

## Supplementary data

Controlled crystallization of mixed-ligand complexes of  
1,3-bis(4-pyridyl)propane-*N,N'*-dioxide with metal(II) thiocyanates:  
isostructurality in coordination networks bearing different mono- and  
di-nuclear nodes

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### Experimental Procedures:

#### General:

As starting materials, 4,4'-trimethylenedipyridine (Aldrich), 35% hydrogen peroxide (Junsei), CoCl<sub>2</sub>·6H<sub>2</sub>O (Merck), MnCl<sub>2</sub>·4H<sub>2</sub>O (Beijing), ZnCl<sub>2</sub> (Riedel), CdCl<sub>2</sub>·2H<sub>2</sub>O (BDH) and KSCN (Beijing) were obtained commercially and used without further purification. Elemental analyses of C, H and N were performed by the MEDAC LTD

Vrunel Science Center, United Kingdom. IR spectra were recorded with a Nicolet Impact 420 FT-IR spectrometer using KBr pellets.  $^1\text{H}$  NMR spectra was taken at 300Hz with a Bruker-300 spectrometer using  $\text{D}_2\text{O}$  as solvent. Thermal stability of samples was measured on a Hi-Res TGA 2950 Thermogravimetric Analyzer from  $50^\circ\text{C}$  to  $900^\circ\text{C}$  under a nitrogen atmosphere at a heating rate of  $15^\circ\text{C}/\text{min}$ .

**Synthesis of  $[\text{CoL}(\text{H}_2\text{O})(\text{SCN})_2]_{\text{y}}$ , **1**.** This complex was obtained by the reaction of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , KSCN and L ligand at the molar ratio 1:2:1. To a solution of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (0.047g, 0.2mmol) in  $\text{H}_2\text{O}$  (3mL), 2mL KSCN (0.04g, 0.41mmol) aqueous solution was added. Then, with stirring, an aqueous solution of L (0.046g, 0.2mmol) 6mL was added. The result solution was stirred at  $70^\circ\text{C}$  for about 10 minutes and then filtered. The filtrate was allowed to stand at room temperature. Several days later, dark purple scale-like crystals of **1** were obtained. Yield: 0.030g (36%). Anal. Calcd. for  $\text{C}_{15}\text{H}_{16}\text{CoN}_4\text{O}_3\text{S}_2$ : C, 42.55; H, 3.81; N, 13.23%. Found: C, 42.50; H, 3.80; N, 13.08%. IR (KBr,  $\text{cm}^{-1}$ ): 3415 $w$ , 3234 $w$ , 3120 $w$ , 2060 $vs$ , 1629 $w$ , 1489 $m$ , 1448 $w$ , 1212 $m$ , 850 $m$ , 789 $w$ , 729 $w$ .

**Synthesis of  $[\text{CdL}(\text{H}_2\text{O})(\text{SCN})_2]_{\text{y}}$ , **2**.** This complex was obtained as colorless scale-like crystals in a similar procedure as for **1** by the reaction of  $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$ , KSCN and L ligand at the molar ratio 1:2:1. Yield: 67%. Anal. Calcd. for  $\text{C}_{15}\text{H}_{16}\text{CdN}_4\text{O}_3\text{S}_2$ : C, 37.78; H, 3.38; N, 11.75%. Found: C, 37.70; H, 3.38; N, 11.75%. IR (KBr,  $\text{cm}^{-1}$ ): 3415-3183 $brw$ , 3102 $m$ , 2941 $w$ , 2858 $w$ , 2111 $s$ , 2057 $vs$ , 1637 $w$ , 1484 $s$ , 1448 $m$ , 1214 $s$ , 1175 $m$ , 1114 $w$ , 844 $m$ , 766 $w$ , 729 $w$ .

**Synthesis of [MnL(H<sub>2</sub>O)(SCN)<sub>2</sub>]<sub>¥</sub>, **3**.** This complex was obtained as pale yellow scaly crystals by the reaction of MnCl<sub>2</sub>·4H<sub>2</sub>O, KSCN and L ligand at the molar ratio 1:2:1 in a similar method as **1**. Yield: 0.040g (48%). Anal. Calcd. for C<sub>15</sub>H<sub>16</sub>MnN<sub>4</sub>O<sub>3</sub>S<sub>2</sub>: C, 42.96; H, 3.85; N, 13.36%. Found: C, 43.09; H, 3.92; N, 12.97%. IR (KBr, cm<sup>-1</sup>): 3415*m*, 3200*w*, 3113*w*, 2049*vs*, 1635*w*, 1488*m*, 1441*w*, 1213*m*, 856*m*, 796*w*, 722*w*.

