two decades [1–3], and particular emphasis has been placed on heterobimetallic complexes. The magnetic interaction between two nonequivalent paramagnetic centers may lead to situations which cannot be encountered in species containing only one kind of center [4]. A successful strategy in obtaining the desired spin topology is the 'complex as ligand' approach. These anionic precursors are particularly suitable for designing heterobimetallic complexes and have played an important role in the development of molecular magnetism [5–10]. Symmetrically *N,N′*-disubstituted oxamidate derivatives are known to be versatile organic ligands which can chelate as well as bridge metal ions to construct discrete and extended structures, depending on their adoption of the *cis*- or *trans*-conformation (Scheme 1) [11].

Owing to synthetic difficulties, only two dissymmetrical oxamidate copper (II) precursors have been both structurally and magnetically characterized by Kahn and co-workers: $[Cu(obze)]^{2-}$ [8], and $[Cu(obzp)]^{2-}$ [12] (Scheme 2). Recently [13], a new copper (II) precursor of this kind has been reported by us. To our knowledge, there is no other reports on dissymmetrical oxamidate-bridged heterobinuclear copper(II)–nickel(II) complexes. Here, we report the synthesis, magnetic and spectroscopic properties of a new heterobinuclear complex $[Cu(oxbe)Ni(phen)_2]ClO_4 \cdot 3H_2O$ (**1**). Moreover, the number of supramolecular systems derived from trinuclear entities is very limited, and with oxamidate

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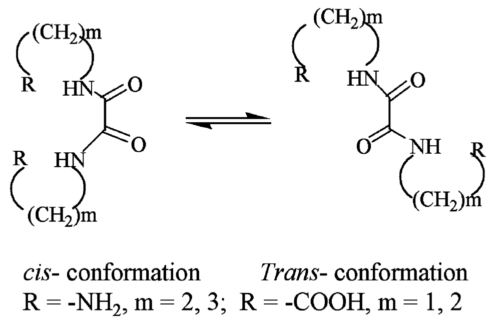


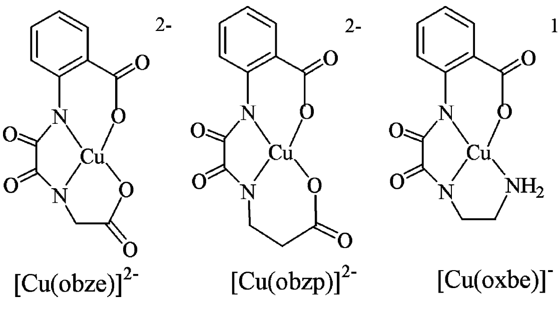
Scheme 1. Symmetrically *N, N′*-disubstituted oxamidate derivatives.

derived ligands only two Cu_3 supramolecular structures are known [14]. We also report the new dissymmetrical oxamidate nickel(II) precursor, Na[Ni(oxbe)]·$1.5H_2O$ (**3**), and assembly of a centrosymmetrical homotrinuclear nickel(II) $\{[Ni(oxbe)]_2Ni(H_2O)_2\}\cdot 2.5DMF$ (**2**), which exhibits a 2D supramolecular structure through hydrogen bonding and π–π stacking interactions.

2. Experimental

2.1. General

All regents used in the synthesis were of analytical grade. The perchlorate complex of nickel ion is prepared by general methods. Elemental analyses for C, H and N were carried out on a Perkin–Elmer elemental analyzer, model 2400II. The metal contents were determined by EDTA titration. The infrared spectrum was recorded on Avater-360 spectrometer using KBr pellets in 400–4000 cm^{-1}. UV–Vis spectra were recorded on Heλions α spectrometer in the 200–850 nm ranges. X-band EPR spectra were recorded on a Varian E-115 EPR spectrometer. Magnetic measurement was carried out on polycrystalline samples with a MPMS-7 SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants for all constituent atoms.



Scheme 2. Some dissymmetrical building blocks.

2.2. Preparation of the complexes

The ligand H_3O oxbe and its copper(II) mononuclear complex Na[Cu(oxbe)]·$1.5H_2O$ were obtained as described in the literature [13].

