Bis[1,2-bis(4-chlorophenyl)ethylene-1,2-dithiolato(1−)]nickel(II)

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The title compound, [Ni(S₂C₂(C₆H₄-p-Cl)₂)₂] or [Ni(C₁₄H₈Cl₂S₂)₂], crystallizes in the triclinic space group Pī as pairs of molecules disposed about an inversion center at the bc face of the cell. Close intermolecular C—H/C1/C1/C1/S (2.884 Å) and C—H/C1/C1/C1/Ni (3.032 Å) contacts that are less than the sum of the van der Waals radii appear to induce slight bowing of the molecular planes toward one another. The angles at which the four p-ClC₆H₄- rings join the NiS₂C₂ chelate rings [39.37 (9)–53.41 (6)] are similarly influenced by these intermolecular contacts. In the larger packing arrangement, sheets of molecules extend in the direction of the ac face diagonal.

Structure description

As seen from a survey of the Cambridge Structural Database, nickel has enjoyed the most extensive development of its coordination chemistry with dithiolene ligands that bear aryl substituents. One reason for the attention given to these nickel complexes is the application they have found as reversibly bleachable Q-switching dyes for near infrared lasers (Mueller-Westerhoff et al., 1991). Their photochemical, thermal, and chemical stability, in conjunction with the relative ease with which they are synthesized, has made such nickel bis(dithiolene) complexes impactful enough that a variety are now sold commercially. Charge-neutral, aryl-substituted nickel dithiolene complexes, [(R₂C₂S₂)₂Ni], that have been structurally characterized include the complexes where R = Ph (Megnamisi-Belombe & Nuber, 1989; Kuramoto & Asao, 1990), p-CH₃C₆H₄- (Miao et al., 2011), p-CH₃OC₆H₄- (Arumugam et al., 2007), p-"BuOC₆H₄- (Perochon et al., 2009), p-CH₃(CH₂)₆C₆H₄- (Perochon et al., 2009), and 3,5-(CH₃O)₂-4-"BuOC₆H₂- (Nakazumi et al., 1992).

Compounds of this type are electrochemically rich and typically support two successive ligand-based one-electron reductions that correspond to the transformations depicted as
The redox-active molecular orbital has rather modest metal character and is best described as being delocalized among both dithiolene ligands, which individually may be regarded as radical monoanions but which collectively have their spins paired such that the charge-neutral state is diamagnetic. In structure (c), both dithiolene ligands are in a fully reduced ene-1,2-dithiolate dianionic state.

The potentials at which these reductions occur are quite sensitive to the nature and placement of ring substituents. As part of an effort to more fully map the potential range in which the electron transfers in these complexes occur, we have undertaken the synthesis and characterization of aryl-substituted nickel(II) bis(dithiolene) complexes bearing electron-withdrawing groups. Although a known compound, the nickel(II) bis(dithiolene) variant with $p$-ClC$_6$H$_4$– substituents has not been the subject of an X-ray diffraction study, nor has a coordination compound of this ligand with any other metal. We briefly relate here the structural and crystal packing features of [(p-ClC$_6$H$_4$)$_2$C$_2$S$_2$]Ni.

Bis[1,2-bis(4-chlorophenylethylene)-1,2-dithiolato(1–)]nickel(II) crystallizes upon a general position in triclinic space group $P\overline{1}$ (Fig. 2). Its idealized point-group symmetry is $D_{2h}$ if the phenyl groups are either perfectly perpendicular to, or fully planar with, the Ni(S$_2$C$_2$)$_2$ core. However, the four arene rings are canted from the NiS$_2$C$_2$ chelate ring to which they are attached by values ranging from 38.39 (9)– 53.41 (6)$^\circ$, the average being 44.87$^\circ$. A similar description is pertinent to the compounds featuring phenyl, $p$-CH$_3$C$_6$H$_4$–, and $p$-CH$_3$OC$_6$H$_4$– substituents. The averaged S–C bond length in [(p-ClC$_6$H$_4$)$_2$C$_2$S$_2$]Ni is 1.707 (1) Å. This intermediate value between S–C thione (1.63 Å, Rindorf & Carlsen, 1979; Fu et al., 1997) and vinyl thioether (1.74 Å; Tian et al., 1995; Yu et al., 2011) bond lengths is due to the presence of some thione character to the bond order in the radical monoaion arising from resonance form (e) (Fig. 1), even as the ligands are coordinating to the metal. Similarly, the C–C$_{chelate}$ bond lengths are between the 1.54 and 1.34 Å values that are typical of carbon–carbon $sp^3$–$sp^3$ single and $sp^2$–$sp^2$ double bonds, respectively (Carey & Sundberg, 2000), further indicating the participation of both resonance forms (d) and (e) in the electronic structure of bis[1,2-bis(4-chlorophenylethylene)-1,2-dithiolato(1–)]nickel(II).

