Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

Bis[1-(4-chlorobenzyl)pyridinium] bis(1,2,5-thiadiazole-3,4-dithiolato)-nickelate(II)

Zhi-min Wang,[a,b]* Fang-quan Wang[b] and Zi-yang Liu[a]

[a]Department of Chemistry, Zhejiang University, Hangzhou, 310027, People's Republic of China, and [b]College of Biology and Environment Engineering, Zhejiang Shuren University, Hangzhou 310015, People's Republic of China
Correspondence e-mail: wangzm168@126.com

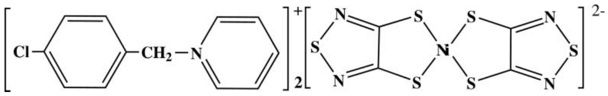
Received 8 July 2011; accepted 17 July 2011

Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.003 Å; R factor = 0.024; wR factor = 0.062; data-to-parameter ratio = 14.1.

The asymmetric unit of the salt, $(C_{12}H_{11}ClN)_2[Ni(C_2N_2S_3)_2]$, comprises one cation and a half of $Ni(tdas)_2$ (tdas = 1,2,5-thiadiazole-3,4-dithiolate) anion. The Ni^{II} atom is located at a centre of inversion. The Ni^{II} atom has a square-planar coordination with Ni—S distances of 2.2052 (4) and 2.1970 (5) Å. In crystal, weak C—H⋯S and C—H⋯Ni contacts are observed between the anions and cations.

Related literature

For background to complexes containing the $[Ni(mnt)_2]$ anion, see: Robertson & Cronin (2002); Xie *et al.* (2002); Ni *et al.* (2005); Chen *et al.* (2010). For details of other square-planar $[Ni(tdas)_2]$ complexes, see: Awaga *et al.* (1994); Yamochi *et al.* (2001); Okuno *et al.* (2003); Ni *et al.* (2004). For C—H⋯Ni contacts, see: Brookhart *et al.* (2007); Yang & Ni (2006).



Experimental

Crystal data

$(C_{12}H_{11}ClN)_2[Ni(C_2N_2S_3)_2]$
M_r = 764.49
Monoclinic, $P2_1/c$
a = 11.3091 (10) Å
b = 12.6699 (12) Å
c = 12.2405 (11) Å
β = 116.005 (1)°
V = 1576.3 (2) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 1.21 mm^{-1}
T = 296 K
0.22 × 0.17 × 0.11 mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)
T_{min} = 0.788, T_{max} = 0.872
11011 measured reflections
2771 independent reflections
2583 reflections with $I > 2\sigma(I)$
R_{int} = 0.023

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.024
$wR(F^2)$ = 0.062
S = 1.03
2771 reflections
196 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.34 e Å^{-3}
$\Delta\rho_{min}$ = −0.34 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C4—H4⋯S2^{i}	0.93	2.86	3.765 (2)	163
C11—H11⋯S2^{ii}	0.93	2.80	3.715 (2)	169
C9—H9B⋯Ni1^{iii}	0.97	2.90	3.818 (3)	159

Symmetry codes: (i) $x, y+1, z$; (ii) $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$; (iii) $-x+2, y+\frac{1}{2}, -z+\frac{3}{2}$.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

This work was funded by the Zhejiang Natural Science Foundation (No. y4090430).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: KP2343).

References

Awaga, K., Okuno, T., Maruyama, Y., Kobayashi, A., Kobayashi, H., Schenk, S. & Underhill, A. E. (1994). *Inorg. Chem.* **33**, 5598–5600.
Brookhart, M., Green, M. L. H. & Parkin, G. (2007). *PNAS*, **104**, 6908–6914.
Bruker (2000). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Chen, X., Zou, H. L., Lin, J. H., Huang, Q., Zuo, H. R., Zhou, J. R., Ni, C. L. & Hu, X. L. (2010). *J. Mol. Struct.* **981**, 139–145.
Ni, C. L., Dang, D. B., Ni, Z. P., Li, Y. Z., Xie, J. L., Meng, Q. J. & Yao, Y. G. (2004). *J. Coord. Chem.* **57**, 1529–1536.
Ni, Z. P., Ren, X. M., Ma, J., Xie, J. L., Ni, C. L., Chen, Z. D. & Meng, Q. J. (2005). *J. Am. Chem. Soc.* **127**, 14330–14338.
Okuno, T., Kuwamoto, K., Fujita, W., Awaga, K. & Nakanishi, W. (2003). *Polyhedron*, **22**, 2311–2315.
Robertson, N. & Cronin, L. (2002). *Coord. Chem. Rev.* **227**, 93–127.
Sheldrick, G. M. (2004). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Xie, J. L., Ren, X. M., Song, Y., Zhang, W. W., Liu, W. L., He, C. & Meng, Q. J. (2002). *Chem. Commun.* pp. 2346–2347.
Yamochi, H., Sogoshi, N., Simizu, Y., Saito, G. & Matsumoto, K. (2001). *J. Mater. Chem.* **11**, 2216–2220.
Yang, S.-B. & Ni, C.-L. (2006). *Acta Cryst.* E**62**, m483–m485.

