



# Polymethylene spacer regulated structural divergence in cadmium complexes: Unusual trigonal prismatic and severely distorted octahedral coordination

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## Abstract

Chelation of the tetradentate pyridyl di-Schiff-base ligands, *N,N'*-bis-(1-pyridin-2-yl-ethylidene)-propane-1,3-diamine ( $L^1$ ) or *N,N'*-bis-(1-pyridin-2-yl-ethylidene)-ethane-1,2-diamine ( $L^2$ ) to a cadmium(II) centre reveals interesting structural deviations from regular octahedral geometry in the resulting hexacoordinated complexes  $[Cd(L^1)(NCS)_2]$  (**1**) and  $[Cd(L^2)(NCS)_2]$  (**2**), respectively. The two tetradentate ligands  $L^1$  and  $L^2$  differ only in the polymethylene chain –  $(CH_2)_3$  and  $(CH_2)_2$ , respectively, which connects the two halves of the symmetric ligands. Complex **1** assumes a trigonal prismatic (TP) geometry. The structure of **2** reveals a severely distorted octahedral geometry. The structural differences between  $[Cd(L^1)(NCS)_2]$  (**1**) and  $[Cd(L^2)(NCS)_2]$  (**2**) can be traced to the length of the polymethylene spacers and the formation of a six- versus a five-membered metal-chelate ring together with the pyramidal  $Cd(L^1)$  and planar  $Cd(L^2)$  arrangement.

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## 1. Introduction

Octahedral coordination geometries are ubiquitous as the fundamental geometries of transition metal hexacoordinated complexes. Non-octahedral structures can be realized by considering a trigonal twist about the three-fold axis of the octahedron (twist angle  $\phi = 60^\circ$ ) with a trigonal prismatic (TP) stereochemistry at  $\phi = 0^\circ$  (cf. Scheme 1). TP coordination was first observed [1] for the layer lattices of heavy metal sulphides ( $MoS_2$  and  $WS_2$ ) but could only be rationalized as peculiarities of

the solid state. Structural authentication of a TP geometry in a discrete molecule was first available in the year 1965 and the concerned work of Eisenberg and Ibers [2] merits paramount importance from a chemical point of view. The breakthrough was then followed by a good number of structurally characterized TP complexes in cases of various 3d, 4d and 5d transition metals under differing ligand environments. Scrutiny of the underlying aspects in favour of TP coordination with much regard to electronic and steric influences of metals and ligands had started earlier [3–12]. Later on, theoretical analyses, i.e., ab initio calculations at the DFT level [13–17], ligand field-based models [18] and continuous symmetry measures [19] efficiently correlated the experimental findings and, of course, provided a sophisticated perspective of optimized structure–energy relationships.

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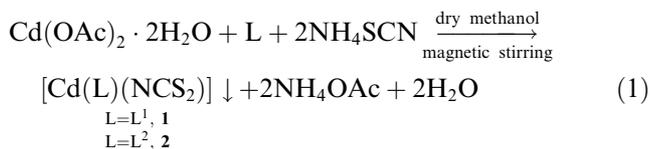
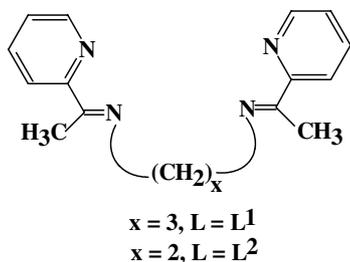
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The trigonal prismatic geometry for a metal ion with a  $d^{10}$  electronic configuration is not unexpected as there is no crystal field stabilization energy. In Zn(II) complexes, the TP geometry has been previously established [20,21]. A perfectly prismatic structure of Cd(II) was found in the potassium salt of the tris(acetylacetonato) complex [22], and distorted trigonal prisms were observed with other ligands such as nitrates, carboxylates, triamines, oxalato and a derivative of triazacyclononane [23,24]. However, to the best of our knowledge no TP geometry with a neutral, tetradentate Schiff-base ligand has been reported up to date. Herein we describe a neutral trigonal prismatic cadmium complex of the formula  $[\text{Cd}(\text{L}^1)(\text{NCS})_2]$  incorporating the tetradentate ligand  $N,N'$ -bis-(1-pyridin-2-yl-ethylidene)-*propane*-1,3-diamine ( $\text{L}^1$ ). Use of the closely related ligand  $N,N'$ -bis-(1-pyridin-2-yl-ethylidene)-*ethane*-1,2-diamine ( $\text{L}^2$ ) in the complex  $[\text{Cd}(\text{L}^2)(\text{NCS})_2]$  resulted in a severely distorted octahedral geometry. The structural differences are investigated in terms of conformational requirements of the ligands.

