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Coordination chemistry and bioactivity of some metal complexes containing two isomeric bidentate NS Schiff bases derived from *S*-benzyldithiocarbazate and the X-ray crystal structures of *S*-benzyl-β-*N*-(5-methyl-2-furylmethylene)dithiocarbazate and bis[*S*-benzyl-β-*N*-(2-furylmethylketone)dithiocarbazato]cadmium(II)

M.T.H. Tarafder [a,1], Teng-Jin Khoo [a], Karen A. Crouse [a,*], A.M. Ali [b], B.M. Yamin [c], H.-K. Fun [d]

[a] *Department of Chemistry, University Putra Malaysia, 43400 Serdang, Selangor, Malaysia*
[b] *Department of Biotechnology, University Putra Malaysia, 43400 Serdang, Selangor, Malaysia*
[c] *School of Chemical Sciences and Food Technology, University Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia*
[d] *X-ray Crystallography Unit, School of Physics, University Sains Malaysia, 11800 Minden, Penang, Malaysia*

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Abstract

Isomeric bidentate ligands having nitrogen–sulfur donor sequence were prepared by condensing *S*-benzyldithiocarbazate (SBDTC) with 5-methyl-2-furyladehyde (NS) and 2-furylmethylketone (NS′). Complexes of these ligands with lead, tin, iron, cobalt and cadmium gave complexes of $[M(L)_2]$ (M = Pb, Fe and Cd) and $[M(L)_2]Cl_n$ (M = Sn, $n = 2$ and Co, $n = 1$) (L = NS and NS′). The compounds have been characterized by spectroscopic studies (infrared, ^{1}H NMR and electronic spectra). X-ray crystallographic analysis of *S*-benzyl-β-*N*-(5-methyl-2-furylmethylene)dithiocarbazate shows the presence of two independent molecules in the asymmetric unit. The molecule adopts a *trans–cis* configuration, as was observed in other analogues, such as SBDTC where the furylmethylene and benzyl groups are *trans* and *cis* about the N–C and C–S bonds, respectively. The molecular structure of bis[*S*-benzyl-β-*N*-(2-furylmethylketone)dithiocarbazato]cadmium(II) shows a tetrahedral geometry about the central cadmium atom with the bidentate ligand coordinating through the thioketo sulfur and the azomethine nitrogen atoms. The lead(II) complex of the NS ligand was highly cytotoxic against leukemic cells (CEM-SS) with a CD_{50} of 3.25 μg cm^{-3} while antimicrobial screening showed that the $[Fe(NS)_2]Cl_2 \cdot H_2O$ complex was effective against *Aspergillus achraceous*.

Keywords: Schiff base ligands; Cadmium(II) complexes; Crystal structures; Dithiocarbazate Schiff base crystal structures; Metal complexes; Bioactivity

1. Introduction

Considerable interest has been shown in metal complexes of thiocarbazate derivatives especially those having NNS donor sequences [1]. These compounds warrant further study because they provide an interesting series of ligands whose properties can be greatly modified by introducing different organic substituents, thereby giving variation in donor properties. These ligands interact with metal ions to give structures of different geometry and properties and they are often biologically active [2,3]. To date, reports of the biological properties of these metal–dithiocarbazato complexes are still lacking since previous studies concentrated on synthesis and characterization [4–6]. Furthermore, limited studies have been done on ligands having ONS donor sequences [7,8]. Therefore, as part of our ongoing

* Corresponding author. Tel.: +603-894-66788; fax: +603-894-35380
E-mail address: crouse@pc.jaring.my (K.A. Crouse).
[1] Present address: Department of Chemistry, Rajshahi University, Rajshahi 6205, Bangladesh.

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study on ligands derived from *S*-benzyldithiocarbazate (SBDTC), we report herein the synthesis, characterization and bioactivity of some transition metal (Fe^{2+} and Co^{2+}) and non-transition metal (Cd^{2+}, Pb^{2+} and Sn^{2+}) complexes of isomeric nitrogen–sulfur donor ligands formed between SBDTC with 5-methyl-2-furaldehyde (NS), (Fig. 1) and 2-furaldehyde (NS′), (Fig. 2). The structures of *S*-benzyl-β-*N*-(5-methyl-2-furyl methylene)dithiocarbazate, NS, free ligand and bis[*S*-benzyl-β-*N*-(2-furylmethylketone) dithiocarbazato] cadmium(II), $[Cd(NS')_2]$, as determined by X-ray analysis of single crystals are also given.

