Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Poly[[μ_4-bis(4-pyridylcarbonyl)piperazine-$\kappa^4N:N':O:O'$]bis(thiocyanato-κN)-cobalt(II)]

Zachary M. Wilseck and Robert L. LaDuca*

Lyman Briggs College, Department of Chemistry, Michigan State University, East Lansing, MI 48825, USA
Correspondence e-mail: laduca@msu.edu

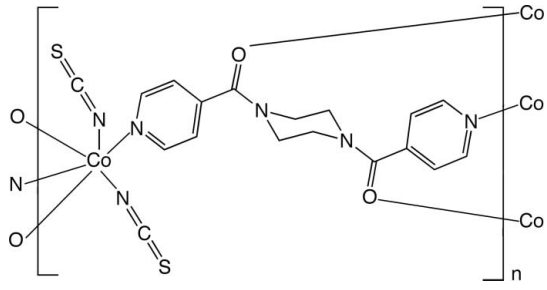
Received 12 May 2010; accepted 21 May 2010

Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.005 Å; R factor = 0.037; wR factor = 0.105; data-to-parameter ratio = 13.2.

In the title compound, $[Co(NCS)_2(C_{16}H_{16}N_4O_2)]_n$, the octahedrally coordinated Co^{II} ion lies on a crystallographic inversion center, with *trans* isothiocyanate ligands. Pyridyl N-donor atoms and formyl O-donor atoms from exotetradentate bis(4-pyridylcarbonyl)piperazine (4-bpfp) ligands link the $Co(NCS)_2$ units into a $[Co(NCS)_2(4\text{-bpfp})]_n$ coordination polymer layer that is oriented parallel to (101). The layers stack along [010] to construct the pseudo-three-dimensional structure.

Related literature

For divalent metal isophthalate coordination polymers containing bis(4-pyridylmethyl)piperazine ligands, see: Martin *et al.* (2007). For a cobalt isothiocyanate coordination polymer containing bis(4-pyridylmethyl)piperazine ligands, see: Martin *et al.* (2009). For the preparation of 4-bpfp, see: Hou *et al.* (2003).



Experimental

Crystal data

$[Co(NCS)_2(C_{16}H_{16}N_4O_2)]$
M_r = 471.44
Triclinic, $P\overline{1}$
a = 7.7410 (14) Å
b = 7.8943 (15) Å
c = 9.801 (3) Å
α = 101.080 (2)°
β = 102.264 (2)°
γ = 119.136 (2)°
V = 479.58 (18) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 1.14 mm^{-1}
T = 173 K
0.42 × 0.19 × 0.07 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.643, T_{max} = 0.928
6955 measured reflections
1753 independent reflections
1646 reflections with $I > 2\sigma(I)$
R_{int} = 0.052

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.105
S = 1.18
1753 reflections
133 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.37 e Å^{-3}
$\Delta\rho_{min}$ = −0.55 e Å^{-3}

Table 1
Selected bond lengths (Å).

Co1—N1	2.1739 (19)	Co1—O1^{i}	2.2034 (16)
Co1—N3	2.026 (2)		

Symmetry code: (i) $-x, -y+1, -z$.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *CrystalMaker* (Palmer, 2007); software used to prepare material for publication: *SHELXL97*.

We gratefully acknowledge the donors of the American Chemical Society Petroleum Research Fund for funding this work. ZMW thanks Dr Richard Staples for instruction in the use of the crystallographic software.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HY2308).

References

Bruker (2007). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Hou, H., Song, Y., Xu, H., Wei, Y., Fan, Y., Zhu, Y., Li, L. & Du, C. (2003). *Macromolecules*, **36**, 999–1008.
Martin, D. P., Braverman, M. A. & LaDuca, R. L. (2007). *Cryst. Growth Des.* **7**, 2609–2619.
Martin, D. P., Knapp, W. R., Supkowski, R. M. & LaDuca, R. L. (2009). *Inorg. Chim. Acta*, **362**, 1559–1564.
Palmer, D. (2007). *CrystalMaker*. CrystalMaker Software, Bicester, England.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supplementary materials

