

# 行政院國家科學委員會專題研究成果報告

\*\*\*\*\*  
\*  
\* 多硫分子導體的製備、物性和結構研究 \*  
\*  
\* Preparative, Physical and Structural \*  
\* Characterization of \*  
\* Multi-sulfur Charge-transfer Complexes (V) \*  
\*  
\*\*\*\*\*

計劃類別： 個別型計劃

計劃編號： NSC-89-2113-M-032-029-

執行期間： 89年 8月 1日 - 90年 10月 31日

個別型計劃： 計畫主持人： 李 榮 熹

處理方式： 可立即對外提供參考

執行單位： 淡 江 大 學 化 學 系

中 華 民 國 九 十 二 年 一 月 日

## ABSTRACT

Reactions of Qimnt<sup>-</sup> with [Ni(II)L<sup>R</sup>]<sup>2+</sup> {Qimnt = 2,2'-(4,8-dihydro-4,8-dioxobenzo[1,2-d:4,5-d']bis[1,3]dithiole-2,6-diylidene)bis[propanenitrile]; L<sup>R</sup> = 3,10-bis(R)-1,3,5,8,10,12-hexaazacyclotetradecane; R = cyanoethyl, **1**, and ethyl, **2**} yield [NiL<sup>R</sup>(Qimnt)<sub>2</sub>] complexes with three-dimensional Supramolecular structures involving  $\sigma$  coordination of Qimnt<sup>-</sup> towards metal,  $\pi$ - $\pi$  interactions between Qimnt<sup>-</sup> molecules, and intermolecular hydrogen bonding among Qimnt<sup>-</sup>, macrocyclic ligands, and lattice water molecules. The structures of [NiL<sup>C<sub>2</sub>H<sub>4</sub>CN</sup>(Qimnt)<sub>2</sub>] (**1**) and [NiL<sup>C<sub>2</sub>H<sub>5</sub></sup>(Qimnt)<sub>2</sub>]·4H<sub>2</sub>O (**2**) are the first examples in which Qimnt groups are coordinated in a monodentate fashion to a nickel atom. The expectation that the sulfur-rich organocyanide Qimnt<sup>-</sup> could function as a  $\sigma$ -coordination ligand to transition metals has been fulfilled.

Key words: Sulfur-Rich Organocyanide, Hexaaza-Macrocyclic Nickel(II) Complexes, Supramolecular Crystal Structures.

## 摘 要

利用  $\text{Qimnt}^{2-}$  和  $[\text{Ni(II)L}^{\text{R}}]^{2+}$  反應，得到  $[\text{NiL}^{\text{R}}(\text{Qimnt})_2]$   $\{\text{L}^{\text{R}} = 3,10\text{-bis(R)-1,3,5,8,10,12-hexaazacyclotetradecane; R = cyanoethyl, 1, and ethyl, 2; Qimnt} = 2,2'-(4,8\text{-dihydro-4,8-dioxobenzo}[1,2\text{-d:4,5-d'}]\text{bis}[1,3]\text{dithiole-2,6-diylidene})\text{bis[propanenitrile]}\}$ 。這些產物具有三維的組合超分子結構。它們涉及  $\text{Qimnt}^{2-}$  與鎳金屬的  $\sigma$  配位， $\text{Qimnt}^{2-}$  分子的  $\pi\text{-}\pi$  堆疊，以及  $\text{Qimnt}^{2-}$ 、大環配位基、晶格水分子間的氫鍵連結。此  $[\text{NiL}^{\text{C}_2\text{H}_4\text{CN}}(\text{Qimnt})_2]$  (1) 和  $[\text{NiL}^{\text{C}_2\text{H}_5}(\text{Qimnt})_2] \cdot 4\text{H}_2\text{O}$  (2) 結構，是  $\text{Qimnt}$  分子以單牙圍的方式，與 Ni 金屬配位的首例。此研究證實了多硫有機氰化物  $\text{Qimnt}^{2-}$  可與過渡金屬形成  $\sigma$  配位鍵的預測。

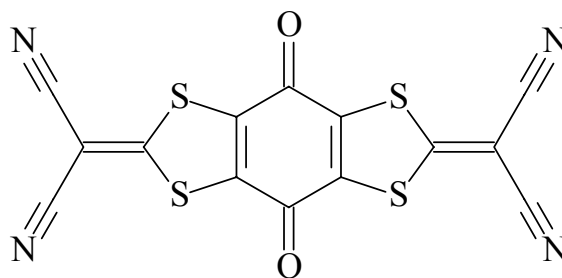
關鍵詞：多硫有機氰化物，含六氮大環鎳(II)錯合物，組合超分子晶體結構。

**The First Supramolecular Assemblies Based-on a Sulfur-Rich  
Organocyanide Radical  $\sigma$ -Bonding to Hexaaza-Macrocyclic  
Nickel(II) Complexes**

In the past two decades, there has been a growing interest in the preparation of new supramolecular materials with novel optical, electrical and magnetic properties.<sup>[1-4]</sup> Special attention have been attracted to the design of supramolecular organizations built by organonitrile radicals and transition metals because of the various possibilities of interaction that can lead to diverse structures.<sup>[5-7]</sup> For examples, the organonitrile radicals derived from acceptor molecules such as 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ), *N,N'*-dicyano-*p*-quinonediimine (DCNQI), and tetracyanoethylene (TCNE) are very unusual in view of their tendency to form complexes with low- and multi-dimensional structures via  $\pi$ - $\pi$  stacking or  $\sigma$  coordination towards metals that gives them a great potential to fabricate molecule-based conducting and magnetic materials.

2,2'-(4,8-Dihydro-4,8-dioxobenzo[1,2-d:4,5-d']bis[1,3]-dithiole-2,6-diylidene)bis[propanenitrile]<sup>[8]</sup> (Qimnt, scheme 1) is an electron acceptor that can be easily reduced to Qimnt<sup>•-</sup> radical-anion and some of its charge-transfer complexes with organic donors exhibit high electrical conductivities.<sup>[9]</sup> We expect that Qimnt<sup>•-</sup>, with four nitrile groups and four sulfur atoms, has a great feasibility to combine with paramagnetic metal complex cations to form multi-dimensional crystal structures with novel macroscopic properties like magnetic ordering or high electrical conductivity. Thus, we have prepared [Ni(II)L<sup>R</sup>(Qimnt)<sub>2</sub>] (L<sup>R</sup> = 3,10-bis(R)-1,3,5,8,10,12-hexaazacyclotetradecane; R = cyanoethyl, **1**, and ethyl, **2**). In this paper we report the synthesis and structural characterization of the two complexes, [NiL<sup>C<sub>2</sub>H<sub>4</sub>CN</sup>(Qimnt)<sub>2</sub>] (**1**) and [NiL<sup>C<sub>2</sub>H<sub>5</sub></sup>(Qimnt)<sub>2</sub>]·4H<sub>2</sub>O (**2**).

Scheme 1

**Qimnt**

## Experimental Section

Synthesis of  $[\text{NiL}^{\text{C}_2\text{H}_4\text{CN}}(\text{Qimnt})_2]$  (**1**) and  $[\text{NiL}^{\text{C}_2\text{H}_5}(\text{Qimnt})_2] \cdot 4\text{H}_2\text{O}$  (**2**).  $[\text{NiL}^{\text{C}_2\text{H}_4\text{CN}}]\text{Cl}_2$ <sup>[10]</sup>,  $[\text{NiL}^{\text{C}_2\text{H}_5}]\text{Cl}_2$ <sup>[11]</sup> and  $\text{Qimnt}$ <sup>[8]</sup> were prepared according to the literature methods. Reagent grade LiI was purchased from Fluka and used without furthered purification. Qimnt 76.8 mg (0.2mmol) and LiI 80.3 mg (0.6mmol) were added to 35 ml solution of  $\text{CH}_3\text{CN}$ , MeOH and  $\text{H}_2\text{O}$  in the volumn ratio of 4:1:1 and  $[\text{NiL}^{\text{C}_2\text{H}_4\text{CN}}]\text{Cl}_2$  38.8 mg (0.1 mmol) for **1** or  $[\text{NiL}^{\text{C}_2\text{H}_5}]\text{Cl}_2$  43.8 mg (0.1 mmol) for **2** was dissolved in another 15 ml of the same solution. The two mixtures were heated to dissolve and combined after filtration. The resulting dark-brown solution was standing at room temperature for several hours and black powder was formed. Black single crystals suitable for x-ray structure determination were obtained by adding 5 ml DMF to each mixture before combining, and the resulting solution was standing to crystallize on a hot plate at  $\sim 50^\circ\text{C}$  for one day.

