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Polyhedron 22 (2003) 1471–1479

POLYHEDRON

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Synthesis and characterization of mono- and bis-ligand zinc(II) and cadmium(II) complexes of the di-2-pyridylketone Schiff base of *S*-benzyl dithiocarbazate (Hdpksbz) and the X-ray crystal structures of the [Zn(dpksbz)$_2$] and [Cd(dpksbz)NCS]$_2$ complexes

Mohammad Akbar Ali[a,*], Aminul Huq Mirza[a], Mohammad Nazimuddin[b], Raju Ahmed[b], Lawrence R. Gahan[c], Paul V. Bernhardt[c]

[a] *Department of Chemistry, Universiti Brunei Darussalam, Jalan Tungku Link, BE 1410, Bander Seri Begawan, Brunei*
[b] *Department of Chemistry, University of Chittagong, Chittagong, Bangladesh*
[c] *Department of Chemistry, The University of Queensland, Brisbane, Qld 4072, Australia*

Received 22 May 2002; accepted 5 March 2003

Abstract

New mono- and bis-chelated zinc(II) and cadmium(II) complexes of formula, [M(dpksbz)NCS] (dpksbz = anionic form of the di-2-pyridylketone Schiff base of *S*-benzyldithiocarbazate) and [M(dpksbz)$_2$] (M = Zn^{II}, Cd^{II}) have been prepared and characterized. The structure of the bis-ligand complex, [Zn(dpksbz)$_2$] has been determined by X-ray diffraction. The complex has a distorted octahedral geometry in which the ligands are coordinated to the zinc(II) ion as uninegatively charged tridentate chelates via the thiolate sulfur atoms, the azomethine nitrogen atoms and the pyridine nitrogen atoms. The distortion from a regular octahedral geometry is attributed to the restricted bite angles of the Schiff base ligands. X-ray structural analysis shows that the [Cd(dpksbz)NCS]$_2$ complex is a centrosymmetric dimer in which each of the cadmium(II) ions adopts a five-coordinate, approximately square-pyramidal configuration with the Schiff base acting as a tetradentate chelating agent coordinating a cadmium(II) ion via one of the pyridine nitrogen atoms, the azomethine nitrogen atom and the thiolate sulfur atom; the second pyridine nitrogen atom is coordinated to the other cadmium(II) ion of the dimer. The fifth coordination position around each cadmium(II) is occupied by an N-bonded thiocyanate ligand.

Keywords: Zinc(II) and cadmium(II) complexes; Di-2-pyridylketone Schiff base of *S*-benzyldithiocarbazate; Schiff bases; Dithiocarbazates

1. Introduction

The wide variety of biological activity exhibited by thiosemicarbazones [1–11] and Schiff bases derived from *S*-alkyldithiocarbazates [12–16] and their interesting coordination chemistry have stimulated considerable research interest in these compounds [17–22]. Previous studies have centred mainly on copper(II) and nickel(II) complexes of these ligands. Complexes of d^{10} metal ions, such as zinc(II) and cadmium(II) are also of interest since they are involved in many biological processes [23]. The chemical similarity of zinc(II) and cadmium(II) suggests that the latter may displace the former from the active site in enzymes containing zinc(II) [24]. Although cadmium has been known as a toxic metal and is often associated with mercury and lead as one of the biologically harmful metal ions, the cadmium(II) ion has recently been found to serve as the catalytic centre in a newly discovered carbonic anhydrase [25]. Recent studies by Perez et al. on zinc(II) and cadmium(II) complexes of thiosemicarbazone ligands have shown that these complexes might overcome cisplatin resistance in murine keratinocytes overexpressing the H-ras oncogene [26]. In addition to their importance in biology, zinc(II) and cadmium(II) complexes of mixed

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* Corresponding author. Tel.: +673-2-24-9001x1341; fax: +673-2-24-9502.
E-mail address: akbar@fos.ubd.edu.bn (M. Akbar Ali).

0277-5387/03/$ - see front matter
doi:10.1016/S0277-5387(03)00125-6

diimine ligands have also been shown to display an interesting type of ligand-to-ligand charge-transfer transition without the involvement of the metal ion [27]. This observation has generated considerable interest in the excited electronic properties of these elements.

In view of sparse literature on zinc(II) and cadmium(II) complexes of tridentate thiosemicarbazone and dithiocarbazate ligands and as part of our continuing work on metal–dithiocarbazates, we report here the synthesis and characterization of some mono- and bis-chelated zinc(II) and cadmium(II) complexes of a nitrogen–sulfur chelating agent derived from *S*-benzyldithiocarbazate, together with the X-ray crystal and molecular structures of the [Zn(dpksbz)$_2$] and [Cd(dpksbz)NCS]$_2$ complexes.

2. Experimental

2.1. Methods

The ^{1}H, ^{13}C [^{1}H] and ^{13}C DEPT NMR spectra were recorded at 301 K on a Bruker AC 200F 200 MHz or Bruker AV 400 MHz spectrometer. Chemical shifts for the ^{1}H NMR spectra (CDCl$_3$ or DMSO-d_6) are reported in ppm as positive downfield of the internal reference, TMS. All other physical measurements and analytical procedures were similar to those described previously [28,29].