**Synthesis of [ZnL(H<sub>2</sub>O)(SCN)<sub>2</sub>]<sub>¥</sub>, **4**.** Complex **4** was synthesized as colorless scaly crystals as the case of **1** with the molar ratio of ZnCl<sub>2</sub>, KSCN and L ligand at 1:2:1. Yield: 64%. Anal. Calcd. for C<sub>15</sub>H<sub>16</sub>ZnN<sub>4</sub>O<sub>3</sub>S<sub>2</sub>: C, 42.06; H, 3.77; N, 13.09%. Found: C, 41.99; H, 3.76; N, 12.92%. IR (KBr, cm<sup>-1</sup>): 3434*m*, 3230*w*, 3121*w*, 2064*vs*, 1630*w*, 1494*m*, 1447*w*, 1213*m*, 856*m*, 782*w*, 722*w*.

**Synthesis of [CoL<sub>2</sub>(SCN)<sub>2</sub>]<sub>¥</sub>, **5**.** Complex **5** was synthesized as red block-like crystals in the same way as **1** but with a starting molar ratio of CoCl<sub>2</sub>·6H<sub>2</sub>O, KSCN and L ligand at 1:2:6. Yield: 0.056g (45%). Between the molar ratios Co(II)/L 1:1 and 1:6, both compounds **1** and **5** were obtained from the same crude solution. During slow evaporation of the filtrate at room temperature, compound **1** crystallized first. After removal of the crystals of compound **1**, red block-like crystals of compound **5** were obtained after several days. When the molar ratio L/Co(II) exceeds 6, compound **5** is the only product. Anal. Calcd. for C<sub>28</sub>H<sub>28</sub>CoN<sub>6</sub>O<sub>4</sub>S<sub>2</sub>: C, 52.91; H, 4.44; N, 13.22%. Found: C, 52.50; H, 4.39; N, 13.09%. IR (KBr, cm<sup>-1</sup>): 3432*w*, 3111*w*, 3052*w*, 2088*vs*, 1622*w*, 1486*s*, 1440*w*, 1210*s*, 850*m*, 802*w*, 729*w*.

**Synthesis of  $[\text{CdL}_2(\text{SCN})_2]_n$ , **6**.** Complex **6** was synthesized as colorless blocks in a similar way as **2**, but with the molar ratio  $\text{CdCl}_2 \cdot 2\text{H}_2\text{O} : \text{KSCN} : \text{L}$  changed from 1:2:1 to 1:2:6. Yield: 60%. And between these two molar ratios, compound **2** and **6** were obtained in the same solution with compound **2** crystallizing out first. Anal. Calcd. for  $\text{C}_{28}\text{H}_{28}\text{CdN}_6\text{O}_4\text{S}_2$ : C, 48.80; H, 4.10; N, 12.20%. Found: C, 48.80; H, 4.01; N, 11.77%. IR (KBr,  $\text{cm}^{-1}$ ): 3469 $m$ , 3113 $w$ , 3046 $w$ , 2072 $vs$ , 1649 $w$ , 1487 $m$ , 1447 $w$ , 1218 $m$ , 846 $m$ , 802 $w$ , 722 $w$ .

**Synthesis of  $[\text{MnL}_2(\text{H}_2\text{O})_2(\text{SCN})_2]$ , **7**.** When the molar ratio between  $\text{MnCl}_2$  and L ligand (1:1) in the synthesis of compound **3** was increased to 1:2, during the slow evaporation of the filtrate at room temperature, compound **3** crystallized first. After removal of the crystals of **3**, yellow block-like crystals of compound **7** were deposited several days later. Yield: 15%. With L/M increasing, compound **7** became the major product, but we could not obtain it as the only product till L/M was equal to 10. Anal. Calcd. for  $\text{C}_{28}\text{H}_{32}\text{MnN}_6\text{O}_6\text{S}_2$ : C, 50.37; H, 4.83; N, 12.59%. Found: C, 50.59; H, 4.91; N, 13.04%. IR (KBr,  $\text{cm}^{-1}$ ): 3422 $w$ , 3100 $w$ , 2938 $w$ , 2065 $vs$ , 1649 $w$ , 1488 $m$ , 1440 $w$ , 1219 $m$ , 1179 $w$ , 850 $w$ , 802 $w$ , 735 $w$ .