2.2.1. Na[Ni(oxbe)]·$1.5H_2O$ (*3*)

Eight millimole (2.00 g) H_3oxbe and 24 mmol (0.96 g) NaOH were dissolved in 100 ml water/ethanol (v/v = 1:1). Ten milliliter aqueous solution containing 7.5 mmol (2.74 g) $Ni(ClO_4)_2\cdot 6H_2O$ was then added. The resulting yellow solution was filtered and concentrated to 20 ml. Ethanol was then added slowly into the filtrate, and Na[Ni(oxbe)]·$1.5H_2O$ precipitated as a yellow polycrystalline powder, which was washed with ethanol and dried under vacuum at room temperature. Yield: 90%. Found: C, 37.07; H, 3.72; N, 11.83; Ni, 16.52%. *Anal*. Calc. for $C_{11}H_{13}N_3O_{5.5}NaNi$: C, 37.01; H, 3.67; N, 11.78; Ni, 16.44%.

2.2.2. [Cu(oxbe)Ni(phen)$_2$]$ClO_4\cdot 3H_2O$ (*1*)

To 1 mmol (0.362 g) Na[Cu(oxbe)] $1.5H_2O$ in 10 ml of methanol was successively added a solution of 2 mmol (0.369 g) phen in 5 ml methanol and 1 mmol (0.366 g) $Ni(ClO_4)_2\cdot 6H_2O$ in 5 ml methanol. The mixture was stirred at room temperature for 2 h, and then filtered. The product was filtered out, and then washed with ethanol. Yield: 90%. Found: C, 47.57; H, 3.72; N, 11.00; Cu, 7.22; Ni, 6.58%. *Anal*. Calc. for $C_{35}H_{32}N_7O_{11}Cl$-CuNi: C, 47.53; H, 3.65; N, 11.09; Cu, 7.19; Ni, 6.64%.

2.2.3. $\{[Ni(oxbe)]_2Ni(H_2O)_2\}\cdot 2.5DMF$ (*2*)

To a solution of 1 mmol (0.357 g) Na[Ni(oxbe)]·$1.5H_2O$ dissolved in 20 ml of water was added slowly a solution of an aqueous solution of 0.5 mmol (0.183 g) $Ni(ClO_4)_2\cdot 6H_2O$ with continuously stirring for 2 h, affording a yellow precipitate, which was filtered, washed with water, and dried in a desiccator containing silica gel. Well-shaped single crystals of this complex were obtained by slow evaporation of the dimethylformamide (DMF) solution of the crude product. Yield: 75%. Found: C, 39.73; H, 4.66; N, 13.34; Ni, 19.79%. *Anal*. Calc. for $C_{29.50}H_{41.50}N_{8.50}O_{12.50}Ni_3$: C, 39.75; H, 4.69; N, 13.36; Ni, 19.75%. *Caution:* although no problem was encounter in this work, nickel perchlorate complex is potentially explosive and should be handled in small quantities.

2.3. Crystal structure determination and refinement of complex 2

A bright yellow single crystal ($0.45 \times 0.26 \times 0.23$ mm^3) of complex **2** was selected, and intensity data were collected in the 2θ range of 3.08°–51.96° at room temperature on Siemens P4 diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda =$

Table 1
Crystal data and structure refinement for complex **2**

Empirical formula	$C_{29.50}H_{41.50}N_{8.50}O_{12.50}Ni_3$
Formula weight	891.34
Cryst system	monoclinic
Space group	$C2/c$
a (Å)	22.684(5)
b (Å)	17.247(2)
c (Å)	10.857(2)
β (°)	115.38(2)
V (Å^3)	3838 (1)
Z	4
D_{calc} (g cm^{-1})	1.543
λ(Mo Kα) (Å)	0.71073
μ(Mo Kα) (mm^{-1})	1.527
T (K)	293(2)
$R_1[(I>2\sigma)]$ [a]	0.0548
wR_2 [b]	0.1623

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$.
[b] $wR_2 = [\Sigma w(|F_o|^2-|F_c|^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

0.71073 Å). A summary of the crystallographic data is given in Table 1. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the SHELXTL-97 program [15]. One DMF molecule appeared to be disordered, and its site occupancy factor was let to 0.5. CCDC: 201431.

