

{4,4',6,6'-Tetrachloro-2,2'-[(spiro[4.4]-nonane-1,6-diyl)bis(nitrilomethylidene)]-diphenolato- $\kappa^4 O, N, N', O'$ }nickel(II)

Fan Ni, Zhi-Qing Wu, Lei Liang and Xiang-Ge Zhou*

Institute of Homogeneous Catalysis, Department of Chemistry, Sichuan University, Chengdu 610064, People's Republic of China

Correspondence e-mail: scuzhouxg@163.com

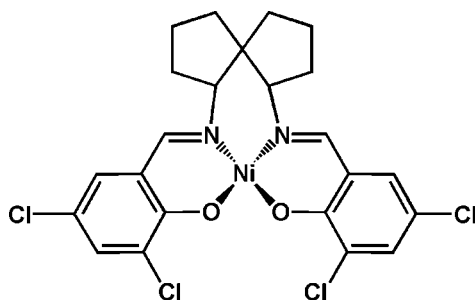
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Key indicators: single-crystal X-ray study; $T = 294$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.039; wR factor = 0.113; data-to-parameter ratio = 18.0.

The title compound, $[\text{Ni}(\text{C}_{23}\text{H}_{20}\text{Cl}_4\text{N}_2\text{O}_2)]$, has an Ni^{II} ion in a square-planar coordination formed by two imine N and two phenolato O atoms.

Related literature

For related literature, see: Gaetani Manfredotti *et al.* (1983), de Castro *et al.* (2001); Lutz (2003); Hoshina *et al.* (2000); Gosden *et al.* (1978, 1981); Healy & Pletcher (1980); Dahm & Peters (1996).



Experimental

Crystal data

$[\text{Ni}(\text{C}_{23}\text{H}_{20}\text{Cl}_4\text{N}_2\text{O}_2)]$
 $M_r = 556.92$

Monoclinic, $P2_1/n$
 $a = 13.344$ (2) Å

$b = 12.073$ (2) Å
 $c = 14.081$ (2) Å
 $\beta = 97.181$ (3)°
 $V = 2250.6$ (6) Å³
 $Z = 4$

Mo $K\alpha$ radiation
 $\mu = 1.36$ mm⁻¹
 $T = 294$ (2) K
 $0.22 \times 0.20 \times 0.12$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
 $T_{\text{min}} = 0.761$, $T_{\text{max}} = 1.000$
(expected range = 0.646–0.849)

20414 measured reflections
5196 independent reflections
3731 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.055$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.113$
 $S = 1.01$
5196 reflections

289 parameters
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.55$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.40$ e Å⁻³

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINTE* (Bruker, 1997); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); 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: IM2062).

References

- Bruker (1997). *SMART* and *SAINTE*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Castro, B. de, Freire, C., Duarte, M. T., Minas da Piedade, M. F. & Santos, I. C. (2001). *Acta Cryst.* **C57**, 370–372.
- Dahm, C. E. & Peters, D. G. (1996). *J. Electroanal. Chem. Interfac. Electrochem.* **406**, 119–121.
- Gaetani Manfredotti, A. & Guastini, C. (1983). *Acta Cryst.* **C39**, 863–865.
- Gosden, C., Healy, K. P. & Pletcher, D. (1978). *J. Chem. Soc. Dalton Trans.* pp. 972–976.
- Gosden, C., Kerr, J. B., Pletcher, D. & Rosas, R. (1981). *J. Electroanal. Chem. Interfac. Electrochem.* **117**, 101–107.
- Healy, K. P. & Pletcher, D. (1980). *J. Organomet. Chem.* **186**, 401–409.
- Hoshina, G., Tsuchimoto, M. & Ohba, S. (2000). *Acta Cryst.* **C56**, e122.
- Lutz, M. (2003). *Acta Cryst.* **E59**, m950–m952.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

supplementary materials

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{4,4',6,6'-Tetrachloro-2,2'-[(spiro[4.4]nonane-1,6-diyl)bis(nitrilomethylidyne)]diphenolato- κ^4 O,N,N',O'}nickel(II)

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Comment

Nickel(II) complexes with N₂O₂ Schiff base ligands derived from salicylaldehyde have long been used as homogenous catalysts (Gosden *et al.*, 1978, 1981; Healy & Pletcher, 1980). More recently, the preparation of metal-salen based modified electrodes by oxidative electropolymerization of the metal complexes prompted their use in heterogenous electrocatalysis (Dahm & Peters, 1996). Work in our laboratory has attempted to introduce spiro[4.4]nonane-1,6-diamine as backbone into the salen system and investigate its coordination feature.