**Synthesis of  $[\text{ZnL}_2(\text{H}_2\text{O})_2(\text{SCN})_2]$ , **8**.** When a starting molar ratio between  $\text{ZnCl}_2$  and L ligand was set at 1:10, slow evaporation of the filtrate at room temperature yielded crystals of compound **4**. After removing the crystals of **4**, colorless block-like crystals of compound **8** were obtained several days later. Yield: 10%. Compound **8** could not be obtained as the only product till L/M reached 10. Anal. Calcd. for  $\text{C}_{28}\text{H}_{32}\text{ZnN}_6\text{O}_6\text{S}_2$ : C,

49.60; H, 4.76; N, 12.39%. Found: C, 49.53; H, 4.47; N, 12.00%. IR (KBr,  $\text{cm}^{-1}$ ): 3415<sub>w</sub>, 3093<sub>w</sub>, 2918<sub>w</sub>, 2085<sub>vs</sub>, 1655<sub>w</sub>, 1488<sub>m</sub>, 1454<sub>w</sub>, 1226<sub>m</sub>, 1179<sub>w</sub>, 856<sub>w</sub>, 809<sub>w</sub>, 735<sub>w</sub>.

### **X-ray Crystallography:**

Single-crystal X-ray diffraction measurement of L and compounds **1**, **2**, **4** and **6** were carried out on a Bruker SMART 1000 CCD diffractometer with graphite monochromatized Mo- $K\alpha$  radiation ( $\lambda = 0.71073\text{\AA}$ ) at 293K. Intensity data was obtained in the range  $1.8 < \theta < 28^\circ$ . An empirical absorption correction was applied using the SADABS program.<sup>1</sup> The data collection of compounds **3**, **5** and **7** was performed on a Rigaku AFC7R four-circle diffractometer in the variable  $\omega$ -scan mode<sup>2</sup> using Mo- $K\alpha$  radiation ( $\lambda = 0.71073\text{\AA}$ ) at 293 K. Intensity data was obtained in the range  $2.3 < \theta < 25^\circ$ , and an empirical absorption correction was applied using  $\psi$ -scan data for selected strong reflections. The data of compound **8** was collected on a Rigaku RAXIS-IIC imaging-plate diffractometer using Mo- $K\alpha$  radiation ( $\lambda = 0.71073\text{\AA}$ ) at 293K.<sup>3</sup> Intensity data was obtained in the range  $2.2 < \theta < 25.5^\circ$ , and a self-consistent semi-empirical absorption correction based on symmetry-equivalent reflections was applied using the REQAB program.<sup>4</sup> All the structures were solved by direct methods and refined by full-matrix least squares based on  $F^2$  using the SHELXTL program package.<sup>5</sup> A summary of the crystallographic data and structure refinement is listed in Table 1.

### **Crystal structure of the L Ligand**

Single-crystal X-ray analysis revealed that the crystal structure of L consists of a hydrogen-bonded two-dimensional framework. All the atoms in the molecule except C10

and C11 lie on a mirror plane, and hence the pyridyl rings are orthogonal to each other (Fig. 4). The L molecules are connected through weak hydrogen bonds: C10...O1b, 3.294 Å, C10-H10A...O1b, 172.1°; C11...O2c, 3.230 Å, C11-H11A...O2c, 176.9°, (b  $-x+1$ ,  $-y$ ,  $-z+2$ ; c  $-x+1$ ,  $-y$ ,  $-z+1$ ) generating a corrugated sheet built of hydrogen-bonded eight-membered, ten-membered and large twenty-two-membered rings (Fig. 5).

### TGA Measurements:

The X-ray single crystal studies have clearly shown that compounds **1** and **5** have different crystal asymmetry units but similar two-dimensional network. In complex **1** there is a coordination water bonded to the Co(II) ion, besides SCN<sup>-</sup> and the ligands, while in complex **5**, no water molecules exist in the structure. The TGA investigation for **1** indicates that the first weight loss of 4.38% from 94°C to 160°C, corresponding to the loss of the coordination water molecule (calculated: 4.27%). Then the remaining framework [CoL(SCN)<sub>2</sub>]<sub>∞</sub> does not lose weight until further heating to 228°C. For complex **5**, the network of [CoL<sub>2</sub>(SCN)<sub>2</sub>]<sub>∞</sub> begins to collapse from 250°C, close to the temperature of complex **1**, because of their similar two-dimensional (4, 4) topology.