Crystal structure analyses of **1** and **2**. **1** ( $\text{C}_{42}\text{H}_{28}\text{N}_{16}\text{O}_4\text{S}_8\text{Ni}$ ):  $M_r = 1135.99$ , black prismatic cystal ( $0.48 \times 0.18 \times 0.13$  mm<sup>3</sup>), monoclinic, space group  $P2_1/n$ ,  $a = 16.105(3)$ ,  $b = 8.8734(11)$ ,  $c = 16.3710(15)$  Å,  $\beta = 91.478(9)^\circ$ ,  $V = 2338.7(5)$  Å<sup>3</sup>,  $Z = 2$ ,  $\rho_{\text{calcd}} = 1.163$  g cm<sup>-3</sup>,  $\mu = 0.836$  mm<sup>-1</sup>, min./max.

transmission = 0.6899/0.8991,  $3.5 < 2\theta < 50^\circ$ ; of 3590 unique reflections, 2840 were assumed observed with  $I > 2\sigma(I)$ ; refinement of 322 variables with anisotropic thermal parameters for all non-hydrogen atoms gave  $R1 = 0.0394$ ,  $wR2 = 0.0968$  and  $S = 1.046$ . **2**( $C_{40}H_{38}N_{14}O_8S_8Ni$ ):  $M_r = 1158.03$ , black columnar crystal ( $0.50 \times 0.30 \times 0.05 \text{ mm}^3$ ), Triclinic, space group  $P \bar{1}$ ,  $a = 9.4820(11)$ ,  $b = 11.224(2)$ ,  $c = 11.705(2) \text{ \AA}$ ,  $\alpha = 90.381(8)^\circ$ ,  $\beta = 93.656(12)^\circ$ ,  $\gamma = 96.880(12)^\circ$ ,  $V = 1234.1(3) \text{ \AA}^3$ ,  $Z = 1$ ,  $\rho_{\text{calcd}} = 1.558 \text{ g cm}^{-3}$ ,  $\mu = 0.798 \text{ mm}^{-1}$ , min./max. transmission = 0.6912/0.9612,  $3.66 < 2\theta < 50^\circ$ ; of 4355 unique reflections, 3187 were assumed observed with  $I > 2\sigma(I)$ ; refinement of 332 variables with anisotropic thermal parameters for all non-hydrogen atoms gave  $R1 = 0.0471$ ,  $wR2 = 0.1170$  and  $S = 1.027$ .

All lattice parameters and intensity data of the complexes were measured on an Siemens P4 automated diffractometer using a graphite monochromated Mo  $K\alpha$  radiation ( $0.71073 \text{ \AA}$ ). Accurate cell constants were obtained from least-squares fitting of 25 well-centered reflections with setting angles  $17.21^\circ \leq 2\theta \leq 22.01^\circ$  and  $11.33^\circ \leq 2\theta \leq 29.84^\circ$  for **1** and **2**, respectively. The intensity data were collected at ambient temperature using

$\theta$ - $2\theta$  scan technique to a maximum  $2\theta$  value of  $50^\circ$ . Three standard reflections were measured after every 100 reflections to check the crystal quality, and no significant decay was found. Semi-empirical absorption corrections ( $\psi$ -scans) were applied in each case. All calculations were performed with SHELXL Version 5.0 package on a personal computer. <sup>[12]</sup> The structures were solved by direct method and expanded using difference Fourier methods. All non-hydrogen atoms were refined with anisotropic thermal parameters using a full-matrix least-squares procedure based on  $F^2$ . Hydrogen atoms were fixed at idealized positions and not refined. Crystallographic data, final atomic coordinates, and equivalent isotropic thermal parameters for complexes **1** and **2** are summarized in the supplementary files 1 and 2, respectively. And selected bond lengths and angles are listed in Table 1. Selected bond lengths and angles are listed in Table 1 and 2.

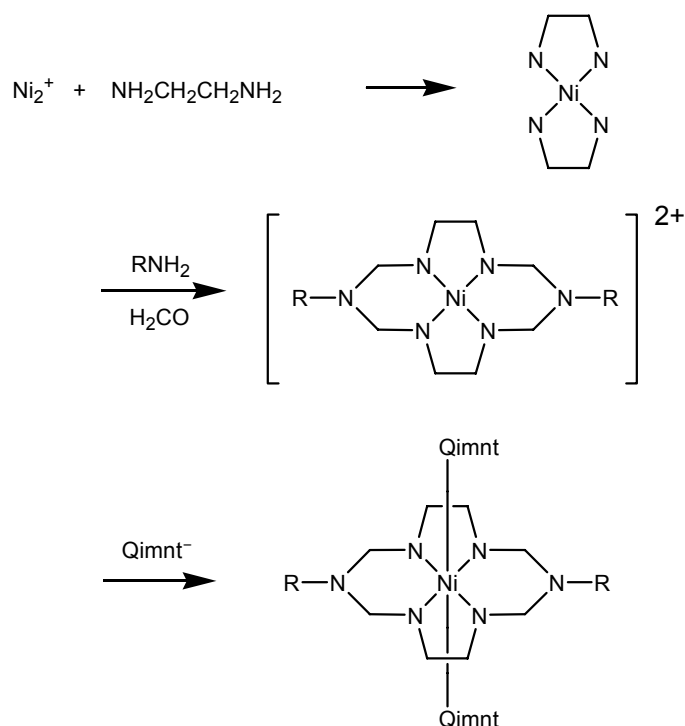
## Results and discussions

The preparative procedures can be described as Scheme 2. A one-pot metal template condensation reaction of ethylenediamine with formaldehyde and various amines,  $\text{RNH}_2$  (R = cyanoethyl, **1**, and ethyl, **2**), in the presence of the nickel(II) ion, produced the corresponding mononuclear



$[\text{NiL}^{\text{R}}]^{2+}$  complexes. The four-coordinate nickel(II) complexes can accept nitrogen donor atoms of two  $\text{Qimnt}^{\cdot-}$  radical ions to give six-coordinate  $[\text{Ni(II)L}^{\text{R}}(\text{Qimnt})_2]$  species. Complexes **1** and **2** are stable in air and slightly soluble in most organic solvents.

### Scheme 2



The Supramolecular structure of **1** consists of mononuclear  $[\text{Ni(II)L}^{\text{C}_2\text{H}_4\text{CN}}(\text{Qimnt})_2]$  building-blocks constructed from  $\sigma$ -bonding of two  $\text{Qimnt}^{\cdot-}$  radicals to a  $[\text{Ni(II)L}^{\text{C}_2\text{H}_4\text{CN}}]^{2+}$  complex (see Figure 1). The  $[\text{Ni(II)L}^{\text{C}_2\text{H}_4\text{CN}}(\text{Qimnt})_2]$  units stack to form two-dimensional sheets

parallel to the *ab* plane, with alternating  $[\text{Ni}(\text{II})\text{L}^{\text{C}_2\text{H}_4\text{CN}}]^{2+}$  and  $\text{Qimnt}^-$  columns along *b* direction (Figure 2). The  $\text{Qimnt}^-$  molecules are dimerized in the column and the overlap modes are shown in Figure 3. The intra- and inter-dimer spacings are 3.192 Å and 3.371 Å, respectively. The closest Ni...Ni distance in the  $[\text{Ni}(\text{II})\text{L}^{\text{C}_2\text{H}_4\text{CN}}]^{2+}$  column is 8.873 Å. In addition to the  $\sigma$ -bonding between Ni and  $\text{Qimnt}^-$  and  $\pi$ - $\pi$  interactions between  $\text{Qimnt}^-$  molecules, the intra-layer intermolecular interactions involve hydrogen bonding  $[\text{N1}\cdots\text{N7}(-x+2, -y+1, -z) = 3.136 \text{ \AA}]$  between  $\text{Qimnt}^-$  and macrocyclic ligand, as shown in Figure 4. Furthermore, a three-dimensional network is resulting from the hydrogen-bonding between macrocyclic ligands in the neighboring layers  $\text{N3}\cdots\text{N4}[(-x+3/2, y+1/2, -z-1/2) = 3.167 \text{ \AA}]$ . It is interesting to note that two  $\text{Qimnt}^-$  planes in the neighboring layers are perpendicular each other, although all those in the same layer are parallel.

In the  $[\text{Ni}(\text{II})\text{L}^{\text{C}_2\text{H}_4\text{CN}}(\text{Qimnt})_2]$  (**1**), the metal atom is located at an inversion center and is six-coordinated. In the equatorial plane the nickel atom is bonded to the four secondary nitrogen atoms of the hexaaza-macrocyclic ligand at 2.052(3) and 2.062(3) Å, similar to those found in other hexaazacyclotetradecane macrocyclic complexes<sup>[11,13-24]</sup>. The

two axial positions are occupied by nitrile groups of two Qimnt<sup>-</sup> molecules with a nickel-nitrogen distance of 2.233(3) Å to complete a distorted octahedral environment. This distance is longer than the axial Ni-N(TCNQ) distances of 2.175(4) and 2.165(2) Å, respectively observed in [NiL<sup>C<sub>2</sub>H<sub>4</sub>OH</sup>(TCNQ)<sub>2</sub>]<sup>[25]</sup> and [Ni(cyclam)(TCNQ)<sub>2</sub>]<sup>[26]</sup>, suggesting that Qimnt<sup>-</sup> is a weaker σ-donor than TCNQ<sup>-</sup>. The axial Ni-N-C bonds is linear with an angle of 169.1(3)°. The six-membered chelate rings of the macrocyclic ligand adopt a chair conformation, while the five-membered chelate rings assume a gauche conformation. The dihedral angle between the equatorial NiN<sub>4</sub> plane and the best Qimnt plane is 74.0°.

