

Short Communication

# The Structure of a Toroidal, Neutral, Homoleptic Ni(II) Complex with a Chelate Dithiolate Ligand, $[\text{Ni}_6(\text{SCH}_2\text{CH}_2\text{CH}_2\text{S})_6]$

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Metal thiolates are of interest as synthetic models, both for the active sites in certain metalloproteins,<sup>1,2</sup> and for metal sulfide catalysts.<sup>3,4</sup> Thiolate ligands have a strong affinity for many metal ions, including Ni(II), and often binds in bridging modes, forming di- and polynuclear complexes.<sup>5</sup>

A number of polynuclear ( $n \geq 3$ ) homoleptic Ni(II) thiolate complexes have been isolated and structurally characterized. With monodentate thiolate ligands a series of neutral, cyclic complexes,  $[\text{Ni}_n(\text{SR})_n]$ ,  $n = 4, 5, 6, 8$ , are known.<sup>6–14</sup> With chelate dithiolate ligands, on the other hand, the homoleptic Ni(II) complexes characterized and reported to date are anionic, acyclic species;  $[\text{Ni}_n(\text{SRS})_{n+1}]^{2-}$ ,  $n = 3, 6$ .<sup>15–17</sup> For heteroleptic species, containing chelating dithiolate and O- or N-containing ligands, both neutral, cyclic Ni(II) complexes<sup>18,19</sup> and an anionic, cyclic Ni(II) complex have been described.<sup>16a,20</sup> The present paper reports, to our knowledge, the first example of a neutral, cyclic, homoleptic Ni(II) complex with a chelate dithiolate ligand;  $[\text{Ni}_6(\text{SCH}_2\text{CH}_2\text{CH}_2\text{S})_6]$ . It has been suggested that toroidal nickel thiolates may function as a monomolecular inclusion hosts.<sup>12,14</sup> Recently, this question and other structural and bonding features in this class of compounds, have been addressed in a theoretical study.<sup>21</sup>

## Experimental

**Preparation of compound.**  $[\text{Ni}_6(\text{pdt})_6]$ , ( $\text{pdt}^{2-} = 1,3$ -propanedithiolate) was isolated as a crystalline side-product from the reaction mixture of  $\{\text{O}(\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{CH}_2\text{SH})_2\}$  and  $\text{NiCl}_2\{\text{P}(\text{C}_6\text{H}_5)_3\}_2$  in a 1:1 molar ratio in  $\text{CH}_2\text{Cl}_2$  under an  $\text{N}_2$  atmosphere, during work aimed at

producing mononuclear, pentacoordinate Ni thiolate complexes.<sup>19,22,23</sup>

**X-Ray data collection and structure determination.** The brown, irregularly shaped crystals rapidly developed an oily surface upon removal from the mother liquid, and had a modest diffraction power even at low reflection angles. A crystal of dimensions  $0.36 \times 0.18 \times 0.12$  mm was sealed in a quartz capillary under an  $\text{N}_2$  atmosphere, and diffraction data were collected at 295 K with an Enraf–Nonius CAD4 diffractometer using monochromatized Mo  $K\alpha$  radiation ( $\lambda = 0.71073$  Å). Unit-cell parameters were determined from a least-squares fit of the setting angles of 24 reflections with  $2\theta$  in the range  $10$ – $32^\circ$ . Originally an orthorhombic C-centred cell was assumed, but, as deviations from  $mmm$  Laue symmetry were observed, the cell was transformed to a primitive monoclinic cell (with  $a$ - and  $c$ -axes of almost equal length), and data were collected accordingly. A total of 2913 unique reflections were recorded in the range  $2 < 2\theta < 50^\circ$ . The intensities of three reference reflections monitored throughout the data collection fluctuated by  $\pm 6\%$  owing to movement of the crystal in the capillary, and decreased in average by 2.6%. The data were corrected for Lorentz and polarization effects and for anisotropic decay. Direct methods gave the starting positions for the Ni and S atoms; the remaining atoms were located through successive Fourier syntheses. After isotropic refinement of non-hydrogen atoms, hydrogen atoms were included at fixed, calculated positions, and an empirical absorption correction was carried out.<sup>24</sup> In the final full-matrix least-squares cycles, which included the adjustment of an extinction parameter, Ni and S were anisotropically refined and C isotropically. 1255 reflections with  $I > 3\sigma$  were used in the refinement, which con-

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Table 1. Crystal data for  $[\text{Ni}_6(\text{SCH}_2\text{CH}_2\text{CH}_2\text{S})_6]$ .