The packing arrangement for bis[1,2-bis(4-chlorophenylethylene)-1,2-dithiolato(1–)]nickel(II) is such that molecules occur in centrosymmetric pairs around the inversion centers that occur at each bc face of the cell (Fig. 3). These pairwise associations juxtapose two molecules in a nearly parallel planar fashion but with an offset that places the phenyl groups of one ligand over the relatively open NiS$_4$ interior of its partner molecule. Relatively close intermolecular C–H–S (2.884 Å) and C–H–Ni (3.032 Å) contacts are made (Fig. 4), two each that are related by the inversion symmetry. The C–H–S and C–N–Ni close contacts are less than the sum of the hydrogen–sulfur and hydrogen–nickel van der Waals radii (Batsanov, 2001) and appear to be favorable interactions that induce a slight but discernible concave bowing of the mol-
The title compound was prepared from 4,4′-dichlorobenzil, P₂S₁₀, and NiCl₂·6H₂O according to the literature procedure (Schrauzer & Mayweg, 1965). Yield: 50%. Intense green column-shaped crystals were grown by the diffusion of tert-butyl methyl ether vapor into a solution of the title compound in 1,2-dichloroethane.

Synthesis and crystallization

The title compound was prepared from 4,4′-dichlorobenzil, P₂S₁₀, and NiCl₂·6H₂O according to the literature procedure (Schrauzer & Mayweg, 1965). Yield: 50%. Intense green column-shaped crystals were grown by the diffusion of tert-butyl methyl ether vapor into a solution of the title compound in 1,2-dichloroethane.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. One reflection affected by the beamstop was omitted from the final refinement.

Acknowledgements

Tulane University is acknowledged for its ongoing support with operational costs for the diffraction facility and for publication costs.

| Crystal data |
|---|---|
| Chemical formula | [Ni(C₁₄H₁₂Cl₂S₂)₂] |
| M₀ | 681.16 |
| Crystal system, space group | Triclinic, PṬ |
| Temperature (K) | 170 |
| a, b, c (Å) | 9.5487 (4), 11.4141 (4), 15.0254 (6) |
| α, β, γ (°) | 107.486 (2), 94.791 (2), 111.423 (2) |
| V (Å³) | 1419.16 (10) |
| Radiation type | Mo Kα |
| μ (mm⁻¹) | 1.37 |
| Crystal size (mm) | 0.27 × 0.15 × 0.10 |

Table 1

Experimental details.

Data collection

| Diffractometer | Bruker D8 QUEST PHOTON 3 diffractometer |
|---|---|
| Absorption correction | Numerical (SADABS; Krause et al., 2015) |
| T_min, T_max | 0.76, 0.88 |
| No. of measured, independent and observed | 89629, 8009, 5941 |
| R(int) | 0.056 |
| (sin θ/λ)max (Å⁻¹) | 0.696 |

Refinement

| R[F² > 2σ(F²)], wR(F²), S | 0.040, 0.112, 1.03 |
| No. of reflections | 8009 |
| No. of parameters | 334 |
| H-atoms treatment | H-atoms parameters constrained |
| Δρ_max, Δρ_min (e Å⁻³) | 0.78, −0.45 |

Computer programs: APEX3 and SAINT (Bruker, 2020), SHELXL (Sheldrick, 2015a), SHELXL2018/1 (Sheldrick, 2015b), DIAMOND (Brandenburg & Putz, 2012), and SHELXTL (Sheldrick, 2008).