The crystal structure of the title compound **1** is shown in Fig. 1, while bond lengths and angles are listed in the supplementary material. As shown in Fig. 1, the mononuclear Ni^{II} ion is tetra-coordinated, showing a nearly perfectly square-planar coordination mode. The planes Ni1—N1—C10—C11—C12—O1 and Ni1—Ni2—C17—C18—C19—O2 are not coplanar due to the steric pressure of the spirocyclic ligand.

The O—Ni—O, N—Ni—N and N—Ni—O angles correspond very well with the familiar Ni-salen complexes based on 1,2-ethanediamine (Gaetani Manfredotti *et al.* 1983, Lutz, 2003), 1,2-cyclohexanediamine (Castro *et al.* 2001), and 1,2-diphenyl-1,2-ethanediamine (Hoshina *et al.* 2000). de Castro *et al.* found that the coordination geometry usually is tetrahedrally distorted the more the substituents in the imine bridge are bulkier or if the substitution is asymmetric. Here we attribute the intensive distortion to the spiro frame which reinforces the asymmetry.

A comparison with the three analogous nickel complexes above indicates that, in the present compound, both the Ni—O bonding distances [1.848 (2) / 1.846 (2), respectively] are in good agreement with those observed in similar Schiff base Ni complexes whereas the Ni—N bonding distances [1.892 (2) / 1.884 (2) Å, respectively] are slightly longer [reported values range from 1.843 (2) to 1.855 (2) Å].

Experimental

The title complex, [*N,N'*-Bis(3,5-dichloro-salicylidene)- spiro[4.4]nonane-1,6-diaminato]-nickel(II), was prepared by the reaction of a hot methanolic solution (30 mL) of nickel(II) acetate tetrahydrate (0.249 g, 1 mmol) with the Schiff base ligand *N,N'*-Bis(3,5-dichloro-salicylidene)-spiro[4.4]nonane-1,6-diamine (0.500 g, 1 mmol). The resulting green precipitate was collected by filtration and washed with methanol and ether (yield 38%). Dark green crystals of **1** were grown by slow diffusion of ether into a solution of **1** in dichloromethane.

Refinement

All hydrogen atoms of the complex were positioned geometrically and refined using a riding model, with C—H = 0.93 Å (aromatic) and 0.98 Å (methylene) with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Figures

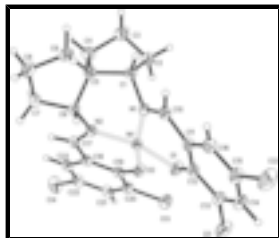


Fig. 1. A view of complex $[\text{Ni}(\text{C}_{23}\text{H}_{20}\text{Cl}_4\text{N}_2\text{O}_2)]$, with displacement ellipsoids drawn at the 30% probability level.

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Crystal data

$[\text{Ni}(\text{C}_{23}\text{H}_{20}\text{Cl}_4\text{N}_2\text{O}_2)]$

$M_r = 556.92$

Monoclinic, $P2_1/n$

Hall symbol: -P 2yn

$a = 13.344$ (2) Å

$b = 12.073$ (2) Å

$c = 14.081$ (2) Å

$\beta = 97.181$ (3)°

$V = 2250.6$ (6) Å³

$Z = 4$

$F_{000} = 1136$

$D_x = 1.644$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 10509 reflections

$\theta = 1-27.5^\circ$

$\mu = 1.36$ mm⁻¹

$T = 294$ (2) K

Prism, black

$0.22 \times 0.20 \times 0.12$ mm

Data collection

Bruker SMART CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 294$ (2) K

φ and ω scans

Absorption correction: multi-scan (SADABS; Sheldrick, 1996)

$T_{\min} = 0.761$, $T_{\max} = 1.000$

20414 measured reflections

5196 independent reflections

3731 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.055$

$\theta_{\text{max}} = 27.6^\circ$

$\theta_{\text{min}} = 2.0^\circ$

$h = -17 \rightarrow 17$

$k = -15 \rightarrow 15$

$l = -18 \rightarrow 18$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.039$