supplementary materials

Acta Cryst. (2011). E**67**, m1143 [**doi:10.1107/S160053681102873X**]

Bis[1-(4-chlorobenzyl)pyridinium] bis(1,2,5-thiadiazole-3,4-dithiolato)nickelate(II)

Z. Wang, F. Wang and Z. Liu

Comment

Much effort has been devoted to the study of bis(1,2-ditholene) transition metal complexes because of their extensive applications in molecular materials showing magnetic, superconducting, and optical properties. Among these complexes, $[M(\text{tdas})_2]^{n-}$ (tdas is 1,2,5-thiadiazole-3,4-dithiolate, n is 1 or 2) complexes show interesting magnetic properties with unusual phase transition and electro-conductive properties in the solid state. As a continuation of our work in this field, we have obtained a new ion-pair complex, $[\text{4ClBzPy}]_2[\text{Ni(tdas)}_2]$ (I), by introducing 1-(4'-chlorobenzyl)pyridinium as a counterion into the system containing the $[\text{Ni(tdas)}_2]^{2-}$ anion.

There are one $[\text{4ClBzPy}]^+$ and a half of $[\text{Ni(tdas)}_2]^{2-}$ anion in an asymmetric unit of (I). The nickel(II) ion of Ni(tdas)_2 anion is situated at a center of symmetry of a square planar complex (Fig. 1). The two $[\text{4ClBzPy}]^+$ ions are related to each other by the symmetry centre. The Ni1—S1 and Ni1—S2 bond distances are 2.205 (1)Å and 2.197 (1) Å (Table 1), and the S1—Ni1—S2 bond angle within the five-membered ring is 93.42 (2)°, as that have been found for other $[\text{Ni(tdas)}_2]^{2-}$ structures. The dihedral angles between the C8—C9—N3 reference plane and these aromatic rings are 87.2 (2)° for a phenyl ring and 5.4 (2)° for a pyridine ring, respectively. The dihedral angle between the phenyl ring and the pyridine ring is 92.1 (2)°. The anions and the cations are involved in C4—H4···S2, C11—H11···S2 and C9—H9···Ni weak contacts (Fig. 2, Table 2). The distances of C9···Ni and H···Ni are 3.819Å and 2.895 (2) Å, respectively, while the bond angle is 159.36 (2)° (Brookhart *et al.*, 2007).

Experimental

The title complex was prepared by the direct reaction of 1:2:2 mol equiv. of $\text{NiCl}_2.6\text{H}_2\text{O}$, Na_2tdas and 1-(4'-chlorobenzyl)pyridinium bromide in methanol. A brown product was given and purified through recrystallisation from the mixed solvent of methanol and water (yield 81%). The brown block single crystals suitable for X-ray analysis were obtained by slow evaporation of methanol solution of (I) at room temperature about 2 weeks.

Refinement

All H-atoms were positioned geometrically and refined using a riding model with d(C—H) = 0.93 Å, $U_{\text{iso}}=1.2U_{\text{eq}}$ (C) for aromatic and 0.97 Å, $U_{\text{iso}} = 1.2U_{\text{eq}}$ (C) for CH_2 atoms.

Figures

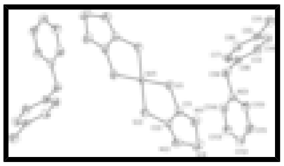


Fig. 1. The molecular structure of (I) with atom labels of an asymmetric units and 30% probability displacement ellipsoids for non-H atoms. The complete is generated by the inversion symmetry operation: -*x* + 2, *y* + 1/2, -*z* + 2.

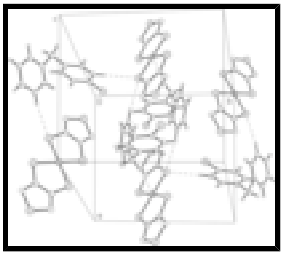


Fig. 2. Crystal packing of (I) showing the C—H···S and C—H···Ni contacts between the anions and cations drawn as dashed lines.