## 2. Results and discussion

### 2.1. Synthesis of the ligands and complexes

Facile condensation of 2-acetylpyridine with 1,3-diaminopropane or 1,2-diaminoethane in a 2:1 molar ratio furnished the two neutral tetradentate ligands  $N,N'$ -bis-(1-pyridin-2-yl-ethylidene)-*propane*-1,3-diamine ( $\text{L}^1$ ) and  $N,N'$ -bis-(1-pyridin-2-yl-ethylidene)-*ethane*-1,2-diamine ( $\text{L}^2$ ), respectively.



At ambient temperature, reaction of  $\text{L}$  with  $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  in dry methanol in the presence of  $\text{NH}_4\text{SCN}$  yielded two neutral cadmium complexes, **1** and **2** (Eq. (1)). The products were insoluble in the reaction medium and were isolated in the pure form via filtration.

### 2.2. Bonding and geometrical features

Compound **1** is a molecular complex with the tetradentate chelating  $N,N'$ -bis-(1-pyridin-2-yl-ethylidene)-*propane*-1,3-diamine ligand and two terminal (N-bound) isothiocyanato groups around the cadmium centre. Thus each cadmium atom is coordinated by six nitrogen donors, two from the *cis*-arranged NCS groups and four from the organic ligand. A molecular view and selected bond parameters of **1** are displayed in Fig. 1 and Table 1, respectively. A mirror plane passes through the molecule which contains Cd1, C9 and the two NCS groups and relates the two halves of the organic ligand. Significant distortion from classical octahedral towards TP geometry is clearly revealed in the molecular structure. An idealized octahedron is made up with two exactly parallel, staggered equilateral triangles of side  $s$  with an inter-triangular distance  $h$  (Scheme 1). Evaluation

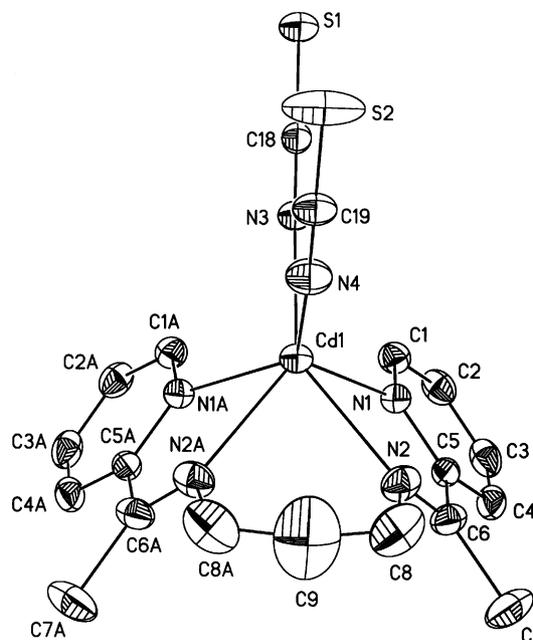
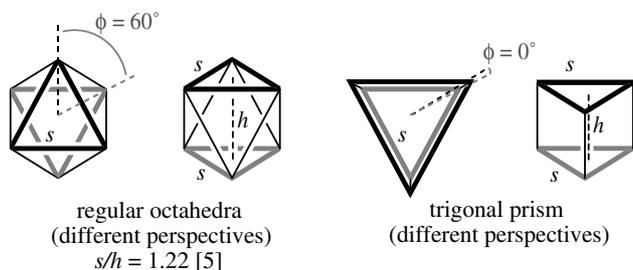


Fig. 1. Perspective view and atom labelling scheme of **1**. All the non-hydrogen atoms are represented by 20% thermal probability ellipsoids.

Table 1  
Selected bond distances (Å) and angles (°) for compound  $[\text{Cd}(\text{L}^1)(\text{NCS})_2]$  (**1**)

Distances			
Cd(1)–N(1)	2.358(2)	Cd(1)–N(4)	2.255(4)
Cd(1)–N(2)	2.393(2)	Cd(1)–N(1A)	2.358(2)
Cd(1)–N(3)	2.316(3)	Cd(1)–N(2A)	2.393(2)
Angles			
N(4)–Cd(1)–N(3)	84.97(13)	N(3)–Cd(1)–N(1)	86.63(8)
N(1)–Cd(1)–N(2)	68.45(8)	N(3)–Cd(1)–N(2)	142.46(7)
N(4)–Cd(1)–N(2)	93.11(9)	N(2)–Cd(1)–N(2A)	75.05(13)
N(4)–Cd(1)–N(1)	134.92(5)	N(1)–Cd(1)–N(1A)	88.47(10)



Scheme 1. Octahedron and trigonal prism with enhanced triangular faces and relevant parameters for the assessment of their relationship and distortion.  $\phi$  is the twist angle between the enhanced triangles around the  $C_3$  axis.

of the  $s/h$  ratio and twist angle ( $\phi$ ) value for the hexacoordinated complexes provides a measure of trigonal distortion [5].