Acta Cryst. (2010). E**66**, m713 [**doi:10.1107/S160053681001915X**]

Poly[[μ_4-bis(4-pyridylcarbonyl)piperazine-$\kappa^4N:N':O:O'$]bis(thiocyanato-κN)cobalt(II)]

Z. M. Wilseck and R. L. LaDuca

Comment

Recently our group has been investigating the synthesis of divalent metal coordination polymers containing aromatic dicarboxylate and bis(4-pyridyl-methyl)piperazine ligands (Martin *et al.*, 2007). To probe the structural effect of the presence of hydrogen-bond accepting formyl oxygen atoms in a similar ligand, we attempted to prepare a cobalt phthalate coordination polymer containing bis(4-pyridylcarbonyl)piperazine (4-bpfp). Use of cobalt(II) thiocyanate as the metal precursor afforded pink plates of the title compound.

The title compound crystallizes in the centrosymmetric triclinic space group with an asymmetric unit consisting of a Co^{II} ion on a crystallographic inversion center, one isothiocyanate ligand bound *via* its N atom, and one-half of a 4-bpfp molecule. The coordination environment at Co is a slightly distorted $[CoN_4O_2]$ octahedron (Fig. 1), with *trans* isothiocyanate ligands, *trans* pyridyl N atom donors from two 4-bpfp ligands, and *trans* formyl O atom donors from two other 4-bpfp ligands.

Each 4-bpfp ligand is exotetradentate, ligating to Co atoms through both pyridyl N atoms and both formyl O atoms. As a result, $[Co(NCS)_2(4\text{-bpfp})]_n$ coordination polymer layers are formed (Fig. 2), which are oriented parallel to the *ac* crystal planes. Fourteen-membered $[CoOC_4N]_2$ circuits, whose centroids rest on crystallographic inversion centers, are evident within the layer motifs. The Co···Co distances across these circuits denote the *a* lattice parameter. The through-ligand Co···Co distances across the full span of the 4-bpfp ligands measure 16.471 (4) Å.

Adjacent $[Co(NCS)_2(4\text{-bpfp})]_n$ layers stack in an *AAA* pattern along the *b* direction (Fig. 3), with the isothiocyanate ligands projecting above and below the layer planes. Crystal packing forces cause aggregation of the layer motifs into *pseudo* three-dimensional crystal structure of the title compound.

Experimental

All starting materials were obtained commercially, except for 4-bpfp, which was prepared by a published procedure (Hou *et al.*, 2003). Cobalt(II) thiocyanate (130 mg, 0.74 mmol), phthalic acid (123 mg, 0.74 mmol) and 4-bpfp (110 mg, 0.37 mmol) were placed into 10 ml H_2O in a 23 ml Teflon-lined Parr acid digestion bomb. The bomb was heated at 393 K for 48 h and was then allowed to cool to room temperature. Pink plates of the title compound were obtained along with a white powdery solid.

Refinement

All H atoms bound to C atoms were placed in calculated positions, with C—H = 0.93 (CH) and 0.97 (CH_2) Å, and refined in a riding mode with $U_{iso}(H) = 1.2U_{eq}(C)$.

Figures

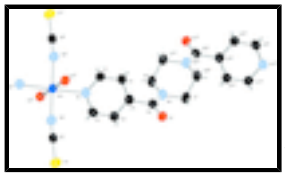


Fig. 1. The coordination environment of the title compound, showing 50% probability ellipsoids. Hydrogen atom positions are shown as grey sticks. [Color codes: dark blue Co, yellow S, red O, light blue N, black C. Symmetry codes: (i) -*x*+1, -*y*+1, -*z*; (ii) -*x*, -*y*+1, -*z*; (iii) *x*+1, *y*, *z*; (iv) -*x*-1, -*y*+1, -*z*-1.]

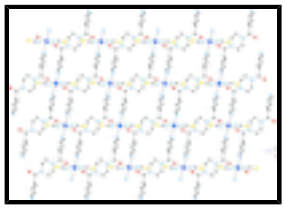


Fig. 2. $[Co(NCS)_2(4\text{-bpfp})]_n$ layer in the title compound.