2. Experimental

All chemicals and solvents were of analytical grade and were used as received.

2.1. Preparation of S-benzyldithiocarbazate (SBDTC)

SBDTC was prepared as previously reported [9].

2.2. General method for synthesizing Schiff bases

A solution of SBDTC (1.98 g, 0.1 mol) in absolute ethanol (40 cm^3) was added to an equimolar solution of 5-methyl-2-furyladehyde or 2-furylmethylketone in 50 cm^3 of the same solvent. The mixture was heated on a steam bath for 10 min and then cooled to 0 °C in an ice bath. Precipitated Schiff bases were filtered, washed with cold ethanol and dried in vacuo over silica gel. The yield and melting point were recorded for each product.

2.3. General method for synthesis of metal complexes

Schiff base (0.0076 mol) prepared as outlined in Section 2.2 was dissolved in ethanol (50 cm^3) in the presence of an equimolar amount of potassium hydroxide (0.4 g). The clear solution was treated with a solution containing a stoichiometric amount of metal salt in the same solvent ($\sim$50 cm^3). The mixture was heated at 90 °C for 5 min and subsequently cooled in an ice–salt bath. The product was isolated and washed with ethanol. It was dried in a vacuum desiccator over P_2O_5. The metal salts used were $SnCl_2$, $FeCl_3$, $CoCl_2$, $Pb(CH_3COO)_2\cdot 3H_2O$ and $Cd(CH_3COO)_2\cdot 2H_2O$.

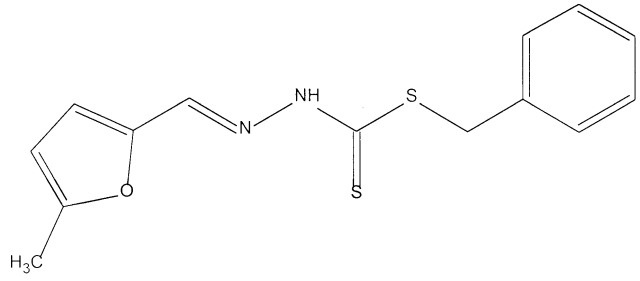

Fig. 1. Chemical structure of *S*-benzyl-β-*N*-(5-methyl-2-furylmethylene) dithiocarbazate.

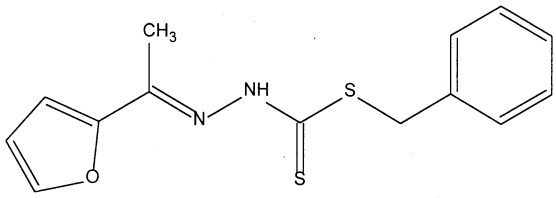

Fig. 2. Chemical structure of *S*-benzyl-β-*N*-(2-furylmethylketone) dithiocarbazate.

2.4. Physical measurements

The analyses for carbon, hydrogen, nitrogen and sulfur were carried out using a LECO CHNS-932 instrument. The IR spectra in KBr pellets were recorded using a Perkin–Elmer FT IR 1750X spectrophotometer (4000–400 cm^{-1}). The molar conductance of 10^{-3} M solutions of the metal complexes in dimethyl sulfoxide (DMSO) were measured at 29 °C using a Jenway 4310 conductivity meter and a dip-type cell with platinized electrode. Magnetic susceptibilities at room temperature were measured using a Sherwood Scientific MSB-AUTO magnetic susceptibility balance. The UV–Vis spectra were run on a Shimadzu UV-2501 PC Recording Spectrophotometer (900–200 nm). All these measurements were done at the Chemistry Department, UPM.

2.5. X-ray structure determination of NS and $[Cd(NS')_2]$

Beautiful dark-yellow crystals of the NS ligand and $[Cd(NS')_2]$ complex were formed after the DMF solutions were allowed to slowly evaporate for a few weeks. A selected crystal was mounted on a SMART CCD diffractometer in each case. Reflection data were measured at 20 °C using graphite monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation with a detector distance of 4 cm and swing angle of $-35°$. The collected data were reduced using the program SAINT [10] and an empirical absorption correction was carried out using SADABS [11]. The structure was solved by direct methods and refined by using the full-matrix least-squares method on F^2_{obs} using the SHELXTL [12] software package. All non-H atoms were anisotropically refined. The hydrogen atoms were located by difference syntheses and refined isotropically. The molecular graphics were created using SHELXTL. Atomic scattering factors and anomalous dispersion correction were taken from the International Table for X-ray Crystallography [13].