2.2. Synthesis of the ligand

Di-2-pyridylketone (1.84 g, 0.01 mol) dissolved in abs. ethanol (50 ml) was mixed with a hot solution of *S*-benzyldithiocarbazate (1.98 g, 0.01 mol) in the same solvent (200 ml). The mixture was heated on a water bath for approximately 1 h and then left to stand overnight whereupon the product that had formed was filtered off and recrystallized from abs. ethanol. Yield, 2.60 g, 70%, m.p. 165 °C. Calc. for $C_{19}H_{16}N_4S_2$: C, 62.6; H, 4.4, N, 15.4; Found: C, 62.5; H, 4.3; N, 15.3%; IR (KBr), ν (cm^{-1}): 3162br, w, 1584m, 1566s, 1478s, 1451s, 1418s, 1339s, 1329m,1293m, 1259s, 1230s, 1193m, 1154m, 1121s, 1089m, 1057s, 1042s, 1029s, 997s, 960m, 901m, 849m, 803s, 785m, 749m, 735s, 720s, 650s, 617s, 567m, 488s, 438m, 400s and 397s; NMR [CDCl$_3$]: δ_H: 15.33 (s, 1H, NH). 4.56 (s, 2H, CH$_2$), 8.80 (d, $^3J = 4$ Hz, 2H, py), 8.62 (d, $^3J = 4$ Hz, 2H, py), 8.02 (t, $^3J = 8$ Hz, py, 2H), 7.44–7.74 (m, 5H, ph); δ_C: 179.4 (CS), 39.2 (CH$_2$), 148.4 (CN), 155.4, 151.1, 148.1, 142.5, 137.2, 136.2, 129.5, 128.6, 127.4, 127.3, 124.5, 124.4, 123.9 (py and ph).

2.3. Preparation of the complexes

2.3.1. Preparation of the [MLNCS]$_2$ complexes

To a solution of the appropriate hydrated metal(II) nitrate salt (1 mmol) in abs. ethanol (50 ml), anhydrous lithium thiocyanate (3.5 mmol) was added and the mixture boiled on a water bath for 10 min. To this solution was added a solution of the ligand (1.98 g, 1 mmol) in abs. ethanol (100 ml) and the resulting yellow solution was heated under reflux for 1 h and then it was left to stand overnight. The product formed was filtered off and dried in a desiccator over anhydrous silica gel. Yield, 60–70%. The [ZnLNCS]$_2$ complex was dissolved in hot DMF and re-precipitated by slowly adding diethyl ether. Crystals of [CdLNCS]$_2$, suitable for X-ray crystallography were obtained by dissolving a small quantity of the complex in hot methyl cyanide and letting the solution evaporate slowly at room temperature over a period of 2–3 days.

2.3.1.1. [Zn·LNCS]$_2$. NMR [DMSO-d_6] δ_H: 4.1 (s, 4H, SCH$_2$), 8.85 (t, $^3J = 4$ Hz, 4H, py), 8.68 (d, $^3J = 4$ Hz, 4H, py), 7.30–7.95 (m, 12H, py and ph), 7.13–7.23 (m, 6H, ph), 6.92–7.0 (m, 4H, ph); δ_C: 34.7 (CH$_2$), 189.6 (CS), 151.5 (CN), 151.4 (CN), 149.3, 148.5, 147.6, 140.6, 139.6, 138.2, 138.0, 136.7, 128.8, 127.0, 126.6, 126.1, 124.8 (py and ph).

2.3.1.2. [Cd·LNCS]$_2$. NMR [DMSO-d_6] δ_H: 4.03 (d, $^3J = 6$ Hz, 2H), 8.84 (d, $^3J = 4$ Hz, 2H, py), 8.61 (d, $^3J = 4$ Hz, 2H, py), 6.86–6.96 (m, 4H, ph), 7.13–7.24 (m, 8H, ph) 7.3–8.00 (m, 12H, py and ph); δ_C: 34.3 (CH$_2$), 154.2 (CN), 152.2 (CN), 187.2 (CS), 149.4. 148.4, 148.2, 139.8, 136.5, 128.7, 128.6, 128.1, 128.0, 126.6, 126.2, 124.4 (py and ph).

2.3.2. Preparation of ML$_2$ (M = Zn^{II} and Cd^{II}; L = anionic form of the Schiff base)

To a boiling solution of the Schiff base (0.72 g; 2 mmol) in abs. ethanol (200 ml) was added a solution of the appropriate metal(II) nitrate salt (1 mmol) in the same solvent (50 ml) and the resulting solution was kept under reflux for about 1 h and then left to stand overnight. The product which had formed was filtered off, washed several times with abs. ethanol and dried in a vacuum desiccator over anhydrous silica gel. Yield, 60–70%. Crystals of the ZnL$_2$ complex, suitable for X-ray diffraction analysis, were obtained by dissolving the complex in hot methyl cyanide and then letting the solution stand at room temperature for 3 days.

Attempts to grow crystals of CdL$_2$ for X-ray analysis were unsuccessful.