$wR(F^2) = 0.113$

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.065P)^2]$

$S = 1.01$

5196 reflections

289 parameters

Primary atom site location: structure-invariant direct methods

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

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

$\Delta\rho_{\max} = 0.55 \text{ e } \text{\AA}^{-3}$

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

Extinction correction: none

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)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Ni1	0.42863 (2)	0.43913 (3)	0.65679 (2)	0.02559 (11)
Cl1	0.10295 (6)	0.32950 (8)	0.53445 (7)	0.0554 (2)
Cl2	-0.05657 (6)	0.63477 (9)	0.75125 (8)	0.0661 (3)
Cl3	0.41217 (6)	0.10984 (6)	0.47916 (6)	0.0453 (2)
Cl4	0.78080 (7)	0.18824 (7)	0.37495 (7)	0.0568 (2)
O1	0.29376 (14)	0.39968 (17)	0.63812 (14)	0.0377 (5)
O2	0.43951 (13)	0.32517 (15)	0.57124 (13)	0.0327 (4)
N1	0.41147 (15)	0.52722 (18)	0.76468 (15)	0.0276 (5)
N2	0.55652 (15)	0.49892 (17)	0.64347 (15)	0.0267 (5)
C1	0.49859 (19)	0.5405 (2)	0.84037 (18)	0.0306 (6)
H1A	0.4785	0.5892	0.8904	0.037*
C2	0.5314 (2)	0.4293 (3)	0.8853 (2)	0.0416 (7)
H2A	0.5236	0.3704	0.8382	0.050*
H2B	0.4928	0.4110	0.9372	0.050*
C3	0.6429 (2)	0.4480 (3)	0.9227 (2)	0.0441 (8)
H3A	0.6505	0.4916	0.9810	0.053*
H3B	0.6786	0.3784	0.9344	0.053*
C4	0.6798 (2)	0.5111 (3)	0.8402 (2)	0.0410 (7)
H4A	0.6944	0.4605	0.7902	0.049*
H4B	0.7405	0.5526	0.8622	0.049*
C5	0.59263 (19)	0.5905 (2)	0.80250 (18)	0.0285 (6)
C6	0.58053 (19)	0.6042 (2)	0.69372 (18)	0.0274 (5)
H6A	0.5229	0.6537	0.6767	0.033*
C7	0.6754 (2)	0.6688 (2)	0.6779 (2)	0.0366 (6)
H7A	0.6677	0.7045	0.6157	0.044*
H7B	0.7343	0.6210	0.6833	0.044*