2.6. Target microorganisms

Eight pathogenic microbials were used to test the biological potential of the ligands and their complexes. They were *Methicillin resistant sthaphylococcus* (MRSA), *Bacillus subtilis wild type* (B29), *Subtilis mutant* (mutant defective DNA repair-B28), *Pseudomonas aeruginosa* (60690), *Candida albicans* (C.A.), *Aspergillus ochraceous* (398), *Saccaromyces ceciricaee* (20341) and *Candida lypolytica* (2075).

2.6.1. Qualitative antimicrobial assay

Antimicrobial activity of each sample was qualitatively determined by a modified disc diffusion method as previously reported [14]. Antimicrobial activity was indicated by the presence of clear inhibition zones around the discs. Commercially available streptomysin (Sigma, USA) was used for antibacterial control while nystatin (Sigma, USA) was used as antifungal control.

2.6.2. Quantitative antimicrobial assay

Compounds that showed positive (>15 mm) antimicrobial activities with the disc diffusion assay were subjected to the broth dilution method for the quantitative measurement of microbiostatic (inhibitory) activity as described by Hufford and Clark [15]. The lowest concentration that completely inhibited visible microbial growth was recorded as the minimum inhibitory concentration (MIC, μg cm^{-3}). Both streptomycin and nystatin were used as positive controls for bacteria and fungi, respectively.

2.6.3. Cytotoxic assay

The CEM-SS (Human T-lymphoblastic leukemia) cell line was obtained from the National Cancer Institute, USA. The cells were cultured in RPMI-1640 medium supplemented with 10% fetal calf serum. Cytotoxicity was determined using the microtitration of 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) assay (Sigma, USA) as reported by Mosmann [16]. Controls that contained only cells were included for each sample.

Cytotoxicity was expressed as CD_{50}, i.e. the concentration that reduced the absorbance of treated cells by 50% with reference to the control (untreated cells). Doxorubicin and tamoxifen were used as control cytotoxins.

3. Results and discussion

The physical and analytical data for the metal complexes are given in Table 1. All the analytical data obtained are in agreement with the proposed empirical formulae. The characterized ligands are soluble in all organic solvents tested and all compounds are stable in air. For both the NS and NS′ free ligands, the physical and analytical data have been reported earlier [17].

3.1. Infrared spectra

Major vibration bands of the free ligands and metal complexes are given in Table 2. For complexation to occur, the free ligand must exibit thiol–thione tautomers which is brought about by the presence of thioamide –NH–C=S functional group [18,19]. The ν(C=S) band at 1096 cm^{-1} and the ν(NH) band at approximately 3150 cm^{-1} were present, indicating that the free ligands remain as the thione tautomer in the solid state. The ν(NH) band present in the free ligand was not observed in any metal complex, indicating deprotonation of the ligand in situ to form the thiol tautomers for the formation of metal complexes to take place.

The ν(C=S) bands at 1096 and 1026 cm^{-1} for NS and NS′ free ligand were also not observed in the metal complexes, thus supporting the suggestion of coordination through the thione sulfur. Sharp bands observed in the spectrum of the free ligand at approximately 1600 cm^{-1} are assigned to ν(C=N) [20]. In the metal complexes this absorption was shifted to lower frequencies indicating coordination of the azomethine nitrogen to the central metal atoms [21,22]. The lowering in frequency of the ν(N–N) band in all the metal complexes is another clear indication that the coordination involves azomethine nitrogen. There was no

Table 1
Analytical data and physical properties of NS and NS′ complexes

Compound	Color	M.p. (°C)	Found (Calc.) (%)				Yield (%)
			C	H	N	S	
$[Pb(NS)_2]\cdot H_2O$	yellow	198.0	41.79(41.83)	3.66(3.24)	6.99(6.97)		75
$[Sn(NS)_2]Cl_2\cdot 2H_2O$	dark yellow	172.0	41.69(41.81)	3.23(3.73)	6.99(6.97)	16.00(15.93)	80
$[Fe(NS)_2]Cl_2\cdot H_2O$	dark brown	173.5	51.25(51.55)	4.18(4.29)	8.62(8.60)	19.68(19.54)	68
$[Co(NS)_2]\cdot Cl$	brown	222.0	54.70(52.75)	4.18(4.38)	8.94(8.80)	20.40(20.10)	65
$[Pb(NS')_2]$	yellow	228.0	42.65(42.79)	3.59(3.31)	7.23(7.13)		72
$[Cd(NS')_2]$	yellow	217.0	48.94(48.67)	3.85(3.77)	8.12(8.11)	19.17(18.54)	70