2.3.2.1. ZnL$_2$. NMR [DMSO-d_6] δ_H: 4.12 (s, 4H, CH$_2$), 8.80 (t, $^3J = 6$ Hz, 4H, py), 8.65 (d, $^3J = 4$ Hz, 2H, py), 7.30 (t, $^3J = 4$ Hz, 2H, py/ph), 6.92–6.99 (m, 5H, ph), 7.14–7.22 (m, 5H, py and ph), 7.50–8.10 (m, 10H, py and ph); δ_C: 189.8 (CS), 151.4 (CN), 150.8 (CN), 150.3, 149.4, 148.5, 147.7, 140.4, 138.2, 136.7, 128.7, 128.1, 126.6, 126.1, 124.8 (py and ph), 34.3 (CH_2).

2.3.2.2. CdL_2. NMR [DMSO-d_6] δ_H: 4.12 (s, 4H, CH_2), 8.90 (d, $^3J = 6$ Hz, 2H, py), 6.96–7.01 (m, 4H, py/Ar.), 7.31 (d, $^3J = 4$ Hz, 2H, ph), 7.47–7.64 (m, 2H, py/ph), 7.89 (m, 8H, py); δ_C: 34.7 (CH_2), 10.0 (CS), 152.8 (CN), 151.4 (CN), 149.4, 147.7, 146.7, 139.6, 138.2, 136.6, 128.8, 128.1, 126.6, 125.9, 124.6.

2.4. X-ray crystal structure analysis

A yellow crystal of the appropriate metal complex was mounted on a glass fibre. Cell constants were determined by a least-squares fit to the setting parameters of 25 independent reflections, measured on an Enraf-Nonius CAD4 four-circle diffractometer using graphite monochromated Mo Kα radiation (0.71073 Å) and operating in the ω–2θ mode within the range $2 < 2\theta < 50°$. Data reduction and empirical absorption corrections (Ψ-scans) were performed with the WINGX [30] suite of programmes. The structures were solved by direct methods with SHELXS-86 [31] and refined by full-matrix least-squares analysis with SHELXL-97 [32]. Non-H atoms were refined with anisotropic thermal parameters whereas H-atoms were included at estimated positions. Drawings of molecules were produced with the programme ORTEP-3 [33]. Crystal data and structure determination are given in Table 1.

Table 1
Crystal data and structure refinement for [Zn(dpksbz)$_2$] and [Cd(dpksbz)NCS]$_2$

Empirical formula	$C_{38}H_{30}N_8S_4Zn$	$C_{20}H_{15}CdN_5S_3$
Formula weight	792.31	533.95
Temperature (K)	297(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$C2/c$	$P2_1/c$
Unit cell dimensions		
a (Å)	21.610(5)	14.7760(10)
b (Å)	13.239(1)	9.8260(10)
c (Å)	14.863(2)	15.1240(10)
β (°)	119.42(1)	108.156(7)
V (Å^3)	3703.87(10)	2086.5(3)
Z	4	4
D_{calc} (Mg m^{-3})	1.438	1.700
Absorption coefficient (mm^{-1})	0.940	1.364
F(0 0 0)	1632	1064
Crystal size (mm)	0.50 × 0.30 × 0.10	0.33 × 0.27 × 0.17
θ range for data collection (°)	1.88–24.97	2.51–24.98
Index ranges	$0 < h < 25$, $0 < k < 15$, $-17 < l < 15$	$0 < h < 17$, $0 < k < 11$, $-17 < l < 17$
Reflections collected	3299	3794
Independent reflections	3210 [$R_{int} = 0.0217$]	644 [$R_{int} = 0.0714$]
Completeness to θ = 24.97° (%)	99.8	99.6
Absorption correction	ψ-scan	ψ-scan
Max/min transmission	0.9118, 0.6507	0.7921, 0.726
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraint/parameters	3210/0/231	3644/0/262
Goodness-of-fit on F^2	0.969	1.002
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0335$, $wR_2 = 0.0793$	$R_1 = 0.0345$, $wR_2 = 0.0823$
R indices (all data)	$R_1 = 0.0814$, $wR_2 = 0.0953$	$R_1 = 0.0712$, $wR_2 = 0.0952$
Largest difference peak and hole (e Å^{-3})	0.256 and −0.216	0.923 and −0.588

3. Results and discussion

Compounds containing the thioamide function, –N(H)–C(S) are capable of exhibiting thione–thiol tautomerism. Therefore, the present Schiff base (Hdpksbz; Fig. 1) can exist either as the thione (1a) or as the thiol form (1b) or as an equilibrium mixture of both.

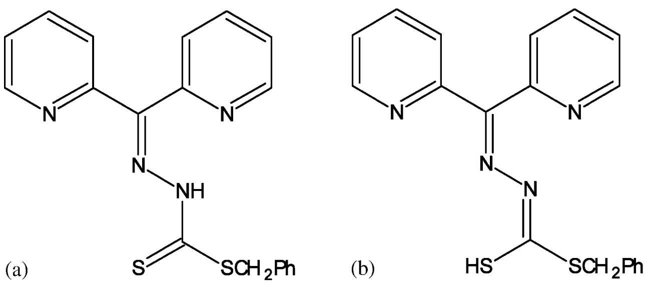

Fig. 1. The thione (1a) and the thiol (1b) forms of Hdpksbz.

