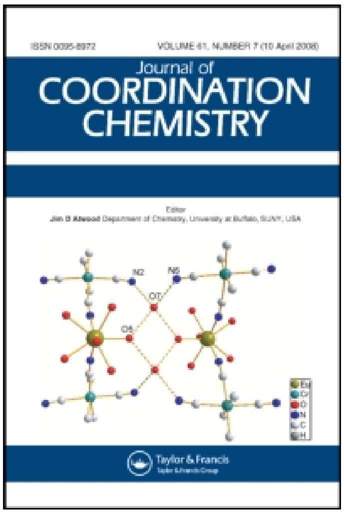

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Synthesis and structure of a Schiff base and its bivalent transition metal complexes

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Synthesis and structure of a Schiff base and its bivalent transition metal complexes

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A Schiff base (HCSmz) was synthesized *via* (*E*)-cinnamaldehyde with S-methyl dithiocarbazate and six bivalent transition metal complexes [M(CSmz)$_2$] (M=Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Hg^{2+}) were prepared. The complexes were characterized by elemental analyses, IR, ^{1}H NMR, and UV-Vis spectra, and the Ni(II) and Zn(II) complexes were also characterized by single crystal X-ray diffraction. After tautomerism of thiotone to thioenol and deprotonization of the thioenol, two ligands chelate the metal by two nitrogens of azomethine and two sulfurs of thioenol. Ni(CSmz)$_2$ crystallizes in the centrosymmetric space group $P2_1/n$ with a perfectly square planar *trans*-configuration with Ni located at the center of the square; crystal packing is stabilized by intra- and intermolecular C–H$\cdots$S hydrogen bonds. Zn(CSmz)$_2$ is in the mirror-symmetric space group $I4_1/a$ in a distorted tetrahedral geometry with two equivalent Zn–N and Zn–S bonds; crystal packing is stabilized by intermolecular C–H$\cdots\pi$ hydrogen bonds.

Keywords: Schiff-base ligand; (*E*)-cinnamaldehyde; S-methyl dithiocarbazate; Synthesis; Complexes of transitional metal ions

1. Introduction

Dithiocarbazic acid, its S-alkyl/aryl esters and their Schiff bases have received considerable attention for: (1) the biological activities of anticancer, antibacterial, antifungal, antiamoebic, and insecticidal activities [1–4], especially S-methyl dithiocarbazate [5–10], (2) they easily form an interesting series of ligands whose properties can be modified by introducing the organic substituents into the molecules, thereby inducing different stereochemistries in the resulting metal complexes [11–14], and (3) their complexes have shown electronic, optical, and magnetic material properties [15–18].

(*E*)-cinnamaldehyde shows not only strong anti-necrosis-tumor and other bioactivities, but also is a food additive [19–21]. In earlier articles, we reported the synthesis and characterization of some metal complexes of Schiff bases derived from the reaction of S-methyl and S-benzyl dithiocarbazate with (*E*)-cinnamonylferrocene or other compounds [22–27]. We report herein a Schiff base (HCSmz) derived from (*E*)-cinnamaldehyde and S-methyldithiocarbazate, its transition metal complexes M(CSmz)$_2$, and the crystal structures of Zn(CSmz)$_2$ and Ni (CSmz)$_2$.

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2. Experimental

2.1. *Reagents and general procedures*

All chemicals used for the preparation of the ligand and complexes were of analytical quality and used without purification. S-methyldithiocarbazate was prepared according to the literature method [22]. The progress of the reaction was monitored by TLC (silica gel H). The analyses for C, H, and N were performed with a Perkin-Elmer PE-2400 SERIES II instrument. IR spectra were recorded on a Bruker TENSOR-27 instrument as KBr discs from 400 to 4000 cm^{-1}. Electronic spectra were measured using a UV-2501 UV-visible spectrophotometer from 200 to 800 nm in $CHCl_3$. ^1H NMR spectra were recorded on a Bruker Avance 600 spectrometer using TMS as an external standard in $CDCl_3$. Molar conductance measurements were made on a DDS-IIA conductometer in $CHCl_3$ or DMF at 20°C. Melting points were measured on a XRC-1 micro-melting point and are uncorrected.