The  $CdN_6$  coordination sphere in **1** can be described as being constituted of two triangles ( $N_3, N_1, N1A$  and  $N_4, N_2, N2A$ ) with an average side ( $s$ ) of 3.228 Å. These two  $N_3$  triangles are slightly tilted with a dihedral angle of 8.8° and an inter-triangular separation between the centroids of 2.802 Å ( $h$ ). A view of the  $CdN_6$  motif showing the twist angles  $\phi$  is represented in Fig. 2. The torsion angles  $N-C_n-C_n'-N'$  ( $C_n, C_n'$  = centroids of the two  $N_3$  triangles;  $N, N'$  = near eclipsed pair of donor atoms) of 0°, 6° and 6° are fairly close to the twist angle of a regular TP geometry ( $\phi = 0^\circ$ ). The average twist angle of 4° in **1** is similar to the trigonal prismatic complex  $Zn[(py)_3tach]$  [20]. The  $s/h$  ratio in **1** is 1.15 indicating an elongation relative to an ideal trigonal prism with square faces ( $s = h, s/h = 1.00$ ). Consideration of the

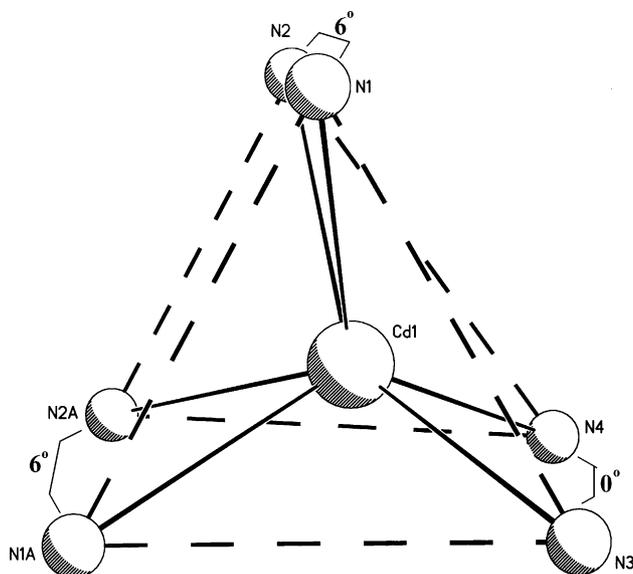


Fig. 2. ORTEP view of the  $CdN_6$  coordination sphere of **1** showing all the individual twist angles. Non-bonded  $N \cdots N$  distances (Å):  $N1 \cdots N1A \cdots N3$  triangle  $N1/N1A \cdots N3$  3.206,  $N1 \cdots N1A$  3.290;  $N2 \cdots N2A \cdots N4$  triangle  $N2/N2A \cdots N4$  3.376,  $N1 \cdots N1A$  2.915.

angular parameters  $\theta, \rho$  and  $\omega$  (Scheme 2) in the comparison between octahedral and trigonal prismatic limiting structures clearly indicates that compound **1** can be regarded as a trigonal prism (see parameters for **1** in Scheme 2).

A molecular view of  $[Cd(L^2)(NCS)_2]$  (**2**) with the tetradentate ligand  $N,N'$ -bis-(1-pyridin-2-yl-ethylidene)-ethane-1,2-diamine ( $L^2$ ) (with a shorter dimethylene spacer in place of  $L^1$ ) is depicted in Fig. 3 and selected

octahedron	trigonal prism (TP)	compound <b>1</b>
		chelate plane 98.5° $N1-Cd1-N1A$ 98.5° $N2-Cd1-N2A$ 90° $N3-Cd1-N4$
ideal $\theta = 54.7^\circ$	ideal $\theta = 90^\circ$	
		135.6° (average)
ideal $\rho = 180^\circ$	ideal $\rho = 135.4^\circ$	
		127.4° (2x) 105.1° 119.9° (average)
ideal $\omega = 180^\circ$	ideal $\omega = 120^\circ$	

Scheme 2. Angular parameters involved in the comparison between the octahedral and trigonal prismatic limiting structures.  $\theta$  = angle between the mean plane of the two  $N_3$  triangles and the chelate planes defined by the metal and each pair of near eclipsed N vertices.  $\rho$  = angle between the metal and *trans* N-donor sites.  $\omega$  = angle between the triangular faces defined by the metal and near eclipsed N atoms.