The layer architecture in the Supramolecular structure of **2**, shown in Figure 5, is similar to that of **1**. The building-block [Ni(II)L<sup>C<sub>2</sub>H<sub>5</sub></sup>(Qimnt)<sub>2</sub>] (Figure 6) stack to form layers parallel to the (01 $\bar{1}$ ) plane, with alternating [Ni(II)L<sup>C<sub>2</sub>H<sub>5</sub></sup>]<sup>2+</sup> and Qimnt<sup>-</sup> columns which are parallel to the a axis. The Qimnt<sup>-</sup> molecules are dimerized in the column and the overlap modes are shown in Figure 7. The intra- and inter-dimer spacings are 3.453 Å and 3.513 Å, respectively. The closest Ni...Ni distance in the [Ni(II)L<sup>C<sub>2</sub>H<sub>4</sub>CN</sup>]<sup>2+</sup> column is 9.482 Å. The intra-layer intermolecular interactions include the σ-bonding between

Ni and Qimnt<sup>-</sup> and  $\pi$ - $\pi$  interactions between Qimnt<sup>-</sup> molecules, but not hydrogen bonding. However, hydrogen bonds between macrocyclic ligand and Qimnt<sup>-</sup> [N3 $\cdots$ N7(x+1, y-1, z), 3.194 Å], macrocyclic ligand and lattice water [N1 $\cdots$ O3(-x, -y+2, -z+1), 3.041 Å], lattice water and Qimnt<sup>-</sup>, [O3 $\cdots$ O2, 2.792 Å; O4 $\cdots$ O1(x, y, z+1), 2.881 Å], and between lattice water molecules [O3 $\cdots$ O4, 2.711 Å; O3 $\cdots$ O4(-x, -y+2, -z+2), 2.836 Å], as shown in Figure 8, lead to the Supramolecular structure of **2**. It very interesting to note that the lattice waters form a square tetrameric cluster residing between adjacent layers. Different from **1**, all Qimnt<sup>-</sup> molecules in **2** stack in the same direction.

In the [NiL<sup>C<sub>2</sub>H<sub>5</sub></sup>(Qimnt)<sub>2</sub>] $\cdot$ 4H<sub>2</sub>O (**2**), the Ni atom is located at an inversion center in an elongated octahedral environment. The axial Ni-N(Qimnt) bond length of 2.869(4) Å is extremely long, but we assume that it is still the bond distance. The axial Ni-N-C bonds deviate slightly from linearity with an angle of 172.7(4)°. The very long Ni-N distance may result from the weak basicity of Qimnt<sup>-</sup> and some possible strain associated with the hydrogen bonding. In the equatorial plane the nickel atom is bonded to the four secondary nitrogen atoms of the hexaaza-macrocyclic ligand at 1.933(3) Å and 1.938(3) Å, shorter

than those found in **1**. But the short Ni-N distances are comparable to those of four-coordinate square-planar nickel(II) complexes of related hexaaza-macrocycles,  $[\text{Ni}(\text{II})\text{L}^{\text{C}_2\text{H}_4\text{NH}_2}](\text{ClO}_4)_2$  [1.931(2)–1.934(2) Å]<sup>[27]</sup> and  $[\text{Ni}(\text{II})\text{L}^{\text{CH}_2\text{C}_6\text{H}_5}](\text{ClO}_4)_2$  [1.9292(2)–1.939(2) Å],<sup>[28]</sup>  $[\text{Ni}(\text{II})\text{L}^{\text{CH}_2\text{C}_5\text{NH}_4}](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$  [1.934(3) Å]<sup>[29]</sup> consistent with the very weak bonding in the axial positions. A similar situation is found in the segregated-stacked  $[\text{NiL}^{\text{CH}_2\text{C}_6\text{H}_5}(\text{CH}_3\text{CN})_2][\text{Qimnt}]_2 \cdot 2\text{CH}_3\text{CN}$ <sup>[30]</sup> ( $\text{L}^{\text{CH}_2\text{C}_6\text{H}_5}$  = 3,10-bis(2-phenylethyl)-1,3,5,8,10,12-hexaazacyclotetradecane) with axial Ni-N(CH<sub>3</sub>CN) = 2.620(5) Å, equatorial Ni-N(macrocyclic) = 1.995(4) and 2.018(4) Å, and axial Ni-N-C = 149.7(5)°, compared with the axial Ni-N(CH<sub>3</sub>CN) = 2.170(5) Å, equatorial Ni-N(macrocyclic) = 2.058(4) and 2.065(4) Å, and axial Ni-N-C = 167.1(5)° observed in  $[\text{NiL}^{\text{CH}_2\text{C}_6\text{H}_5}(\text{CH}_3\text{CN})_2][\text{Qimnt}]_2 \cdot \text{CH}_3\text{CN} \cdot 2\text{H}_2\text{O}$ .<sup>[30]</sup> The six-membered chelate rings of the macrocyclic ligand adopt a chair conformation, while the five-membered chelate rings assume a gauche conformation. The dihedral angle between the equatorial NiN<sub>4</sub> plane and the best Qimnt<sup>2-</sup> plane is 85.4(1)°.

Reaction of Qimnt<sup>2-</sup> with  $[\text{NiL}^{\text{R}}]^{2+}$  gives the three-dimensional network structures involving  $\sigma$  coordination towards metal,  $\pi$ - $\pi$  stacking and hydrogen bonding. The

structures of  $[\text{Ni}(\text{II})\text{L}^{\text{R}}(\text{Qimnt})_2]$  ( $\text{L}^{\text{R}} = 3,10\text{-bis}(\text{R})\text{-}1,3,5,8,10,12\text{-hexaazacyclotetradecane}$ ;  $\text{R} = \text{cyanoethyl}$ , **1**, and ethyl, **2**) are the first examples in which Qimnt groups are coordinated in a monodentate fashion to a nickel atom. The expectation that the sulfur-rich organocyanide Qimnt<sup>-</sup> could function as a  $\sigma$ -coordination ligand to transition metals has been fulfilled.

## References

- [1] J. M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*; VHC: Weinheim, **1995**.
- [2] D. B. Amabilino, J. F. Stoddart, *Chem. Rev.*, **1995**, *95*, 2725.
- [3] P. J. STANG, B. OLENYUK, *Acc. Chem. Res.*, **1997**, *30*, 502.
- [4] G. F. Swiegers, T. J. Malefetse, *Chem. Rev.*, **2000**, *100*, 3483
- [5] W. Kaim, M. Moscherosch, *Coord. Chem. Rev.*, **1994**, *129*, 157.
- [6] K. R. Dunbar, *Angew. Chem., Int. Ed. Engl.*, **1996**, *35*, 1659.
- [7] L. Ballester, A. Gutierrez, M. F. Perpnan, M. T. Azcondo, *Coord. Chem. Rev.*, **1999**, *190-192*, 447.
- [8] T. Mukai, T. Yamashita, T. Suzuki, *Jpn. Kokai Tokkyo Koho*, JP63-225382 (Int.Cl. C07D495/04), **1988**.
- [9] T. Yamashita, T. Suzuki, G. Saito, T. Mukai, *J. Chem. Soc., Chem. Comm.*, **1986**, 1489.
- [10] R. W. Hay, M. J. Armstrong and M. M. Hassan, *Transition Metal Chem.* **1992**, *17*, 270.

- [11] M. P. Suh, B. Y. Shim, T. Yoon, *Inorg. Chem.*, 1994, 33, 5509.
- [12] *SHELXTL-PLUS Version 5.03*: Siemens Analytical X-Ray Instruments Inc., Madison, Wisconsin, USA, **1994**.
- [13] M. P. Suh, B. Y. Shim, T. S. Yoon, *Inorg. Chem.* **1994**, 33, 5509.
- [14] H. Z. Kou, S. Gao, W. M. Bu, D. Z. Liao, B. Q. Ma, Z. H. Jiang, S. P. Yan, Y. G. Fan, G. L. Wang, *J. Chem. Soc., Dalton Trans.*, **1999**, 2477.
- [15] H. Z. Kou, S. Gao, B. Q. Ma and D. Z. Liao, *Chem. Commun.*, **2000**, 713.
- [16] H. Z. Kou, S. Gao, B. Q. Ma and D. Z. Liao, *Chem. Commun.* **2000**, 1309.
- [17] H. Z. Kou, W. M. Bu, S. Gao, D. Z. Liao, Z. H. Jiang, S. P. Yan, Y. G. Fan and G. L. Wang, *J. Chem. Soc., Dalton Trans.*, **2000**, 2996.
- [18] J. C. Kim, A. J. Lough, J. C. Fettinger, K. Y. Choi, D. Kim, S. Y. Pyun, J. Cho, *Inorg. Chim. Acta*, **2000**, 303, 163.
- [19] T. Lu, H. Xiang, C. Su, P. Cheng, Z. Mao and L. Ji, *New J. Chem.*, **2001**, 25, 216.
- [20] H. Xiang, S. Gao, T. B. Lu, R. L. Luck, Z. W. Mao, X. M. Chen, L. N. Ji, *New J. Chem.*, **2001**, 25, 875.
- [21] H. Z. Kou, S. Gao, O. Bai, Z. M. Wang *Inorg. Chem.* **2001**, 40, 6287.
- [22] J. Liu, T. B. Lu, H. Xiang, Z. W. Mao, L. N. Ji, *Cryst. Eng. Comm.*, **2002**, 4, 64.
- [23] J. Cho, U. Lee, J. C. Kim, *Trans. Met. Chem.*, **2002**, 27, 429.
- [24] H. Z. Kou, S. F. Si, S. Gao, D. Z. Liao, Z. H. Jiang, S. P. Yan, Y. G. Fan, G. L. Wang *Eur. J. Inorg. Chem.* **2002**, 699.
- [25] L. Ballester, M. C. Banal, A. Gutierrez, A. Monge, M. F. Perpnan, C. Ruiz-Valero, A. E. Sanchez-Pelaez, *Inorg. Chem.*, **1994**, 33, 2142.
- [26] L. Ballester, A. Gutierrez, M. F. Perpnan, U. Amador,

M. T. Azcondo, A. E. Sanchez, C. Bellitto, *Inorg. Chem.*, **1997**, *36*, 6390.

[27] S. G. Kang, K. Ryu, S. K. Jung, J. Kim, *Inorg. Chim. Acta*, **1999**, *293*, 140.

[28] T. Lu, H. Xiang, X. Li, Z. Mao, L. Ji, *Inorg. Chem. Comm.*, **2000**, *3*, 597.