Bis[1-(4-chlorobenzyl)pyridinium] bis(1,2,5-thiadiazole-3,4-dithiolato)nickelate(II)

Crystal data

$(C_{12}H_{11}ClN)_2[Ni(C_2N_2S_3)_2]$	$F(000) = 780$
$M_r = 764.49$	$D_x = 1.611$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 8963 reflections
$a = 11.3091$ (10) Å	$\theta = 2.5$–$27.6°$
$b = 12.6699$ (12) Å	$\mu = 1.21$ mm^{-1}
$c = 12.2405$ (11) Å	$T = 296$ K
$\beta = 116.005$ (1)°	Block, brown
$V = 1576.3$ (2) Å^3	0.22 × 0.17 × 0.11 mm
$Z = 2$	

Data collection

Bruker Smart AAPEX CCD diffractometer	2771 independent reflections
Radiation source: fine-focus sealed tube	2583 reflections with $I > 2\sigma(I)$
graphite	$R_{\text{int}} = 0.023$
φ and ω scans	$\theta_{\text{max}} = 25.0°$, $\theta_{\text{min}} = 2.0°$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)	$h = -11 \rightarrow 13$
$T_{\text{min}} = 0.788$, $T_{\text{max}} = 0.872$	$k = -15 \rightarrow 15$
11011 measured reflections	$l = -14 \rightarrow 14$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map

$R[F^2 > 2\sigma(F^2)] = 0.024$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.062$	H-atom parameters constrained
$S = 1.03$	$w = 1/[\sigma^2(F_o^2) + (0.0288P)^2 + 0.688P]$ where $P = (F_o^2 + 2F_c^2)/3$
2771 reflections	$(\Delta/\sigma)_{max} = 0.001$
196 parameters	$\Delta\rho_{max} = 0.34$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.34$ e Å^{-3}

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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Ni1	1.0000	0.0000	1.0000	0.03315 (10)
S1	0.92227 (4)	0.11624 (3)	0.85099 (4)	0.04375 (12)
S2	0.80993 (4)	−0.08083 (4)	0.94044 (4)	0.04587 (13)
S3	0.52625 (5)	0.07090 (6)	0.64534 (5)	0.06730 (18)
Cl1	0.81302 (6)	0.64372 (5)	1.10601 (5)	0.06886 (17)
N1	0.66806 (17)	0.13162 (15)	0.68113 (15)	0.0560 (4)
N2	0.57869 (16)	−0.02144 (15)	0.75207 (15)	0.0570 (4)
N3	0.71207 (14)	0.36476 (11)	0.59981 (13)	0.0386 (3)
C1	0.75730 (17)	0.08146 (14)	0.77589 (16)	0.0414 (4)
C2	0.70635 (18)	−0.00619 (13)	0.81645 (17)	0.0419 (4)
C3	0.8199 (2)	0.57027 (15)	0.79196 (18)	0.0511 (5)
H3	0.8155	0.6055	0.7236	0.061*
C4	0.8134 (2)	0.62703 (16)	0.88550 (19)	0.0550 (5)
H4	0.8048	0.7001	0.8807	0.066*
C5	0.81978 (17)	0.57358 (15)	0.98640 (17)	0.0470 (4)
C6	0.83425 (19)	0.46580 (16)	0.99634 (18)	0.0507 (4)
H6	0.8390	0.4309	1.0650	0.061*
C7	0.84157 (19)	0.41026 (15)	0.90237 (18)	0.0479 (4)
H7	0.8525	0.3374	0.9087	0.057*
C8	0.83301 (17)	0.46093 (15)	0.79884 (16)	0.0420 (4)
C9	0.84261 (18)	0.39821 (16)	0.69918 (17)	0.0464 (4)
H9A	0.8950	0.3356	0.7343	0.056*
H9B	0.8886	0.4401	0.6636	0.056*
C10	0.59709 (18)	0.38027 (15)	0.60462 (18)	0.0471 (4)