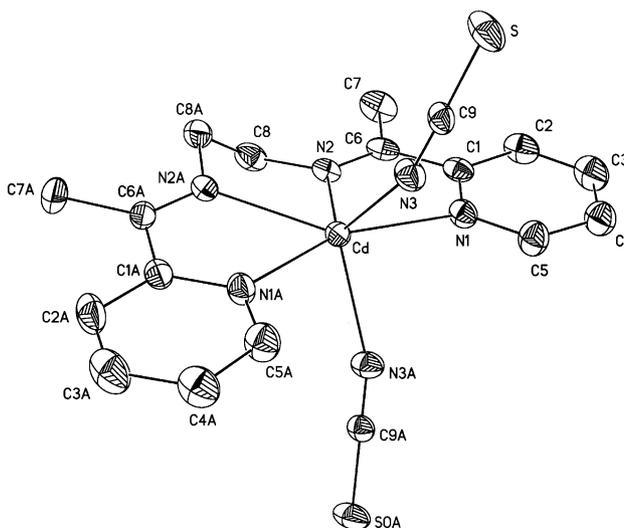


Fig. 3. Perspective view and atom labelling scheme of **2**. All the non-hydrogen atoms are represented by 20% thermal probability ellipsoids.

bond parameters are listed in Table 2. The  $\text{CdN}_6$  coordination sphere is strongly distorted from an octahedron with a crystallographic twofold symmetry axis passing through the metal atom and the midpoint of the C8–C8A bond of  $L^2$ . The six nitrogen atoms in **2** at an average distance of 2.356 Å define a polyhedron that is neither close to the octahedral nor the TP geometry. The structure may be imagined to consist of two symmetry related  $\text{N}_3$  triangles (N1, N2, N3 and N1A, N2A, N3A) with an average side ( $s$ ) of 3.246 Å and separated by a distance ( $h$ ) of 2.786 Å. Then the  $s/h$  ratio of  $\sim 1.17$  ( $< 1.22$ ) indicates an elongated octahedral structure. The triangular twist angle  $\phi$  measured at the donor atoms N1, N3A or N1A, N3 is only  $8.3^\circ$  with the imaginary  $C_3$  axis passing through the centroids of the imagined triangles. Such a small angle would be close to the prismatic limit ( $\phi = 0^\circ$ , Scheme 1). Yet, the third donor set N2, N2A is twisted by  $41.3^\circ$  about the threefold axis towards the octahedral extreme ( $60^\circ$ ). The average *trans* angles  $\angle\text{N1–Cd–N1A}$  and  $\angle\text{N3–Cd–N3A}$  at  $\sim 133^\circ$  are also close to the prismatic limit ( $\rho = 135.4^\circ$ , Scheme 2). The deviation in **2** mimics the benzenedithiolato-chelated  $d^0\text{–Ta(V)}$  ion [25] where an average twist angle  $\phi$  of  $19.3^\circ$  also indicated a significant departure from a regular octahedral coordination. In **2** the average dihedral angle  $\theta$  of  $59.8^\circ$  is closer to an octahedral than to a TP geometry. Dihedral angles  $\omega$  between the individual  $\text{CdN}_2$  planes are averaged at only  $60.3^\circ$ , consistent with severe distortion.

### 2.3. Comparison of ligand binding in **1** and **2**

In the following the structural divergence in the cadmium complexes **1** and **2** will be comparatively discussed on the basis of the geometrical selectivity and bonding aspects of the concerned ligands.

- (i) The  $\text{Cd}(L^1)$  moiety in **1** defines a square pyramidal geometry. The metal atom is displaced upward by  $\sim 1.2$  Å from the plane comprised of the  $L^1$  donor atoms N1, N2, N2A and N1A. This does not allow the coordination polyhedron to be completed to an octahedron via the  $(\text{NCS})_2$  coordination. In **2** the metal atom along with the  $L^2$  donor atoms

N1, N2, N2A and N1A constitutes a planar arrangement (mean deviation = 0.09 Å) and would welcome the two NCS groups to complete a close to octahedral geometry. The two  $\text{Cd}(L)$  situations are portrayed by space-filling models represented in Fig. 4. It is well known that chelate ligands giving rise to a five-membered chelate ring (e.g. an N–C–C–N ligand moiety) are better suited for larger metal ions whereas a chelate ligand yielding a six-membered chelate ring (e.g. an N–C–C–C–N ligand moiety) is better for smaller metal ions [26]. This assumes the metal ion at the intersection of the N lone-pairs and the chelate ring near its energy minimum. Thus, the N–C–C–C–N ligand moiety simply cannot accommodate the large Cd ion within its plane. The N lone-pairs and with it the pyridylimine moieties are tilted out of the N–C–C–C–N plane, so that the TP structure results (Fig. 4). On the other hand, the N–CH<sub>2</sub>–CH<sub>2</sub>–N ligand moiety in compound **2** is much better suited for accommodating the large Cd ion in the plane of a five-membered chelate ring. Therefore, the tetradentate ligand in compound **2**, with its five-membered chelate rings could span the equatorial plane in a distorted octahedral geometry.