[29] K. S. Min, M. P. Suh, *Chem. Eur. J.*, **2001**, *7*, 303.

[30] Will be published.



Table 1. Selected Bond lengths [Å] and angles [°] for **1**.

---

Ni(1)-N(1)	2.052(3)
Ni(1)-N(3)	2.062(3)
Ni(1)-N(5)	2.233(3)
O(1)-C(8)	1.244(4)
O(2)-C(11)	1.258(4)
N(5)-C(16)	1.153(5)
N(6)-C(17)	1.144(5)
N(7)-C(20)	1.143(5)
N(8)-C(21)	1.141(5)
N(1)-Ni(1)-N(1)#1	180.0(2)
N(1)-Ni(1)-N(3)	94.92(11)
N(1)-Ni(1)-N(3)#1	85.08(11)
N(3)-Ni(1)-N(3)#1	180.0(2)
N(1)-Ni(1)-N(5)	88.16(12)
N(3)-Ni(1)-N(5)	89.17(12)
N(1)-Ni(1)-N(5)#1	91.84(12)
N(3)-Ni(1)-N(5)#1	90.83(12)
N(5)-Ni(1)-N(5)#1	180.0(2)
C(16)-N(5)-Ni(1)	169.1(3)

---

Symmetry transformations used to generate equivalent atoms:  
#1 -x+1,-y,-z

Table 2. Selected Bond lengths [Å] and angles [°] for **2**.

---

Ni-N(3)	1.933(3)
Ni-N(1)	1.936(3)
Ni-N(4)	2.868(4)
O(1)-C(7)	1.253(4)
O(2)-C(10)	1.249(4)
N(4)-C(15)	1.122(6)
N(5)-C(16)	1.131(6)
N(6)-C(19)	1.136(5)
N(7)-C(20)	1.145(5)
N(3)#1-Ni-N(3)	180.00(17)
N(3)-Ni-N(1)	93.59(13)
N(3)-Ni-N(1)#1	86.41(13)
N(1)-Ni-N(1)#1	180.00(16)
N(3)#1-Ni-N(4)	99.19(13)
N(3)-Ni-N(4)	80.81(13)
N(1)-Ni-N(4)	84.60(13)
N(1)#1-Ni-N(4)	95.40(13)
N(4)-Ni-N(4)#1	180.0(16)
C(15)-N(4)-Ni	172.7(4)

---

Symmetry transformations used to generate equivalent atoms:  
#1 -x, -y+1, -z

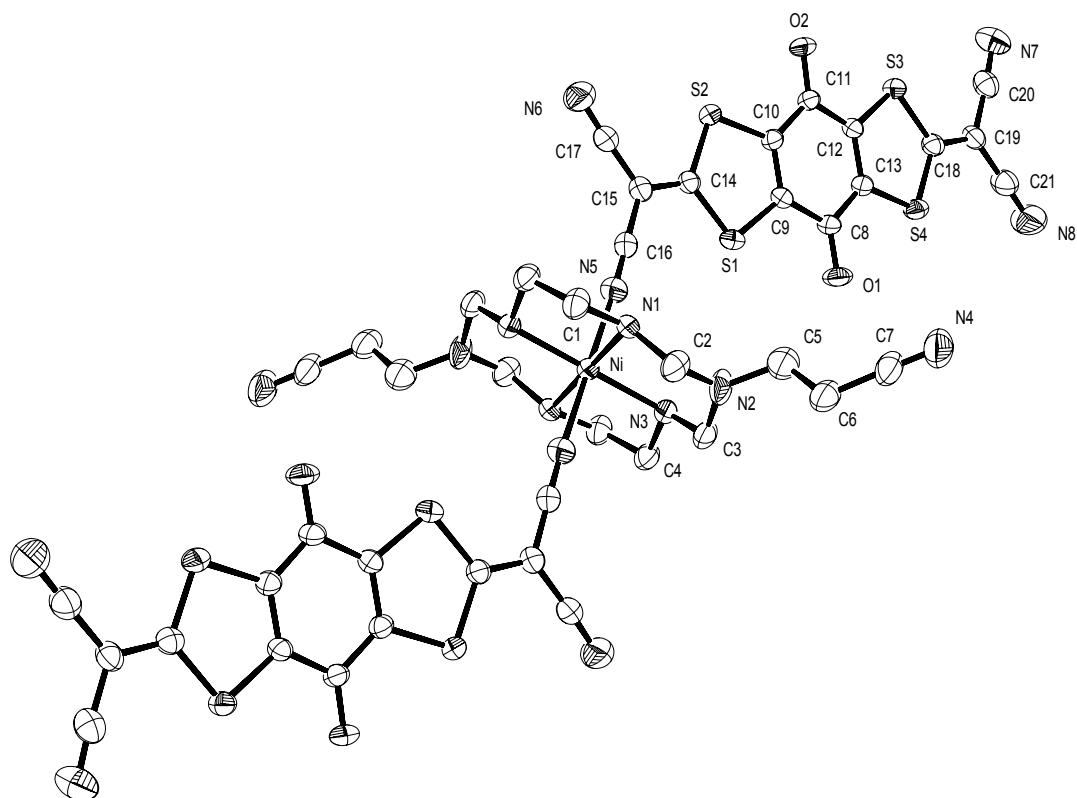


Fig. 1 ORTEP drawing of the  $[\text{Ni}(\text{II})\text{L}^{\text{C}_2\text{H}_4\text{CN}}(\text{Qimnt})_2]$  (**1**) with atomic numbering scheme.

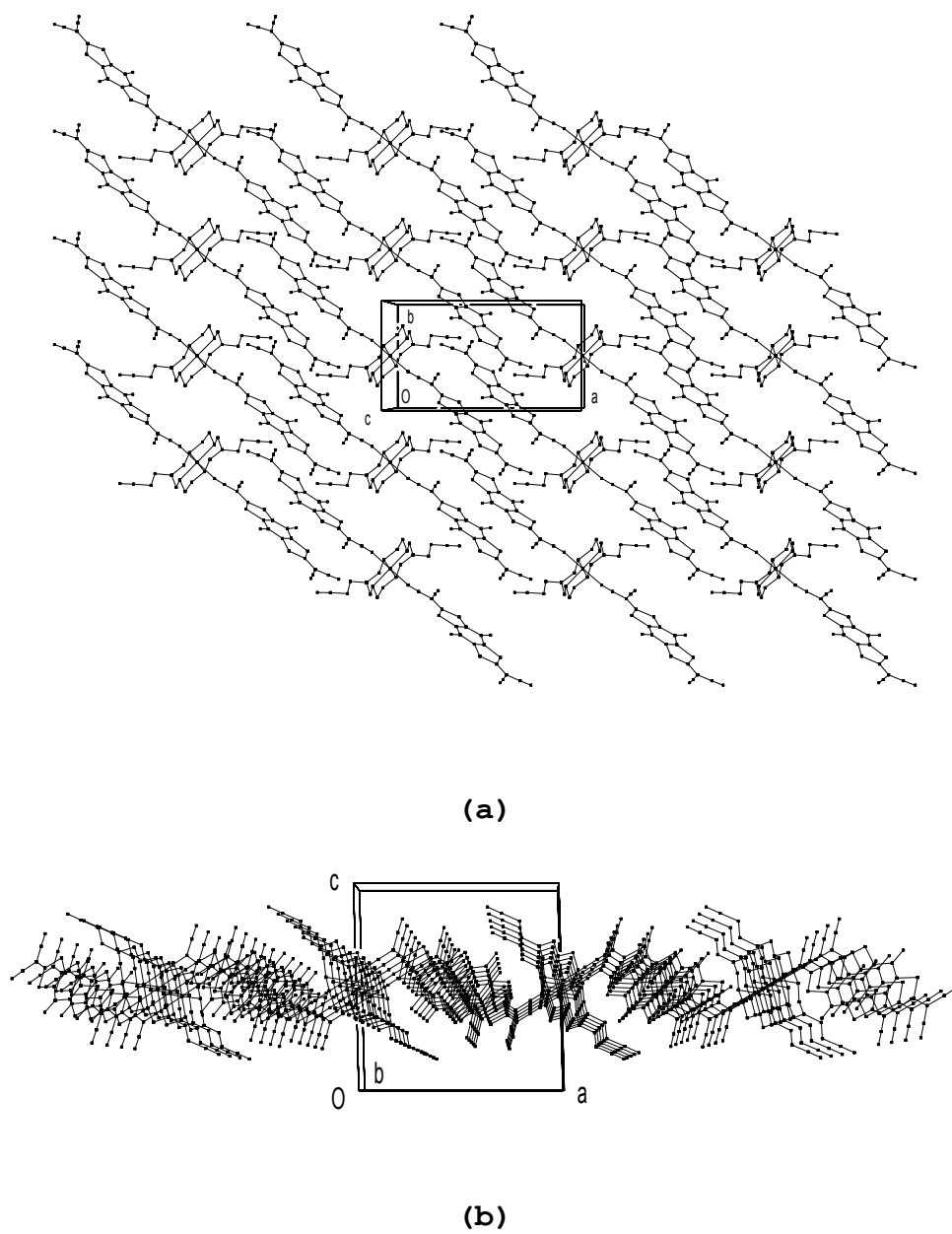


Fig. 2 Molecular packing arrangement of the two-dimensional sheets parallel to the  $ab$  plane for **1**. (a) Viewed along the  $c$  axis. (b) Viewed along the  $b$  axis.