H10	0.5951	0.4172	0.6695	0.057*
C11	0.48229 (19)	0.34190 (18)	0.51417 (19)	0.0564 (5)
H11	0.4028	0.3531	0.5178	0.068*
C12	0.4847 (2)	0.28709 (17)	0.41842 (19)	0.0560 (5)
H12	0.4075	0.2604	0.3572	0.067*
C13	0.6037 (2)	0.27238 (17)	0.41461 (18)	0.0549 (5)
H13	0.6077	0.2358	0.3504	0.066*
C14	0.71548 (19)	0.31201 (15)	0.50599 (17)	0.0485 (4)
H14	0.7957	0.3023	0.5033	0.058*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.03566 (17)	0.02727 (16)	0.04445 (18)	0.00239 (11)	0.02487 (14)	0.00392 (11)
S1	0.0409 (2)	0.0400 (2)	0.0576 (3)	0.00339 (18)	0.0282 (2)	0.0144 (2)
S2	0.0434 (3)	0.0386 (2)	0.0568 (3)	−0.00545 (18)	0.0230 (2)	0.00919 (19)
S3	0.0467 (3)	0.0940 (5)	0.0522 (3)	0.0000 (3)	0.0134 (2)	0.0145 (3)
Cl1	0.0629 (3)	0.0786 (4)	0.0630 (3)	0.0043 (3)	0.0258 (3)	−0.0204 (3)
N1	0.0504 (9)	0.0693 (11)	0.0502 (9)	0.0087 (8)	0.0237 (8)	0.0178 (8)
N2	0.0454 (9)	0.0700 (11)	0.0526 (10)	−0.0095 (8)	0.0188 (8)	0.0016 (8)
N3	0.0401 (8)	0.0377 (7)	0.0441 (8)	0.0038 (6)	0.0240 (7)	0.0060 (6)
C1	0.0431 (10)	0.0454 (10)	0.0435 (9)	0.0059 (7)	0.0262 (8)	0.0043 (8)
C2	0.0422 (10)	0.0437 (10)	0.0450 (10)	−0.0019 (7)	0.0238 (8)	−0.0020 (7)
C3	0.0558 (11)	0.0458 (11)	0.0493 (11)	0.0039 (9)	0.0208 (9)	0.0107 (8)
C4	0.0566 (12)	0.0397 (10)	0.0609 (12)	0.0055 (9)	0.0185 (10)	0.0014 (9)
C5	0.0345 (9)	0.0545 (11)	0.0487 (11)	0.0003 (8)	0.0152 (8)	−0.0068 (8)
C6	0.0530 (11)	0.0528 (11)	0.0511 (11)	−0.0024 (9)	0.0274 (9)	0.0048 (9)
C7	0.0536 (11)	0.0390 (9)	0.0566 (11)	−0.0019 (8)	0.0292 (9)	0.0053 (8)
C8	0.0354 (9)	0.0437 (9)	0.0477 (10)	−0.0011 (7)	0.0190 (8)	0.0034 (8)
C9	0.0388 (9)	0.0537 (11)	0.0513 (11)	0.0012 (8)	0.0239 (8)	0.0035 (8)
C10	0.0431 (10)	0.0535 (11)	0.0518 (11)	0.0087 (8)	0.0274 (9)	0.0012 (9)
C11	0.0392 (10)	0.0688 (14)	0.0630 (13)	0.0102 (9)	0.0240 (9)	0.0005 (10)
C12	0.0478 (11)	0.0634 (13)	0.0510 (11)	0.0030 (9)	0.0164 (9)	0.0025 (9)
C13	0.0597 (12)	0.0629 (13)	0.0484 (11)	0.0013 (10)	0.0294 (10)	−0.0047 (9)
C14	0.0500 (11)	0.0541 (11)	0.0549 (11)	0.0028 (9)	0.0354 (9)	−0.0002 (9)

Geometric parameters (Å, °)

Ni1—S2	2.1970 (5)	C4—H4	0.9300
Ni1—S2^{i}	2.1970 (5)	C5—C6	1.374 (3)
Ni1—S1	2.2052 (4)	C6—C7	1.382 (3)
Ni1—S1^{i}	2.2052 (4)	C6—H6	0.9300
S1—C1	1.7367 (19)	C7—C8	1.386 (3)
S2—C2	1.7351 (19)	C7—H7	0.9300
S3—N1	1.6552 (18)	C8—C9	1.499 (3)
S3—N2	1.6576 (19)	C9—H9A	0.9700
Cl1—C5	1.7428 (19)	C9—H9B	0.9700
N1—C1	1.320 (2)	C10—C11	1.374 (3)

N2—C2	1.321 (2)	C10—H10	0.9300
N3—C10	1.342 (2)	C11—C12	1.373 (3)
N3—C14	1.344 (2)	C11—H11	0.9300
N3—C9	1.505 (2)	C12—C13	1.379 (3)
C1—C2	1.436 (2)	C12—H12	0.9300
C3—C4	1.381 (3)	C13—C14	1.364 (3)
C3—C8	1.392 (3)	C13—H13	0.9300
C3—H3	0.9300	C14—H14	0.9300
C4—C5	1.382 (3)		