Table 2
Infrared spectral data (band maxima) and molar conductance

Compound	Absorption bands (frequency, cm^{-1})					Molar conductance (Ω^{-1} cm^2 mol^{-1})	Ion ratio
	ν(NH)	ν(C=N)	ν(C=S)	ν(N–N)	ν(C–O–C)		
NS	3102	1618	1096	1023	1232 [17,24]		
NS′	3200	1600	1026	1062	1232 [17,24]		
$[Pb(NS)_2]\cdot H_2O$		1612		934	1234	18	
$[Sn(NS)_2]Cl_2\cdot 2H_2O$		1612		936	1234	85	2:1
$[Fe(NS)_2]Cl_2\cdot H_2O$		1592		962	1236	88	2:1
$[Co(NS)_2]\cdot Cl$		1598		962	1230	20	
$[Pb(NS')_2]$		1584		990	1230	22	
$[Cd(NS')_2]$		1590		998	1230	20	

significant displacement of the frequency of the ring breathing and ν(C–O–C) vibrations at 1230 cm^{-1} [7] and no presence of metal oxygen bond stretching observed at 440–450 cm^{-1} [8] in any complex. This shows that there was no coordination by the furanic oxygen. Indeed there is no indication of oxygen bonding to the central metal atom in the crystal structure of the $[Cd(NS)_2]$ complex.

3.2. Magnetic and conductivity data and electronic spectra

At room temperature, magnetic susceptibility (Table 3) measurements show that all the complexes are diamagnetic and low spin except for $[Fe(NS)_2]Cl_2\cdot H_2O$ which has paramagnetic properties with μ_{eff} of 1.77 B.M., characteristic of a square planar structure. All the diamagnetic complexes are four-coordinated and expected to be distorted tetrahedral, as proved for our cadmium complex by its crystal structure. For the iron(II) ion which has a $3d^6$ electron configuration, the magnetic moment (1.77 B.M.) suggests that the iron(II) ion is in a low-spin iron(II) state.

The complexes $[Sn(NS)_2]Cl_2\cdot H_2O$ and $[Fe(NS)_2]Cl_2\cdot H_2O$ exhibit molar conductance values corresponding to 2:1 electrolytes in DMSO. The conductivity presumably arises from solvation according to the following scheme:

$$[Sn(NS)_2]Cl_2\cdot H_2O + DMSO \rightarrow [Sn(NS)_2](DMSO)_2\cdot H_2O + 2Cl^-$$

and

$$[Fe(NS)_2]Cl_2\cdot H_2O + DMSO \rightarrow [Fe(NS)_2](DMSO)_2\cdot H_2O + 2Cl^-$$

The electronic spectrum of the $[Co(NS)_2]$ complex displays two diagnostic absorptions at 393 and 339 nm corresponding to $^1A_{1g}\rightarrow{}^1T_{1g}$ and $^1A_{1g}\rightarrow{}^1T_{2g}$ transitions. The remaining compounds showed bands that are caused by charge transfer.

3.3. Crystal structure studies

3.3.1. Crystal structure of NS (see Table 6)

A perspective view of the ligand with the numbering scheme is shown in Fig. 3. The relevant bond distances and bond angles are given in Table 7. The asymmetric unit consists of two independent *S*-benzyl-β-*N*(5-methyl-2-furylmethylene)dithiocarbazate molecules. The methylfurylmethylenedithiocarbazate moiety of the two molecules are not exactly planar. The methylfuryl plane of (O1–C10–C11–C12–C13–C9) is planar with C14 atom deviated by only −0.030(3) Å. This plane makes a dihedral angle of 11.33(9)° with the S1–S2–N1–N2–C7–C8 plane. Similarly, in the second molecule the methylfuryl O2–C24–C25–C26–C27–C28 is planar with maximum deviation of 0.04(2) Å at the C28

Table 3
UV–Vis spectral of band maxima (λ, nm (log ε)) and magnetic susceptibility of metal complexes

Compound	λ_{max} (nm)	μ_{eff} (B.M.) [a]
$[Pb(NS)_2]\cdot H_2O$	355.5(4.817), 588.0(4.738)	diamagnetic
$[Sn(NS)_2]Cl_2\cdot 2H_2O$	357.5(4.821), 295.5(4.056), 585.0(1.523)	diamagnetic
$[Fe(NS)_2]Cl_2\cdot H_2O$	354.5(6.045), 418.0(5.574), 587.0(5.097)	1.77
$[Co(NS)_2]\cdot Cl$	339.0(4.402), 393.0(4.385)	diamagnetic
$[Pb(NS')_2]$	303.5(4.434), 347.5(4.569)	diamagnetic
$[Cd(NS')_2]$	307.5(4.320), 359.5(4.420)	diamagnetic

Beer's law: $A = \varepsilon bc$ where A, absorption, $b = 1$ cm and c, concentration (M), log ε (cm^{-1} mol^{-1} l) are given in parentheses.
[a] Tetrahedral complex, 1.94–2.00 B.M.; distorted square-planar, 1.90–1.93 B.M.; square-planar, 1.85–1.89 B.M.

