

Bis[μ -2,2'-[ethane-1,2-diylbis(nitrilomethylidene)]diphenolato]dinickel(II)

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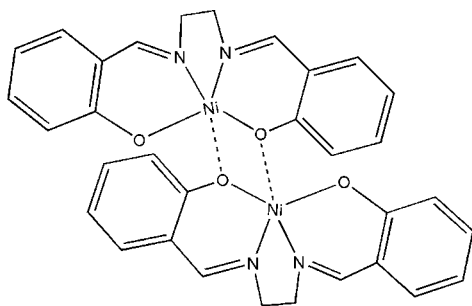
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Key indicators: single-crystal X-ray study; $T = 273$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.024; wR factor = 0.056; data-to-parameter ratio = 16.2.

The asymmetric unit of the title compound, $[\text{Ni}_2(\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_2)_2]$, contains an Ni^{II} cation which is coordinated by two imine N atoms and by two phenolate O atoms of the salen ligand {salen = N,N' -bis(salicylidene)ethane-1,2-diamine or 2,2'-[ethane-1,2-diylbis(nitrilomethylidene)]diphenol}, leading to a distorted square-planar conformation. When a secondary Ni—O interaction > 2.41 Å to the neighbouring phenolate O atom is considered, two molecules are linked into a centrosymmetric dimer with an overall square-pyramidal coordination for the Ni^{II} cation. Weak π – π interactions with a shortest interplanar distance of 3.704 Å help to stabilize the crystal structure.

Related literature

For a review on metal–salen complexes used in catalysis, see: Cozzi (2004).



Experimental

Crystal data

$[\text{Ni}_2(\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_2)_2]$
 $M_r = 650.00$
 Monoclinic, $C2/c$
 $a = 26.639$ (2) Å
 $b = 6.9775$ (6) Å
 $c = 14.7094$ (12) Å
 $\beta = 97.501$ (1)°

$V = 2710.7$ (4) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 1.44$ mm⁻¹
 $T = 273$ (2) K
 $0.34 \times 0.21 \times 0.07$ mm

Data collection

Bruker SMART CCD diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2001)
 $T_{\text{min}} = 0.641$, $T_{\text{max}} = 0.906$

8437 measured reflections
 3090 independent reflections
 2607 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.023$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.024$
 $wR(F^2) = 0.056$
 $S = 1.03$
 3090 reflections

191 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.39$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.18$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Ni1—O2	1.9115 (11)	Ni1—N2	1.9484 (13)
Ni1—O1	1.9412 (10)	Ni1—N1	1.9560 (13)
O2—Ni1—O1	91.35 (5)	O2—Ni1—N1	92.53 (5)
O2—Ni1—N2	171.05 (5)	O1—Ni1—N1	170.36 (5)
O1—Ni1—N2	91.21 (5)	N2—Ni1—N1	83.67 (6)

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* ((Bruker, 2001); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2168).

References

- Bruker (2001). *SAINT* (Version 6.45), *SMART* (Version 5.628), *SHELXTL* (Version 6.12) and *SADABS* (Version 2.03). Bruker AXS Inc., Madison, Wisconsin, USA.
- Cozzi, P. G. (2004). *Chem. Soc. Rev.* **33**, 410–421.
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supplementary materials

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Bis{ μ -2,2'-[ethane-1,2-diylbis(nitrilomethylidene)]diphenolato}dinickel(II)

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Comment

A review on metal-salen complexes in catalysis was given recently by Cozzi (2004). Herein, we report on synthesis and crystal structure of [Ni(salen)]₂, (I).

As shown in Fig. 1, the molecular structure of (I) is made up of a centrosymmetric dimer. The Ni^{II} cation is surrounded by two N atoms and two O atoms from the salen ligands leading to a distorted square coordination with mean Ni—O distances of 1.927 Å, and somewhat longer mean Ni—N distances of 1.952 Å. Secondary Ni1—O1(-*x*, *y*, 1/2 - *z*) interactions of 2.4106 (11) Å of one salen ligand to the neighbouring Ni^{II} center link two molecules to a centrosymmetric dimer with an Ni1...Ni1(-*x*, *y*, 1/2 - *z*) separation of 3.1946 (4) Å. The resulting overall coordination sphere of the Ni^{II} cation can thus be described as a distorted square pyramid.

As shown in Fig. 2, there are weak π - π interactions, with plane-to-plane distances and displacement angles for the planes Cg4...Cg5 and Cg5...Cg6 of 3.704 Å and 11.85°, and 4.022 Å and 6.72°, respectively. The planes Cg4, Cg5 and Cg6 consist of atoms C3—O2/N1, C1—C6 and C7—C12.