The IR spectrum of the free ligand in KBr does not exhibit a ν(SH) band at 2700 cm^{-1}, but shows a broad and weak band at 3160 cm^{-1} attributable to ν(NH), indicating that in the solid state it remains as the thione form. However, in solution and in the presence of a zinc(II) or cadmium(II) salt, it quickly converts to the thiol form and coordinates to the metal ion in its deprotonated thiolate form. The related α-N-heterocyclic carboxyaldehyde thiosemicarbazones have been shown to coordinate to metal ions in both protonated [34] and deprotonated [35] forms. There are examples of metal–thiosemicarbazone complexes in which the thiosemicarbazone ligands have been found to coordinate to a metal ion both in their thiolate and thione forms in the same complex [36]. Although Schiff bases derived from S-alkyl esters of dithiocarbazic acid are structurally very similar to thiosemicarbazones, they invariably deprotonate in the presence of metal ions forming metal complexes of their deprotonated thiolate forms. To our knowledge, there has not been any example of a metal complex of a Schiff base ligand derived from an *S*-alkyl ester of dithiocarbazic acid in which a neutral protonated form of the ligand has been found. Our attempts to isolate zinc(II) and cadmium(II) complexes of the neutral protonated form of Hdpksbz have also been unsuccessful.

The Schiff base Hdpksbz reacts readily with zinc(II) and cadmium(II) salts in ethanol producing stable compounds, the compositions of which depend on the nature of the anion present in the reaction mixture. Thus, with a coordinating anion such as the thiocyanate ion, mono-ligand complexes of empirical formula, [M(dpksbz)NCS] ($M = Zn^{II}$, Cd^{II}) were obtained, whereas in the presence of a weakly coordinating anion such as the nitrate ion, bis-ligand complexes of formula, $[M(dpksbz)_2]$ resulted. These complexes are sparingly soluble in dichloromethane and methyl cyanide but they readily dissolve in DMF and DMSO. Their molar conductances in CH_2Cl_2 (Table 2) indicate that they are essentially non-electrolytes in this solvent. The non-electrolytic nature of these complexes indicates that the Schiff base is coordinated to the zinc(II) and cadmium(II) ions in its deprotonated thiolate form and that in the mono-ligated complexes, the NCS^- ions are also coordinated to the zinc(II) and cadmium(II) ions. Coordination of the thiocyanate ions is further supported by the IR spectra of the thiocyanato-complexes, which show strong bands in the 2030–2091 cm^{-1} range indicating that the NCS^- anions are coordinated to the zinc(II) ion and cadmium(II) ions *vide infra*.

The IR bands that are considered most useful in ascertaining the mode of coordination of the Schiff base to the zinc(II) and cadmium(II) ions are summarized in Table 3. A comparison of the IR spectrum of the ligand with those of its complexes shows that the broad and weak band at 3162 cm^{-1} attributable to ν(NH), is not present in the spectra of the complexes indicating that the ligand is coordinated in its deprotonated form. Coordination via the pyridine nitrogen atom is indicated by the shift of the pyridine band of the ligand from 596 to 610 cm^{-1} in the spectra of the complexes. In the past, evidence of coordination of thiosemicarbazone and dithiocarbazate ligands to metal ions via the azomethine nitrogen atom was based on shifting of the azomethine C=N band of the free ligand from higher to lower wave numbers in the spectra of metal complexes [37]. However, shifting of this band to both higher [38] and lower [39] wave numbers have been reported. Since the ν(C=N) band is expected to couple with other bands, the shifting of this band will be dependent on how much it is in combination with other bands. In the IR spectra of the present complexes, the ν(C=N) band is not shifted but the ν(N–N) band of the free ligand shifts considerably to higher wave numbers supporting coordination via the azomethine nitrogen atom [40].

The thiocyanate ion is known to coordinate to metal ions in different modes [41] and IR spectroscopy has proved an effective method of distinguishing between these modes [42]. Complexes containing N-bonded thiocyanate exhibit a C–N stretching frequency generally in the 2040–2080 cm^{-1} range and S-bonded complexes exhibit this frequency in the 2080–2120 cm^{-1} range. As bridging ligands, the NCS^- anions can also link a pair of metal ions in either an end-on (μ-1,1) via either the sulfur end or the nitrogen end or a side-on (μ-1,3) bonded manner. The IR spectra of end-on S-bridged thiocyanato-complexes, whose structures have been determined by X-ray diffraction, have been shown to exhibit only one C–N stretching band at approximately 2091 cm^{-1} [43]. The side-on NCS bridging mode (μ-1,3) has been found to be most common for copper(II) complexes [44]. Thus, the spectrum of the polymeric $[Cu(bpm)(NCS)]_n$ complex (bpm = bipyrimidine), whose structure has been determined by X-ray crystallography [44], displays two C–N bands at 2120 and 2100 cm^{-1}. For the zinc(II) complex, [Zn(dpksbz)NCS] the presence of two C–N bands at 2076 and 2030 cm^{-1} in its IR spectrum suggests that the thiocyanate ions are coordinated to the zinc(II) ion as bridging ligands in a side-on manner, the complex being either a μ-1,3 linked dimer or a polymer [45].