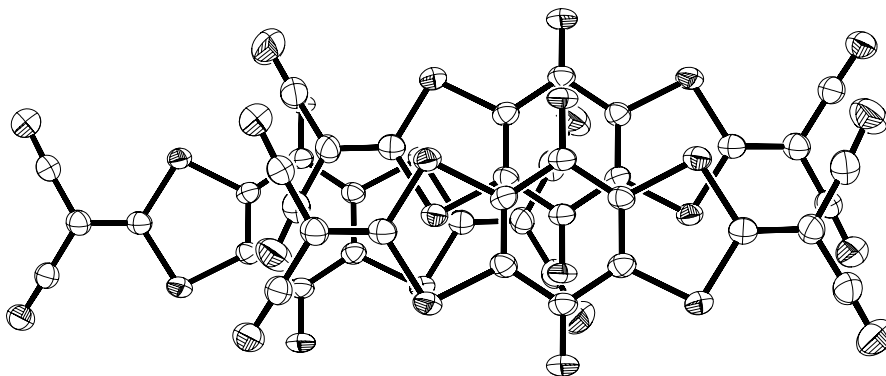


Fig. 3 The overlap modes of Qimnt<sup>2-</sup> molecules in **1**.

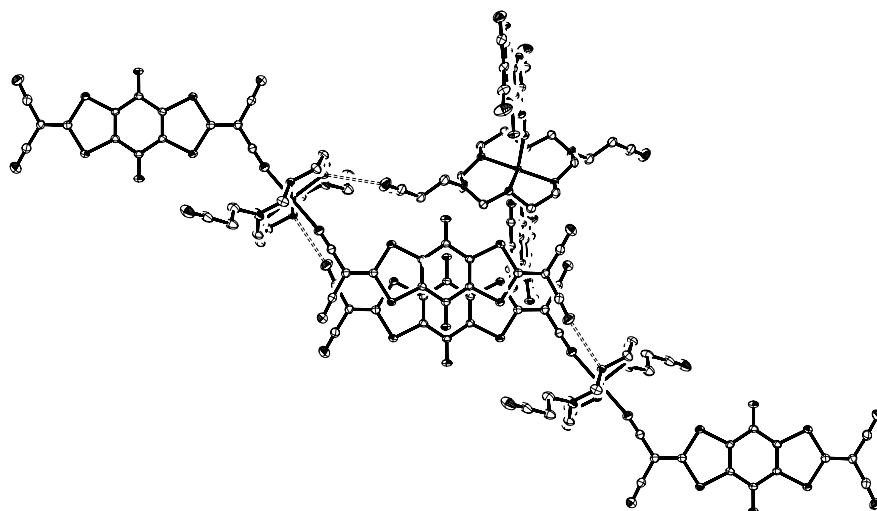


Fig. 4 ORTEP view of hydrogen bonding in **1**. For clarity the hydrogen atoms are omitted.

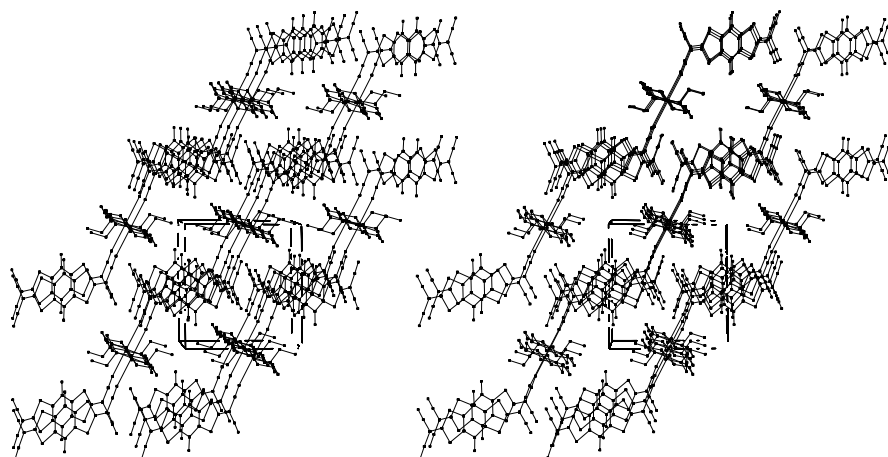


Fig. 5 Stereoview of the molecular packing of **2**, viewed along the *a* axis.

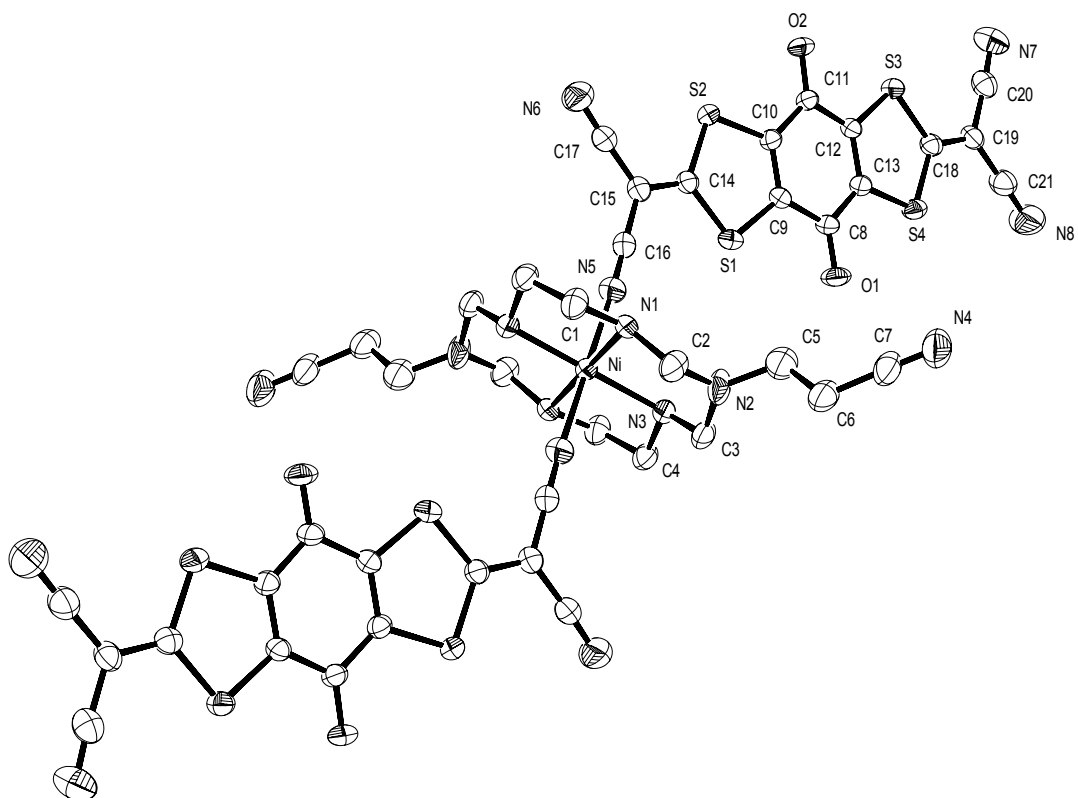


Fig. 6 ORTEP drawing of the  $[\text{Ni}(\text{II})\text{L}^{\text{C}_2\text{H}_5}(\text{Qimnt})_2]$  (**2**) and lattice water oxygens with atomic numbering scheme.



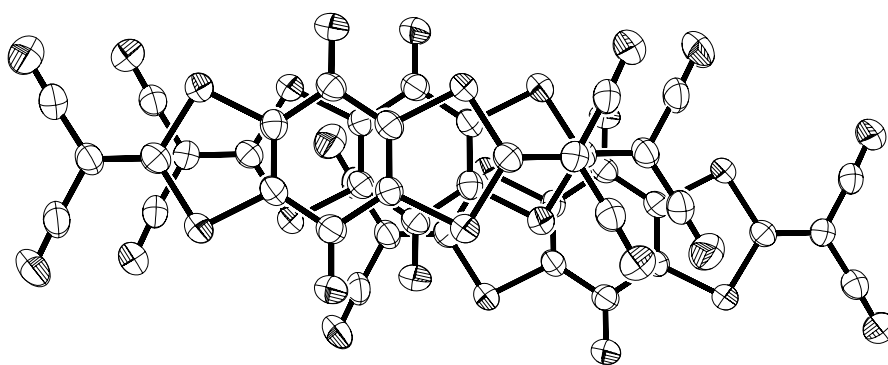


Fig. 7 The overlap modes of  $Qimnt''$  molecules in **2**.

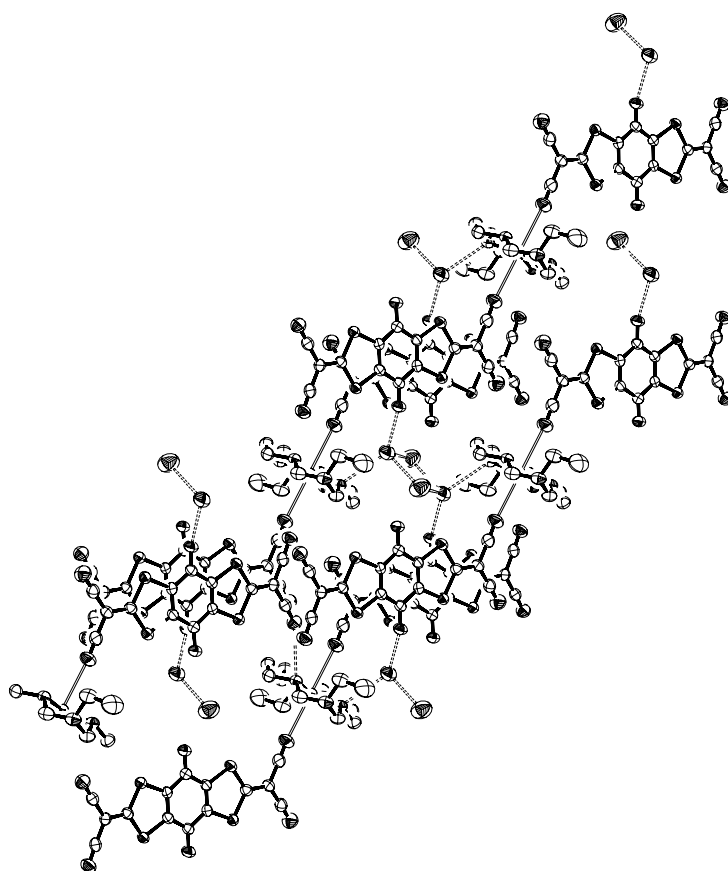


Fig. 8 View of the crystal structure **2**, highlighting the intermolecular H-bonds. For clarity the hydrogen atoms are omitted.