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C8	0.6830 (2)	0.7548 (3)	0.7596 (2)	0.0480 (8)
H8A	0.6586	0.8264	0.7355	0.058*
H8B	0.7525	0.7627	0.7886	0.058*
C9	0.6165 (2)	0.7099 (3)	0.8331 (2)	0.0431 (7)
H9A	0.6526	0.7124	0.8973	0.052*
H9B	0.5549	0.7529	0.8317	0.052*
C10	0.32576 (19)	0.5653 (2)	0.78429 (19)	0.0295 (6)
H10A	0.3273	0.6123	0.8368	0.035*
C11	0.22883 (19)	0.5419 (2)	0.73250 (19)	0.0302 (6)
C12	0.21902 (19)	0.4569 (2)	0.66395 (19)	0.0304 (6)
C13	0.1189 (2)	0.4320 (2)	0.6213 (2)	0.0367 (6)
C14	0.0362 (2)	0.4869 (3)	0.6479 (2)	0.0421 (7)
H14A	-0.0285	0.4692	0.6193	0.051*
C15	0.0498 (2)	0.5684 (3)	0.7173 (2)	0.0397 (7)
C16	0.1439 (2)	0.5968 (2)	0.7601 (2)	0.0354 (6)
H16A	0.1517	0.6517	0.8068	0.043*
C17	0.6168 (2)	0.4638 (2)	0.58462 (18)	0.0290 (6)
H17A	0.6717	0.5085	0.5757	0.035*
C18	0.6061 (2)	0.3617 (2)	0.53205 (18)	0.0280 (6)
C19	0.51800 (19)	0.2961 (2)	0.53137 (18)	0.0278 (5)
C20	0.5172 (2)	0.1946 (2)	0.4804 (2)	0.0321 (6)
C21	0.5954 (2)	0.1621 (2)	0.4321 (2)	0.0355 (6)
H21A	0.5921	0.0955	0.3988	0.043*
C22	0.6801 (2)	0.2305 (2)	0.4335 (2)	0.0359 (6)
C23	0.6860 (2)	0.3287 (2)	0.48250 (19)	0.0324 (6)
H23A	0.7428	0.3734	0.4829	0.039*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.02081 (18)	0.02942 (19)	0.02673 (19)	0.00060 (13)	0.00379 (13)	-0.00226 (14)
Cl1	0.0407 (4)	0.0607 (6)	0.0629 (5)	-0.0066 (4)	-0.0008 (4)	-0.0221 (4)
Cl2	0.0264 (4)	0.0838 (7)	0.0887 (7)	0.0125 (4)	0.0095 (4)	-0.0225 (6)
Cl3	0.0416 (4)	0.0319 (4)	0.0620 (5)	-0.0045 (3)	0.0044 (4)	-0.0038 (3)
Cl4	0.0631 (5)	0.0467 (5)	0.0688 (6)	0.0084 (4)	0.0402 (5)	-0.0077 (4)
O1	0.0227 (10)	0.0430 (11)	0.0477 (12)	-0.0003 (8)	0.0057 (8)	-0.0123 (9)
O2	0.0251 (9)	0.0325 (10)	0.0416 (11)	-0.0006 (8)	0.0077 (8)	-0.0089 (8)
N1	0.0216 (11)	0.0342 (12)	0.0274 (11)	-0.0005 (9)	0.0044 (9)	0.0002 (9)
N2	0.0244 (11)	0.0294 (12)	0.0262 (11)	0.0014 (9)	0.0030 (9)	0.0002 (9)
C1	0.0239 (13)	0.0420 (16)	0.0258 (13)	0.0021 (11)	0.0023 (10)	-0.0030 (11)
C2	0.0359 (16)	0.0485 (18)	0.0393 (17)	-0.0031 (13)	0.0006 (13)	0.0122 (14)
C3	0.0333 (16)	0.059 (2)	0.0385 (17)	0.0051 (14)	-0.0034 (13)	0.0139 (15)
C4	0.0268 (15)	0.0538 (19)	0.0418 (17)	0.0066 (13)	0.0012 (12)	0.0058 (15)
C5	0.0217 (12)	0.0345 (15)	0.0287 (14)	0.0004 (10)	0.0003 (10)	-0.0017 (11)
C6	0.0236 (13)	0.0274 (13)	0.0308 (14)	-0.0008 (10)	0.0020 (10)	-0.0008 (11)
C7	0.0332 (15)	0.0364 (16)	0.0406 (16)	-0.0072 (12)	0.0065 (12)	0.0014 (13)
C8	0.0472 (19)	0.0435 (18)	0.054 (2)	-0.0134 (15)	0.0088 (15)	-0.0082 (15)
C9	0.0445 (18)	0.0451 (18)	0.0392 (17)	-0.0112 (14)	0.0030 (13)	-0.0129 (14)