Formula	$\text{Ni}_6\text{S}_{12}\text{C}_{18}\text{H}_{36}$
FW	989.52
Unit cell	Monoclinic
$a/\text{\AA}$	9.964(2)
$b/\text{\AA}$	17.440(2)
$c/\text{\AA}$	9.975(2)
$\beta/^\circ$	112.57(2)
$V/\text{\AA}^3$	1601(1)
$Z$	2
$D_{\text{calc}}/\text{g cm}^{-3}$	2.05
Space group	$P2_1/c$
Scan mode	$\theta-2\theta$
Scan range	$\Delta\theta = 0.80^\circ + 0.347 \tan \theta$
Scan rate/ $^\circ \text{min}^{-1}$	1.4
Absorption coefficient, $\mu/\text{mm}^{-1}$	4.2463
Transmission factors	0.782–1.222 (av. = 0.990)
Unique observed reflections ( $I > 3\sigma_I$ )	1255
No. of parameters refined	119
Secondary extinction coefficient	$1.03(46) \times 10^{-7}$
$R^a$	0.090
$R_w^b$	0.126
Goodness of fit	2.378

<sup>a</sup>  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ . <sup>b</sup>  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2}$  where  $w^{-1} = [\sigma^2_{\text{count}} + (0.06F^2)^2] / 4F^2$ .

verged at  $R = 0.090$ . The scattering curves, with anomalous scattering terms included, were those of Cromer and Mann.<sup>25</sup> All calculations were carried out using the SPD/Vax package of programs supplied by Enraf–Nonius.<sup>26</sup> Crystal parameters and refinement results are summa-

Table 2. Positional and equivalent isotropic thermal parameters.<sup>a</sup>

Atom	x	y	z	$B/\text{\AA}^{2b}$
Ni1	0.3669(4)	0.3696(2)	0.3756(4)	2.70(8)
Ni2	0.6291(4)	0.3426(2)	0.6333(4)	2.42(8)
Ni3	0.7630(4)	0.4786(2)	0.7582(4)	3.02(9)
S1	0.3386(8)	0.4283(5)	0.1717(8)	3.2(2)
S2	0.1623(8)	0.4301(5)	0.3458(8)	3.3(2)
S3	0.4027(7)	0.3091(5)	0.5780(7)	3.0(2)
S4	0.5682(8)	0.3061(4)	0.4088(7)	2.9(2)
S5	0.8563(8)	0.3770(5)	0.6869(8)	3.1(2)
S6	0.6909(8)	0.3809(5)	0.8570(7)	2.9(2)
C1	0.179(4)	0.385(2)	0.031(4)	5.4(9)*
C2	0.090(3)	0.333(2)	0.102(3)	2.9(6)*
C3	0.028(4)	0.379(2)	0.183(3)	4.7(8)*
C4	0.321(3)	0.358(2)	0.693(3)	4.3(8)*
C5	0.396(3)	0.421(2)	0.780(3)	3.1(6)*
C6	0.530(3)	0.405(2)	0.901(3)	2.9(6)*
C7	0.687(3)	0.346(2)	0.328(3)	3.6(7)*
C8	0.772(3)	0.420(2)	0.396(3)	4.4(8)*
C9	0.896(4)	0.396(2)	0.529(4)	5.4(9)*

<sup>a</sup> Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter, defined as:

$$4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}].$$

<sup>a</sup>  $B$ -values marked with an asterisk denote isotropically refined atoms.