3. Result and discussion

3.1. IR Spectra

3.1.1. [Cu(oxbe)Ni(phen)$_2$]ClO$_4$·3H$_2$O (*1*)

The $\nu_{C=O}$ vibration (oxamidate group and ionized carboxylate group) at 1649 cm^{-1} for Na[Cu(oxbe)] 1.5H$_2$O and the –N=C– stretching vibration at 1450–1500 cm^{-1} were shifted to higher frequencies in the binuclear complex, 1665 and 1522 cm^{-1}, respectively. In addition, the –NH$_2$ vibration at about 3314 cm^{-1} for Na[Cu(oxbe)] 1.5H$_2$O and ClO$_4^-$ group vibration at 1100 cm^{-1} were all observed.

3.1.2. Na[Ni(oxbe)]·1.5H$_2$O) (*3*) and {[Ni(oxbe)]$_2$Ni(H$_2$O)$_2$}·2.5DMF (*2*)

The ligand H$_3$oxbe exhibits one $\nu_{C=O}$ vibration of oxamidate group at approximately 1636 cm^{-1} [13,16], one $\nu_{as(COO)}$ vibration band at approximately 1700 cm^{-1} ($\nu_{(COOH)}$ un-ionized) [13,17] and the bands of ν_{N-H} group (oxamidate group) at approximately 2955, 3017, 3083 cm^{-1} [13]. These bands are all missing in the spectrum of the mononuclear complex because of the losing of the protons from both COOH and N–H (oxamidate group) groups, indicating the formation of the mononuclear Ni(II) complex. It must be stressed that one new sharp strong band observed in mononuclear Na[Ni(oxbe)]·1.5H$_2$O (**3**) (1663 cm^{-1}) and trinuclear complex {[Ni(oxbe)]$_2$Ni(H$_2$O)$_2$}·2.5DMF (**2**) (1660 cm^{-1}) is the result of overlapping between $\nu_{as(COO)}$ of ionized carboxylate group and the vibration of oxamidate group ($\nu_{C=O}$) acting as a bidendate mode. The –NH$_2$ vibration at approximately 3307 cm^{-1} for H$_3$oxbe was present for both complexes (3289 and 3277 cm^{-1} for **3** and **2**, respectively).

3.2. Electronic spectra

The electronic absorption spectra of complexes **1**, **2** and **3** were measured in DMF solutions in the 200–850 nm range. All complexes exhibit two intense bands at approximately 308 and 340 nm ($\varepsilon > 10^3$ l mol^{-1} cm^{-1}), which can be assigned to charge-transfer transitions and/or intraligand π–π* transitions.

3.2.1. Na[Ni(oxbe)]·1.5H$_2$O) (*3*)

The electronic absorption spectra exhibits two bands at 450 nm ($\varepsilon = 21.1$ l mol^{-1} cm^{-1}) and 520 nm ($\varepsilon = 12.2$ l mol^{-1} cm^{-1}), which can be ascribed to the d–d transition of Ni(II) atom in the square planar environment [18,19].

3.2.2. {[Ni(oxbe)]$_2$Ni(H$_2$O)$_2$}·2.5DMF (*2*)

The electronic absorption spectra of complex **2** consists of four d–d transitions at 455 nm ($\varepsilon = 20.8$ l mol^{-1} cm^{-1}), 520 nm ($\varepsilon = 12.8$ l mol^{-1} cm^{-1}), 385 nm ($\varepsilon = 17.5$ l mol^{-1} cm^{-1}) and 590 nm ($\varepsilon = 8.6$ l mol^{-1} cm^{-1}). The former two bands belong to the Ni(II) atom in square planar coordination while the latter two are due to Ni(II) coordinated octahedrally [18,19].

3.2.3. [Cu(oxbe)Ni(phen)$_2$]ClO$_4$·3H$_2$O (*1*)

A relatively strong band centered at 560 nm ($\varepsilon = 55.4$ l mol^{-1} cm^{-1}) is attributed to the overlap of two spin allowed d–d transitions: $^2B_2(Cu) \rightarrow {}^2B_1(Cu)$ and $^3A_2(Ni) \rightarrow {}^3T_1(Ni)$. A very weak band at around 790 nm ($\varepsilon = 5.4$ l mol^{-1} cm^{-1}) is attributed to the spin-forbidden transition $^3A_2(Ni) \rightarrow {}^1E_2(Ni)$, which is activated by an exchange mechanism [20,21].