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full crystallographic data

IUCrData (2022). 7, x220148  [https://doi.org/10.1107/S2414314622001481]

Bis[1,2-bis(4-chlorophenyl)ethylene-1,2-dithiolato(1−)]nickel(II)

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Bis[1,2-bis(4-chlorophenyl)-2-sulfanylideneethane-1-thiolato]nickel(II)

Crystal data

\[
\begin{align*}
&\text{[Ni(C}_{14}\text{H}_{8}\text{Cl}_{2}\text{S}_{2}]_{2} \\
&M_r = 681.16 \\
&\text{Triclinic, } P\overline{1} \\
&a = 9.5487 (4) \text{ Å} \\
&b = 11.4141 (4) \text{ Å} \\
&c = 15.0254 (6) \text{ Å} \\
&\alpha = 107.486 (2) ^\circ \\
&\beta = 94.791 (2) ^\circ \\
&\gamma = 111.423 (2) ^\circ \\
&V = 1419.16 (10) \text{ Å}^3
\end{align*}
\]

\[Z = 2\]

\[F(000) = 688\]

\[D_x = 1.594 \text{ Mg m}^{-3}\]

Mo Kα radiation, λ = 0.71073 Å

Cell parameters from 9023 reflections

\[\theta = 2.4-29.5^\circ\]

\[\mu = 1.37 \text{ mm}^{-1}\]

\[T = 170 \text{ K}\]

Column, intense green

0.27 × 0.15 × 0.10 mm

Data collection

Bruker D8 QUEST PHOTON 3
diffractometer

Radiation source: fine-focus sealed tube
Graphite monochromator

Detector resolution: 7.3910 pixels mm\(^{-1}\)
\(\phi\) and \(\omega\) scans

Absorption correction: numerical
\((SADABS; \text{Krause et al., 2015})\)

\[T_{\text{min}} = 0.76, T_{\text{max}} = 0.88\]

Refinement

Refinement on \(F^2\)
Least-squares matrix: full

\[R(F^2 > 2\sigma(F^2)) = 0.040\]

\[wR(F^2) = 0.112\]

\[S = 1.03\]

8009 reflections
334 parameters
0 restraints

Primary atom site location: dual

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained

\[w = 1/[\sigma(F_c^2) + (0.0524P)^2 + 1.0724P]\]

where \(P = (F_c^2 + 2F_s^2)/3\)

\[(\Delta/\sigma)_{\text{max}} = 0.001\]

\[\Delta \rho_{\text{max}} = 0.78 \text{ e Å}^{-3}\]

\[\Delta \rho_{\text{min}} = -0.45 \text{ e Å}^{-3}\]
**Special details**

**Experimental.** The diffraction data were obtained from sets 11 of frames, each of width 0.5° in \( \omega \) or \( \phi \), collected with scan parameters determined by the "strategy" routine in APEX3. The scan time was 15 sec/frame.

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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\(^2\) > 2sigma(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. H-atoms attached to carbon were placed in calculated positions (C—H = 0.95 Å). All were included as riding contributions with isotropic displacement parameters 1.2 times those of the attached atoms.