- (ii) The ratio of the ligand bite ( $b$  = distance between the donor atoms) to the average  $\text{Cd1–N}$  distance ( $a$ ) in **1** is not compatible with the chelate being able to span the edge of the octahedron ( $b/a = 1.41$  for the ideal octahedron). In **1** the bite

Table 2  
Selected bond distances (Å) and angles ( $^\circ$ ) for compound  $[\text{Cd}(L^2)(\text{NCS})_2]$  (**2**)

Distances			
Cd–N(1)	2.460(3)	Cd–N(2)	2.372(3)
Cd–N(3)	2.236(3)		
Angles			
N(3)–Cd–N(3A)	109.83(18)	N(1)–Cd–N(1A)	156.01(17)
N(3)–Cd–N(2)	120.99(12)	N(2)–Cd–N(2A)	70.99(16)
N(3)–Cd–N(2A)	114.90(11)	N(3)–Cd–N(1A)	85.02(11)
N(3)–Cd–N(1)	81.25(11)	N(2)–Cd–N(1A)	137.03(12)
N(2)–Cd–N(1)	66.84(12)		

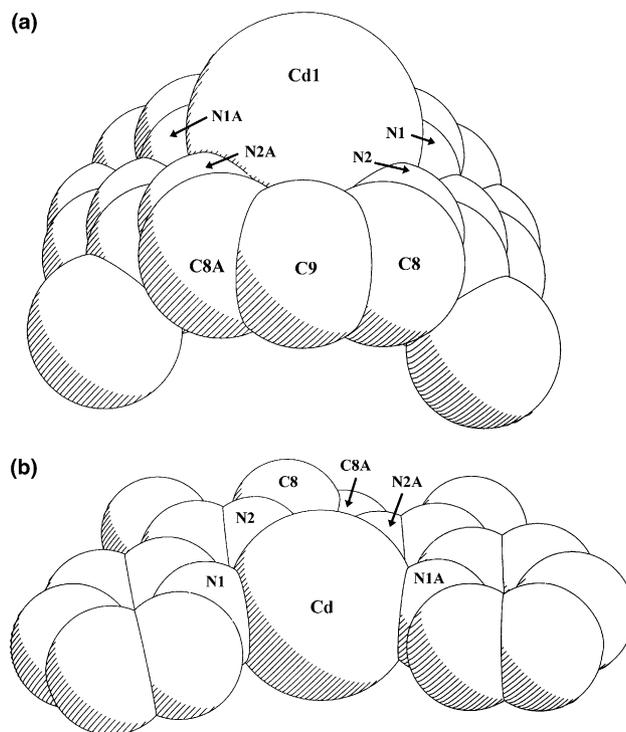


Fig. 4. Space-filling model of metal–L moiety for **1** (a) and **2** (b).

is quite short ( $b/a = 1.24$ ) and  $L^1$  encapsulates the metal atom in a TP fashion ( $b/a = 1.31$  for ideal TP). In **2** the ratio ( $b/a = 1.37$ ) is much closer to the octahedral limit.

- (iii) In complex **1** the intermolecular packing along the crystallographic  $b$ -direction is controlled by  $\pi$ -stacking interactions [27] between the pyridyl planes (Figs. 5(a) and (b)). The overlapping ring planes are related by a center of inversion, thus, are exactly parallel. The ring slippage has a slip angle of  $24.6^\circ$  and a vertical displacement between the ring centroids of  $1.58 \text{ \AA}$  (centroid separation  $3.796 \text{ \AA}$ , interplanar distance  $3.45 \text{ \AA}$ ). [27,28]. The shortest overlapping carbon contact  $C5-C1^3$  is  $3.45 \text{ \AA}$ . Therefore, the  $\pi$ -stacking in **1** corresponds closely to strong  $\pi$ -interactions which are classified

by centroid–centroid contacts  $<3.8 \text{ \AA}$ , slip angles  $<25^\circ$  and vertical displacements  $<1.5 \text{ \AA}$  [27]. On the other hand, the intermolecular packing in **2** exhibits only very weak  $\pi$ -stacking interactions between the pyridyl planes deduced by rather long centroid–centroid distances ( $>4.2 \text{ \AA}$ ), large interplanar distances ( $>3.65 \text{ \AA}$ ) together with large slip angles ( $=30^\circ$ ) and vertical displacements ( $>2.1 \text{ \AA}$ ) between the ring centroids [27].

#### 2.4. $^1\text{H}$ NMR spectra

The  $^1\text{H}$  NMR spectrum of diamagnetic  $[\text{Cd}(L^1)(\text{NCS})_2]$  (**1**), in  $\text{DMSO}-d_6$  at room temperature exhibits sharp singlets at  $\delta = 3.92$  and  $2.36$  ppm due to six methylene protons which is fully consistent with the crystallographically imposed mirror symmetry. The eight pyridyl proton signals do not exhibit spin structure and appear as broad singlets at  $8.95$ ,  $8.29$  and  $7.83$  ppm with the relative intensities 1:2:1. The methyl resonance is observed at  $2.46$  ppm as a sharp singlet as expected.