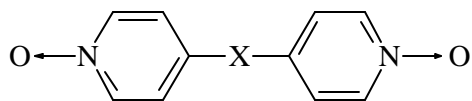
### References:

1. G. M. Sheldrick, SADABS: Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Germany, 1996.
2. R. A. Sparks, in F. R. Ahmed (Ed.), Crystallography, Computing Techniques, Munksgaard, Copenhagen, 1976, p.452.
3. (a) J. Tanner, K. L. Krause, *The Rigaku Journal* **1994**, *11*, 4. *ibid.* **1990**, 7,28; (b) K.

- Kraus, G.N. Phillips, *Jr. Appl. Crysta.* **1992**, *25*, 146.
4. L. L. Miller, R.A. Jacobson, *Computer Chem.* **1989**, *13*, 1.
  5. G.M. Sheldrick, SHELXTL: Structure Determination Software Programs, Bruker Analytical X-ray Systems, Inc., Madison, WI, U. S. A., 1997

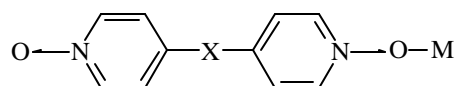
**Scheme 1.** The coordination modes of the di-pyridine based di-*N*-oxide ligands with transition and rare-earth metal ions.

**Di-pyridine based di-*N*-oxide ligands:**

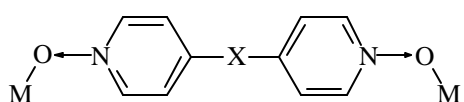


X represent: I. none.  
 II. -CH<sub>2</sub>-CH<sub>2</sub>-  
 III. -CH=CH-  
 IV. -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-

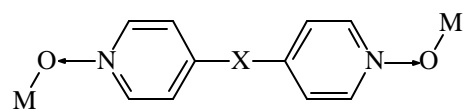
**Coordination modes:**



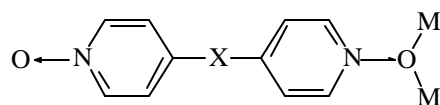
terminal monodentate (M = Mn, Co, Cu)



*cis*

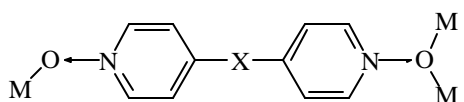


*trans*

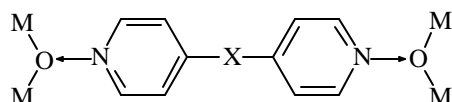


end-to-end bidentate,  $\mu$  -*O,O'*  
 (M = Co, Ni, Cu, Zn, La, Pr, Yb, Sm, Er)

( $\mu = \mu_2$ )



$\mu_3$ -*O,O,O'* (M = Mn, Co, Zn)



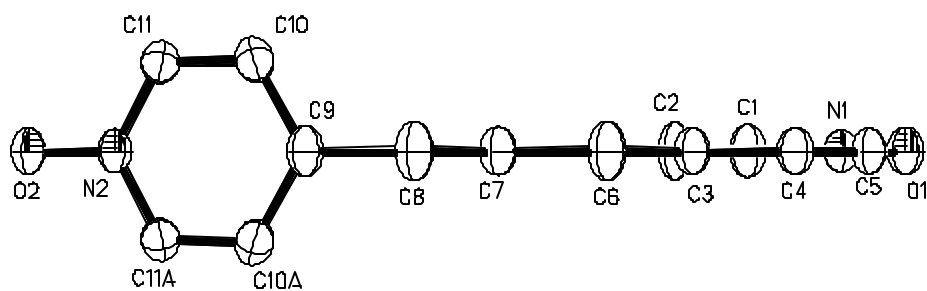
$\mu_4$ -*O,O,O',O'* (M = La, Ce, Gd)



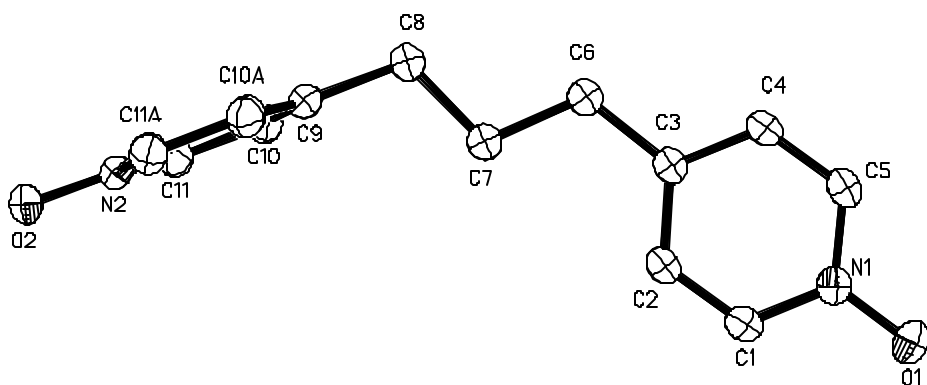
**Table 1.** Crystallographic data of **L** and complexes **1-8**.