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

|   | x       | y       | z       | U\(_{eq}\) |
|---|---------|---------|---------|-----------|
| Ni1| 0.35173 (3) | 0.63386 (3) | 0.56629 (2) | 0.03136 (9) |
| Cl1| 1.01198 (10) | 0.89129 (9) | 1.11457 (5) | 0.0646 (2) |
| Cl2| 0.44766 (10) | 0.05522 (7) | 0.82193 (5) | 0.05315 (18) |
| Cl3| -0.27660 (10) | 0.36001 (13) | 0.00470 (6) | 0.0866 (3) |
| Cl4| 0.00224 (9) | 1.14473 (7) | 0.34765 (5) | 0.05241 (18) |
| S1| 0.51018 (7) | 0.75530 (5) | 0.69986 (4) | 0.03387 (13) |
| S2| 0.35562 (7) | 0.45659 (5) | 0.58196 (4) | 0.03250 (13) |
| S3| 0.19444 (7) | 0.50969 (5) | 0.43335 (4) | 0.03449 (13) |
| S4| 0.32801 (6) | 0.80720 (5) | 0.55486 (4) | 0.03159 (12) |
| C1| 0.6573 (3) | 0.7049 (2) | 0.83698 (16) | 0.0316 (4) |
| C2| 0.6637 (3) | 0.8171 (2) | 0.91031 (18) | 0.0402 (5) |
| H2| 0.591392 | 0.854176 | 0.902039 | 0.048* |
| C3| 0.7730 (3) | 0.8754 (3) | 0.99479 (19) | 0.0458 (6) |
| H3| 0.776586 | 0.952416 | 1.043937 | 0.055* |
| C4| 0.8768 (3) | 0.8206 (3) | 1.00694 (18) | 0.0423 (6) |
| C5| 0.8749 (3) | 0.7106 (3) | 0.9358 (2) | 0.0460 (6) |
| H5| 0.947798 | 0.674405 | 0.944845 | 0.055* |
| C6| 0.7664 (3) | 0.6533 (3) | 0.85115 (18) | 0.0392 (5) |
| H6| 0.765655 | 0.577825 | 0.801890 | 0.047* |
| C7| 0.5440 (3) | 0.6456 (2) | 0.74536 (16) | 0.0307 (4) |
| C8| 0.4672 (3) | 0.5076 (2) | 0.69248 (16) | 0.0314 (4) |
| C9| 0.4672 (2) | 0.3986 (2) | 0.72654 (16) | 0.0296 (4) |
| C10| 0.4301 (3) | 0.3963 (2) | 0.81393 (16) | 0.0334 (5) |
| H10| 0.410317 | 0.468058 | 0.853727 | 0.040* |
| C11| 0.4218 (3) | 0.2903 (2) | 0.84348 (17) | 0.0353 (5) |
| H11| 0.394413 | 0.288101 | 0.902488 | 0.042* |
| C12| 0.4541 (3) | 0.1880 (2) | 0.78565 (17) | 0.0343 (5) |
| C13| 0.4911 (3) | 0.1876 (2) | 0.69874 (17) | 0.0349 (5) |
| H13| 0.512544 | 0.116288 | 0.659864 | 0.042* |
| C14| 0.4966 (3) | 0.2923 (2) | 0.66892 (17) | 0.0325 (5) |
| H14| 0.520569 | 0.292032 | 0.608783 | 0.039* |
| C15| 0.0353 (3) | 0.5525 (2) | 0.29789 (17) | 0.0330 (5) |
|       | x      | y      | z      | U₁₁    | U₂₂    | U₃₃    | U₁₂    | U₁₃    | U₂₃    |
|-------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| C16   | -0.0885 (3) | 0.4265 (3) | 0.27169 (19) | 0.0409 (5) |
| H16   | -0.106881  | 0.381348 | 0.316152 | 0.049* |
| C17   | -0.1839 (3) | 0.3672 (3) | 0.1819 (2) | 0.0527 (7) |
| H17   | -0.268122  | 0.281852 | 0.164421 | 0.063* |
| C18   | -0.1553 (3) | 0.4339 (3) | 0.11759 (19) | 0.0512 (7) |
| C19   | -0.0334 (3) | 0.5563 (3) | 0.14068 (19) | 0.0475 (6) |
| H19   | -0.015078  | 0.600008 | 0.095417 | 0.057* |
| C20   | 0.0625 (3)  | 0.6152 (3) | 0.23024 (18) | 0.0395 (5) |
| H20   | 0.147957   | 0.699344 | 0.246213 | 0.047* |
| C21   | 0.1388 (2)  | 0.6145 (2) | 0.39363 (16) | 0.0308 (4) |
| C22   | 0.1954 (2)  | 0.7506 (2) | 0.45073 (16) | 0.0304 (4) |
| C23   | 0.1474 (2)  | 0.8490 (2) | 0.42788 (15) | 0.0295 (4) |
| C24   | -0.0076 (3) | 0.8158 (2) | 0.39296 (17) | 0.0343 (5) |
| H24   | -0.082964  | 0.729787 | 0.385917 | 0.041* |
| C25   | -0.0535 (3) | 0.9061 (2) | 0.36839 (17) | 0.0353 (5) |
| H25   | -0.159136  | 0.882127 | 0.344000 | 0.042* |
| C26   | 0.0569 (3)  | 1.0315 (2) | 0.37998 (17) | 0.0349 (5) |
| C27   | 0.2113 (3)  | 1.0700 (2) | 0.41777 (18) | 0.0349 (5) |
| C28   | 0.2555 (3)  | 0.9781 (2) | 0.44116 (17) | 0.0319 (4) |
| H28   | 0.360993   | 1.003321 | 0.466667 | 0.038* |