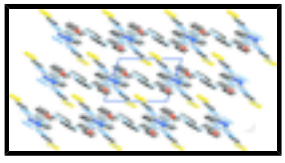


Fig. 3. Packing diagram of the title compound.

Poly[[μ_4-bis(4-pyridylcarbonyl)piperazine- $\kappa^4N:N':O:O'$]bis(thiocyanato- κN)cobalt(II)]

Crystal data

$[Co(NCS)_2(C_{16}H_{16}N_4O_2)]$	$Z = 1$
$M_r = 471.44$	$F(000) = 241$
Triclinic, $P\overline{1}$	$D_x = 1.632$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 7.7410$ (14) Å	Cell parameters from 6955 reflections
$b = 7.8943$ (15) Å	$\theta = 2.3$–$25.3°$
$c = 9.801$ (3) Å	$\mu = 1.14$ mm^{-1}
$\alpha = 101.080$ (2)°	$T = 173$ K
$\beta = 102.264$ (2)°	Plate, pink
$\gamma = 119.136$ (2)°	0.42 × 0.19 × 0.07 mm
$V = 479.58$ (18) Å^3	

Data collection

Bruker APEXII CCD diffractometer	1753 independent reflections
Radiation source: fine-focus sealed tube	1646 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.052$
ω and φ scans	$\theta_{max} = 25.3°$, $\theta_{min} = 2.3°$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$h = -9 \rightarrow 9$
$T_{min} = 0.643$, $T_{max} = 0.928$	$k = -9 \rightarrow 9$
6955 measured reflections	$l = -11 \rightarrow 11$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.037$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.105$	H-atom parameters constrained
$S = 1.18$	$w = 1/[\sigma^2(F_o^2) + (0.0458P)^2 + 0.1032P]$ where $P = (F_o^2 + 2F_c^2)/3$
1753 reflections	$(\Delta/\sigma)_{max} < 0.001$
133 parameters	$\Delta\rho_{max} = 0.37$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.55$ e Å^{-3}

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Co1	0.5000	0.5000	0.0000	0.03453 (19)
S1	0.75373 (12)	1.06782 (11)	0.44195 (8)	0.0504 (2)
N1	0.2531 (3)	0.5500 (3)	−0.0887 (2)	0.0359 (4)
N2	−0.3493 (3)	0.6090 (3)	−0.3539 (2)	0.0384 (5)
N3	0.6324 (3)	0.7503 (3)	0.1850 (2)	0.0409 (5)
C1	0.0560 (4)	0.3911 (4)	−0.1764 (3)	0.0391 (5)
H1	0.0304	0.2594	−0.2075	0.047*
C2	−0.1098 (4)	0.4140 (4)	−0.2225 (3)	0.0389 (5)
H2	−0.2440	0.2996	−0.2828	0.047*
C3	−0.0749 (4)	0.6093 (4)	−0.1781 (2)	0.0364 (5)
C4	0.1289 (4)	0.7751 (4)	−0.0883 (3)	0.0402 (5)
H4	0.1589	0.9085	−0.0564	0.048*
C5	0.2849 (4)	0.7384 (4)	−0.0476 (3)	0.0402 (5)
H5	0.4208	0.8506	0.0119	0.048*
C6	−0.2526 (4)	0.6408 (3)	−0.2131 (3)	0.0366 (5)
C7	−0.5284 (4)	0.6312 (4)	−0.3955 (3)	0.0418 (6)
H7A	−0.4879	0.7492	−0.4281	0.050*
H7B	−0.5682	0.6550	−0.3099	0.050*
C8	−0.2853 (4)	0.5629 (4)	−0.4802 (3)	0.0407 (6)
H8A	−0.1706	0.5438	−0.4478	0.049*
H8B	−0.2349	0.6781	−0.5163	0.049*
C9	0.6850 (4)	0.8842 (4)	0.2928 (3)	0.0368 (5)
O1	−0.3046 (2)	0.6962 (2)	−0.10853 (17)	0.0385 (4)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0345 (3)	0.0389 (3)	0.0305 (3)	0.0226 (2)	0.0083 (2)	0.0097 (2)
S1	0.0535 (4)	0.0462 (4)	0.0441 (4)	0.0265 (4)	0.0163 (3)	0.0048 (3)
N1	0.0353 (10)	0.0408 (11)	0.0334 (10)	0.0222 (9)	0.0114 (8)	0.0142 (8)