Complex	L	1	2	3	4	5	6	7	8
Empirical formula	C <sub>13</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub>	C <sub>15</sub> H <sub>16</sub> CoN <sub>4</sub> O <sub>3</sub> S <sub>2</sub>	C <sub>15</sub> H <sub>16</sub> CdN <sub>4</sub> O <sub>3</sub> S <sub>2</sub>	C <sub>15</sub> H <sub>16</sub> MnN <sub>4</sub> O <sub>3</sub> S <sub>2</sub>	C <sub>15</sub> H <sub>16</sub> ZnN <sub>4</sub> O <sub>3</sub> S <sub>2</sub>	C <sub>28</sub> H <sub>28</sub> CoN <sub>6</sub> O <sub>4</sub> S <sub>2</sub>	C <sub>28</sub> H <sub>28</sub> CdN <sub>6</sub> O <sub>4</sub> S <sub>2</sub>	C <sub>28</sub> H <sub>32</sub> MnN <sub>6</sub> O <sub>6</sub> S <sub>2</sub>	C <sub>28</sub> H <sub>32</sub> ZnN <sub>6</sub> O <sub>6</sub> S <sub>2</sub>
Formula weight	230.26	423.37	476.84	419.38	429.81	635.61	689.08	667.66	678.08
Crystal size	0.95×0.42×0.39	0.68×0.24×0.20	0.32×0.31×0.31	0.60×0.40×0.20	0.40×0.40×0.20	0.50×0.40×0.40	0.58×0.24×0.22	0.50×0.40×0.30	0.50×0.40×0.30
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>Pnma</i> (No.62)	<i>P2(1)/c</i> (No.14)	<i>P2(1)/c</i> (No.14)	<i>P2(1)/c</i> (No.14)	<i>P2(1)/c</i> (No.14)	<i>P2(1)/c</i> (No.14)	<i>P2(1)/c</i> (No.14)	<i>P2(1)/c</i> (No.14)	<i>P2(1)/c</i> (No.14)
<i>a</i> (Å)	9.159(2)	12.510(7)	15.375(2)	12.544(3)	12.555(3)	6.925(1)	7.115(1)	12.773(3)	12.564(3)
<i>b</i> (Å)	7.799(1)	12.446(7)	14.926(2)	12.644(3)	12.529(3)	22.460(5)	22.521(4)	14.033(3)	14.136(3)
<i>c</i> (Å)	16.794(3)	13.185(8)	8.16969(8)	13.219(3)	13.159(3)	9.688(2)	9.708(2)	8.734(2)	8.779(2)
<i>a</i> (°)	90	90	90	90	90	90	90	90	90
<i>b</i> (°)	90	114.40(1)	91.079(2)	114.18(3)	114.779(5)	98.24(3)	99.210(3)	94.66(3)	94.28(3)
<i>g</i> (°)	90	90	90	90	90	90	90	90	90
<i>V</i> (Å <sup>3</sup> )	1199.5(4)	1870(2)	1874.5(3)	1912.5(7)	1879.4(7)	1491.1(5)	1535.5(5)	1560.4(5)	1554.8(5)
<i>Z</i>	4	4	4	4	4	2	2	2	2
<i>D</i> <sub>calc</sub> (g/cm <sup>3</sup> )	1.275	1.504	1.690	1.456	1.519	1.416	1.490	1.421	1.448
<i>m</i> (Mo-Kα) (mm <sup>-1</sup> )	0.088	1.162	1.409	0.929	1.550	0.759	0.890	0.607	0.975
<i>F</i> (000)	488	868	952	860	880	658	700	694	704
Reflections collected	7739	12512	12357	3523	12649	2860	10405	2958	4834
Independent reflections ( <i>R</i> <sub>int</sub> )	1548(0.0260)	4556(0.0496)	4514(0.0289)	3361(0.0416)	4535(0.0663)	2633 (0.0271)	3723(0.0375)	2760(0.0355)	2761(0.0294)
Observed reflections [ <i>I</i> > 2σ( <i>I</i> )]	1134	3202	3785	2204	2338	1873	2944	2138	2637
Parameters	98	226	235	234	226	188	187	197	197
Goodness-of-fit	1.041	0.969	1.011	1.027	0.913	1.034	1.071	1.057	1.070
<i>R</i> <sub>1</sub> [ <i>I</i> > 2σ( <i>I</i> )] <sup>a</sup>	0.0440	0.0403	0.0326	0.0446	0.0465	0.0471	0.0423	0.0374	0.0347
<i>wR</i> <sub>2</sub> (all data) <sup>b</sup>	0.1434	0.1086	0.0877	0.1260	0.1190	0.1332	0.1303	0.1047	0.0947