C10	0.0271 (13)	0.0315 (14)	0.0306 (14)	0.0006 (11)	0.0059 (11)	-0.0010 (11)
C11	0.0232 (13)	0.0360 (15)	0.0323 (14)	0.0008 (11)	0.0067 (11)	0.0031 (11)
C12	0.0239 (13)	0.0332 (15)	0.0350 (15)	-0.0011 (11)	0.0069 (11)	0.0024 (12)
C13	0.0312 (15)	0.0387 (16)	0.0393 (16)	-0.0040 (12)	0.0007 (12)	-0.0018 (13)
C14	0.0224 (14)	0.0531 (19)	0.0500 (18)	-0.0021 (13)	0.0015 (12)	-0.0004 (15)
C15	0.0233 (14)	0.0472 (18)	0.0493 (18)	0.0057 (12)	0.0077 (12)	0.0011 (14)
C16	0.0306 (15)	0.0394 (16)	0.0368 (16)	0.0069 (12)	0.0067 (12)	0.0010 (12)
C17	0.0269 (13)	0.0313 (14)	0.0292 (14)	-0.0031 (11)	0.0055 (11)	0.0014 (11)
C18	0.0301 (14)	0.0283 (14)	0.0259 (13)	0.0054 (11)	0.0043 (11)	0.0020 (11)
C19	0.0284 (13)	0.0278 (13)	0.0275 (13)	0.0039 (11)	0.0042 (11)	0.0019 (11)
C20	0.0324 (14)	0.0295 (14)	0.0339 (15)	0.0015 (11)	0.0017 (11)	0.0028 (11)
C21	0.0465 (17)	0.0272 (14)	0.0338 (15)	0.0060 (13)	0.0093 (13)	0.0000 (12)
C22	0.0398 (16)	0.0356 (16)	0.0348 (15)	0.0108 (13)	0.0146 (12)	0.0024 (12)
C23	0.0325 (15)	0.0343 (15)	0.0321 (15)	0.0014 (12)	0.0109 (12)	0.0052 (12)

Geometric parameters (Å, °)

Ni1—O2	1.8463 (18)	C6—H6A	0.9800
Ni1—O1	1.8484 (19)	C7—C8	1.544 (4)
Ni1—N2	1.884 (2)	C7—H7A	0.9700
Ni1—N1	1.892 (2)	C7—H7B	0.9700
Cl1—C13	1.734 (3)	C8—C9	1.544 (4)
Cl2—C15	1.747 (3)	C8—H8A	0.9700
Cl3—C20	1.733 (3)	C8—H8B	0.9700
Cl4—C22	1.739 (3)	C9—H9A	0.9700
O1—C12	1.302 (3)	C9—H9B	0.9700
O2—C19	1.297 (3)	C10—C11	1.432 (4)
N1—C10	1.294 (3)	C10—H10A	0.9300
N1—C1	1.484 (3)	C11—C12	1.403 (4)
N2—C17	1.296 (3)	C11—C16	1.409 (4)
N2—C6	1.470 (3)	C12—C13	1.426 (4)
C1—C2	1.525 (4)	C13—C14	1.379 (4)
C1—C5	1.546 (4)	C14—C15	1.383 (4)
C1—H1A	0.9800	C14—H14A	0.9300
C2—C3	1.532 (4)	C15—C16	1.366 (4)
C2—H2A	0.9700	C16—H16A	0.9300
C2—H2B	0.9700	C17—C18	1.436 (4)
C3—C4	1.522 (4)	C17—H17A	0.9300
C3—H3A	0.9700	C18—C23	1.403 (4)
C3—H3B	0.9700	C18—C19	1.416 (4)
C4—C5	1.548 (4)	C19—C20	1.420 (4)
C4—H4A	0.9700	C20—C21	1.372 (4)
C4—H4B	0.9700	C21—C22	1.397 (4)
C5—C9	1.527 (4)	C21—H21A	0.9300
C5—C6	1.529 (4)	C22—C23	1.368 (4)
C6—C7	1.526 (4)	C23—H23A	0.9300
O2—Ni1—O1	82.52 (8)	H7A—C7—H7B	109.2
O2—Ni1—N2	94.27 (8)	C7—C8—C9	105.9 (2)
O1—Ni1—N2	164.28 (9)	C7—C8—H8A	110.6