3.3. The electron paramagnetic resonance spectra of *1*

The powder EPR spectra are depicted in Fig. 1. At room temperature the spectrum exhibits a very large and intense signal centered at $g = 2.17$ and a smaller one at $g = 4.34$. The intensity of the first signal is independent of the temperature but becomes narrower and sharper upon cooling down. The intensity of the second signal disappears at 77 K. Obviously, the temperature dependence of the EPR spectra do not correspond to that expected for a single doublet ground state. This fact can be explained in a satisfactory way by assuming the

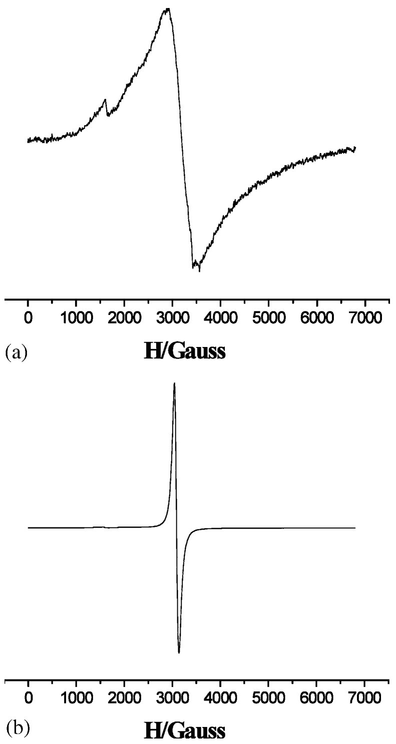


Fig. 1. Powder X-band EPR spectra of **1** at (a) room temperature (b) 77 K.

existence of a moderately strong zero-field splitting (ZFS) within the quartet state, which leads to two Kramer doublets, |3/2, ±1/2⟩ and |3/2, ±3/2⟩. If axial symmetry is assumed in the ZFS, the allowed |3/2, ±1/2⟩→|3/2, ±3/2⟩ transition may produce two anisotropic signals, one near to the g_e value and other one at about half-field ($g = 4.40$) [22]. For complex **1**, the first signal can be seen as the overlap of the signals of the $S = 1/2$ and 3/2 states at room temperature, and the latter one is tentatively attributed to the allowed |3/2, ±1/2⟩→|3/2, ±3/2⟩ transition. When the temperature is lowed to 77 K, the quartet is depopulated, as revealed by the magnetic study, and then both signals of $S = 3/2$ state disappear and only the $S = 1/2$ ground state remains in the spectrum [23].

Based on the discussion above (including elemental analysis, IR, electronic and EPR spectra), complex **1** is proposed to have an extended oxamido-bridged structure and contain copper(II) atom in a planar environment and Ni(II) atom in an octahedral environment, as shown in Scheme 3.

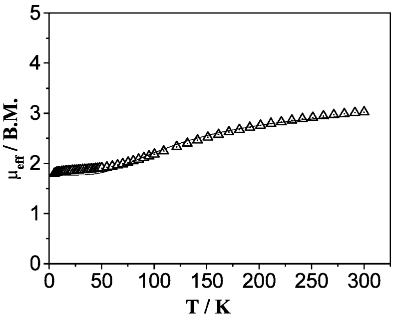
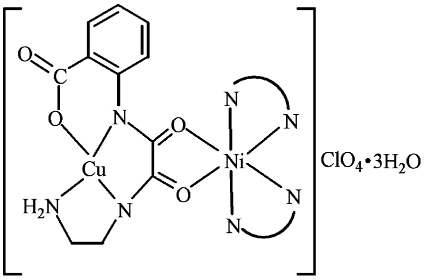


Fig. 2. μ_{eff} versus T plots for complex **1**.

3.4. Magnetic properties of complex *1*

The magnetic susceptibility of complex **1** was measured in the temperature range 5–300 K on a MPMS-7 SQUID magnetometer. The room temperature value for μ_{eff} (3.00 BM where μ_{eff} is the effective magnetic moment) is slightly smaller than that expected for uncoupled Cu(II)–Ni(II) binuclear ions (3.32 BM). Upon cooling, the μ_{eff} value decreases steadily and reach a plateau below 50 K. These features are typical of Cu(II)–Ni(II) pairs with antiferromagnetic interaction [4]. The plateau indicates that only the doublet ground state is thermally populated at low temperature.