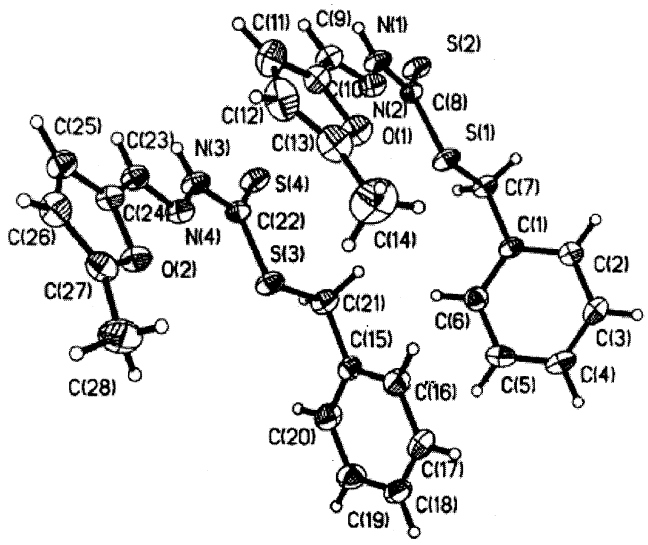

Fig. 3. Molecular structure and atom numbering scheme of (NS).

atom. However, the S3–S4–N3–N4–C4–C5–C6–C7 plane showed large deviation from the planar S3–N3–C21–C22 group at the S4 and N4 atoms of 0.126(1) and −0.119(1) Å, respectively. The dihedral angle between the methylfurfuryl O2–C24–C25–C26–C27–C28 plane and S3–N3–C21–C22 is 6.41(16)° which is smaller than in the first molecule. The phenyl ring C1–C2–C3–C4–C5–C6–C7 is nearly perpendicular to the methylene-dithiocarbazate S1–S2–N1–N2–C7–C8 of 80.21(6)°. In the second molecule, the phenyl ring C15–C16–C17–C18–C19–C20 makes a dihedral angle of 74.12(9)° with the S3–N3–C21–C22 plane.

The C8–S2 and C22–S4 bond lengths in the two molecules of 1.6669(15) and 1.6667(15) Å, respectively, are intermediate between 1.82 Å for C–S single bond and 1.56 Å for C=S double bond [23] and is in agreement with the reported value in SBDTC [24]. Thus, the compound exits as a thioketo tautomeric form. The furylmethylene and benzyl groups are *trans* and *cis* with respect to the ion about the the C–N and C–S bonds, respectively. A similar configuration was also reported for SBDTC [24]. The N1–N2 and N3–N4

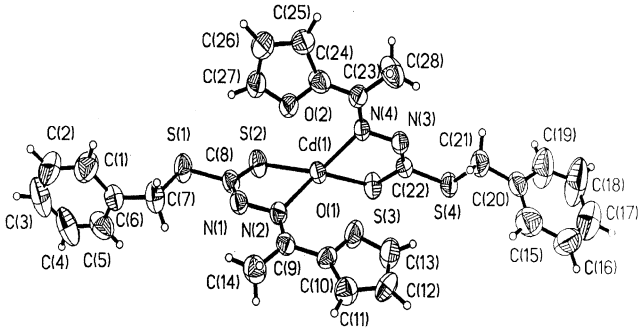

Fig. 4. Molecular structure and atom numbering scheme of $[Cd(NS')_2]$.