N2	0.0369 (11)	0.0495 (12)	0.0346 (10)	0.0276 (10)	0.0121 (8)	0.0157 (9)
N3	0.0404 (11)	0.0456 (11)	0.0369 (11)	0.0262 (10)	0.0100 (9)	0.0114 (10)
C1	0.0401 (13)	0.0394 (12)	0.0372 (12)	0.0234 (11)	0.0121 (10)	0.0102 (10)
C2	0.0365 (12)	0.0426 (13)	0.0315 (12)	0.0212 (11)	0.0071 (10)	0.0082 (10)
C3	0.0384 (12)	0.0459 (13)	0.0300 (12)	0.0250 (11)	0.0141 (10)	0.0158 (10)
C4	0.0393 (13)	0.0399 (13)	0.0408 (13)	0.0225 (11)	0.0105 (10)	0.0149 (10)
C5	0.0352 (12)	0.0393 (13)	0.0403 (13)	0.0185 (11)	0.0083 (10)	0.0139 (10)
C6	0.0344 (12)	0.0361 (12)	0.0363 (12)	0.0186 (10)	0.0092 (10)	0.0124 (10)
C7	0.0438 (14)	0.0579 (15)	0.0361 (13)	0.0358 (13)	0.0143 (11)	0.0181 (11)
C8	0.0368 (12)	0.0589 (15)	0.0363 (13)	0.0308 (12)	0.0153 (10)	0.0207 (11)
C9	0.0322 (12)	0.0415 (13)	0.0374 (13)	0.0210 (11)	0.0109 (10)	0.0147 (11)
O1	0.0394 (9)	0.0435 (9)	0.0352 (9)	0.0253 (8)	0.0122 (7)	0.0124 (7)

Geometric parameters (Å, °)

Co1—N1	2.1739 (19)	C2—H2	0.9300
Co1—N3	2.026 (2)	C3—C4	1.391 (3)
Co1—O1^{i}	2.2034 (16)	C3—C6	1.496 (3)
S1—C9	1.620 (3)	C4—C5	1.372 (4)
N1—C1	1.343 (3)	C4—H4	0.9300
N1—C5	1.344 (3)	C5—H5	0.9300
N2—C6	1.331 (3)	C6—O1	1.256 (3)
N2—C7	1.464 (3)	C7—C8^{ii}	1.515 (3)
N2—C8	1.475 (3)	C7—H7A	0.9700
N3—C9	1.170 (3)	C7—H7B	0.9700
C1—C2	1.377 (3)	C8—C7^{ii}	1.515 (3)
C1—H1	0.9300	C8—H8A	0.9700
C2—C3	1.388 (3)	C8—H8B	0.9700
N3^{iii}—Co1—N3	180.0	C3—C2—H2	120.3
N3^{iii}—Co1—N1	90.06 (8)	C2—C3—C4	118.0 (2)
N3—Co1—N1	89.94 (8)	C2—C3—C6	121.7 (2)
N3^{iii}—Co1—N1^{iii}	89.94 (8)	C4—C3—C6	120.1 (2)
N3—Co1—N1^{iii}	90.06 (8)	C5—C4—C3	118.8 (2)
N1—Co1—N1^{iii}	180.00 (9)	C5—C4—H4	120.6
N3^{iii}—Co1—O1^{i}	90.43 (7)	C3—C4—H4	120.6
N3—Co1—O1^{i}	89.57 (7)	N1—C5—C4	123.9 (2)
N1—Co1—O1^{i}	89.79 (7)	N1—C5—H5	118.0
N1^{iii}—Co1—O1^{i}	90.21 (7)	C4—C5—H5	118.0
N3^{iii}—Co1—O1^{iv}	89.57 (7)	O1—C6—N2	122.7 (2)
N3—Co1—O1^{iv}	90.43 (7)	O1—C6—C3	118.7 (2)
N1—Co1—O1^{iv}	90.21 (7)	N2—C6—C3	118.7 (2)
N1^{iii}—Co1—O1^{iv}	89.79 (7)	N2—C7—C8^{ii}	109.9 (2)
O1^{i}—Co1—O1^{iv}	180.00 (9)	N2—C7—H7A	109.7
C1—N1—C5	116.8 (2)	C8^{ii}—C7—H7A	109.7
C1—N1—Co1	121.35 (15)	N2—C7—H7B	109.7