## Supplementary File 1

Table 1. Crystal data and structure refinement for  $[\text{NiL}^{\text{C}_{2}\text{H}_{4}\text{CN}}(\text{Qimnt})_2]$  (1).

Identification code	tku153
Empirical formula	C <sub>42</sub> H <sub>28</sub> N <sub>16</sub> Ni <sub>4</sub> S <sub>8</sub>
Formula weight	1135.99
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 16.105(3) Å    alpha = 90 deg. b = 8.8734(11) Å    beta = 91.478(9) deg. c = 16.3710(15) Å    gamma = 90 deg.
Volume	2338.7(5) Å <sup>3</sup>
Z, Calculated density	2, 1.613 Mg/m <sup>3</sup>
Absorption coefficient	0.836 mm <sup>-1</sup>
F(000)	1160
Crystal size	0.48 x 0.18 x 0.13 mm
Theta range for data collection	1.75 to 25.00 deg.
Limiting indices	0 ≤ h ≤ 13, 0 ≤ k ≤ 10, -19 ≤ l ≤ 19
Reflections collected / unique	3748 / 3590 [R(int) = 0.0190]
Completeness to theta = 25.00	87.1 %
Absorption correction	Empirical
Max. and min. transmission	0.8991 and 0.6899

Refinement method	Full-matrix least-squares on $F^2$
Data / restraints / parameters	3590 / 0 / 322
Goodness-of-fit on $F^2$	1.046
Final R indices [ $I > 2\sigma(I)$ ]	R1 = 0.0394, wR2 = 0.0968
R indices (all data)	R1 = 0.0556, wR2 = 0.1059
Largest diff. peak and hole	0.459 and -0.235 e. $\text{\AA}^{-3}$

Table 2. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for tkul53. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Ni(1)	5000	0	0	28(1)
N(1)	5881(2)	-1656(3)	-103(2)	32(1)
N(2)	6078(2)	-1103(4)	-1523(2)	54(1)
N(3)	5222(2)	958(3)	-1121(2)	33(1)
N(4)	8408(3)	-1759(6)	-3284(2)	81(2)
C(1)	5705(3)	-2795(4)	536(2)	42(1)
C(2)	5935(3)	-2279(4)	-945(2)	44(1)
C(3)	5405(3)	-159(5)	-1769(2)	42(1)
C(4)	4519(3)	1971(4)	-1310(2)	40(1)
C(5)	6870(3)	-940(5)	-1909(3)	54(1)
C(6)	6951(3)	-1969(6)	-2636(2)	55(1)
C(7)	7779(3)	-1824(6)	-2995(3)	62(1)
S(1)	7531(1)	4406(1)	-12(1)	35(1)
S(2)	8666(1)	4311(1)	1417(1)	31(1)
S(3)	10726(1)	8366(1)	-50(1)	31(1)
S(4)	9588(1)	8512(1)	-1484(1)	35(1)
O(1)	8094(2)	6409(3)	-1390(2)	42(1)
O(2)	10278(2)	6040(3)	1214(1)	38(1)
N(5)	5984(2)	1474(4)	559(2)	43(1)
N(6)	7684(3)	1676(5)	2741(2)	67(1)
N(7)	12290(3)	11063(5)	-518(3)	63(1)
N(8)	10598(3)	11294(6)	-2743(3)	84(2)
C(8)	8586(2)	6355(4)	-792(2)	31(1)
C(9)	8438(2)	5453(4)	-71(2)	30(1)
C(10)	8979(2)	5390(4)	589(2)	29(1)
C(11)	9757(2)	6174(4)	633(2)	29(1)
C(12)	9873(2)	7160(4)	-55(2)	28(1)
C(13)	9333(2)	7236(4)	-720(2)	30(1)
C(14)	7756(2)	3684(4)	948(2)	31(1)
C(15)	7253(2)	2632(4)	1313(2)	36(1)
C(16)	6545(3)	2023(4)	895(2)	36(1)
C(17)	7474(3)	2086(5)	2107(2)	42(1)

C(18)	10478(2)	9158(4)	-998(2)	31(1)
C(19)	10979(2)	10248(4)	-1329(2)	37(1)
C(20)	11713(3)	10727(4)	-898(3)	42(1)
C(21)	10776(3)	10853(5)	-2108(3)	49(1)

---

Table 3. Bond lengths [Å] and angles [deg] for tkul53.

---

Ni(1)-N(1)	2.052(3)
Ni(1)-N(1)#1	2.052(3)
Ni(1)-N(3)	2.062(3)
Ni(1)-N(3)#1	2.062(3)
Ni(1)-N(5)	2.233(3)
Ni(1)-N(5)#1	2.233(3)
N(1)-C(1)	1.487(4)
N(1)-C(2)	1.490(4)
N(2)-C(3)	1.421(5)
N(2)-C(2)	1.431(5)
N(2)-C(5)	1.444(6)
N(3)-C(4)	1.472(5)
N(3)-C(3)	1.486(4)
N(4)-C(7)	1.131(6)
C(1)-C(4)#1	1.515(5)
C(4)-C(1)#1	1.515(5)
C(5)-C(6)	1.508(6)
C(6)-C(7)	1.476(7)
S(1)-C(14)	1.726(3)
S(1)-C(9)	1.736(4)
S(2)-C(14)	1.729(4)
S(2)-C(10)	1.745(3)
S(3)-C(12)	1.740(4)
S(3)-C(18)	1.741(3)
S(4)-C(18)	1.721(4)
S(4)-C(13)	1.744(3)
O(1)-C(8)	1.244(4)
O(2)-C(11)	1.258(4)
N(5)-C(16)	1.153(5)
N(6)-C(17)	1.144(5)
N(7)-C(20)	1.143(5)
N(8)-C(21)	1.141(5)
C(8)-C(13)	1.438(5)
C(8)-C(9)	1.450(5)
C(9)-C(10)	1.372(5)
C(10)-C(11)	1.433(5)
C(11)-C(12)	1.443(5)
C(12)-C(13)	1.376(5)
C(14)-C(15)	1.382(5)
C(15)-C(16)	1.421(5)

C(15)-C(17)	1.424(5)
C(18)-C(19)	1.379(5)
C(19)-C(21)	1.414(5)
C(19)-C(20)	1.427(6)
N(1)-Ni(1)-N(1)#1	180.0(2)
N(1)-Ni(1)-N(3)	94.92(11)
N(1)#1-Ni(1)-N(3)	85.08(11)
N(1)-Ni(1)-N(3)#1	85.08(11)
N(1)#1-Ni(1)-N(3)#1	94.92(11)
N(3)-Ni(1)-N(3)#1	180.0(2)
N(1)-Ni(1)-N(5)	88.16(12)
N(1)#1-Ni(1)-N(5)	91.84(12)
N(3)-Ni(1)-N(5)	89.17(12)
N(3)#1-Ni(1)-N(5)	90.83(12)
N(1)-Ni(1)-N(5)#1	91.84(12)
N(1)#1-Ni(1)-N(5)#1	88.16(12)
N(3)-Ni(1)-N(5)#1	90.83(12)
N(3)#1-Ni(1)-N(5)#1	89.17(12)
N(5)-Ni(1)-N(5)#1	180.0(2)
C(1)-N(1)-C(2)	114.5(3)
C(1)-N(1)-Ni(1)	106.5(2)
C(2)-N(1)-Ni(1)	113.5(2)
C(3)-N(2)-C(2)	118.9(3)
C(3)-N(2)-C(5)	119.5(3)
C(2)-N(2)-C(5)	121.4(3)
C(4)-N(3)-C(3)	115.0(3)
C(4)-N(3)-Ni(1)	106.8(2)
C(3)-N(3)-Ni(1)	113.7(2)
N(1)-C(1)-C(4)#1	108.3(3)
N(2)-C(2)-N(1)	110.8(3)
N(2)-C(3)-N(3)	110.8(3)
N(3)-C(4)-C(1)#1	108.5(3)
N(2)-C(5)-C(6)	112.4(4)
C(7)-C(6)-C(5)	111.1(4)
N(4)-C(7)-C(6)	177.7(6)
C(14)-S(1)-C(9)	95.33(17)
C(14)-S(2)-C(10)	95.19(16)
C(12)-S(3)-C(18)	94.68(17)
C(18)-S(4)-C(13)	95.31(17)
C(16)-N(5)-Ni(1)	169.1(3)
O(1)-C(8)-C(13)	123.9(3)
O(1)-C(8)-C(9)	123.2(3)