Experimental

Compound (I) was prepared by adding Ni(Ac)₂·2H₂O (0.110 g, 0.5 mmol) to a solution of H₂(salen) 0.122 mg (0.5 mmol) in methanol (20 mL) and DMF (20 ml). After stirring the mixture for 2 h, the solution was filtered and kept for several days at ambient temperature to evaporate. Brown block-like crystals were obtained.

Refinement

H atoms were placed in geometrically idealized positions and were refined in the riding mode with C—H = 0.97 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for C14 and C15. All other H atoms were refined with C—H = 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Figures

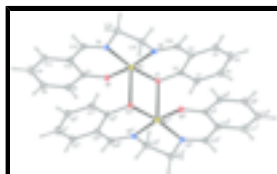


Fig. 1. The molecular structure of (I), showing displacement ellipsoids at the 30% probability level [symmetry code: (i) -*x*, *y*, 1/2 - *z*].

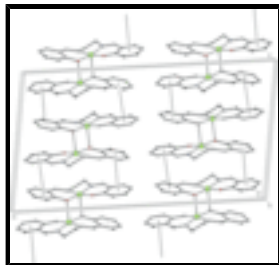


Fig. 2. The packing diagram of (I).

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Crystal data

[Ni₂(C₁₆H₁₄N₂O₂)₂]

$M_r = 650.00$

Monoclinic, $C2/c$

Hall symbol: $-C\ 2yc$

$a = 26.639\ (2)\ \text{\AA}$

$b = 6.9775\ (6)\ \text{\AA}$

$c = 14.7094\ (12)\ \text{\AA}$

$\beta = 97.501\ (1)^\circ$

$V = 2710.7\ (4)\ \text{\AA}^3$

$Z = 4$

$F_{000} = 1344$

$D_x = 1.593\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073\ \text{\AA}$

Cell parameters from 3127 reflections

$\theta = 2.8\text{--}26.6^\circ$

$\mu = 1.44\ \text{mm}^{-1}$

$T = 273\ (2)\ \text{K}$

Block, brown

$0.34 \times 0.21 \times 0.07\ \text{mm}$

Data collection

Bruker SMART CCD
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 273\ (2)\ \text{K}$

ϕ - and ω - scans

Absorption correction: multi-scan
(SADABS; Bruker, 2001)

$T_{\min} = 0.641$, $T_{\max} = 0.906$

8437 measured reflections

3090 independent reflections

2607 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.023$

$\theta_{\max} = 27.5^\circ$

$\theta_{\min} = 2.8^\circ$

$h = -34 \rightarrow 32$

$k = -7 \rightarrow 9$

$l = -16 \rightarrow 19$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.024$

$wR(F^2) = 0.056$

$S = 1.03$

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0243P)^2 + 0.8084P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.39\ \text{e \AA}^{-3}$

3090 reflections

$$\Delta\rho_{\min} = -0.18 \text{ e } \text{\AA}^{-3}$$

191 parameters

Extinction correction: SHELXL,
 $F_c^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Primary atom site location: structure-invariant direct methods

Extinction coefficient: 0.00018 (7)

Secondary atom site location: difference Fourier map

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Ni1	0.267171 (7)	0.20529 (3)	0.402119 (12)	0.02626 (7)
C1	0.13571 (6)	0.5214 (3)	0.42203 (12)	0.0431 (4)
H1	0.1505	0.6316	0.4492	0.052*
O1	0.21557 (4)	0.37606 (15)	0.43757 (7)	0.0331 (2)
C3	0.14245 (6)	0.1972 (2)	0.36791 (11)	0.0381 (4)
C2	0.16650 (6)	0.3629 (2)	0.40947 (10)	0.0333 (3)
C6	0.08435 (7)	0.5180 (3)	0.39534 (14)	0.0560 (5)
H6	0.0650	0.6253	0.4050	0.067*
C4	0.08991 (7)	0.1999 (3)	0.34122 (14)	0.0520 (5)
H4	0.0743	0.0914	0.3138	0.062*
C5	0.06105 (7)	0.3565 (3)	0.35422 (15)	0.0611 (6)
H5	0.0263	0.3551	0.3358	0.073*
C7	0.36315 (6)	0.3962 (2)	0.39857 (10)	0.0341 (4)
C12	0.38590 (6)	0.2332 (2)	0.36206 (12)	0.0383 (4)
C9	0.44526 (7)	0.5552 (3)	0.40933 (14)	0.0560 (5)
H9	0.4651	0.6624	0.4261	0.067*
C8	0.39502 (7)	0.5555 (3)	0.42134 (13)	0.0459 (4)
H8	0.3815	0.6644	0.4453	0.055*
C11	0.43741 (7)	0.2396 (3)	0.34965 (15)	0.0538 (5)
H11	0.4518	0.1331	0.3251	0.065*
N1	0.31197 (5)	0.03112 (18)	0.34648 (9)	0.0342 (3)
O2	0.31572 (4)	0.40839 (15)	0.41080 (8)	0.0386 (3)
N2	0.21745 (5)	0.00240 (18)	0.37265 (9)	0.0360 (3)
C13	0.35815 (6)	0.0617 (2)	0.33554 (11)	0.0392 (4)
H13	0.3750	-0.0349	0.3082	0.047*
C14	0.28630 (7)	-0.1438 (2)	0.30878 (12)	0.0430 (4)
H14A	0.3096	-0.2513	0.3158	0.052*