C5—N1—Co1	121.59 (15)	C8^{ii}—C7—H7B	109.7
C6—N2—C7	121.13 (19)	H7A—C7—H7B	108.2
C6—N2—C8	125.8 (2)	N2—C8—C7^{ii}	109.98 (19)
C7—N2—C8	112.94 (18)	N2—C8—H8A	109.7
C9—N3—Co1	171.96 (19)	C7^{ii}—C8—H8A	109.7
N1—C1—C2	123.1 (2)	N2—C8—H8B	109.7
N1—C1—H1	118.4	C7^{ii}—C8—H8B	109.7
C2—C1—H1	118.4	H8A—C8—H8B	108.2
C1—C2—C3	119.4 (2)	N3—C9—S1	179.0 (2)
C1—C2—H2	120.3	C6—O1—Co1^{v}	127.28 (15)
N3^{iii}—Co1—N1—C1	32.05 (18)	Co1—N1—C5—C4	−173.16 (18)
N3—Co1—N1—C1	−147.95 (18)	C3—C4—C5—N1	−0.4 (4)
O1^{i}—Co1—N1—C1	−58.38 (17)	C7—N2—C6—O1	−1.9 (4)
O1^{iv}—Co1—N1—C1	121.62 (17)	C8—N2—C6—O1	174.0 (2)
N3^{iii}—Co1—N1—C5	−154.13 (18)	C7—N2—C6—C3	178.1 (2)
N3—Co1—N1—C5	25.87 (18)	C8—N2—C6—C3	−6.1 (3)
O1^{i}—Co1—N1—C5	115.44 (18)	C2—C3—C6—O1	110.4 (3)
O1^{iv}—Co1—N1—C5	−64.56 (18)	C4—C3—C6—O1	−64.0 (3)
C5—N1—C1—C2	−0.9 (3)	C2—C3—C6—N2	−69.5 (3)
Co1—N1—C1—C2	173.23 (17)	C4—C3—C6—N2	116.0 (3)
N1—C1—C2—C3	0.3 (4)	C6—N2—C7—C8^{ii}	−126.9 (2)
C1—C2—C3—C4	0.2 (3)	C8—N2—C7—C8^{ii}	56.8 (3)
C1—C2—C3—C6	−174.4 (2)	C6—N2—C8—C7^{ii}	127.0 (2)
C2—C3—C4—C5	−0.2 (3)	C7—N2—C8—C7^{ii}	−56.8 (3)
C6—C3—C4—C5	174.5 (2)	N2—C6—O1—Co1^{v}	100.8 (2)
C1—N1—C5—C4	0.9 (3)	C3—C6—O1—Co1^{v}	−79.1 (2)

Symmetry codes: (i) −*x*, −*y*+1, −*z*; (ii) −*x*−1, −*y*+1, −*z*−1; (iii) −*x*+1, −*y*+1, −*z*; (iv) *x*+1, *y*, *z*; (v) *x*−1, *y*, *z*.