2.2. *Synthesis of (HCSmz)*

(*E*)-cinnamaldehyde (0.01 mol) was dissolved in boiling ethanol (30 mL) and the solution was mixed with a solution of the appropriate S-methyldithiocarbazate (0.01 mol) in methanol (35 mL). The mixture was stirred for 30 min and then left to stand overnight in a refrigerator. The product that formed was filtered off and washed with cold ethanol. After recrystallization from chloroform, yellow crystals of HCSmz (1.69 g) were obtained.

2.3. *Synthesis of the complexes*

$M(OAc)_2 \cdot nH_2O$ ($M=Co^{2+}$, Ni^{2+}, Zn^{2+}, Cd^{2+}, Cu^{2+}, and Hg^{2+}) (0.001 mol) dissolved in ethanol (20 mL) was mixed with a hot solution of the Schiff base (0.002 mol) in the same solvent (30 mL) and the mixture was then refluxed for 1–2 h. On cooling to room temperature, crystals of the transition metal complexes $[M(CSmz)_2]$ were obtained, filtered off, washed with cold ethanol, and dried in a desiccator over silica gel. Yield: 75.0–81.5%.

2.4. *Crystal structure determination*

Single crystals of $Zn(CSmz)_2$ and $Ni(CSmz)_2$ for X-ray analysis were obtained by slow evaporation of their solution in CH_2Cl_2 and ether at room temperature. X-ray data were collected on a Bruker SMART 1000 CCD diffractometer using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) operating in the ω–2θ mode within the range $3.2 \leq 2\theta \leq 55.3$ at 293 K. Data collection and reduction were performed using SMART and SAINT software [28]. An empirical absorption correction was applied using SADABS [29]. The structures were solved by direct methods using SHELXS-97 [30] and refinement was carried out by full-matrix least-squares methods, based on F^2 with anisotropic thermal parameters for all non-hydrogen atoms, and hydrogen atoms were included in the model at their calculated positions and refined isotropically using the SHELXL-97 program package [31]. The molecular and crystal structures are illustrated by PLANTO [32], ORTEP3 [33], and MERCURY [34]. Crystal structure data and refinement details for both complexes are summarized in table 1. Selected bond distances and angles are given in table 2.

3. Results and discussion

3.1. *Synthesis, physical, and electrical properties*

The title complexes can be easily formed by refluxing a mixture of HCSmz and metal(II) acetate in ethanol. Their elemental analyses and physical properties are listed in table 3. The elemental analytical data shows that in every molecule two ligands are bidentate to the metal ion. The formula of the complexes agree with $M(Csmz)_2$ and all compounds are non-electrolytes, that are supported by their molar conductivity data [35].

3.2. *IR spectra*

A partial listing of IR spectra of the ligand and its complexes is given in table 4. In the free ligand, the band appearing at 3168 cm^{-1} may be assigned to ν(N–H) of the thioamide. The ligand does not show any band at *ca* 2550 cm^{-1} indicative of S–H, implying that the ligand remains in the thione form in the solid state. Bands at 2933, 1616, 1065, 1027,

Table 1. Crystal data and structure refinement of $Ni(CSmz)_2$ and $Zn(CSmz)_2$.

Compound	$Ni(CSmz)_2$	$Zn(CSmz)_2$
Empirical formula	$C_{22}H_{22}N_4S_4Ni$	$C_{22}H_{22}N_4S_4Zn$
Formula weight	529.39	536.11
Color	Brown	Yellow
Crystal size (mm^3)	0.30 × 0.30 × 0.20	0.30 × 0.30 × 0.20
Crystal system	Monoclinic	Tetragonal
Space group	$P2_1/n$	$I4_1/a$
Unit cell dimensions (Å, °)		
a	15.2720(17)	16.7831(11)
b	7.2379(8)	16.7831(11)
c	21.663(3)	18.018(2)
α	90	90
β	90.779(2)	90
γ	90	90
Volume (Å^3), Z	2394.4(5), 4	5075.1(8), 8
Calculated density ($g\,cm^{-1}$)	1.469	1.574
$F(000)$	1096	2208
Temperature (K)	296(2)	296(2)
Absorption coefficient (mm^{-1})	1.177	1.314
Limiting indices	$-19 \le h \le 18$; $-9 \le k \le 9$; $-28 \le l \le 28$	$-21 \le h \le 21$; $-21 \le k \le 21$; $-23 \le l \le 23$
Completeness to θ	99.20%	99.90%
θ range for data collection (°)	1.62–27.68	1.66–27.63
Absorption correction	Multi-scan	Multi-scan
Reflections collected	20,393	21,914
Independent reflection	5560 [R(int) = 0.036]	2953 [R(int) = 0.04]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5560/0/282	2953/0/142
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0344$, $wR_2 = 0.0735$	$R_1 = 0.0340$, $wR_2 = 0.0854$
R indices (all data)	$R_1 = 0.0560$, $wR_2 = 0.0823$	$R_1 = 0.0582$, $wR_2 = 0.1027$
Goodness-of-fit on F^2	1.01	1.03
Largest difference peak and hole (e Å^{-3})	0.284 and −0.265	0.306 and −0.165