S2—Ni1—S2^{i}	180.0	C5—C6—H6	120.6
S2—Ni1—S1	93.419 (17)	C7—C6—H6	120.6
S2^{i}—Ni1—S1	86.581 (17)	C6—C7—C8	121.32 (18)
S2—Ni1—S1^{i}	86.581 (17)	C6—C7—H7	119.3
S2^{i}—Ni1—S1^{i}	93.419 (17)	C8—C7—H7	119.3
S1—Ni1—S1^{i}	180.0	C7—C8—C3	118.64 (17)
C1—S1—Ni1	102.38 (6)	C7—C8—C9	119.85 (17)
C2—S2—Ni1	102.90 (6)	C3—C8—C9	121.48 (16)
N1—S3—N2	98.58 (8)	C8—C9—N3	114.31 (14)
C1—N1—S3	106.72 (13)	C8—C9—H9A	108.7
C2—N2—S3	106.67 (14)	N3—C9—H9A	108.7
C10—N3—C14	120.12 (16)	C8—C9—H9B	108.7
C10—N3—C9	123.34 (15)	N3—C9—H9B	108.7
C14—N3—C9	116.44 (14)	H9A—C9—H9B	107.6
N1—C1—C2	114.09 (17)	N3—C10—C11	120.30 (18)
N1—C1—S1	124.97 (14)	N3—C10—H10	119.9
C2—C1—S1	120.93 (14)	C11—C10—H10	119.9
N2—C2—C1	113.95 (17)	C12—C11—C10	120.10 (18)
N2—C2—S2	125.75 (14)	C12—C11—H11	119.9
C1—C2—S2	120.30 (14)	C10—C11—H11	119.9
C4—C3—C8	120.74 (18)	C11—C12—C13	118.82 (19)
C4—C3—H3	119.6	C11—C12—H12	120.6
C8—C3—H3	119.6	C13—C12—H12	120.6
C3—C4—C5	118.99 (18)	C14—C13—C12	119.31 (19)
C3—C4—H4	120.5	C14—C13—H13	120.3
C5—C4—H4	120.5	C12—C13—H13	120.3
C6—C5—C4	121.56 (18)	N3—C14—C13	121.34 (17)
C6—C5—Cl1	118.66 (16)	N3—C14—H14	119.3
C4—C5—Cl1	119.76 (15)	C13—C14—H14	119.3
C5—C6—C7	118.73 (18)		

Symmetry codes: (i) $-x+2, -y, -z+2$.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4···S2^{ii}	0.93	2.86	3.765 (2)	163
C11—H11···S2^{iii}	0.93	2.80	3.715 (2)	169
C9—H9B···Ni1^{iv}	0.97	2.90	3.818 (3)	159

Symmetry codes: (ii) *x*, *y*+1, *z*; (iii) −*x*+1, *y*+1/2, −*z*+3/2; (iv) −*x*+2, *y*+1/2, −*z*+3/2.

Fig. 1

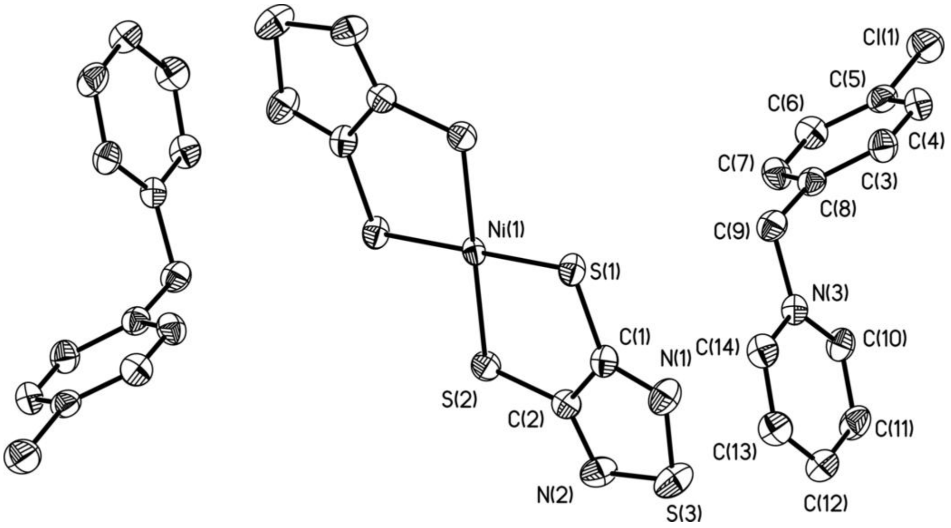


Fig. 2