$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} \quad ^b wR_2 = \left[ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right]^{1/2}$$

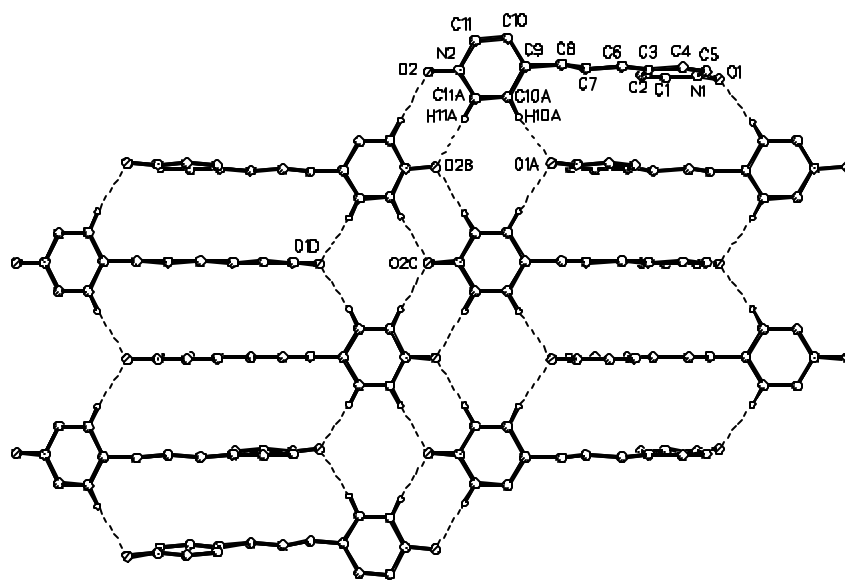


(a)

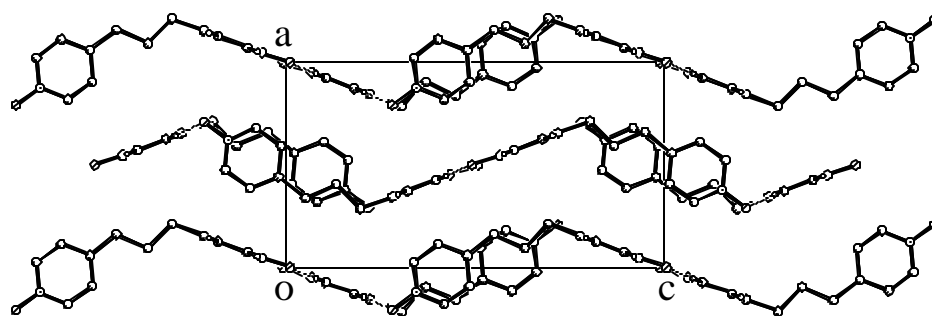


(b)

**Fig. 4** (a) Molecular structure of L viewed in the *a* direction; atoms C10a and C11a are generated by the symmetry operator  $x, 0.5-y, z$ . (b) Molecular structure of L view along the *b* axis.

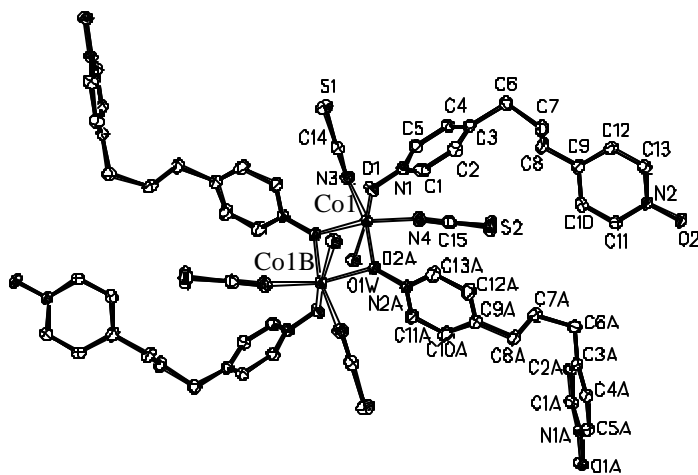


(a)