Table 2. Selected bond lengths (Å) and angles (°) of Ni(CSmz)$_2$ and Zn(CSmz)$_2$.

Ni(CSmz)$_2$			
Bond lengths			
Ni1–N3	1.901(2)	S1–C11	1.749(2)
Ni1–N1	1.909(2)	S1–C10	1.795(3)
Ni1–S3	2.161(1)	N3–C9	1.306(3)
Ni1–S2	2.195(1)	N3–N4	1.413(2)
S3–C12	1.724(2)	N1–C14	1.299(3)
S2–C11	1.720(2)	N1–N2	1.413(2)
S4–C12	1.743(2)	N4–C11	1.290(3)
S4–C13	1.795(2)	C12–N2	1.289(3)
Bond angles			
N1–Ni1–N3	177.35(8)	N3–Ni1–S3	91.87(5)
S2–Ni1–S3	172.29(3)	C12–S3–Ni1	96.30(7)
N1–Ni1–S3	86.41(5)	C11–S2–Ni1	94.18(8)
N3–Ni1–S2	85.76(5)	N2–N1–Ni1	120.8(1)
N1–Ni1–S2	95.68(5)		
Zn(CSmz)$_2$			
Bond lengths			
Zn1–N3	2.045(2)	S3–C12	1.742(3)
Zn1–S3	2.280(1)	C12–N2	1.289(3)
S2–C12	1.749(2)	N3–C9	1.281(3)
S2–C13	1.790(3)	N2–N3	1.393(3)
Bond angles			
N3–Zn1–N3a	109.78(10)	N3–N2–C12	114.53(18)
N3–Zn1–S3a	86.45(5)	N2–C12–S3	129.09(19)
N3–Zn1–S3	124.50(6)	C12–S3–Zn1	92.69(9)
S3a–Zn1–S3	127.97(5)	S2–C12–N2	118.39(18)
Zn1–N3–C9	128.42(15)	S2–C12–S3	112.52(13)
Zn1–N3–N2	117.10(13)	C12–S1–C11	102.89(13)
N2–N3–C9	114.48(18)		

and 1288 cm^{-1} are attributed to ν(H–C of HC=N), ν(C=N), ν(C=S), ν(C–S), and ν(SC–N), respectively [21, 36]; ν(N–N) and ν(*trans*-H–C of HC=CH) may be in the same peak at 978 cm^{-1}. In addition, the stretch and bending absorptions of C–H bond in methyl group appear at 2850 and 1431 cm^{-1}, respectively [36], and the bands at 1590 and 1486, 734, and 968 cm^{-1} are attributed to stretch and bending absorptions of C–H in phenyl.

The IR spectra of the complexes show significant changes to the free ligand. Bands attributed to ν(N–H), ν(C–N), and ν(C=S) disappear and a new band attributed to ν(S–C) is observed at *ca* 1039–1052 cm^{-1}. The ν(C=N) band in free ligand at 1616 cm^{-1} shifts to lower frequency by 4–14 cm^{-1} in its complexes and the ν(N–N) band at 968 cm^{-1} is higher by 4–20 cm^{-1}, due to the formation of a longer conjugated chain of Ph–CH=CH=N–N=C, *via* nitrogen in amide (N–CS$_2$Me), after deprotonation and further reduction of electron density and frequency of C=N, and an increase of electron density and frequency in the N–N single bond [17, 36–38]. All other bands are largely unchanged in both position and intensity, relative to the free ligand.