Attempts to grow crystals of this compound suitable for X-ray diffraction have been unsuccessful. The IR spectrum of the $[Cd(dpksbz)NCS]_2$ complex, on the otherhand, exhibits a strong unsplit band at 2073 cm^{-1} indicating that the thiocyanate ion is coordinated to the cadmium(II) ion as a unidentate ligand via the nitrogen atom. This mode of bonding of the NCS^- ion in the

Table 2
Colour, conductivities and analytical data for the zinc(II) and cadmium(II) complexes

Compound	Colour	M.p. (dec. temperature)	Λ [a]	Found (calc.) (%)		
				C	H	N
[Zn(dpksbz)NCS]	yellow	245	1.8	49.0 (49.3)	3.4 (3.1)	14.2 (14.4)
$[Zn(dpksbz)_2]$	yellow	243	1.4	57.5 (57.6)	3.7 (3.8)	14.0 (14.1)
$[Cd(dpksbz)NCS]_2$	orange	246	1.7	54.2 (54.4)	3.7 (3.6)	13.1 (13.3)
$[Cd(dpksbz)_2]$	orange–yellow	240	1.0	54.4 (54.4)	3.7 (3.6)	13.1 (13.3)

[a] Molar conductance of (ohm^{-1} cm^2 mol^{-1}) approximately 10^{-3} M solutions in CH_2Cl_2.

Table 3
IR and electronic spectral data for Hdpksbz and its zinc(II) complexes

Compound	IR					Electronic spectra [a]	
	ν(NH)	ν(CN)	ν(NN)	ν(CSS)	ν(py)	State	λ_{max} (nm)
Hdpksbz	3162br, w	1584m	1057s	960m	596s	N D	376, 342, 257 364(5.5), 318(4.4), 284(5.5)
[Zn(dpksbz)NCS]		1602m	1092s	1021m 987s	601s	N D	439, 366, 301. 432(4.5), 358(4.5), approximately 250sh
$[Zn(dpksbz)_2]$		1599s	1097s	995s 1020s	610s	N D	439, 366, 304, 20 428(3.6), 356(3.6), 232(3.0)
$[Cd(dpksbz)NCS]_2$		1600s	1092s	1002s	610s	N	440, 366, 301
$[Cd(dpksbz)_2]$		1583s	1079s	960s 993s	 613m	N D	438, 361, 299,250 414(4.6), 346(4.1), 234(4.2)

[a] Log ε ($mol^{-1}\,l\,cm^{-1}$) are in parentheses; N, Nujol; D, dichloromethane.

$[Cd(dpksbz)NCS]_2$ complex has also been confirmed by X-ray crystallography (Vide Section 3.2).

The electronic spectra of the Schiff base and its zinc(II) and cadmium(II) complexes are compiled in Table 3. The spectra of the ligand, both in the solid state and in solution, exhibit bands at ~374 and 342 nm attributable to the n→π* and π→π* transitions, respectively. In the complexes, these bands do not shift significantly but a new band at approximately 440 nm, probably a CT band, is observed. Such bands are common in the electronic spectra of metal–thiosemicarbazone and metal–dithiocarbazate complexes [46].

Table 4
Selected bond lengths (Å) and bond angles (°) for $[Zn(dpksbz)_2]$

Zn1–N2	2.307(3)	N4–C12	1.309(4)
Zn1–N1	2.108(2)	C12–S1	1.715(3)
Zn1–S1	2.4199(10)	N1–N4	1.390(3)
C1–N1	1.291(4)		
N1–Zn1–S1	81.11(7)	N1–Zn1–N1#	154.56(13)
N2–Zn1–S1	154.79(7)	N1#–Zn1–N2	88.32(9)
N2–Zn1–N1	73.70(9)	N1–Zn1–N2#	73.70(9)
N2#–Zn1–S1#	154.79(7)	N1#–Zn1–N2#	115.89(7)
N1#–Zn1–S1#	81.11(7)	N1–Zn1–S1#	89.83(7)
N2#–Zn1–N2#	90.54(13)	N2–Zn1–S1#	89.83(7)
N(2)#–Zn1–S1	88.32(9)		

3.1. The structure of $[Zn(dpksbz)_2]$

The structure of $[Zn(dpksbz)_2]$, together with the atom numbering scheme adopted, is shown in Fig. 2 and selected bond lengths and bond angles are summarized in Table 4. The crystal structure of $[Zn(dpksbz)_2]$ shows that the zinc(II) ion is six-coordinate. The two