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H14B	0.2747	-0.1270	0.2440	0.052*
C15	0.24182 (7)	-0.1823 (2)	0.35987 (13)	0.0443 (4)
H15A	0.2181	-0.2688	0.3250	0.053*
H15B	0.2532	-0.2407	0.4188	0.053*
C10	0.46695 (7)	0.3965 (3)	0.37237 (16)	0.0618 (6)
H10	0.5009	0.3974	0.3634	0.074*
C16	0.16935 (7)	0.0228 (2)	0.35544 (11)	0.0402 (4)
H16	0.1504	-0.0832	0.3332	0.048*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.02833 (11)	0.02401 (11)	0.02671 (11)	0.00003 (8)	0.00461 (7)	-0.00381 (8)
C1	0.0403 (9)	0.0467 (10)	0.0431 (10)	0.0081 (8)	0.0082 (8)	0.0044 (8)
O1	0.0303 (6)	0.0334 (6)	0.0356 (6)	0.0004 (5)	0.0048 (4)	-0.0036 (5)
C3	0.0359 (9)	0.0435 (10)	0.0343 (9)	-0.0052 (7)	0.0030 (7)	0.0054 (7)
C2	0.0326 (8)	0.0405 (9)	0.0271 (8)	0.0013 (7)	0.0056 (6)	0.0068 (7)
C6	0.0404 (10)	0.0672 (14)	0.0615 (13)	0.0172 (10)	0.0112 (9)	0.0118 (11)
C4	0.0390 (10)	0.0646 (13)	0.0510 (12)	-0.0112 (9)	0.0007 (8)	0.0094 (10)
C5	0.0288 (9)	0.0842 (16)	0.0691 (14)	0.0010 (10)	0.0019 (9)	0.0164 (12)
C7	0.0328 (8)	0.0386 (9)	0.0309 (8)	-0.0011 (7)	0.0037 (7)	0.0026 (7)
C12	0.0357 (9)	0.0395 (9)	0.0403 (10)	0.0041 (7)	0.0066 (7)	0.0034 (7)
C9	0.0434 (11)	0.0600 (13)	0.0637 (13)	-0.0162 (9)	0.0043 (9)	0.0022 (10)
C8	0.0433 (10)	0.0445 (10)	0.0505 (11)	-0.0054 (8)	0.0082 (8)	-0.0047 (8)
C11	0.0390 (10)	0.0576 (12)	0.0667 (13)	0.0083 (9)	0.0143 (9)	0.0018 (10)
N1	0.0396 (7)	0.0309 (7)	0.0323 (7)	0.0024 (6)	0.0052 (6)	-0.0032 (6)
O2	0.0349 (6)	0.0327 (6)	0.0499 (7)	-0.0017 (5)	0.0119 (5)	-0.0051 (5)
N2	0.0425 (8)	0.0318 (7)	0.0342 (7)	-0.0048 (6)	0.0071 (6)	-0.0026 (6)
C13	0.0438 (10)	0.0365 (9)	0.0387 (9)	0.0109 (7)	0.0110 (7)	-0.0005 (7)
C14	0.0542 (11)	0.0333 (9)	0.0419 (10)	0.0018 (8)	0.0083 (8)	-0.0087 (7)
C15	0.0583 (12)	0.0301 (9)	0.0455 (10)	-0.0035 (8)	0.0102 (9)	-0.0035 (7)
C10	0.0330 (10)	0.0720 (14)	0.0817 (16)	-0.0024 (10)	0.0124 (10)	0.0065 (12)
C16	0.0447 (10)	0.0394 (9)	0.0361 (9)	-0.0142 (8)	0.0037 (7)	-0.0004 (7)