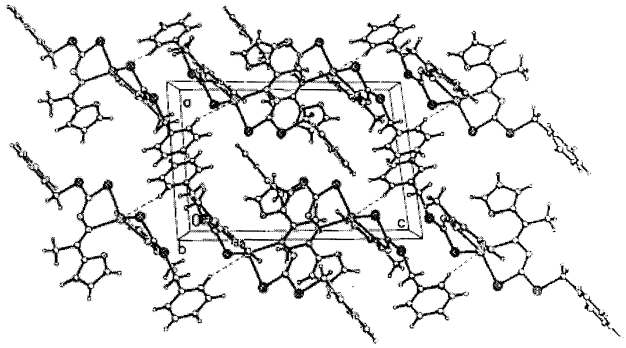

Fig. 5. Packing arrangement of $[Cd(NS')_2]$.

bond distances of 1.3820(16) and 1.3824(17) Å are slightly shorter than the corresponding bond lengths in unsubstituted SBDTC (1.406(3) Å) [24] due to the delocalised electrons of the furan ring. The two molecules are connected by hydrogen bondings, N1–H1A···S4 (H1A···S4 2.578 Å) and N3–H3A···S2 (H3A···S2 2.589 Å), and therefore, are arranged as dimers parallel to the *b* and *c* axes in the lattice.

3.3.2. Crystal structure of the $[Cd(NS')_2]$ complex

The molecular structure of the $[Cd(NS')_2]$ complex is shown in Fig. 4, while Fig. 5 shows the packing arrangement of the molecules on the ac plane. The central cadmium atom is bis-chelated by the uninegatively charged bidentate ligand through the azomethine nitrogen atoms, N2 and N4, and the thiolate sulfur atoms, S2 and S3. Both nitrogen atoms (N2, N4) and sulfur atoms (S2 and S3) from the two ligands are coordinated at opposite positions. The formation of this complex gives a distorted tetrahedral geometry about the central cadmium atom with angles of 78.89(10)°–137.72(11)°. The bond lengths of the complex are comparable to the analogous complex bis[*S*-benzyl-β-*N*(5-methyl-2-furylmethylene)dithiocarbazato]cadmium(II) reported earlier [17]. Both complexes show non-participation of the furanic oxygen in the coordination to the central cadmium atom. This observation, however, is in contrast to the one proposed by Jouad et al. [25]. There is slight variation in corresponding bond lengths in the C9–N2–N1–C8–S1–C17 and C23–N4–N3–C22–S4–C21 moieties in the complex. The largest variation is shown by the C9–C10 and C23–C24 of 1.466(6) and 1.419(7) Å, respectively. The C8–N1 and C22–N3 bond lengths of 1.257(6) and 1.300(7) Å clearly indicate the complexation involves deprotonation at N1 and N3 atoms of the ligand. The conjugation system of the moieties is influenced by the coordination with the metal as shown by the slight bond lengthenings compared with the uncomplexed ligand. The N1–N2 and N3–N4 distances of of 1.424(5) and 1.417(5) Å are slightly longer than the normal values of about 1.36–1.38 Å [22,26]. The corresponding bond lengths in

octahedral tridentate bis[*S*-benzyl-β-*N*(2-pyridylmethylene)dithiocarbazato]zinc(II) are 1.379(4) and 1.374(4) Å, respectively [1]. The cadmium atom makes a linear plane with the furyl groups Cd1–O1–N1–N2–C9–C10–C11–C12–C13–C14, with maximum deviation of 0.048(4) Å at C11, and Cd1–O2–N3–N4–C23–C24–C25–C26–C27 with maximum deviation of 0.032(7) Å at N4, respectively. The cadmium-bidentate rings are less planar. The Cd1–S2–N1–N2–C8 has a minimum deviation of 0.085(5) Å at the N1 atom and maximum deviation of 0.181(4) Å at the S4 atom. For the Cd1–S3–N3–N4–C22 plane the minimum deviation is 0.096(5) Å at the N3 atom and the maximum deviation is 0.219(9) Å at the N4 atom. The dihedral angles between the planar benzyl planes C1–C2–C3–C4–C5–C6–C7 and C15–C16–C17–C18–C19–C20–C21 with their corresponding furyl planes O1–C10–C11–C12–C13–C14 (maximum deviation at C9, 0.021(5) Å) and O2–C32–C24–C25–C26–C27 (maximum deviation at C24, 0.047(6) Å) are quite different with values of 83.9(4)° and 67.7(4)°, respectively. The intramolecular interaction of C14–H14A···N1 (H14A···N1, 2.259 Å) and C28–H28A···N3 (H28A···N3, 2.248 Å) result in the formation of six-membered rings in the ligand moieties and may contribute to the planarity of the furyl-Schiff base group of the complex.