C(13)-C(8)-C(9)	112.8(3)
C(10)-C(9)-C(8)	123.3(3)
C(10)-C(9)-S(1)	116.9(3)
C(8)-C(9)-S(1)	119.8(3)
C(9)-C(10)-C(11)	123.8(3)
C(9)-C(10)-S(2)	116.4(3)
C(11)-C(10)-S(2)	119.8(2)
O(2)-C(11)-C(10)	123.9(3)
O(2)-C(11)-C(12)	123.4(3)
C(10)-C(11)-C(12)	112.7(3)
C(13)-C(12)-C(11)	123.7(3)
C(13)-C(12)-S(3)	117.1(3)
C(11)-C(12)-S(3)	119.2(2)
C(12)-C(13)-C(8)	123.3(3)
C(12)-C(13)-S(4)	116.3(3)
C(8)-C(13)-S(4)	120.4(2)
C(15)-C(14)-S(1)	122.2(3)
C(15)-C(14)-S(2)	121.7(3)
S(1)-C(14)-S(2)	116.1(2)
C(14)-C(15)-C(16)	121.4(3)
C(14)-C(15)-C(17)	119.2(3)
C(16)-C(15)-C(17)	119.3(3)
N(5)-C(16)-C(15)	177.3(4)
N(6)-C(17)-C(15)	177.1(4)
C(19)-C(18)-S(4)	122.7(3)
C(19)-C(18)-S(3)	120.8(3)
S(4)-C(18)-S(3)	116.5(2)
C(18)-C(19)-C(21)	119.8(4)
C(18)-C(19)-C(20)	120.0(3)
C(21)-C(19)-C(20)	120.2(4)
N(7)-C(20)-C(19)	176.3(5)
N(8)-C(21)-C(19)	177.5(5)

---

Symmetry transformations used to generate equivalent atoms:

#1  $-x+1, -y, -z$

Table 4. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for tkul53. The anisotropic displacement factor exponent takes the form:  
 $-2 \pi^2 [ h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12} ]$

	U11	U22	U33	U23	U13	U12
Ni(1)	25(1)	35(1)	24(1)	-1(1)	0(1)	2(1)
N(1)	22(2)	44(2)	30(2)	0(1)	2(1)	2(1)
N(2)	48(3)	75(3)	39(2)	16(2)	21(2)	32(2)
N(3)	30(2)	43(2)	27(1)	3(1)	2(1)	3(1)
N(4)	60(4)	131(4)	53(2)	25(3)	18(2)	36(3)
C(1)	46(3)	43(2)	37(2)	7(2)	7(2)	12(2)
C(2)	49(3)	47(2)	35(2)	-6(2)	6(2)	19(2)
C(3)	42(3)	59(2)	25(2)	1(2)	6(2)	11(2)
C(4)	42(3)	49(2)	30(2)	7(2)	2(2)	10(2)
C(5)	52(3)	61(3)	50(2)	5(2)	2(2)	17(2)
C(6)	53(3)	75(3)	38(2)	3(2)	2(2)	25(2)
C(7)	58(4)	91(4)	36(2)	16(2)	10(2)	32(3)
S(1)	26(1)	45(1)	33(1)	3(1)	-6(1)	0(1)
S(2)	28(1)	42(1)	23(1)	1(1)	-1(1)	-1(1)
S(3)	28(1)	36(1)	30(1)	-1(1)	-4(1)	1(1)
S(4)	33(1)	40(1)	31(1)	7(1)	-6(1)	0(1)
O(1)	38(2)	52(2)	36(1)	8(1)	-16(1)	-2(1)
O(2)	34(2)	53(2)	28(1)	2(1)	-11(1)	-4(1)
N(5)	35(2)	54(2)	39(2)	-4(2)	-1(2)	-3(2)
N(6)	59(3)	90(3)	50(2)	21(2)	-7(2)	-20(2)
N(7)	43(3)	65(3)	81(3)	1(2)	-13(2)	-5(2)
N(8)	68(3)	108(4)	76(3)	50(3)	-11(2)	-11(3)
C(8)	26(2)	37(2)	30(2)	2(1)	-5(2)	5(2)
C(9)	23(2)	36(2)	31(2)	1(1)	0(2)	3(2)
C(10)	28(2)	33(2)	24(2)	2(1)	0(1)	4(2)
C(11)	29(2)	35(2)	24(2)	-2(1)	-3(1)	2(2)
C(12)	22(2)	34(2)	28(2)	-1(1)	-1(1)	3(2)
C(13)	27(2)	36(2)	28(2)	3(1)	-1(1)	5(2)
C(14)	26(2)	38(2)	28(2)	-4(1)	1(1)	4(2)
C(15)	29(3)	43(2)	34(2)	-2(2)	3(2)	0(2)
C(16)	33(3)	43(2)	32(2)	-1(2)	5(2)	-1(2)
C(17)	31(3)	55(2)	40(2)	6(2)	1(2)	-7(2)
C(18)	28(2)	32(2)	34(2)	-1(1)	0(2)	6(2)

C(19)	26(3)	40(2)	44(2)	7(2)	3(2)	1(2)
C(20)	37(3)	37(2)	53(2)	4(2)	6(2)	2(2)
C(21)	38(3)	54(3)	55(3)	16(2)	-1(2)	-5(2)

---

Table 5. Hydrogen bonds for tkul53 [A and deg.].

---

Hydrogen bonds with  $H..A < r(A) + 2.000$  Angstroms and  $\langle DHA \rangle > 110$  deg.

D-H	d(D-H)	d(H..A)	$\langle DHA \rangle$	d(D..A)	A
N1-H1N	0.910	2.270	158.87	3.136	N7 [-x+2, -y+1, -z]
N3-H3N	0.910	2.378	144.93	3.167	N4 [-x+3/2, y+1/2, -z-1/2]

---

## Supplementary File 2

Table 1. Crystal data and structure refinement for  $[\text{NiL}^{\text{C}_{2}\text{H}_5}][\text{Qimnt}]_2 \cdot 4\text{H}_2\text{O}$  (2).

Identification code	tku156
Empirical formula	C40 H38 N14 Ni 08 S8
Formula weight	1158.03
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 9.4820(11) Å    alpha = 90.381(8) deg. b = 11.2235(17) Å    beta = 93.656(12) deg. c = 11.7052(18) Å    gamma = 96.880(12) deg.
Volume	1234.1(3) Å <sup>3</sup>
Z, Calculated density	1, 1.558 Mg/m <sup>3</sup>
Absorption coefficient	0.798 mm <sup>-1</sup>
F(000)	596
Crystal size	0.50 x 0.30 x 0.05 mm
Theta range for data collection	1.83 to 25.00 deg.
Limiting indices	0 ≤ h ≤ 11, -13 ≤ k ≤ 13, -13 ≤ l ≤ 13
Reflections collected / unique	4641 / 4355 [R(int) = 0.0221]
Completeness to theta = 25.00	100.0 %
Absorption correction	Empirical
Max. and min. transmission	0.9612 and 0.6912

Refinement method	Full-matrix least-squares on $F^2$
Data / restraints / parameters	4355 / 6 / 332
Goodness-of-fit on $F^2$	1.027
Final R indices [ $I > 2\sigma(I)$ ]	R1 = 0.0471, wR2 = 0.1170
R indices (all data)	R1 = 0.0734, wR2 = 0.1321
Largest diff. peak and hole	0.665 and -0.419 e.Å <sup>-3</sup>

Table 2. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for tkul56. U(eq) is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	x	y	z	U(eq)
Ni	0	5000	0	37(1)
N(1)	911(3)	6524(3)	-507(3)	43(1)
N(2)	3381(4)	6098(3)	-168(3)	51(1)
N(3)	1753(3)	4518(3)	677(3)	40(1)
C(1)	-86(5)	7037(4)	-1342(4)	51(1)
C(2)	2356(4)	6532(4)	-965(3)	50(1)
C(3)	3076(4)	4856(4)	57(4)	54(1)
C(4)	1525(5)	3213(4)	898(4)	50(1)
C(5)	3832(5)	6861(5)	849(4)	64(1)
C(6)	4646(7)	8052(6)	545(5)	102(2)
S(1)	-1681(1)	8594(1)	3169(1)	48(1)
S(2)	-1043(1)	8607(1)	5656(1)	41(1)
S(3)	-4280(1)	12311(1)	6121(1)	42(1)
S(4)	-4939(1)	12295(1)	3634(1)	43(1)
O(1)	-3499(3)	10487(3)	2316(2)	57(1)
O(2)	-2347(3)	10507(3)	6953(2)	56(1)
N(4)	76(6)	6192(4)	2182(4)	81(1)
N(5)	1269(5)	6197(4)	5921(4)	72(1)
N(6)	-6304(5)	14511(4)	7154(3)	66(1)
N(7)	-7395(4)	14559(4)	3362(3)	62(1)
C(7)	-3274(4)	10464(3)	3381(3)	41(1)
C(8)	-2422(4)	9650(3)	3961(3)	39(1)
C(9)	-2130(4)	9651(3)	5126(3)	37(1)
C(10)	-2641(4)	10470(3)	5897(3)	38(1)
C(11)	-3840(4)	11256(3)	4158(3)	37(1)
C(12)	-3544(4)	11261(3)	5322(3)	37(1)
C(13)	-846(4)	7979(3)	4330(3)	42(1)
C(14)	-52(4)	7036(4)	4201(3)	45(1)
C(15)	40(5)	6548(4)	3076(4)	55(1)
C(16)	680(5)	6548(4)	5148(4)	49(1)
C(17)	-5188(4)	12880(3)	4967(3)	38(1)
C(18)	-6076(4)	13754(3)	5115(3)	39(1)

C(19)	-6240(4)	14190(4)	6238(4)	45(1)
C(20)	-6822(4)	14210(4)	4159(4)	45(1)
O(3)	-912(4)	11223(3)	9048(3)	80(1)
O(4)	-1802(6)	9590(5)	10623(5)	115(2)

---



Table 3. Bond lengths [Å] and angles [deg] for tkul56.