3.3. ^{1}*H NMR spectra*

The ^{1}H NMR spectra of the ligand and its complexes recorded using CDCl$_3$ are shown in table 5. Compared with the proton signals of (*E*)-Ph–C$^{\beta}$H=C$^{\alpha}$H–C^{1}HO [21], the free

Table 3. Elemental analyses and physical properties of the ligand and complexes.

				Analysis (Anal. Calcd %)			Λm ($\Omega\,cm^2\,mol^{-1}$)	
Compound	Color	Yield (%)	m.p. (°C)	C	H	N	in DMF	in CH_3Cl
HCSmz	Yellow	70.3	172–174	55.77 (55.90)	4.98 (5.12)	11.62 (11.85)	16. 0	0.50
$Co(CSmz)_2$	Brown-red	76.0	168–170	49.76 (49.89)	4.06 (4.19)	10.45 (10.58)	2.30	0.38
$Ni(CSmz)_2$	Brown	81.5	250–252	49.60 (49.81)	4.16 (4.19)	10.36 (10.58)	2.55	0.20
$Cu(CSmz)_2$	Black	78.4	188–190	49.26 (49.46)	4.05 (4.15)	10.27 (10.49)	2.45	0.18
$Zn(CSmz)_2$	Yellow	75.0	202–204	49.16 (49.29)	4.19 (4.14)	10.38 (10.45)	1.85	0.16
$Cd(CSmz)_2$	Bright-yellow	80.1	200–202	45.25 (45.32)	3.92 (3.80)	9.70 (9.61)	1.95	0.70
$Hg(CSmz)_2$	Yellow	78.2	158–160	49.26 (49.36)	4.05 (4.30)	10.27 (10.35)	2.30	0.64

ligand HCSmz has two protons β-H and H–C=N with large upfield shift and α-H with a slight downfield shift; their coupling constants are much larger [39].

The free Schiff bases also have two peaks at 10.23 ppm and 4.85 ppm that are attributable to the thioamide N–H and the S–H, respectively; these peaks disappear on deuteration [40], indicating that in solution the ligand exists predominantly as thione–thiol tautomer [41]. The lower S–H resonance also shows that the N···H–S hydrogen bond forms after thione–thiol tautomerism of the ligand. The proton signal of the S–Me is at 2.71 ppm [39].

The ligand undergoes enolization and the protons of N–H and S–H disappear upon coordination with metal ions, and α-H, β-H, and H–C=N are shifted downfield; α-H is shifted downfield slightly more than β-H in complexes, reverse of the free ligand, fromnitrogen of H–C=N becoming more electron-withdrawing and making the electron cloud of α-C smaller than that of β-C after coordination. $Co(CSmz)_2$ and $Cu(CSmz)_2$ are paramagnetic.

3.4. *UV spectra*

UV spectral data of the ligand and its complexes are listed in table 6. Compared with its parent compound (*E*)-cinnamaldehyde which has B-band $\pi \rightarrow \pi^*$ transition of the phenyl ring at 285 nm [21], the ligand has 294.3 nm and 353.5 nm from the R-band $n \rightarrow \pi^*$ transition of a long conjugated chain of –CH=CH–CH=N and making the B-band red shift. After coordination with metal(II), the B-band and the R-band show a bathochromic shift of *ca* 19.1–26.2 nm and 15.5–60.4 nm, respectively, due to the formation of a large conjugated system Ph–CH=CH–CH=N–N=C–S^- and the charge transfer of ligand to the metal ions *via* sulfur and nitrogen. $Ni(CSmz)_2$ d–d transitions at *ca* 486.0 nm shows square-planar configuration [25], proved by the crystal structure.

3.5. *Crystal structures*

3.5.1. Crystal structure of $Ni(CSmz)_2$. An ORTEP of $Ni(CSmz)_2$ with atom numbering is shown in figure 1 and a view of the molecular packing in the crystal

Table 4. Some IR frequencies of the ligand and complexes (cm^{-1}).