The  $^1\text{H}$  NMR spectrum of  $[\text{Cd}(L^2)(\text{NCS})_2]$  (**2**), in  $\text{DMSO}-d_6$  at room temperature revealed well resolved spin-spin structures for the pyridyl protons in the domain of  $8.82$ – $7.43$  ppm. The methylene proton resonance appeared as a singlet at  $3.84$  ppm, in agreement with the presence of a twofold axis bisecting the C–C bond of the dimethylene moiety of the ligand. Like **1**, the methyl resonance was observed as a sharp singlet at  $2.42$  ppm.

### 3. Experimental

#### 3.1. Materials and measurements

$\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ , 2-acetylpyridine and 1,3-diaminopropane were purchased from Fluka AG (Switzerland). Ammonium thiocyanate and 1,2-diaminoethane were obtained from S.D. Fine Chemicals (India). Reagent grade solvents were distilled and dried by standard methods and were used for all reactions. Spectral measurements were carried out using the following equipment: IR (KBr disc), Perkin–Elmer RXI FT-IR spectrometer;  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ , s = singlet, d = doublet, t = triplet), Bruker 300 MHz FT NMR, FAB Mass spectra JEOL JMS 600 spectrometer. A Perkin–Elmer 2400 Series II elemental analyzer was used for microanalysis (C, H, N).

#### 3.2. Preparations

##### 3.2.1. Ligands

$L^1$ : 1,3-Diaminopropane (1.11 g, 15 mmol) and 2-acetylpyridine (3.63 g, 30 mmol) were refluxed in 30 mL of dry methanol for 8 h. The resulting solution

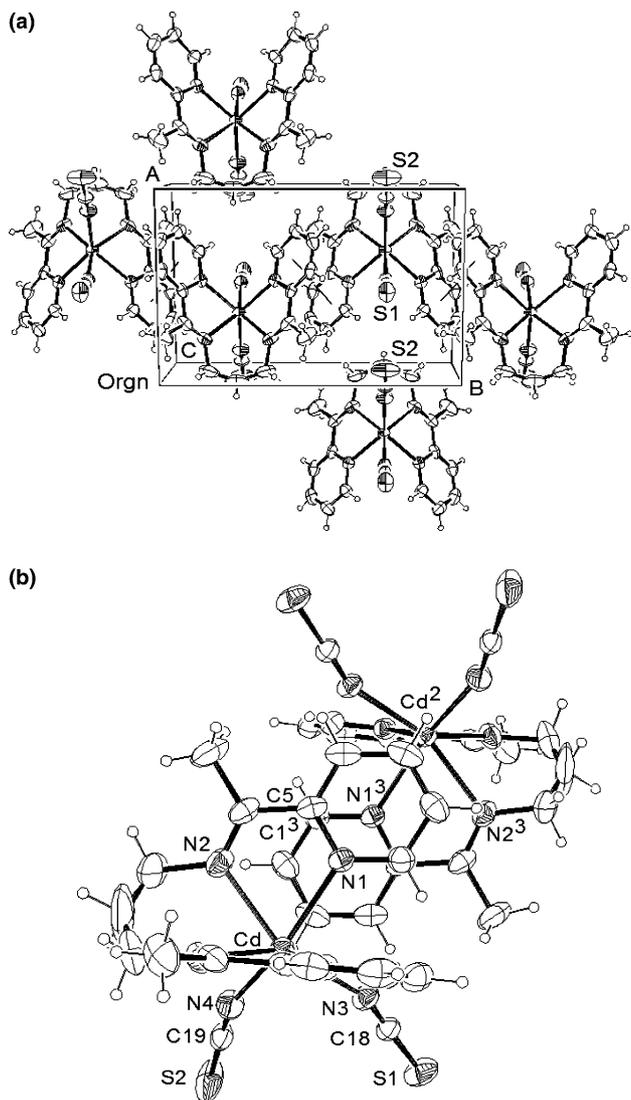


Fig. 5. (a) Intermolecular  $\pi$ -stacking (thin lines) along  $b$  in **1**. (b) Perpendicular view of the  $\pi$ -overlap between two molecules to show the typical ring slippage; symmetry transformation  $^2 = 1 - x, y - 1/2, 1 - z$ ;  $^3 = 1 - x, 1 - y, 1 - z$ .