**Atomic displacement parameters (Å²)**

|      | U₁₁    | U₂₂    | U₃₃    | U₁₂    | U₁₃    | U₂₃    |
|------|--------|--------|--------|--------|--------|--------|
| Ni1  | 0.0357 (16) | 0.02817 (15) | 0.03695 (16) | 0.01568 (12) | 0.01086 (12) | 0.01650 (12) |
| Cl1  | 0.0720 (5)  | 0.0606 (5)  | 0.0441 (4)  | 0.0149 (4)  | 0.0112 (3)  | 0.0158 (3)  |
| Cl2  | 0.0827 (5)  | 0.0370 (3)  | 0.0519 (4)  | 0.0335 (3)  | 0.00122 (3) | 0.0021 (3)  |
| Cl3  | 0.0569 (5)  | 0.1278 (9)  | 0.0417 (4)  | 0.0310 (5)  | 0.0044 (3)  | 0.00022 (5) |
| Cl4  | 0.0680 (4)  | 0.0482 (4)  | 0.0639 (4)  | 0.0402 (3)  | 0.0187 (3)  | 0.0293 (3)  |
| S1   | 0.0401 (3)  | 0.0266 (3)  | 0.0392 (3)  | 0.0155 (2)  | 0.0100 (2)  | 0.0150 (2)  |
| S2   | 0.0382 (3)  | 0.0270 (3)  | 0.0364 (3)  | 0.0152 (2)  | 0.0095 (2)  | 0.0143 (2)  |
| S3   | 0.0407 (3)  | 0.0255 (3)  | 0.0398 (3)  | 0.0148 (2)  | 0.0085 (2)  | 0.0136 (2)  |
| S4   | 0.0346 (3)  | 0.0263 (3)  | 0.0358 (3)  | 0.0140 (2)  | 0.0065 (2)  | 0.0121 (2)  |
| C1   | 0.0365 (11) | 0.0275 (10) | 0.0344 (11) | 0.0145 (9)  | 0.0131 (9)  | 0.0126 (9)  |
| C2   | 0.0494 (14) | 0.0340 (12) | 0.0426 (13) | 0.0231 (11) | 0.0139 (11) | 0.0126 (10) |
| C3   | 0.0614 (17) | 0.0352 (13) | 0.0393 (13) | 0.0203 (12) | 0.0158 (12) | 0.0095 (11) |
| C4   | 0.0470 (14) | 0.0411 (13) | 0.0370 (12) | 0.0132 (11) | 0.0078 (11) | 0.0183 (11) |
| C5   | 0.0453 (14) | 0.0478 (15) | 0.0491 (15) | 0.0244 (12) | 0.0081 (12) | 0.0169 (12) |
| C6   | 0.0429 (13) | 0.0389 (13) | 0.0388 (12) | 0.0226 (11) | 0.0015 (10) | 0.0000 (10) |
| C7   | 0.0331 (11) | 0.0318 (11) | 0.0379 (11) | 0.0182 (9)  | 0.0062 (9)  | 0.0018 (9)  |
| C8   | 0.0366 (11) | 0.0325 (11) | 0.0360 (11) | 0.0201 (9)  | 0.0060 (9)  | 0.0017 (9)  |
| C9   | 0.0310 (10) | 0.0260 (10) | 0.0358 (11) | 0.0143 (8)  | 0.0010 (9)  | 0.0025 (9)  |
| C10  | 0.0403 (12) | 0.0303 (11) | 0.0365 (11) | 0.0199 (10) | 0.0037 (9)  | 0.0013 (9)  |
| C11  | 0.0448 (13) | 0.0326 (11) | 0.0346 (11) | 0.0197 (10) | 0.0010 (10) | 0.0015 (9)  |
| C12  | 0.0384 (12) | 0.0292 (11) | 0.0386 (12) | 0.0163 (9)  | 0.0027 (9)  | 0.0014 (9)  |
| C13  | 0.0378 (12) | 0.0283 (11) | 0.0408 (12) | 0.0180 (9)  | 0.0081 (10) | 0.0009 (9)  |
| C14  | 0.0341 (11) | 0.0297 (11) | 0.0369 (11) | 0.0159 (9)  | 0.0012 (9)  | 0.0011 (9)  |
|     | U (Å²)       | U (Å²)       | U (Å²)       | U (Å²)       | U (Å²)       | U (Å²)       |
|-----|--------------|--------------|--------------|--------------|--------------|--------------|
| C15 | 0.0331 (11)  | 0.0297 (11)  | 0.0371 (12)  | 0.0164 (9)   | 0.0089 (9)   | 0.0082 (9)   |
| C16 | 0.0363 (12)  | 0.0365 (12)  | 0.0449 (14)  | 0.0140 (10)  | 0.0136 (10)  | 0.0079 (11)  |
| C17 | 0.0325 (13)  | 0.0517 (16)  | 0.0531 (16)  | 0.0120 (12)  | 0.0110 (12)  | −0.0032 (13) |
| C18 | 0.0410 (14)  | 0.0702 (19)  | 0.0369 (13)  | 0.0308 (14)  | 0.0056 (11)  | 0.0028 (13)  |
| C19 | 0.0536 (16)  | 0.0589 (17)  | 0.0385 (13)  | 0.0344 (14)  | 0.0107 (12)  | 0.0145 (12)  |
| C20 | 0.0444 (13)  | 0.0385 (13)  | 0.0404 (13)  | 0.0219 (11)  | 0.0105 (10)  | 0.0139 (10)  |
| C21 | 0.0303 (10)  | 0.0281 (10)  | 0.0397 (12)  | 0.0141 (9)   | 0.0116 (9)   | 0.0161 (9)   |
| C22 | 0.0286 (10)  | 0.0309 (11)  | 0.0385 (11)  | 0.0149 (9)   | 0.0119 (9)   | 0.0170 (9)   |
| C23 | 0.0318 (11)  | 0.0277 (10)  | 0.0327 (11)  | 0.0142 (9)   | 0.0107 (9)   | 0.0121 (9)   |
| C24 | 0.0307 (11)  | 0.0293 (11)  | 0.0458 (13)  | 0.0127 (9)   | 0.0127 (10)  | 0.0157 (10)  |
| C25 | 0.0307 (11)  | 0.0374 (12)  | 0.0408 (12)  | 0.0177 (9)   | 0.0073 (9)   | 0.0132 (10)  |
| C26 | 0.0466 (13)  | 0.0349 (12)  | 0.0363 (12)  | 0.0270 (10)  | 0.0141 (10)  | 0.0161 (10)  |
| C27 | 0.0372 (12)  | 0.0255 (10)  | 0.0453 (13)  | 0.0128 (9)   | 0.0168 (10)  | 0.0152 (9)   |
| C28 | 0.0301 (10)  | 0.0278 (10)  | 0.0393 (12)  | 0.0131 (9)   | 0.0106 (9)   | 0.0117 (9)   |