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O2—Ni1—N1	165.98 (9)	C9—C8—H8A	110.6
O1—Ni1—N1	92.62 (9)	C7—C8—H8B	110.6
N2—Ni1—N1	93.82 (9)	C9—C8—H8B	110.6
C12—O1—Ni1	126.14 (18)	H8A—C8—H8B	108.7
C19—O2—Ni1	128.15 (17)	C5—C9—C8	105.0 (2)
C10—N1—C1	116.2 (2)	C5—C9—H9A	110.7
C10—N1—Ni1	124.76 (18)	C8—C9—H9A	110.7
C1—N1—Ni1	118.34 (16)	C5—C9—H9B	110.7
C17—N2—C6	118.3 (2)	C8—C9—H9B	110.7
C17—N2—Ni1	125.51 (19)	H9A—C9—H9B	108.8
C6—N2—Ni1	115.40 (15)	N1—C10—C11	126.0 (3)
N1—C1—C2	111.2 (2)	N1—C10—H10A	117.0
N1—C1—C5	113.0 (2)	C11—C10—H10A	117.0
C2—C1—C5	106.5 (2)	C12—C11—C16	121.6 (2)
N1—C1—H1A	108.7	C12—C11—C10	119.7 (2)
C2—C1—H1A	108.7	C16—C11—C10	118.2 (3)
C5—C1—H1A	108.7	O1—C12—C11	124.8 (2)
C1—C2—C3	103.2 (2)	O1—C12—C13	118.7 (2)
C1—C2—H2A	111.1	C11—C12—C13	116.5 (2)
C3—C2—H2A	111.1	C14—C13—C12	121.6 (3)
C1—C2—H2B	111.1	C14—C13—Cl1	120.2 (2)
C3—C2—H2B	111.1	C12—C13—Cl1	118.3 (2)
H2A—C2—H2B	109.1	C13—C14—C15	119.7 (3)
C4—C3—C2	101.8 (2)	C13—C14—H14A	120.2
C4—C3—H3A	111.4	C15—C14—H14A	120.2
C2—C3—H3A	111.4	C16—C15—C14	121.5 (3)
C4—C3—H3B	111.4	C16—C15—Cl2	119.8 (2)
C2—C3—H3B	111.4	C14—C15—Cl2	118.7 (2)
H3A—C3—H3B	109.3	C15—C16—C11	119.1 (3)
C3—C4—C5	105.7 (2)	C15—C16—H16A	120.4
C3—C4—H4A	110.6	C11—C16—H16A	120.4
C5—C4—H4A	110.6	N2—C17—C18	125.5 (2)
C3—C4—H4B	110.6	N2—C17—H17A	117.3
C5—C4—H4B	110.6	C18—C17—H17A	117.3
H4A—C4—H4B	108.7	C23—C18—C19	121.3 (2)
C9—C5—C6	99.9 (2)	C23—C18—C17	117.9 (2)
C9—C5—C1	114.9 (2)	C19—C18—C17	120.9 (2)
C6—C5—C1	113.5 (2)	O2—C19—C18	124.0 (2)
C9—C5—C4	111.5 (2)	O2—C19—C20	119.8 (2)
C6—C5—C4	113.0 (2)	C18—C19—C20	116.1 (2)
C1—C5—C4	104.4 (2)	C21—C20—C19	122.6 (3)
N2—C6—C7	120.4 (2)	C21—C20—Cl3	119.4 (2)
N2—C6—C5	112.2 (2)	C19—C20—Cl3	118.0 (2)
C7—C6—C5	102.5 (2)	C20—C21—C22	119.2 (3)
N2—C6—H6A	107.0	C20—C21—H21A	120.4
C7—C6—H6A	107.0	C22—C21—H21A	120.4
C5—C6—H6A	107.0	C23—C22—C21	121.0 (2)
C6—C7—C8	102.3 (2)	C23—C22—Cl4	119.6 (2)
C6—C7—H7A	111.3	C21—C22—Cl4	119.4 (2)