Geometric parameters (\AA , $^\circ$)

Ni1—O2	1.9115 (11)	C12—C13	1.433 (2)
Ni1—O1	1.9412 (10)	C9—C8	1.373 (3)
Ni1—N2	1.9484 (13)	C9—C10	1.392 (3)
Ni1—N1	1.9560 (13)	C9—H9	0.9300
C1—C6	1.373 (2)	C8—H8	0.9300
C1—C2	1.403 (2)	C11—C10	1.364 (3)
C1—H1	0.9300	C11—H11	0.9300
O1—C2	1.3217 (18)	N1—C13	1.279 (2)
C3—C4	1.403 (2)	N1—C14	1.472 (2)
C3—C2	1.421 (2)	N2—C16	1.281 (2)
C3—C16	1.436 (2)	N2—C15	1.466 (2)
C6—C5	1.387 (3)	C13—H13	0.9300
C6—H6	0.9300	C14—C15	1.508 (3)

C4—C5	1.364 (3)	C14—H14A	0.9700
C4—H4	0.9300	C14—H14B	0.9700
C5—H5	0.9300	C15—H15A	0.9700
C7—O2	1.3021 (18)	C15—H15B	0.9700
C7—C8	1.412 (2)	C10—H10	0.9300
C7—C12	1.426 (2)	C16—H16	0.9300
C12—C11	1.409 (2)		
O2—Ni1—O1	91.35 (5)	C9—C8—C7	122.30 (18)
O2—Ni1—N2	171.05 (5)	C9—C8—H8	118.9
O1—Ni1—N2	91.21 (5)	C7—C8—H8	118.9
O2—Ni1—N1	92.53 (5)	C10—C11—C12	122.30 (19)
O1—Ni1—N1	170.36 (5)	C10—C11—H11	118.8
N2—Ni1—N1	83.67 (6)	C12—C11—H11	118.8
C6—C1—C2	121.78 (18)	C13—N1—C14	119.87 (14)
C6—C1—H1	119.1	C13—N1—Ni1	126.75 (11)
C2—C1—H1	119.1	C14—N1—Ni1	113.21 (10)
C2—O1—Ni1	125.41 (10)	C7—O2—Ni1	127.05 (10)
C4—C3—C2	119.15 (16)	C16—N2—C15	121.38 (14)
C4—C3—C16	118.13 (16)	C16—N2—Ni1	126.61 (12)
C2—C3—C16	122.67 (15)	C15—N2—Ni1	111.57 (11)
O1—C2—C1	118.39 (15)	N1—C13—C12	125.11 (15)
O1—C2—C3	124.28 (15)	N1—C13—H13	117.4
C1—C2—C3	117.33 (15)	C12—C13—H13	117.4
C1—C6—C5	120.74 (18)	N1—C14—C15	108.46 (14)
C1—C6—H6	119.6	N1—C14—H14A	110.0
C5—C6—H6	119.6	C15—C14—H14A	110.0
C5—C4—C3	122.08 (19)	N1—C14—H14B	110.0
C5—C4—H4	119.0	C15—C14—H14B	110.0
C3—C4—H4	119.0	H14A—C14—H14B	108.4
C4—C5—C6	118.93 (17)	N2—C15—C14	107.30 (13)
C4—C5—H5	120.5	N2—C15—H15A	110.3
C6—C5—H5	120.5	C14—C15—H15A	110.3
O2—C7—C8	118.69 (15)	N2—C15—H15B	110.3
O2—C7—C12	124.88 (15)	C14—C15—H15B	110.3
C8—C7—C12	116.43 (15)	H15A—C15—H15B	108.5
C11—C12—C7	119.51 (16)	C11—C10—C9	118.58 (18)
C11—C12—C13	117.88 (16)	C11—C10—H10	120.7
C7—C12—C13	122.60 (15)	C9—C10—H10	120.7
C8—C9—C10	120.87 (19)	N2—C16—C3	124.89 (15)
C8—C9—H9	119.6	N2—C16—H16	117.6
C10—C9—H9	119.6	C3—C16—H16	117.6
O2—Ni1—O1—C2	148.07 (12)	O1—Ni1—N1—C14	-54.8 (3)
N2—Ni1—O1—C2	-23.36 (12)	N2—Ni1—N1—C14	3.41 (11)
N1—Ni1—O1—C2	34.3 (4)	C8—C7—O2—Ni1	-170.58 (11)
Ni1—O1—C2—C1	-164.26 (11)	C12—C7—O2—Ni1	10.4 (2)
Ni1—O1—C2—C3	16.4 (2)	O1—Ni1—O2—C7	177.25 (13)
C6—C1—C2—O1	-179.44 (16)	N2—Ni1—O2—C7	-76.1 (4)
C6—C1—C2—C3	-0.1 (3)	N1—Ni1—O2—C7	-11.58 (13)