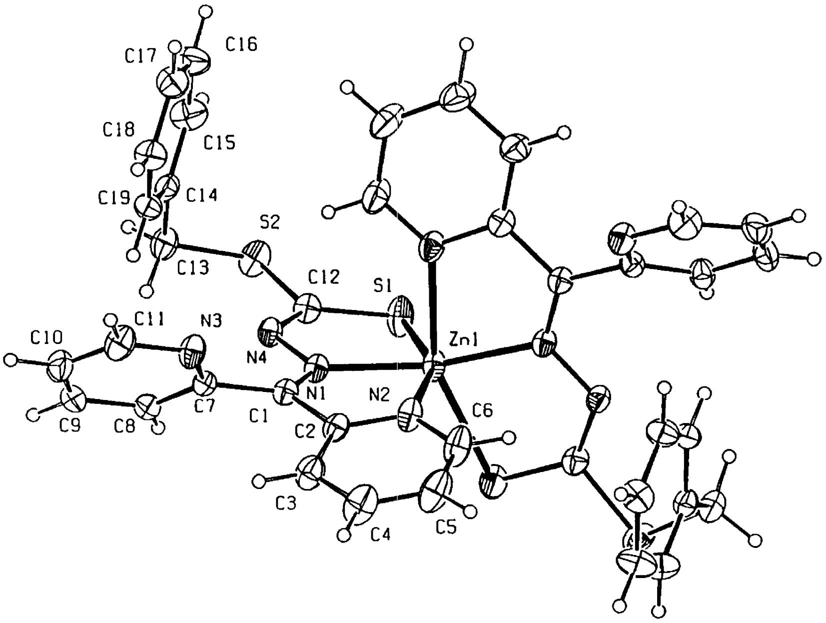

Fig. 2. The X-ray crystal structure of $[Zn(dpksbz)_2]$.

Schiff base ligands coordinate the zinc(II) ion in a meridional configuration with the thiolate sulfur and pyridine nitrogen atoms *cis* and the azomethine nitrogen atoms *trans* to each other. Similar meridional configurations have also been observed in other bis-ligand octahedral complexes of NNS-donor thiosemicarbazones [47] and dithiocarbazates [48]. In the [Zn(dpksbz)$_2$] complex, each ligand is coordinated to the zinc(II) ion in its iminothiolate form via the thiolate sulfur atom, the azomethine nitrogen atom and one of the pyridine nitrogen atoms, similar to the bis-ligand zinc(II) and cadmium(II) complexes of related ligands [47,48]. While coordinating in their iminothiolate forms, the negative charges generated by deprotonation are delocalized in the C–N–N–C system as shown by the intermediate C(1)–N(1) [1.292(4) Å], N(1)–N(4) [1.390(4) Å] and N(4)–C(12) [1.309(4) Å] bond distances. In contrast with the related bis-ligand cadmium(II) complex, [Cd(dpksme)$_2$]·0.5MeOH (dpksme = deprotonated form of the di-2-pyridylketone Schiff base of *S*-methyldithiocarbazate) [29] in which pairs of Cd–S, Cd–N$_{azo}$ and Cd–N$_{py}$ bonds have different lengths, the pairs of Zn–S, Zn–N$_{azo}$ and Zn–N$_{py}$ bonds in [Zn(dpksbz)$_2$] have equal lengths. However, as found previously with other bis-ligand six-coordinate metal complexes of tridentate thiosemicarbazone and dithiocarbazate ligands [46–48], the Zn–N$_{azomethine}$ bonds in this complex are also shorter than the Zn–N$_{py}$ bonds.

Although X-ray crystallographic data on several four- and five-coordinate zinc(II) complexes of thiosemicarbazone ligands are available [49–53], there is no X-ray crystallographic report of an octahedral zinc(II) complex of an NNS tridentate thiosemicarbzone or dithiocarbazate ligand. Therefore, a meaningful comparison of bond lengths and bond angles of [Zn(dpksbz)$_2$] with those of a similar bis-ligand zinc(II) complex is not possible. However, a comparison of the Zn–S and Zn–N$_{azomethine}$ bond distances in this complex with those of the six-coordinate zinc(II) complex of the pyruvic acid thiosemicarbazone (Hpatsc), which has an ONS donor sequence and whose structure has been reported by Ferrari et al. [54], shows that the lengths of these bonds are comparable. However, the Zn–S bonds in [Zn(dpksbz)$_2$] are shorter than those in the [Zn(patsc)$_2$] complex but, the Zn–N$_{azomethine}$ bond lengths in both complexes compare favourably (Table 5). In thiosemicarbazone and dithiocarbazate complexes, the bonds that are expected to be most affected by coordination are the imine C=N and the thiolate C–S bonds. Enethiolization of thiosemicarbazone or dithiocarbazate ligands is expected to lengthen the C=S bond, but the length of the C(12)–S(1) bond, [1.715(3) Å] in the present complex is intermediate between a C–S single and C=S double bond indicating that electron delocalization in the dithiocarbazate side chain extends to the C–S bond.

Table 5
Comparison of bond lengths (Å) in bis-ligand six-coordinate zinc(II) complexes

Bond	[Zn(patsc)$_2$] [a]	[Zn(dpksbz)$_2$]
Zn–S	2.474(2)	2.4199(10)
Zn–N$_{azomethine}$	2.120(4)	2.108(2)
C1–N1	1.285(4)	1.292(4)
N1–N4	1.367(4)	1.390(3)
N4–C12	1.363(4)	1.309(4)
C12–S1	1.685(5)	1.715(3)
Ref.	[49]	this work

[a] patsc, Anionic form of the pyruvic acid thiosemicarbazone.