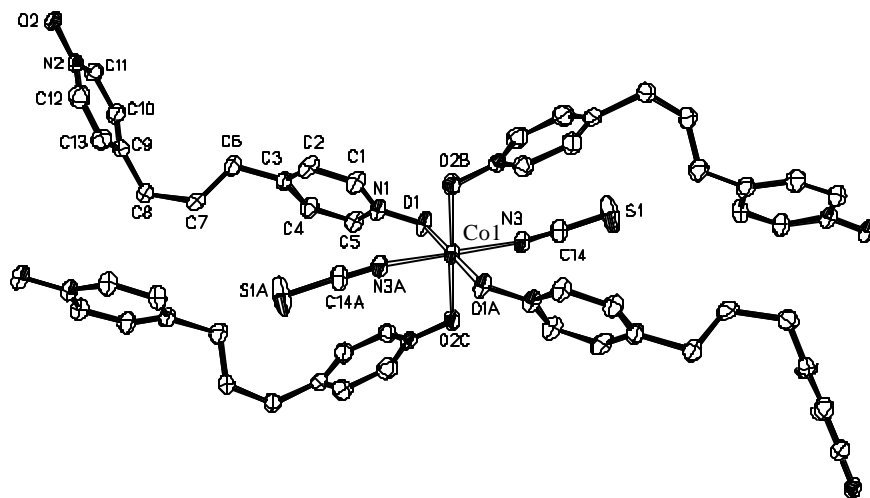


(b)

**Fig. 5** (a) Two-dimensional network of L showing hydrogen-bonded rings; the structure is viewed in the *a* direction. (b) Packing of corrugated sheets of L viewed along the *b* axis. Hydrogen atoms that are not involved in hydrogen bonding are omitted for clarity.

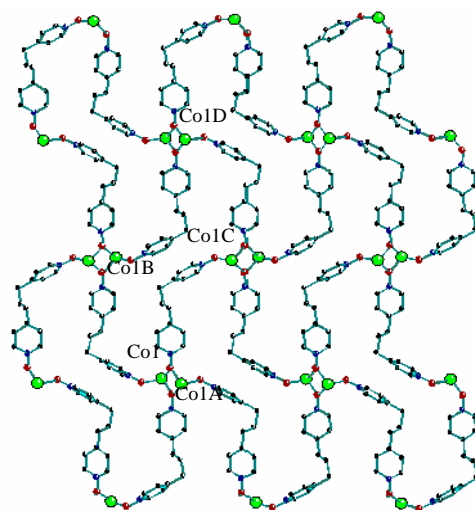


(a)

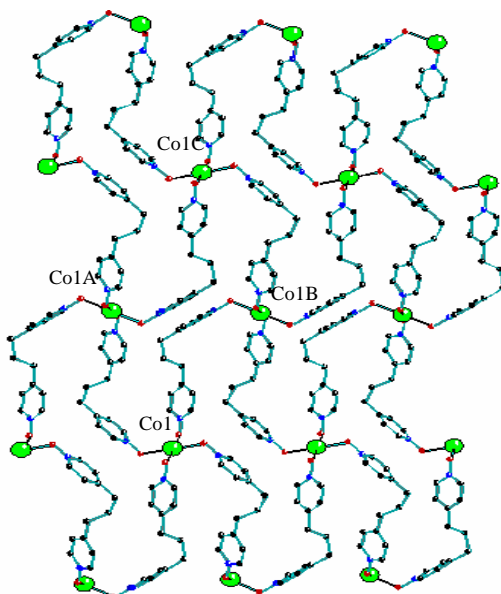


(b)

**Fig. 6** (a) The dinuclear subunit of complex **1**, showing the coordination environment of Co(II) ions (Symmetry operation: A  $-x+1, y+1/2, -z+3/2$ ; B  $-x, -y+2, -z+1$ ). (b) The mononuclear subunit of complex **5**, showing the coordination environment of Co(II) ions (Symmetry operation: A  $-x, -y+1, -z+1$ ; B  $-x, y+1/2, -z+1/2$ ; C  $x, -y+1/2, z+1/2$ ).