---

Ni-N(3)#1	1.933(3)
Ni-N(3)	1.933(3)
Ni-N(1)	1.936(3)
Ni-N(1)#1	1.936(3)
Ni-N(4)	2.868(4)
N(1)-C(1)	1.484(5)
N(1)-C(2)	1.501(5)
N(2)-C(3)	1.418(6)
N(2)-C(2)	1.434(5)
N(2)-C(5)	1.472(5)
N(3)-C(4)	1.482(5)
N(3)-C(3)	1.499(5)
C(1)-C(4)#1	1.487(6)
C(4)-C(1)#1	1.487(6)
C(5)-C(6)	1.517(7)
S(1)-C(13)	1.721(4)
S(1)-C(8)	1.739(4)
S(2)-C(13)	1.731(4)
S(2)-C(9)	1.743(4)
S(3)-C(17)	1.723(4)
S(3)-C(12)	1.736(4)
S(4)-C(17)	1.730(4)
S(4)-C(11)	1.744(4)
O(1)-C(7)	1.253(4)
O(2)-C(10)	1.249(4)
N(4)-C(15)	1.122(6)
N(5)-C(16)	1.131(6)
N(6)-C(19)	1.136(5)
N(7)-C(20)	1.145(5)
C(7)-C(8)	1.436(5)
C(7)-C(11)	1.439(5)
C(8)-C(9)	1.374(5)
C(9)-C(10)	1.430(5)
C(10)-C(12)	1.446(5)
C(11)-C(12)	1.374(5)
C(13)-C(14)	1.383(5)
C(14)-C(16)	1.418(6)
C(14)-C(15)	1.435(6)
C(17)-C(18)	1.384(5)

C(18)-C(20)	1.417(5)
C(18)-C(19)	1.424(6)
N(3)#1-Ni-N(3)	180.00(17)
N(3)#1-Ni-N(1)	86.41(13)
N(3)-Ni-N(1)	93.59(13)
N(3)#1-Ni-N(1)#1	93.59(13)
N(3)-Ni-N(1)#1	86.41(13)
N(1)-Ni-N(1)#1	180.00(16)
N(3)#1-Ni-N(4)	99.19(13)
N(3)-Ni-N(4)	80.81(13)
N(1)-Ni-N(4)	84.60(13)
N(1)#1-Ni-N(4)	95.40(13)
C(1)-N(1)-C(2)	111.1(3)
C(1)-N(1)-Ni	108.5(2)
C(2)-N(1)-Ni	117.1(3)
C(3)-N(2)-C(2)	113.1(3)
C(3)-N(2)-C(5)	114.9(4)
C(2)-N(2)-C(5)	116.2(4)
C(4)-N(3)-C(3)	111.7(3)
C(4)-N(3)-Ni	108.5(2)
C(3)-N(3)-Ni	117.1(2)
N(1)-C(1)-C(4)#1	106.4(3)
N(2)-C(2)-N(1)	113.4(3)
N(2)-C(3)-N(3)	115.1(3)
N(3)-C(4)-C(1)#1	106.6(3)
N(2)-C(5)-C(6)	112.3(4)
C(13)-S(1)-C(8)	95.29(18)
C(13)-S(2)-C(9)	94.82(18)
C(17)-S(3)-C(12)	95.05(18)
C(17)-S(4)-C(11)	94.87(18)
C(15)-N(4)-Ni	172.7(4)
O(1)-C(7)-C(8)	123.9(3)
O(1)-C(7)-C(11)	123.5(4)
C(8)-C(7)-C(11)	112.7(3)
C(9)-C(8)-C(7)	124.0(3)
C(9)-C(8)-S(1)	116.5(3)
C(7)-C(8)-S(1)	119.5(3)
C(8)-C(9)-C(10)	123.5(3)
C(8)-C(9)-S(2)	116.8(3)
C(10)-C(9)-S(2)	119.7(3)
O(2)-C(10)-C(9)	124.2(4)
O(2)-C(10)-C(12)	123.1(3)

C(9)-C(10)-C(12)	112.7(3)
C(12)-C(11)-C(7)	123.3(3)
C(12)-C(11)-S(4)	116.5(3)
C(7)-C(11)-S(4)	120.2(3)
C(11)-C(12)-C(10)	123.7(3)
C(11)-C(12)-S(3)	116.9(3)
C(10)-C(12)-S(3)	119.3(3)
C(14)-C(13)-S(1)	121.3(3)
C(14)-C(13)-S(2)	122.2(3)
S(1)-C(13)-S(2)	116.6(2)
C(13)-C(14)-C(16)	121.8(4)
C(13)-C(14)-C(15)	118.9(4)
C(16)-C(14)-C(15)	119.4(4)
N(4)-C(15)-C(14)	177.5(5)
N(5)-C(16)-C(14)	177.6(5)
C(18)-C(17)-S(3)	121.0(3)
C(18)-C(17)-S(4)	122.4(3)
S(3)-C(17)-S(4)	116.6(2)
C(17)-C(18)-C(20)	120.4(3)
C(17)-C(18)-C(19)	119.5(3)
C(20)-C(18)-C(19)	120.1(3)
N(6)-C(19)-C(18)	176.2(4)
N(7)-C(20)-C(18)	177.6(4)

---

Symmetry transformations used to generate equivalent atoms:

#1 -x, -y+1, -z

Table 4. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for tkul56. The anisotropic displacement factor exponent takes the form:  
 $-2 \pi^2 [ h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12} ]$

	U11	U22	U33	U23	U13	U12
Ni	34(1)	48(1)	31(1)	-2(1)	0(1)	13(1)
N(1)	42(2)	53(2)	34(2)	-3(1)	0(1)	9(2)
N(2)	41(2)	67(2)	44(2)	-4(2)	1(2)	8(2)
N(3)	38(2)	50(2)	35(2)	-4(1)	-1(1)	14(2)
C(1)	54(3)	55(3)	46(2)	5(2)	-5(2)	9(2)
C(2)	44(2)	65(3)	42(2)	0(2)	7(2)	4(2)
C(3)	42(2)	76(3)	46(2)	-4(2)	2(2)	22(2)
C(4)	53(3)	53(3)	47(2)	-2(2)	-2(2)	20(2)
C(5)	46(3)	87(4)	55(3)	-10(2)	-12(2)	5(2)
C(6)	94(5)	107(5)	92(4)	-16(4)	-7(4)	-34(4)
S(1)	62(1)	47(1)	39(1)	-5(1)	6(1)	19(1)
S(2)	44(1)	39(1)	40(1)	-3(1)	0(1)	9(1)
S(3)	49(1)	43(1)	35(1)	-6(1)	1(1)	14(1)
S(4)	51(1)	42(1)	37(1)	-2(1)	1(1)	12(1)
O(1)	81(2)	58(2)	35(2)	-2(1)	2(1)	23(2)
O(2)	71(2)	61(2)	36(2)	-7(1)	-6(1)	17(2)
N(4)	114(4)	82(3)	57(3)	-10(2)	22(2)	45(3)
N(5)	69(3)	83(3)	70(3)	7(2)	1(2)	27(2)
N(6)	76(3)	76(3)	53(2)	-11(2)	6(2)	34(2)
N(7)	63(3)	67(3)	57(2)	1(2)	-6(2)	18(2)
C(7)	47(2)	39(2)	38(2)	-1(2)	4(2)	5(2)
C(8)	44(2)	36(2)	38(2)	-5(2)	6(2)	7(2)
C(9)	35(2)	32(2)	43(2)	-2(2)	3(2)	3(2)
C(10)	37(2)	38(2)	38(2)	-5(2)	3(2)	0(2)
C(11)	44(2)	30(2)	38(2)	-3(2)	0(2)	5(2)
C(12)	38(2)	34(2)	39(2)	-5(2)	4(2)	2(2)
C(13)	42(2)	42(2)	41(2)	-2(2)	8(2)	3(2)
C(14)	46(2)	45(2)	44(2)	-4(2)	10(2)	11(2)
C(15)	59(3)	54(3)	58(3)	4(2)	15(2)	27(2)
C(16)	46(2)	46(2)	56(3)	-1(2)	10(2)	12(2)
C(17)	37(2)	37(2)	39(2)	-3(2)	4(2)	1(2)
C(18)	37(2)	38(2)	43(2)	1(2)	2(2)	7(2)
C(19)	42(2)	42(2)	55(3)	-1(2)	4(2)	13(2)

C(20)	40(2)	44(2)	50(2)	-6(2)	4(2)	6(2)
0(3)	98(3)	78(2)	64(2)	-11(2)	-10(2)	17(2)
0(4)	115(4)	140(5)	99(3)	24(3)	31(3)	37(3)

---

Table 5. Hydrogen bonds for tkul56 [A and deg.].

---

Hydrogen bonds with  $H..A < r(A) + 2.000$  Angstroms and  $\langle DHA \rangle > 110$  deg.

D-H	d(D-H)	d(H..A)	$\langle DHA \rangle$	d(D..A)	A
N1-H1N	0.910	2.208	151.98	3.041	03 [ -x, -y+2, -z+1 ]
N3-H3N	0.910	2.422	142.73	3.194	N7 [ x+1, y-1, z ]
N3-H3N	0.910	2.614	122.16	3.192	N4
O3-H31	0.822	2.067	155.74	2.836	04 [ -x, -y+2, -z+2 ]
O3-H32	0.823	2.017	157.02	2.792	02
O4-H41	0.842	1.953	149.20	2.711	03
O4-H42	0.830	2.081	161.69	2.881	01 [ x, y, z+1 ]

---