**Geometric parameters (Å, °)**

| Bond/Angle                     | Value 1 | Value 2 | Value 3 | Value 4 | Value 5 | Value 6 |
|--------------------------------|---------|---------|---------|---------|---------|---------|
| Ni1—S2                         | 2.1192 (6) |         |         |         |         |         |
| Ni1—S3                         | 2.1207 (7) |         |         |         |         |         |
| Ni1—S4                         | 2.1261 (6) |         |         |         |         |         |
| Ni1—S1                         | 2.1277 (7) |         |         |         |         |         |
| C11—C12                        | 1.383 (3) |         |         |         |         |         |
| C11—H11                        | 0.9500   |         |         |         |         |         |
| C12—C13                        | 1.380 (3) |         |         |         |         |         |
| C13—C14                        | 1.382 (3) |         |         |         |         |         |
| C14—C15                        | 1.400 (3) |         |         |         |         |         |
| C15—C16                        | 1.400 (3) |         |         |         |         |         |
| C16—C17                        | 1.479 (3) |         |         |         |         |         |
| C17—C18                        | 1.380 (4) |         |         |         |         |         |
| C18—C19                        | 1.371 (4) |         |         |         |         |         |
| C19—C20                        | 1.379 (4) |         |         |         |         |         |
| C20—C21                        | 0.9500   |         |         |         |         |         |
| C21—C22                        | 0.9500   |         |         |         |         |         |
| C22—C23                        | 1.397 (3) |         |         |         |         |         |
| C23—C24                        | 1.397 (3) |         |         |         |         |         |
| C24—C25                        | 1.386 (3) |         |         |         |         |         |
| C25—C26                        | 1.386 (3) |         |         |         |         |         |