supplementary materials

C4—C3—C2—O1	179.69 (15)	O2—Ni1—N2—C16	-86.3 (4)
C16—C3—C2—O1	2.5 (3)	O1—Ni1—N2—C16	20.29 (14)
C4—C3—C2—C1	0.4 (2)	N1—Ni1—N2—C16	-151.53 (15)
C16—C3—C2—C1	-176.84 (15)	O2—Ni1—N2—C15	86.0 (3)
C2—C1—C6—C5	-0.4 (3)	O1—Ni1—N2—C15	-167.35 (11)
C2—C3—C4—C5	-0.3 (3)	N1—Ni1—N2—C15	20.84 (11)
C16—C3—C4—C5	177.11 (18)	C14—N1—C13—C12	174.47 (15)
C3—C4—C5—C6	-0.2 (3)	Ni1—N1—C13—C12	-0.4 (2)
C1—C6—C5—C4	0.5 (3)	C11—C12—C13—N1	176.60 (17)
O2—C7—C12—C11	178.16 (16)	C7—C12—C13—N1	-4.5 (3)
C8—C7—C12—C11	-0.8 (2)	C13—N1—C14—C15	158.62 (15)
O2—C7—C12—C13	-0.7 (3)	Ni1—N1—C14—C15	-25.82 (17)
C8—C7—C12—C13	-179.72 (15)	C16—N2—C15—C14	133.16 (16)
C10—C9—C8—C7	1.0 (3)	Ni1—N2—C15—C14	-39.67 (16)
O2—C7—C8—C9	-179.08 (17)	N1—C14—C15—N2	41.36 (18)
C12—C7—C8—C9	0.0 (3)	C12—C11—C10—C9	0.2 (3)
C7—C12—C11—C10	0.8 (3)	C8—C9—C10—C11	-1.1 (3)
C13—C12—C11—C10	179.71 (19)	C15—N2—C16—C3	178.62 (15)
O2—Ni1—N1—C13	6.72 (14)	Ni1—N2—C16—C3	-9.7 (2)
O1—Ni1—N1—C13	120.4 (3)	C4—C3—C16—N2	176.60 (17)
N2—Ni1—N1—C13	178.60 (14)	C2—C3—C16—N2	-6.1 (3)
O2—Ni1—N1—C14	-168.47 (11)		

Fig. 1

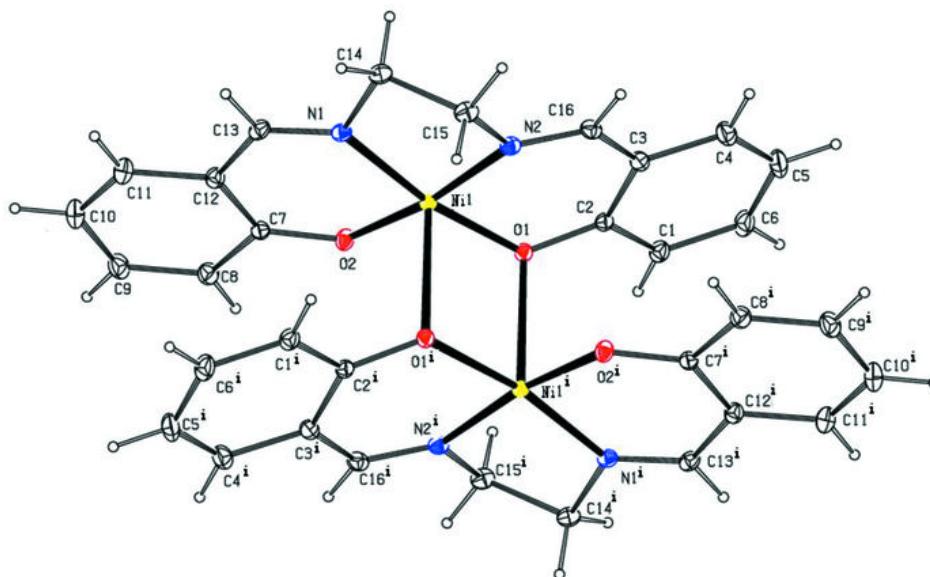


Fig. 2