It is evident from the bond length and bond angle data for [Zn(dpksbz)$_2$] (Table 4) that, in the [Zn(dpksbz)$_2$] complex, the environment about the zinc(II) ion is considerably distorted from an ideal octahedral geometry. Of the 12 bond angles subtended at the zinc(II) ion, only four are close to that expected for a regular octahedral geometry and the rest vary substantially from ideal values. Similar observation has also been made in almost all six-coordinate metal complexes of NNS thiosemicarbazone and dithiocarbazate ligands whose structures have been reported [46–48]. The deviation from an octahedral geometry in the present complex can be ascribed to the small bite angles of the two Schiff bases.

3.2. *The structure of the [Cd(dpksbz)NCS]$_2$ complex*

The structure of the [Cd(dpksbz)NCS]$_2$ complex is shown in Fig. 3 and selected bond lengths and bond angles are listed in Table 6. The crystal structure shows that the complex is a centrosymmetric dimer in which each of the cadmium(II) ions adopts a five-coordinate geometry. In contrast with the [Zn(dpksbz)$_2$] complex in which the Schiff base coordinates to the Zn(II) ion as an NNS tridentate chelating agent, in the [Cd(dpksbz)NCS]$_2$ complex, it acts as an N$_3$S quadridentate chelating agent providing three of its donor atoms, N(1), N(3) and S(1) to one cadmium(II) ion and the fourth donor atom, N(2) to the other. The coordination geometry of each cadmium(II) ion is square pyramidal. Addison et al. [55] have used an angular structural parameter τ (index of trigonality) for distinguishing between a trigonal-bipyramidal and square-pyramidal geometry in five-coordinate metal complexes. $\tau = \beta - \alpha/60°$, where α and β are the two largest angles. $\tau = 0$ for an ideal square-pyramid ($\alpha = \beta = 180°$) and $\tau = 1$ for an ideal trigonal-bipyramid ($\alpha = 120°$ and $\beta = 180°$). Using this criterion, the τ value is found to be 0.03 for the [Cd(dpksbz)NCS]$_2$ complex, indicating that each cadmium(II) ion in the dimer has a near square pyramidal geometry. The pyridine nitrogen atom N(1), the azomethine nitrogen atom N(3) and the thiolate

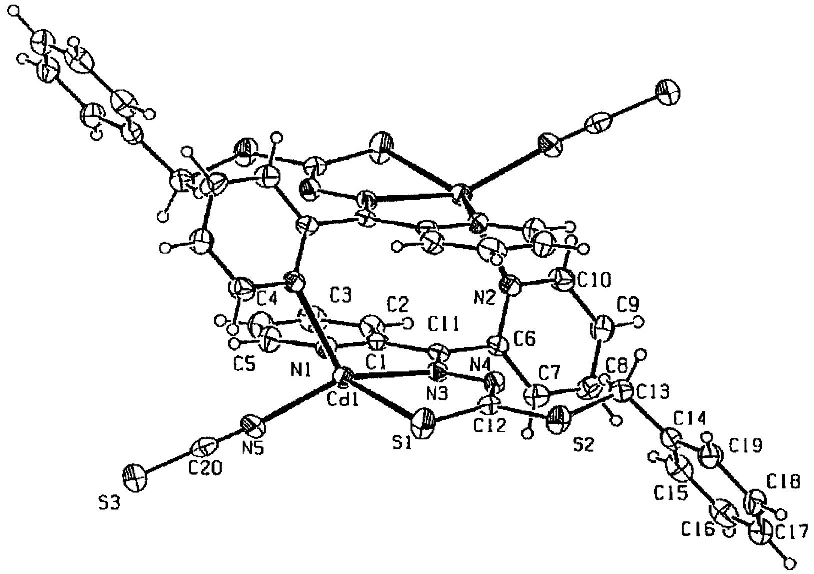

Fig. 3. The X-ray crystal structure of $[Cd(dpksbz)NCS]_2$.

Table 6
Selected bond lengths (Å) and bond angles (°) for $[Cd(dpksbz)NCS]_2$

Cd(1)–N(1)	2.357(4)	Cd(1)–N(2)#	2.373(4)
Cd(1)–N(3)	2.322(3)	Cd(1)#1–N(2)	2.373(4)
Cd(1)–N(5)	2.198(4)	C(12)–S(1)	1.739(5)
Cd(1)–S(1)	2.5302(13)	N(3)–N(4)	1.374(5)
C(11)–N(3)	1.290(5)	C(12)–S(2)	1.740(4)
C(1)–C(11)	1.481(6)	C(6)–C(11)	1.479(6)
N(5)–Cd(1)–N(1)	95.03(15)	N(5)–Cd(1)–S(1)	109.32(13)
N(5)–Cd(1)–N(3)	145.66(15)	N(1)–Cd(1)–S(1)	143.34(9)
N(3)–Cd(1)–N(1)	69.11(12)	N(1)–Cd(1)–N(2)#1	90.47(13)
N(3)–Cd(1)–S(1)	75.54(12)	N(2)#1–Cd(1)–S(1)	115.73(10)
N(3)–Cd(1)–N(2)#1	119.33(12)	N(5)–Cd(1)–N(2)#1	89.95(14)