Scheme 3. Suggested chemical structure for complex **1**

Table 2
Structure and magnetic information of other oxamidato-bridged Cu(II)–Ni(II) complexes

Complexes	Coordination environment	J (cm^{-1})	References
$[Cu(oxpn)Ni(phen)_2](ClO_4)_2 \cdot H_2O$	N_4	−47.22	[24]
$[Cu(oxap)Ni(phen)_2](ClO_4)_2$	N_4	−92.4	[25]
$[Cu(Me_2oxpn)Ni(\mu\text{-}NCS)(H_2O)(tmen)]_2(ClO_4)_2$	N_4	−107	[26]
$[Cu(PEoxd)Ni(bpy)_2](ClO_4)_2 \cdot 1/2H_2O$	N_4	−42.7	[27]
$NiCu(obp)(H_2O)_3 \cdot 3.5H_2O$	N_2O_2	−100.5	[28]
Complex **1**	N_3O	−57.1	this work

*oxpn, N,*N*′-bis(3-aminopropy)oxamido; oxap, *N*,*N*′-bis(2-aminopropy)oxamido; PEoxd, *N*,*N*′-bis(2-pyridyl-ethyl)oxamido; Me_2oxpn, *N*,*N*′-bis(3-amino-2,2′-dimethy(propyl)oxamido; tmen, *N*,*N*,*N*′,*N*′-tetramethylethylenediamine; bpy, 2,2′-bipyridine.

Table 3
Bond length (Å) and angles (°) around the metal atoms for complex **2**

Bond lengths			
Ni(1)–N(2)	1.829(5)	Ni(1)–O(2)	1.839(4)
Ni(1)–N(1)	1.886(6)	Ni(1)–N(3)	1.930(6)
Ni(2)–O(4)	2.063(5)	Ni(2)–O(3)	2.081(4)
Ni(2)–OW	2.081(5)		
Bond angles			
N(2)–Ni(1)–O(2)	174.2(3)	N(2)–Ni(1)–N(1)	86.2(2)
O(2)–Ni(1)–N(1)	97.6(2)	N(2)–Ni(1)–N(3)	82.8(3)
O(2)–Ni(1)–N(3)	94.0(2)	N(1)–Ni(1)–N(3)	167.0(2)
O(4)–Ni(2)–O(3)	81.5(2)	O(4)–Ni(2)–OW	91.3(2)
O(3)–Ni(2)–OW	90.8(2)		

On the basis of the isotropic spin Hamiltonian $\hat{H} = -2J\hat{S}_{\mathrm{Ni}}\hat{S}_{\mathrm{Cu}}$, the expression of the magnetic susceptibility for a Cu(II)–Ni(II) system is

$$\chi_{\mathrm{M}} = (N\beta^2/4KT) \times \{[g_{1/2}^2 + 10g_{3/2}^2 \exp(3J/KT)]/[1 + 2\exp(3J/KT)]\} + N_\alpha$$

where $g_{1/2} = (4g_{\mathrm{Ni}} - g_{\mathrm{Cu}})/3$, and $g_{3/2} = (2g_{\mathrm{Ni}} + g_{\mathrm{Cu}})/3$, N_α is the temperature-independent paramagnetism (120×10^{-6} cm^3 mol^{-1}). The best fit to the experimental data gives $J = -57.1$ cm^{-1}, $g_{\mathrm{Ni}} = 2.02$, $g_{\mathrm{Cu}} = 2.03$. The agreement factor $R = \Sigma(\chi_{\mathrm{obsd}} - \chi_{\mathrm{calc}})^2/\Sigma\chi_{\mathrm{obsd}}^2$ is 3.74×10^{-3}, which corresponds to a good agreement as seen in Fig. 2. Structure and magnetic information of other oxamidato-bridged Cu(II)–Ni(II) complexes already reported have been given in Table 2. As shown in table, it can be found that complex **1** has a reasonable J value among oxamidato-bridged Cu(II)–Ni(II) complexes.

3.5. *Crystal structure of complex* **2**

The crystal structure of complex **2** consists of centrosymmetrical homotrinuclear neutral molecules [Ni(oxbe)]$_2$Ni(H$_2$O)$_2$ and DMF molecules. A perspective view of the trinuclear unit is depicted in Fig. 3 and selected bond lengths and angles are listed in Table 3.