**S2—Ni1—S3**                     | 87.80 (2) |         |         |         |         |         |

**C12—C13—H13**                   | 120.4    |         |         |         |         |         |

*Data reports*
S2—Ni1—S4 174.64 (3)  C14—C13—H13 120.4
S3—Ni1—S4 91.24 (2)  C13—C14—C9 120.6 (2)
S2—Ni1—S1 91.15 (2)  C13—C14—H14 119.7
S3—Ni1—S1 178.94 (2)  C9—C14—H14 119.7
S4—Ni1—S1 89.82 (2)  C20—C15—C16 118.6 (2)
C7—S1—Ni1 105.72 (8)  C20—C15—C21 121.0 (2)
C8—S2—Ni1 105.67 (8)  C16—C15—C21 120.4 (2)
C21—S3—Ni1 105.66 (8)  C17—C16—C15 120.6 (3)
C22—S4—Ni1 105.76 (8)  C17—C16—H16 119.7
C2—C1—C6 117.9 (2)  C15—C16—H16 119.7
C2—C1—C7 121.3 (2)  C16—C17—C18 119.1 (3)
C6—C1—C7 120.7 (2)  C16—C17—H17 120.5
C3—C2—C1 121.3 (2)  C18—C17—H17 120.5
C3—C2—H2 119.3  C19—C18—C17 121.6 (3)
C1—C2—H2 119.3  C19—C18—Cl3 119.3 (2)
C4—C3—C2 119.2 (2)  C17—C18—Cl3 119.1 (2)
C4—C3—H3 120.4  C18—C19—C20 119.3 (3)
C2—C3—H3 120.4  C18—C19—H19 120.3
C5—C4—C3 121.1 (2)  C20—C19—H19 120.3
C5—C4—C11 119.5 (2)  C19—C20—C15 120.8 (3)
C3—C4—C11 119.4 (2)  C19—C20—H20 119.6
C4—C5—C6 119.6 (2)  C21—C15—C20 119.6
C4—C5—H5 120.2  C22—C21—C15 124.79 (19)
C6—C5—H5 120.2  C22—C21—S3 119.14 (17)
C5—C6—C1 120.9 (2)  C15—C21—S3 116.05 (16)
C5—C6—H6 119.6  C21—C22—C23 124.3 (2)
C1—C6—H6 119.6  C21—C22—S4 118.07 (16)
C8—C7—C1 124.84 (19)  C22—C23—C28 117.60 (17)
C8—C7—S1 118.29 (17)  C24—C23—C28 118.3 (2)
C1—C7—S1 116.84 (16)  C24—C23—C22 120.7 (2)
C7—C8—C9 125.3 (2)  C28—C23—C22 120.95 (19)
C7—C8—S2 118.86 (16)  C25—C24—C23 121.3 (2)
C9—C8—S2 115.76 (17)  C25—C24—H24 119.4
C10—C9—C14 118.9 (2)  C23—C24—H24 119.4
C10—C9—C8 120.74 (19)  C26—C25—C24 118.9 (2)
C14—C9—C8 120.3 (2)  C26—C25—H25 120.6
C11—C10—C9 120.8 (2)  C24—C25—H25 120.6
C11—C10—H10 119.6  C25—C26—C27 121.5 (2)
C9—C10—H10 119.6  C25—C26—C14 119.58 (18)
C12—C11—C10 118.9 (2)  C27—C26—C14 118.88 (18)
C12—C11—H11 120.5  C28—C27—C26 118.8 (2)
C10—C11—H11 120.5  C28—C27—H27 120.6