sulfur atom S(1) of the Schiff base, together with the N(5) atom of the thiocyanate ligand, comprise the basal plane of the square-pyramid whereas the pyridine nitrogen atom N(2) of another ligand occupies the apical position. Like the $[Zn(dpksbz)_2]$ complex, the ligand is also coordinated to the cadmium(II) ion in its iminothiolate form. The C–S distance of 1.739(5) Å (Table 5) agrees well with those found in related compounds being intermediate between 1.82 Å for a C–S single bond and 1.56 Å for a C=S double bond [56]. The C(11)–N(3) [1.28(1) Å] and C(12)–N(4) [1.36(1) Å] bond distances are indicative of considerable double bond character. The Cd–S distance, 2.5302(13) Å is shorter than that found in the related five-coordinate cadmium(II) complex of 2-formylpyridine-thiosemicarbazone (Hfptsc), whose structure has been reported [57]. The shorter Cd–S bond in the present complex compared to that in $[Cd(fptsc)Cl_2]$ can be attributed to the different nature of the sulfur donor. In $[Cd(dpksbz)NCS]_2$, the Schiff base is bonded to the cadmium(II) via the thiolate sulfur atom, whereas in $[Cd(fptsc)Cl_2]$, a thione sulfur is involved in bonding. Since a metal–thiolate bond is expected to be stronger than a metal–thione bond, especially with a *Class b* metal ion like the cadmium(II) ion, the Cd–S bond in the present complex is expected to be shorter than that in $[Cd(fptsc)Cl_2]$. The $Cd–N_{py}$ and $Cd–N_{azomethine}$ bond distances, 2.357(4) and 2.322(3) Å, respectively, in $[Cd(dpksbz)NCS]_2$ compare well with those in $[Cd(fptsc)Cl_2]$. For the purpose of comparison, bond distances in some five-coordinate cadmium(II) complexes of related ligands whose structures have been determined by X-ray crystallography are given in Table 7. It is evident that most bonds compare well with each other although bonds in $[Cd(dpksbz)NCS]_2$ are generally shorter than those in related five-coordinate complexes. An examination of the bond length data in Table 7 also shows that the $Cd–N_{py}$ distances in all these complexes are significantly different from the $Cd–N_{imine}$ distances. This difference in the metal–nitrogen bond lengths has also been observed in almost all bis- and mono-ligand metal complexes of tridentate thiosemicarbazone and dithiocarbazate ligands. A comparison of bond distances in the hydrazine side chain of the ligand (Table 7) shows that, while there is little variation in the N(3)–C(11) and N(4)–N(3) bonds, the largest variation occurs in the C(12)–N(4) and C(12)–S(1) bonds. The $[Cd(dpksbz)NCS]_2$ complex has the shortest C(12)–N(4) bond but the C(12)–S(1) bond is longer than in most complexes. Tautomerization of thiosemicarbazone or dithiocarbazate ligand to the iminiothiolate form is expected to cause a lengthening of the C–S bond, but in most complexes, the length of the C–S bond falls between a C–S single bond and C=S double bond indicating extensive electron delocalization over the C–N–N–C–S chain.

Table 7
Comparison of bond lengths (Å) in some five-coordinate cadmium(II) complexes of sulfur–nitrogen chelating agents

Bond	$[Cd(Hfptsc)Cl_2]$ [a]	$[Cd(dpksbz)NCS]_2$ [b]	$[Cd(pftsc)Cl_2]$ [c]	$[Cd(pftsc)Br_2]$	$[Cd(pftsc)I_2]$
Cd–S	2.583(1)	2.5302(13)	2.596(3)	2.579(2)	2.601(3)
$Cd–N_{py}$	2.374(3)	2.357(4)	2.384(6)	2.385(7)	2.325(12)
$Cd–N_{imine}$	2.359(3)	2.322(3)	2.307(6)	2.327(6)	2.313(12)
C(12)–N(4)	1.356(4)	1.294(5)	1.332(9)	1.337(10)	1.340(15)
N(3)–C(11)	1.282(4)	1.290(5)	1.281(9)	1.288(9)	1.322(16)
N(4)–N(3)	1.355(4)	1.374(5)	1.380(9)	1.375(8)	1.399(11)
C(12)–S(1)	1.687(4)	1.739(5)	1.706(8)	1.693 (7)	1.671(15)
Ref.	[57]	this work	[58]	[58]	[58]

[a] Hfptsc, the 2-formylpyridine thiosemicarbazone.
[b] dpksbz, anionic form of the di-2-pyridylketone Schiff base of *S*-benzyldithiocarbazate.
[c] pftsc, 2-pyridineformamide thiosemicarbazone.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos., $[Zn(dpksbz)_2]$: 180639 and $[Cd(dpksbz)NCS]_2$: 180637. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www http://www.ccdc.cam.ac.uk).

Acknowledgements

M.A.A. and A.H.M. thank Universiti Brunei Darussalam for partial support and Awg Mohd Jamil Bin Hj Abd Hamid, Technical Officer, Department of Chemistry, Univeristi Brunei Darussalam, for technical assistance.

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