3.4. Biological activity

3.4.1. Cytotoxic activity

$PbNO_3$ salt is inactive, but chelation by the NS is active, but chelation by Nsfree ligand gives $[Pb(NS)_2]\cdot H_2O$ complex of high cytoxicity against CEM-SS with a CD_{50} of 3.25 μg cm^{-1}. Most of our recent research on cadmium(II) complexes [17] showed high cytotoxic activity on all of the cell lines, but the activity of the $[Cd(NS')_2]$ complex was greatly reduced and was even much lower than the simple cadmium(II) salt. The remainder of the complexes investigated do not possess any significant activity against CEM-SS, with the exception of $[Sn(NS)_2]Cl_2\cdot 2H_2O$ and $[Pb(NS')_2]$ complexes which are toxic at higher concentrations. Detailed results against CEM-SS cell lines are shown in Table 4.

Table 4
Results of screening against leukemic cells (CEM-SS)

Compound	CD_{50} (μg cm^{-3}) [a] CEM-SS
$[Fe(NS)_2]Cl_2\cdot H_2O$	–
$[Sn(NS)_2]Cl_2\cdot 2H_2O$	29
$[Co(NS)_2]\cdot Cl$	–
$[Pb(NS)_2]\cdot H_2O$	3.25
$[Cd(NS')_2]$	–
$[Pb(NS')_2]$	29.7
Metal salts	
$SnCl_2$	–
$FeCl_2$	–
$PbNO_3$	–
$CoCl_3$	12.00
$CdBr_2$	14.00
Standard	
Doxorubicin	0.10
Tamoxifen	36.00

–, inactive.
[a] CD_{50} (μg cm^{-3}), cytotoxic dose at 50%, i.e. the concentration to reduce growth of cancer cells by 50%.

3.4.2. Antimicrobial assay

Preliminary screening for antimicrobial activity was done on all compounds. All the compounds showed clear inhibition zones of 10 mm and above against *A. ochraceous* except the $[Cd(NS')_2]$ complex. $[Fe(NS)_2]Cl_2\cdot H_2O$ was active against *A. ochraceous* with a clear inhibition zone of 21 mm. The qualitative screening results are shown in Table 5.

Only $[Fe(NS)_2]Cl_2\cdot H_2O$ was used for quantitative measurement of MIC. Its MIC value of 100 000 μg cm^{-3} towards *A. ochraceous* is higher than that for the standard drug nystatin (3125 μg cm^{-3}).

Table 5
Qualitative antimicrobial assay results [a] (diameter in mm)

Compound	MRSA	B29	B28	60690	C.A.	398	20341	2075
$[Fe(NS)_2]Cl_2\cdot H_2O$	8	7	8	8	13.5	21	11	11
$[Pb(NS)_2]\cdot H_2O$	–	8	7	–	–	12	–	–
$[Sn(NS)_2]Cl_2\cdot 2H_2O$	8	8	9		8	12	8	–
$[Cd(NS')_2]$	–	–	–	–	11	8	11	–
$[Pb(NS')_2]$	8	7	8	8	7	12	–	8
Streptomysin (antibacterial control)	31	30	30	30	–	–	–	–
Nystatin (antifungal control)	–	–	–	–	21	25	24	27

Methicillin resistant sthaphylococcus (MRSA); *Bacillus subtilis wild* type (B29); *Subtilis mutant* (mutant defective DNA repair-B28); *P. aeruginosa* (60690); *C. albicans* (C.A); *A. ochraceous* (398); *S. ceciricaee* (20341); *C. lypolytica* (2075); '–', inactive.
[a] Diameter of 15 mm and above considered active.

Table 6
Summary of crystal data and structure refinement parameters for NS and $[Cd(NS')_2]$

Compound	NS	$[Cd(NS')_2]$
Chemical formula	$C_{14}H_{14}N_2OS_2$	$C_{28}H_{26}CdN_4O_2S_4$
Formula weight	290.39	691.17
Crystal class	Monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$
a (Å)	9.7144(2)	10.5620(2)
b (Å)	23.26670(10)	10.5926(2)
c (Å)	12.93790(10)	14.9458(3)
α (°)	90	95.377(1)
β (°)	97.2500(10)	93.468(1)
γ (°)	90	114.156(1)
V (Å^3)	2900.87(7)	1509.97(5)
Z	8	2
Mo Kα (Å)	0.71073	0.71073
T (K)	293(2)	293(2)
ρ_{calc} (Mg m^{-3})	1.330	1.520
μ (mm^{-1})	0.360	1.032
Sample dimension (mm)	0.48 × 0.46 × 0.42	0.46 × 0.34 × 0.32
$F(000)$	1216	700
Total number of reflections collected	19 747	10 658
Independent reflections	6962 [$R_{int} = 0.0669$]	7007 [$R_{int} = 0.0845$]
Number of data used for refinement	6962	7007
Number of parameters refined	346	353
Goodness-of-fit on F^2	0.944	0.970
Correction	empirical	empirical
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0416$, $wR_2 = 0.1090$	$R_1 = 0.0716$, $wR_2 = 0.1670$
R indices (all data)	$R_1 = 0.0643$, $wR_2 = 0.1184$	$R_1 = 0.0919$, $wR_2 = 0.1845$
Largest and smallest peak (e Å^{-3})	0.326 and −0.265	1.259 and −1.990