Two oxamidate anions act as bridges between the central and the outer nickel(II) ions. The central Ni2 atom is coordinated by two pairs of oxamide oxygens and two water molecules in *trans* positions. The Ni–O distances are almost equivalent (2.063–2.081 Å). Each terminal Ni atom occupies an inner site of the trideprotonated ligand with a NiN$_3$O distorted square planar environment. The deviations of four donor atoms from their mean plane are in the range of −0.219–0.171 Å, and the nickel atom is displaced out of the plane by 0.162 Å. These slight deviations from planarity are tetrahedral-like, and the N1–Ni1–N3 and N2–Ni1–O2 angles are 167.0(2) and 174.2°, respectively. The Ni1–N1 and Ni1–N2 distance (1.886 and 1.829 Å, respectively) are significantly shorter than the Ni1–N3 one (1.930 Å), consistent with the greater basicity of the deprotonated amido group.

Complex **2** shows an interesting supramolecular structure in the lattice. Firstly, the aryl rings of benzoate anion from different cations are parallel, as seen in Fig. 4. Intermolecular π–π interaction probably exists because the averaged distance between carbon atoms of benzene ring is the aromatic rings of the neighboring molecules is averaged 3.684 Å. Through π–π stacking interactions, a 1D infinite chain is formed. Then, this chain is strengthened by the hydrogen bonding interactions resulting from the water oxygen coordinated to Ni2 atom and the 'free' oxygen of carboxylate of an adjacent molecule in the same layer. Moreover, The –NH$_2$ group is linked to the O3* atom of the adjacent chain, and the N3···O4* distance is 2.925 Å. The interchain hydrogen bonding interactions result in an unusual quasi-2D supramolecular 'double' chain, as can be seen in Fig. 4. And the water oxygen coordinated to Ni2 atom is also linked to the oxygen of DMF by hydrogen bonding, and the distance OW···O5 is 2.656 Å.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Nos. 201431 for **2**. Copies of the data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax:

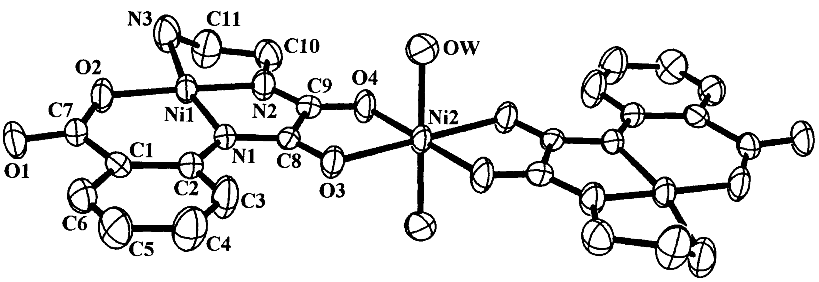


Fig. 3. The molecular structure of complex **2**, DMF molecules were omitted for clarity.

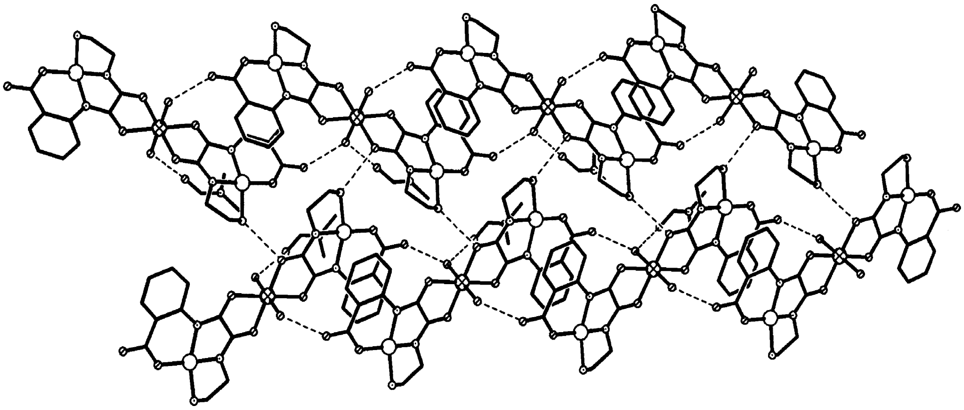


Fig. 4. View of the 2D structure of complex **2**.

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