Table 3. Bond distances (in  $\text{\AA}$ ).

Atom	Atom <sup>a</sup>	Distance	Atom	Atom	Distance
Ni1	S1	2.196(9)	S1	C1	1.83(3)
Ni1	S2	2.211(9)	S2	C3	1.89(3)
Ni1	S3	2.183(8)	S3	C4	1.84(4)
Ni1	S4	2.203(8)	S4	C7	1.80(4)
Ni2	S3	2.186(8)	S5	C9	1.80(4)
Ni2	S4	2.179(8)	S6	C6	1.86(3)
Ni2	S5	2.200(8)	C1	C2	1.62(5)
Ni2	S6	2.179(8)	C2	C3	1.43(5)
Ni3	S1 <sup>i</sup>	2.167(9)	C4	C5	1.43(4)
Ni3	S2 <sup>i</sup>	2.181(10)	C5	C6	1.44(3)
Ni3	S5	2.241(9)	C7	C8	1.56(4)
Ni3	S6	2.222(9)	C8	C9	1.48(4)

<sup>a</sup> Superscript i refers to the symmetry operation  $1-x, 1-y, 1-z$ .

rized in Table 1, atomic coordinates, bond lengths and bond angles are listed in Tables 2–4. Supplementary material comprises tables of anisotropic thermal parameters, coordinates of hydrogen atoms, least-squares planes, observed and calculated structure factors (Tables S1–S4).

## Results and discussion

**Preparation.** The Ni(II)/propanedithiolate system has previously been explored, and binuclear  $[\text{Ni}_2(\text{pdt})_3]^{2-}$  and acyclic hexanuclear  $[\text{Ni}_6(\text{pdt})_7]^{2-}$  were isolated, depending on the Ni/pdt ratio.<sup>17</sup> In the present study  $\text{pdt}^{2-}$  was not originally present in the reaction mixture. However, the species may have been formed by Ni-promoted cleavage of the thioether C–S bond of  $\{\text{O}(\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{CH}_2\text{SH})_2\}$ . Such cleavage reactions have been investigated in closely related systems.<sup>22,27</sup>

**Structural aspects.** In the hexanuclear molecule  $\text{Ni}_6(\text{SCH}_2\text{CH}_2\text{CH}_2\text{S})_6$  (Fig. 1) there is a distorted, planar hexagon of six nickel atoms, bridged by twelve sulfur atoms. The sulfur atoms are arranged in planes (to within 0.04  $\text{\AA}$ ) 1.41  $\text{\AA}$  above and below the plane of the nickel atoms. Each nickel atom is coordinated to four sulfur atoms in an approximately planar, rectangular arrangement. The dihedral angles between the  $S_4$  least-squares planes clearly demonstrate the distortion of the hexagon;  $\text{Ni1S}_4/\text{Ni2S}_4 = 119.1^\circ$ ,  $\text{Ni2S}_4/\text{Ni3S}_4 = 106.5^\circ$ ,  $\text{Ni1S}_4/\text{Ni3S}_4 = 134.4^\circ$ . The nickel atoms deviate only slightly, 0.011–0.023  $\text{\AA}$ , from the planes defined by the four sulfur ligands; Ni2 and Ni3 outward from the torus, Ni1 inward. The separation between adjacent metal atoms are  $\text{Ni1}\cdots\text{Ni2} = 2.916(4)$   $\text{\AA}$ ,  $\text{Ni2}\cdots\text{Ni3} = 2.773(5)$   $\text{\AA}$  and  $\text{Ni1}\cdots\text{Ni3}^i = 3.022(5)$   $\text{\AA}$ , while distances between the centrosymmetrically related metal atoms in the molecule are  $\text{Ni1}\cdots\text{Ni1}^i = 5.369(5)$   $\text{\AA}$ ,  $\text{Ni2}\cdots\text{Ni2}^i = 6.212(5)$   $\text{\AA}$  and  $\text{Ni3}\cdots\text{Ni3}^i = 5.817(4)$   $\text{\AA}$ . The  $\text{pdt}^{2-}$  groups all act as chelating ligands, but bridge the nickel atoms in two different modes. The molecular structure may be derived by assembling in an all-*cis* fashion two of each of the

Table 4. Bond Angles (in °).