Fig. 1

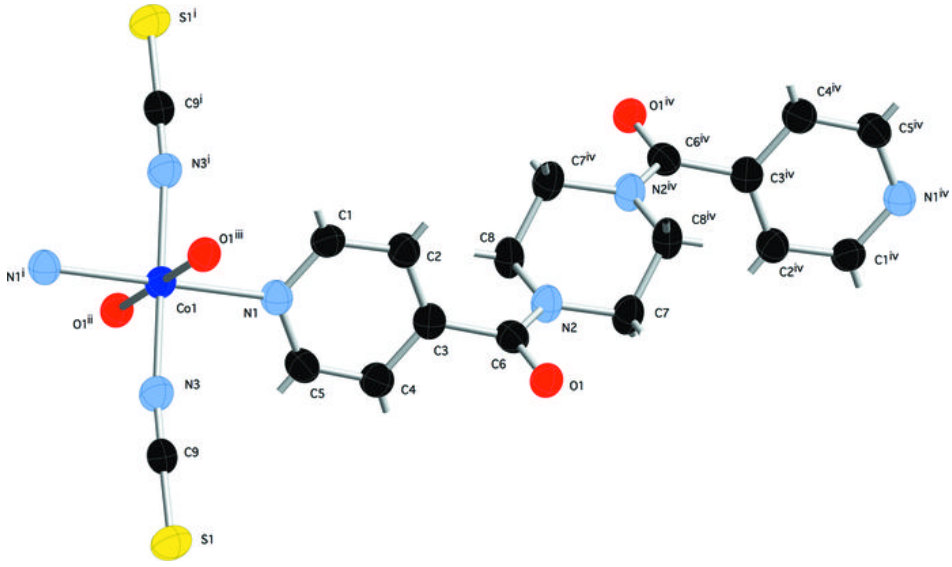

S1i
C9i
N3i
O1iii
N1i
Co1
O1ii
N1
C1
C2
C3
C5
C4
C6
O1
N2
C8
C7
O1iv
C6iv
C7iv
N2iv
C4iv
C5iv
C3iv
N1iv
C8iv
C2iv
C1iv
N3
C9
S1

Fig. 2

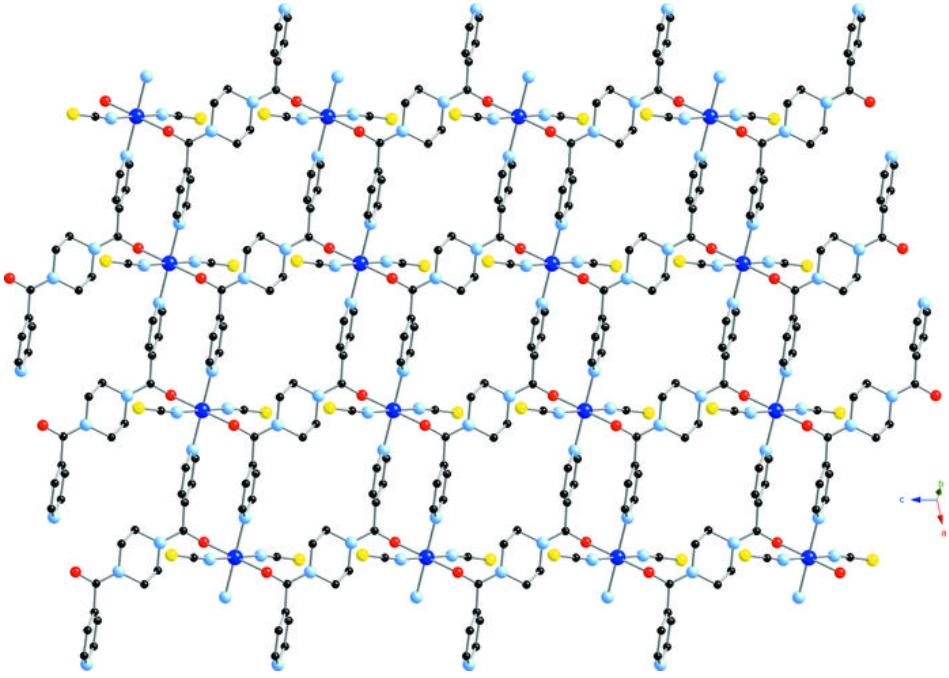


Fig. 3