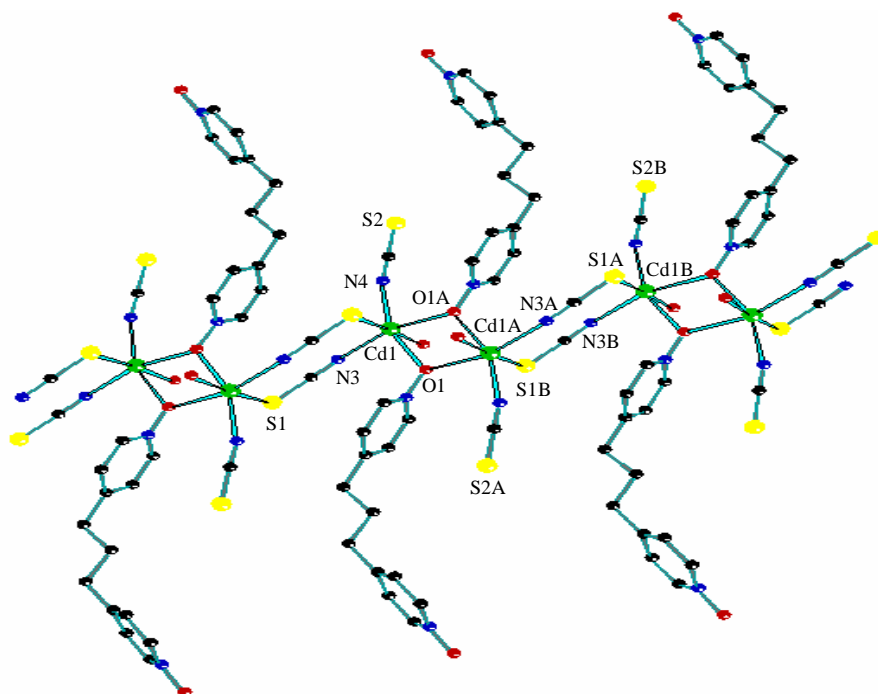


(a)



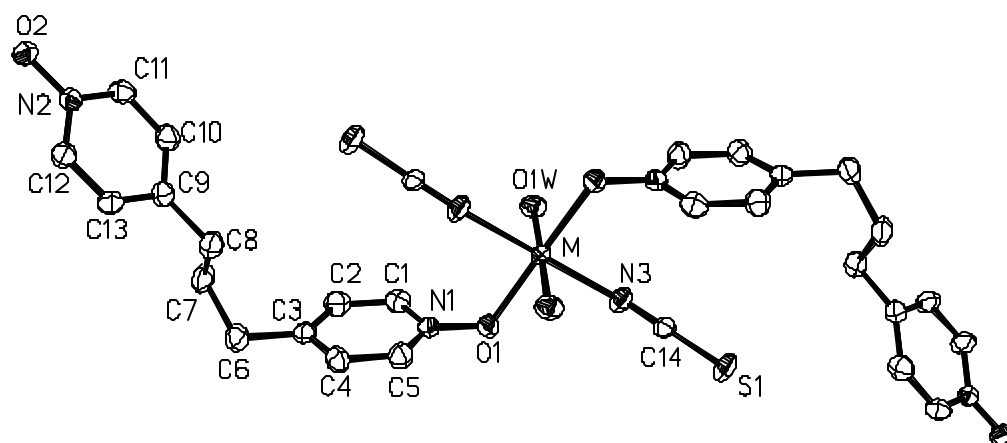
(b)

**Fig. 7** (a) Two-dimensional coordination network with 56-membered S-shaped rings and dinuclear nodes in complex **1** viewed along the *c* axis. (Symmetry operation: A  $-x, -y+2, -z+1$ ; B  $-x+1, y+1/2, -z+3/2$ ; C  $x+1, -y+3/2, z+1/2$ ; D  $-x+2, -y+2, -z+2$ ). (b) Analogous (4, 4) net with 56-membered rings and mononuclear nodes in complex **5** viewed along the *a* axis (Symmetry operation: A  $x, -y+1/2, z+1/2$ ; B  $-x, y-1/2, -z+1/2$ ; C  $-x, -y, -z+1$ ). Hydrogen atoms, *N*-bonded thiocyanate ligands and water molecules are omitted for clarity.



**Fig. 8** An infinite chain in complex **2** with dinuclear centers bridged by  $\mu$ -*N,S* thiocyanate ligands

(Symmetry operation: A  $-x, -y+1, -z; x, y, z-1$ ).



**Fig. 9.** The coordination environment of metal ions in complex **7** and **8** (M = Mn(**7**), Zn(**8**)).