was evaporated under reduced pressure to obtain a yellowish-brown semi-solid mass. The mass was then extracted thrice ( $3 \times 10$  mL) with *n*-hexane, which on slow evaporation afforded deep yellow needles. The product was finally dried under vacuum over fused  $\text{CaCl}_2$ . Yield: 2.77 g (65%). *Anal. Calc.* (%) for  $\text{C}_{17}\text{N}_4\text{H}_{20}$ : C, 72.83; H, 7.19; N, 19.98. Found: C, 72.91; H, 7.13; N, 19.93. IR ( $\nu/\text{cm}^{-1}$ ): 1680 ( $\nu_{\text{C}=\text{N}}$ ). FAB Mass spectrum:  $m/z$  281 ( $\text{L}^1 + 1$ )<sup>+</sup>. <sup>1</sup>H NMR  $\{\delta(\text{J/Hz}), \text{DMSO}-d_6\}$ : Pyridyl protons, 8.52 (d,  $J = 7.0$ , 2H), 7.96 (d,  $J = 7.8$ , 2H), 7.80 (t,  $J = 7.4$ , 2H), 7.37 (t,  $J = 6.8$ , 2H); methylene protons, 3.82 (s, 4H), 3.48 (s, 2H); methyl protons, 2.34 (s, 6H).

$\text{L}^2$ : The ligand was prepared by a procedure similar as that for  $\text{L}^1$ , by starting with 1,2-diaminoethane (0.9 g, 15 mmol) and 2-acetylpyridine (3.63 g, 30 mmol) to obtain a yellow semi-solid mass, which on recrystallization from *n*-hexane gave pale yellow product. Yield: 2.44 g (61%). *Anal. Calc.* (%) for  $\text{C}_{16}\text{N}_4\text{H}_{18}$ : C, 72.22; H, 6.75; N, 21.09. Found: C, 72.15; H, 6.81; N, 21.04. IR ( $\nu/\text{cm}^{-1}$ ): 1681 ( $\nu_{\text{C}=\text{N}}$ ). FAB Mass spectrum:  $m/z$  267 ( $\text{L}^2 + 1$ )<sup>+</sup>. <sup>1</sup>H NMR  $\{\delta(\text{J/Hz}), \text{DMSO}-d_6\}$ : Pyridyl protons, 8.56 (d,  $J = 7.0$ , 2H), 7.98 (d,  $J = 8.2$ , 2H), 7.79 (t,  $J = 7.8$ , 2H), 7.32 (d,  $J = 7.8$ , 2H); methylene protons, 3.75 (s, 4H); methyl protons, 2.32 (s, 6H).

### 3.2.2. Complexes

$[\text{Cd}(\text{L}^1)(\text{NCS})_2]$  (**1**). To a solution of  $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  (0.133 g, 0.5 mmol) in 15 mL dry methanol was added (0.006 g, 1 mmol) of  $\text{NH}_4\text{SCN}$ . To the resulting solution (0.140 g, 0.5 mmol) of  $\text{L}^1$  dissolved in 10 mL dry methanol was added in one go. The solution gradually became turbid and to ensure complete reaction magnetic stirring was continued for 3 h, and the reaction was left overnight at room temperature for complete precipitation. The solid was then collected by filtration, thoroughly washed with cold methanol and finally dried under vacuum over fused  $\text{CaCl}_2$ . Yield: 234 mg (92% with respect to  $\text{L}^1$ ). *Anal. Calc.* (%) for  $\text{C}_{19}\text{N}_6\text{H}_{20}\text{S}_2\text{Cd}$ : C, 44.84; H, 3.96; N, 16.51. Found: C, 44.88; H, 3.89; N, 16.57. IR ( $\nu/\text{cm}^{-1}$ ): 2072 ( $\nu_{\text{NCS}}$ ). FAB Mass spectrum:  $m/z$  510 ( $\mathbf{1} + 1$ )<sup>+</sup>. <sup>1</sup>H NMR  $\{\delta(\text{J/Hz}), \text{DMSO}-d_6\}$ : Pyridyl protons, 8.95 (s, 2H) 8.29 (s, 4H), 7.83 (s, 2H); methylene protons, 3.92 (s, 4H of C8 and C8A atoms); 2.36 (s, 2H of C9 atom); methyl protons, 2.46 (s, 6H).

$[\text{Cd}(\text{L}^2)(\text{NCS})_2]$  (**2**). The complex was prepared by a similar procedure. Yield: 222 mg (90% with respect to  $\text{L}^2$ ). *Anal. Calc.* (%) for  $\text{C}_{18}\text{N}_6\text{H}_{18}\text{S}_2\text{Cd}$ : C, 43.68; H, 3.67; N, 16.98. Found: C, 43.73; H, 3.61; N, 17.04. IR ( $\nu/\text{cm}^{-1}$ ): 2070 ( $\nu_{\text{NCS}}$ ). FAB Mass spectrum:  $m/z$  496 ( $\mathbf{2} + 1$ )<sup>+</sup>. <sup>1</sup>H NMR  $\{\delta(\text{J/Hz}), \text{DMSO}-d_6\}$ : Pyridyl protons, 8.82 (d,  $J = 6.8$ , 2H), 8.12 (t,  $J = 7.5$ , 2H), 7.87 (t,  $J = 7.2$ , 2H), 7.43 (d,  $J = 8.0$ , 2H); methylene protons, 3.84 (s, 4H); methyl protons, 2.42 (s, 6H).