C13—C12—C11 121.6 (2)  C26—C27—H27 120.6
C13—C12—C12 118.56 (18)  C27—C28—C23 121.1 (2)
C11—C12—C12 119.87 (18)  C27—C28—H28 119.4
C12—C13—C14 119.3 (2)  C23—C28—H28 119.4
C6—C1—C2—C3 −0.5 (4)  C20—C15—C16—C17 −1.7 (4)
C7—C1—C2—C3 −177.8 (2) C21—C15—C16—C17 −179.0 (2)
C1—C2—C3—C4 −0.6 (4) C15—C16—C17—C18 0.3 (4)
C2—C3—C4—C5 1.2 (4) C16—C17—C18—C19 0.9 (4)
C2—C3—C4—Cl1 −178.4 (2) C17—C18—C19—C20 −0.6 (4)
C3—C4—C5—C6 179.0 (2) C13—C18—C19—C20 179.73 (19)
C11—C4—C5—C6 179.0 (2) C15—C16—C17—C18 −179.4 (2)
C4—C5—C6—C1 1.1 (4) C18—C19—C20—C15 −0.9 (4)
C2—C1—C6—C5 178.4 (2) C16—C15—C20—C19 2.0 (3)
C7—C1—C6—C5 178.4 (2) C21—C15—C20—C19 179.3 (2)
C2—C1—C7—C8 −142.3 (2) C20—C15—C21—C22 44.4 (3)
C6—C1—C7—C8 40.5 (3) C16—C15—C21—C22 −138.4 (2)
C2—C1—C7—S1 39.8 (3) C20—C15—C21—S3 −133.8 (2)
C6—C1—C7—S1 −137.4 (2) C21—C15—C20—C19 43.5 (3)
Ni1—S1—C7—C8 −0.78 (19) Ni1—S3—C21—C22 2.11 (19)
Ni1—S1—C7—C1 177.20 (14) Ni1—S3—C21—C15 176.18 (15)
C1—C7—C8—C9 10.5 (3) Ni1—S2—C21—C22 −138.4 (2)
S1—C7—C8—C9 −171.64 (17) Ni1—S2—C21—C23 6.6 (3)
C1—C7—C8—S2 −172.99 (17) S3—C21—C22—C23 175.30 (17)
S1—C7—C8—S2 4.8 (3) C15—C21—C22—S4 −174.10 (17)
Ni1—S2—C8—C7 −6.26 (19) Ni1—S4—C22—C21 175.60 (14)
Ni1—S2—C8—C9 170.53 (14) Ni1—S4—C22—C23 42.9 (3)
C7—C8—C9—C10 51.3 (3) C2—C22—C23—C24 43.1 (3)
S2—C8—C9—C10 −125.3 (2) C2—C22—C23—C28 136.43 (19)
C7—C8—C9—C14 −132.1 (2) C2—C22—C23—C28 −137.6 (2)
S2—C8—C9—C14 51.3 (3) C2—C22—C23—C28 43.1 (3)
C14—C9—C10—C11 −0.2 (3) C2—C22—C23—C28 −138.0 (2)
C8—C9—C10—C11 176.4 (2) C2—C22—C23—C28 −178.0 (2)
C9—C10—C11—C12 1.3 (4) C2—C22—C23—C28 −0.7 (4)
C10—C11—C12—C13 −1.3 (4) C2—C22—C23—C28 −1.7 (4)
C10—C11—C12—C12 178.92 (18) C2—C22—C23—C28 178.84 (18)
C11—C12—C13—C14 0.2 (4) C2—C22—C23—C28 2.2 (4)
C12—C12—C13—C14 −179.98 (18) C2—C22—C23—C28 −178.26 (18)
C12—C13—C14—C9 0.9 (3) C2—C22—C23—C28 −0.4 (3)
C10—C9—C14—C13 −0.9 (3) C2—C22—C23—C28 −1.9 (3)
C8—C9—C14—C13 −177.6 (2) C2—C22—C23—C28 178.5 (2)