C8—C7—H7A	111.3	C22—C23—C18	119.8 (3)
C6—C7—H7B	111.3	C22—C23—H23A	120.1
C8—C7—H7B	111.3	C18—C23—H23A	120.1
O2—Ni1—O1—C12	-167.0 (2)	C6—C5—C9—C8	-37.3 (3)
N2—Ni1—O1—C12	-87.9 (4)	C1—C5—C9—C8	-159.1 (2)
N1—Ni1—O1—C12	26.2 (2)	C4—C5—C9—C8	82.4 (3)
O1—Ni1—O2—C19	172.9 (2)	C7—C8—C9—C5	12.0 (3)
N2—Ni1—O2—C19	8.3 (2)	C1—N1—C10—C11	-165.9 (3)
N1—Ni1—O2—C19	-116.8 (4)	Ni1—N1—C10—C11	4.6 (4)
O2—Ni1—N1—C10	-88.5 (4)	N1—C10—C11—C12	11.5 (4)
O1—Ni1—N1—C10	-19.3 (2)	N1—C10—C11—C16	-175.7 (3)
N2—Ni1—N1—C10	146.4 (2)	Ni1—O1—C12—C11	-18.5 (4)
O2—Ni1—N1—C1	81.9 (4)	Ni1—O1—C12—C13	162.3 (2)
O1—Ni1—N1—C1	151.08 (19)	C16—C11—C12—O1	-177.0 (3)
N2—Ni1—N1—C1	-43.26 (19)	C10—C11—C12—O1	-4.5 (4)
O2—Ni1—N2—C17	4.1 (2)	C16—C11—C12—C13	2.2 (4)
O1—Ni1—N2—C17	-73.4 (4)	C10—C11—C12—C13	174.7 (2)
N1—Ni1—N2—C17	172.7 (2)	O1—C12—C13—C14	177.7 (3)
O2—Ni1—N2—C6	174.05 (17)	C11—C12—C13—C14	-1.5 (4)
O1—Ni1—N2—C6	96.6 (4)	O1—C12—C13—C11	-2.0 (4)
N1—Ni1—N2—C6	-17.40 (18)	C11—C12—C13—C11	178.8 (2)
C10—N1—C1—C2	109.6 (3)	C12—C13—C14—C15	0.2 (5)
Ni1—N1—C1—C2	-61.6 (3)	C11—C13—C14—C15	179.9 (2)
C10—N1—C1—C5	-130.8 (2)	C13—C14—C15—C16	0.5 (5)
Ni1—N1—C1—C5	58.1 (3)	C13—C14—C15—C12	-178.8 (2)
N1—C1—C2—C3	154.6 (2)	C14—C15—C16—C11	0.2 (5)
C5—C1—C2—C3	31.1 (3)	C12—C15—C16—C11	179.5 (2)
C1—C2—C3—C4	-42.6 (3)	C12—C11—C16—C15	-1.6 (4)
C2—C3—C4—C5	38.5 (3)	C10—C11—C16—C15	-174.2 (3)
N1—C1—C5—C9	107.9 (3)	C6—N2—C17—C18	178.2 (2)
C2—C1—C5—C9	-129.7 (3)	Ni1—N2—C17—C18	-12.2 (4)
N1—C1—C5—C6	-6.2 (3)	N2—C17—C18—C23	-170.7 (2)
C2—C1—C5—C6	116.1 (3)	N2—C17—C18—C19	8.5 (4)
N1—C1—C5—C4	-129.7 (2)	Ni1—O2—C19—C18	-13.3 (4)
C2—C1—C5—C4	-7.4 (3)	Ni1—O2—C19—C20	169.04 (18)
C3—C4—C5—C9	105.1 (3)	C23—C18—C19—O2	-176.0 (2)
C3—C4—C5—C6	-143.2 (2)	C17—C18—C19—O2	4.8 (4)
C3—C4—C5—C1	-19.4 (3)	C23—C18—C19—C20	1.8 (4)
C17—N2—C6—C7	-1.1 (4)	C17—C18—C19—C20	-177.4 (2)
Ni1—N2—C6—C7	-171.80 (19)	O2—C19—C20—C21	176.2 (2)
C17—N2—C6—C5	-121.8 (2)	C18—C19—C20—C21	-1.7 (4)
Ni1—N2—C6—C5	67.5 (2)	O2—C19—C20—C13	-3.3 (3)
C9—C5—C6—N2	179.9 (2)	C18—C19—C20—C13	178.82 (19)
C1—C5—C6—N2	-57.2 (3)	C19—C20—C21—C22	0.7 (4)
C4—C5—C6—N2	61.4 (3)	C13—C20—C21—C22	-179.8 (2)
C9—C5—C6—C7	49.4 (3)	C20—C21—C22—C23	0.2 (4)
C1—C5—C6—C7	172.2 (2)	C20—C21—C22—C14	178.4 (2)
C4—C5—C6—C7	-69.2 (3)	C21—C22—C23—C18	-0.1 (4)
N2—C6—C7—C8	-167.4 (2)	C14—C22—C23—C18	-178.3 (2)

supplementary materials

C5—C6—C7—C8	-42.0 (3)	C19—C18—C23—C22	-1.0 (4)
C6—C7—C8—C9	18.2 (3)	C17—C18—C23—C22	178.3 (2)

Fig. 1