Table 3  
Crystal data for complexes **1** and **2**

	<b>1</b>	<b>2</b>
Formula	$\text{C}_{19}\text{H}_{20}\text{CdN}_6\text{S}_2$	$\text{C}_{18}\text{H}_{18}\text{CdN}_6\text{S}_2$
<i>M</i>	508.93	494.93
System	monoclinic	orthorhombic
Space group	$P2(1)/m$	$Pccn$
<i>Unit cell dimensions</i>		
<i>a</i> (Å)	8.7047(16)	10.1510(19)
<i>b</i> (Å)	13.090(2)	12.370(2)
<i>c</i> (Å)	9.4678(17)	16.058(3)
$\alpha$ (°)	90.00	90.00
$\beta$ (°)	101.313(3)	90.00
$\gamma$ (°)	90.00	90.00
<i>V</i> (Å <sup>3</sup> )	1057.9(3)	2016.4(6)
<i>Z</i>	2	4
<i>D</i> ( $\text{Mg m}^{-3}$ )	1.598	1.630
<i>T</i> (K)	233(2)	243(2)
$\mu$ ( $\text{mm}^{-1}$ )	1.246	1.305
Collected reflections	9494	16895
Independent reflections	2658	2526
<i>R</i> <sub>int</sub>	0.0165	0.0399
Observed reflections [ $I > 2\sigma(I)$ ]	2281	1505
Parameters	139	123
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ $I > 2\sigma(I)$ ]	0.0293, 0.0818	0.0367, 0.0727
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [all data]	0.0343, 0.0838	0.0697, 0.0818
Goodness-of-fit	1.068	1.065

### 3.3. Crystal structure determination

Crystals of **1** and **2** were grown by slow evaporation of solvent from DMSO solution. Data collection were performed by the  $\omega$ -scan method within the limits  $2.19^\circ \leq \theta \leq 28.66^\circ$  and  $2.54^\circ \leq \theta \leq 28.87^\circ$  for **1** and **2**, respectively, on a Bruker AXS CCD diffractometer with graphite monochromated Mo  $\text{K}\alpha$  radiation ( $\lambda = 0.71073$  Å) radiation. Data collection and cell refinement were carried out with SMART [29], data reduction with SAINT [29], and experimental absorption correction with SADABS [30].

*Structure analysis and refinement.* The structure was solved by direct methods (SHELXS-97) [31]; refinement was done by full-matrix least squares on  $F^2$  using the SHELXL-97 program suite [31]. All non-hydrogen positions were found and refined with anisotropic temperature factors. The hydrogen atoms were calculated with appropriate riding models (AFIX 43 for aromatic hydrogens on pyridine, AFIX 23 for  $\text{CH}_2$  and AFIX 33 for  $\text{CH}_3$ ) and  $U_{\text{eq}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$  for CH and  $\text{CH}_2$  and  $U_{\text{eq}}(\text{H}) = 1.5 U_{\text{eq}}(\text{C})$  for  $\text{CH}_3$ . Significant crystal data are listed in Table 3. Graphics were obtained with ORTEP 3 for Windows [32–34]. Supramolecular interactions ( $\pi$ -contacts) were calculated with PLATON for Windows [35–37].

## 4. Conclusion

The effect of variation of the polymethylene spacer length in the pyridyl Schiff-base ligands  $\text{L}^1$  (spacer

–(CH<sub>2</sub>)<sub>3</sub>–) and L<sup>2</sup> (spacer –(CH<sub>2</sub>)<sub>2</sub>–) was studied in the case of neutral hexacoordinated structures with the Cd(NCS)<sub>2</sub> fragment. The molecular structures of the resulting complexes strongly deviate from the classical octahedron, with [Cd(L<sup>1</sup>)(NCS)<sub>2</sub>] showing a trigonal prismatic coordination polyhedron around cadmium. This and the structural differences between [Cd(L<sup>1</sup>)(NCS)<sub>2</sub>] (**1**) and [Cd(L<sup>2</sup>)(NCS)<sub>2</sub>] (**2**) can be traced to the length of the methylene spacers and the formation of a six- versus a five-membered metal-chelate ring together with the pyramidal Cd(L<sup>1</sup>) and planar Cd(L<sup>2</sup>) arrangement.

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### Appendix A. Supplementary data

CCDC reference numbers are 216947 and 228070 for **1** and **2**, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; email: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>). Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.poly.2005.01.005.

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