Atom <sup>a</sup>	Atom	Atom <sup>a</sup>	Angle	Atom <sup>a</sup>	Atom	Atom <sup>a</sup>	Angle
S1	Ni1	S2	82.5(3)	Ni3 <sup>i</sup>	S2	C3	101.2(1.2)
S1	Ni1	S3	177.7(4)	Ni1	S3	Ni2	83.7(3)
S1	Ni1	S4	99.2(3)	Ni1	S3	C4	113.4(1.0)
S2	Ni1	S3	99.8(4)	Ni2	S3	C4	112.1(9)
S2	Ni1	S4	178.0(4)	Ni1	S4	Ni2	83.5(3)
S3	Ni1	S4	78.5(3)	Ni1	S4	C7	117.1(1.0)
S3	Ni2	S4	79.0(3)	Ni2	S4	C7	112.1(9)
S3	Ni2	S5	179.4(3)	Ni2	S5	Ni3	77.3(3)
S3	Ni2	S6	101.5(3)	Ni2	S5	C9	113.1(1.0)
S4	Ni2	S5	100.6(3)	Ni3	S5	C9	112.8(1.2)
S4	Ni2	S6	179.1(3)	Ni2	S6	Ni3	78.1(3)
S5	Ni2	S6	78.9(3)	Ni2	S6	C6	112.3(8)
S1 <sup>i</sup>	Ni3	S2 <sup>i</sup>	83.9(4)	Ni3	S6	C6	112.7(1.0)
S1 <sup>i</sup>	Ni3	S5	176.0(3)	S1	C1	C2	111(2)
S1 <sup>i</sup>	Ni3	S6	99.2(4)	C1	C2	C3	111(3)
S2 <sup>i</sup>	Ni3	S5	99.7(3)	S2	C3	C2	116(2)
S2 <sup>i</sup>	Ni3	S6	176.8(3)	S3	C4	C5	119(3)
S5	Ni3	S6	77.2(4)	C4	C5	C6	117(3)
Ni1	S1	Ni3 <sup>i</sup>	87.7(3)	S6	C6	C5	117(2)
Ni1	S1	C1	106.5(1.3)	S4	C7	C8	118(2)
Ni3 <sup>i</sup>	S1	C1	100.4(1.3)	C7	C8	C9	107(3)
Ni1	S2	Ni3 <sup>i</sup>	87.0(4)	S5	C9	C8	117(3)
Ni1	S2	C3	101.6(1.2)				

<sup>a</sup> Superscript i refers to the symmetry operation 1-x, 1-y, 1-z.