Table 7
Selected bond lengths (Å) and bond angles (°) for NS and $[Cd(NS')_2]$

NS		$[Cd(NS')_2]$	
Bond lengths			
S(1)–C(8)	1.7506(14)	Cd(1)–N(4)	2.285(4)
S(1)–C(7)	1.8197(17)	Cd(1)–N(2)	2.315(4)
S(2)–C(8)	1.6669(195)	Cd(1)–S(2)	2.4813(13)
S(3)–C(22)	1.7528(15)	Cd(1)–S(3)	2.4827(13)
S(3)–C(21)	1.8149(18)	S(1)–C(8)	1.770(5)
S(4)–C(22)	1.6667(15)	S(1)–C(7)	1.812(6)
N(1)–C(8)	1.3348(19)	S(2)–C(8)	1.747(6)
N(1)–N(2)	1.3820(16)	S(3)–C(22)	1.755(6)
N(2)–C(9)	1.275(2)	S(4)–C(22)	1.730(5)
N(3)–C(22)	1.337(2)	S(4)–C(21)	1.837(6)
N(3)–N(4)	1.3824(17)	N(1)–C(8)	1.257(6)
N(4)–C(23)	1.285(2)	N(1)–N(2)	1.424(5)
		N(2)–C(9)	1.261(6)
		N(3)–C(22)	1.300(7)
		N(3)–N(4)	1.417(5)
		N(4)–C(23)	1.292(7)
Bond angles			
C(8)–S(1)–C(7)	102.37(7)	N(4)–Cd(1)–N(2)	115.98(15)
C(22)–S(3)–C(21)	101.91(8)	N(4)–Cd(1)–S(2)	137.20(11)
C(8)–N(1)–N(2)	119.36(12)	N(2)–Cd(1)–S(2)	79.11(10)
C(9)–N(2)–N(1)	115.86(13)	N(4)–Cd(1)–S(3)	78.89(10)
C(10)–O(1)–C(13)	106.65(15)	N(2)–Cd(1)–S(3)	136.04(11)
C(27)–O(2)–C(24)	106.23(13)	S(2)–Cd(1)–S(3)	119.26(5)
C(8)–N(1)–N(2)	119.36(12)	C(8)–S(1)–C(7)	104.6(3)
C(9)–N(2)–N(1)	115.86(13)	C(8)–S(2)–Cd(1)	93.15(17)
C(22)–N(3)–N(4)	120.74(13)	C(22)–S(3)–Cd(1)	93.15(17)
C(23)–N(4)–N(3)	114.38(13)	C(22)–S(4)–C(21)	104.5(3)
C(1)–C(7)–S(1)	106.30(10)	C(10)–O(1)–C(13)	106.3(4)
N(1)–C(8)–S(2)	121.75(11)	C(27)–O(2)–C(24)	107.8(4)
N(1)–C(8)–S(1)	112.96(11)	C(8)–N(1)–N(2)	115.3(4)
S(2)–C(8)–S(1)	125.29(9)	C(9)–N(2)–N(1)	114.3(4)
N(2)–C(9)–C(10)	121.32(15)	C(9)–N(2)–Cd(1)	131.3(3)
C(11)–C(10)–O(1)	109.51(15)	N(1)–N(2)–Cd(1)	114.4(3)
N(3)–C(22)–S(4)	121.48(12)	C(22)–N(3)–N(4)	114.6(4)
S(4)–C(22)–S(3)	125.23(10)	C(23)–N(4)–N(3)	113.6(4)
N(4)–C(23)–C(24)	123.11(15)	C(23)–N(4)–Cd(1)	130.7(3)
		N(3)–N(4)–Cd(1)	115.3(3)

4. Supplementary material

Crystallographic data for the structural analyses of NS ligand and $[Cd(NS')_2]$ complex have been deposited with the Cambridge Crystallographic Data Center, CCDC 164801 and CCDC 164800. 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).

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