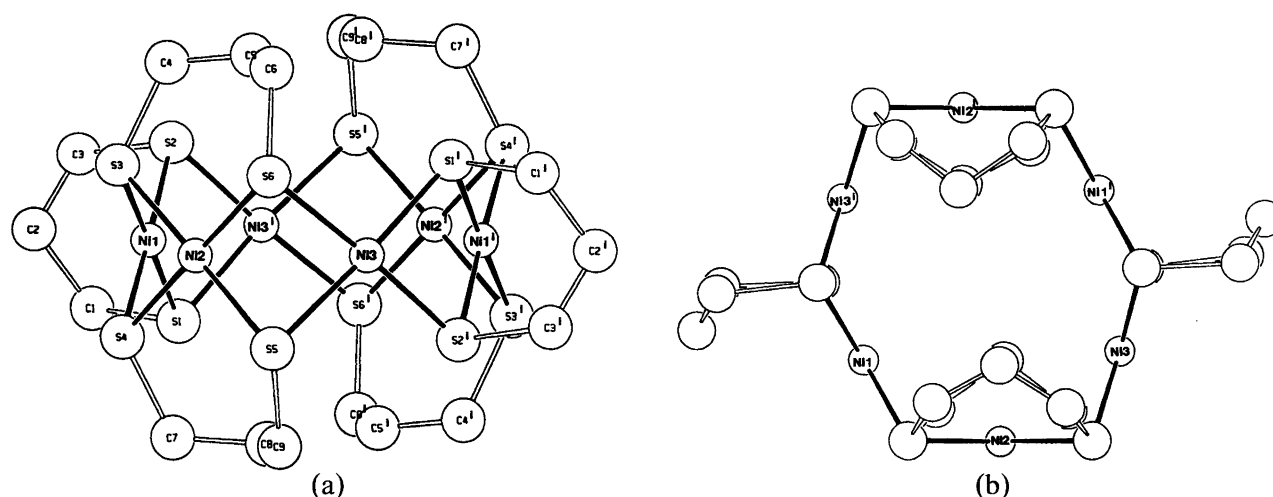


Fig. 1. (a) Hexanuclear unit with the atomic numbering scheme used. Superscript i refers to symmetry operation 1-x, 1-y, 1-z. (b) The molecule projected on to the Ni<sub>6</sub> plane.

hypothetical units  $[\text{Ni}(\text{pdt})_2]^{2-}$  and  $[\text{Ni}(\text{pdt})\text{Ni}]^{2+}$ . This gives an arrangement where four of the S-C bonds are approximately parallel to the toroidal axis (axial ligand), while two of the bonds extend approximately normal to this axis (equatorial ligand). The largest of the NiS<sub>4</sub>/NiS<sub>4</sub> dihedral angles occurs between planes whose sharing edge is defined by an equatorial ligand. The Ni-S bond lengths are in the range 2.167–2.241 Å, but within the limit of errors do not depend systematically on the bridging mode of the connected dithiolate.

Comparison of the neutral, cyclic nickel(II) hexanuclear complexes containing monodentate thiolate ligands<sup>10–13</sup> with the nickel dithiolate shown in Fig. 1 re-

veals several differences. Whereas the tiara skeletons of the former group of compounds all have close to hexagonal symmetry, deviation from this symmetry is appreciable in the latter compound. This deviation is probably related to the occurrence of two different bridging modes of the dithiolate. Furthermore, in the compounds with monodentate thiolate ligands the S-Ni-S angles involving sulfur atoms situated on the same side of the plane of nickel atoms have been found to be in average 15° larger than those with sulfur atoms lying on opposite sides of the plane. This difference is even larger in Ni<sub>6</sub>(pdt)<sub>6</sub>, the average of the two groups of angles being 100.0 and 80.0°, respectively. One may also notice that the S-Ni-S

angles involving a dithiolate chelate ring are systematically larger than the other angles within the same group. In the complexes with monofunctional thiolates the S–C bonds point alternately axially and equatorially, while this is not so in Ni<sub>6</sub>(pdt)<sub>6</sub>, even though both axial and equatorial bonds are present. The ranges of Ni–S–C<sub>equatorial</sub> angles (100.4–106.5°) and Ni–S–C<sub>axial</sub> angles (112.1–117.1°) found in the present compound are close to those found in the hexamers containing monofunctional thiolates. Also, the average Ni–S bond distance of 2.196 Å in Ni<sub>6</sub>(pdt)<sub>6</sub> agrees well with the corresponding average of 2.201 Å for the other group of compounds.

It is also of interest to compare the present compound with the non-cyclic, anionic species, [Ni<sub>6</sub>(pdt)<sub>7</sub>]<sup>2-</sup>,<sup>17</sup> as the same two types of bridging modes of the dithiolate occur in the two compounds. If one terminal dithiolate of the anion were removed, and the NiS<sub>4</sub> units were rearranged from their *cis-trans-cis* orientation to an all-*cis* orientation, the structure of the present compound would in principle be realized. The general feature of larger S–Ni–S angles when both sulfur atoms are on the same side of the nickel plane is also present in the open-chain anion, and Ni–S bond lengths are similar to those in the present compound.

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