Compound	ν(N–H)	ν(C–H of C=N)	ν(C=N)	ν(N–N)	ν(C=S)	ν(C–SM)	ν(C–S)	ν(SC–N)	ν(H–C of HC$^{\alpha}$=C$^{\beta}$H)	ν(CH$_3$)	δ(CH$_3$)	ν(C=C of Ph–)		δ(C–H of Ph–)	
HCSmz	3168s	2933 m	1616 w	978 vs	1065 vs		1027 m	1288 m	978 vs	2850 w	1431 s	1590 vs	1486 s	734 s	698 s
Co(CSmz)$_2$		2921 w	1608 m	1002 s		1052 s	1012 vs		975 vs	2855 w	1430 w	1575 vs	1474 vs	751 s	690 s
Ni(CSmz)$_2$		2919 w	1605 s	1003 s		1048 w	1018 vs		970 vs	2853 w	1430 m	1565 vs	1490 vs	748 s	684 s
Cu(CSmz)$_2$		2906 w	1602 m	1005 s		1047 s	1017 m		977 vs	2848 w	1431 m	1593 vs	1472 s	774 s	700 s
Zn(CSmz)$_2$		2922 w	1608 s	1004 s		1050 s	1018 m		968 vs	2852 w	1432 m	1583 vs	1450 s	750 s	697 s
Cd(CSmz)$_2$		2917 w	1607 w	1003 s		1046 w	1020 m		964 vs	2850 w	1431 m	1577 vs	1467 s	746 s	686 s
Hg(CSmz)$_2$		2921 w	1612 s	998 s		1039 m	1024 m		975 s	2850 w	1431 m	1562 s	1452 vs	750 s	686 s

vs: very strong; s: strong; m: medium; w: weak; br: broad; sh: sharp.

Table 5. ^{1}H NMR data of (*trans*)-cinnamaldehyde, the ligand, and its complexes.

Compound	NH and SH	C_6H_5	$C^{\alpha}H$	$C^{\beta}H$	CH_3	$H^1C{=}N$
Ph–CH=CH– CHO [21]		7.40–7.41 (m, 2H), 7.41 (d, 1H), 7.53–7.55 (m, 2H)	6.67 (dd, 1H, $J_{1\alpha} = 7.7$ Hz, $J_{\alpha\beta} = 16$ Hz)	7.45 (d, 1H, $J_{\alpha\beta} = 16$ Hz)		9.67 (d, 1–H, $J_{1\alpha} = 7.7$ Hz)
HCSmz	10.41(s), 4.86(s), (1H)	7.49 (d, 2H, $J = 7.32$ Hz), 7.33–7.38 (m, 3H)	6.96 (dd, 1H, $J_{1\alpha} = 8.24$ Hz, $J_{\alpha\beta} = 16.0$ Hz)	6.99 (d, 1H, $J_{\alpha\beta} = 15.9$ Hz)	2.67 (s, 3H)	7.71 (d, 1H, $J_{1\alpha} = 8.23$ Hz)
Ni(CSm)$_2$		7.51 (d, 4H, $J = 7.05$ Hz), 7.34–7.41 (m, 6H)	7.14 (dd, 2H, $J_{1\alpha} = 8.84$ Hz, $J_{\alpha\beta} = 15.6$ Hz)	7.04 (dd, 2H, $J_{\alpha\beta} = 15.6$ Hz)	2.64 (s, 6H)	8.40 (dd, 1H, $J_{1\alpha} = 8.83$ Hz)
Zn(CSm)$_2$		7.48 (d, 4H, $J = 7.03$ Hz), 7.38–7.48 (m, 6H)	7.13 (dd, 2H, $J_{1\alpha} = 8.94$ Hz, $J_{\alpha\beta} = 15.6$ Hz)	7.09 (d, 2H, $J_{\alpha\beta} = 15.5$ Hz)	2.64 (s, 6H)	8.45 (dd, 2H, $J_{1\alpha} = 8.93$ Hz)
Cd(CSm)$_2$		7.49 (d, 4H, $J = 6.68$ Hz), 7.39–7.49 (m, 6H)	7.15 (dd, 2H, $J_{1\alpha} = 9.98$ Hz, $J_{\alpha\beta} = 15.6$ Hz)	7.05 (d, 2H, $J_{\alpha\beta} = 15.6$ Hz)	2.59 (s, 6H)	8.42 (d, 2H, $J_{1\alpha} = 9.97$ Hz)
Hg(CSm)$_2$		7.49 (d, 4H, $J = 7.25$ Hz), 7.34–7.40 (m, 6H)	7.13 (dd, 2H, $J_{1\alpha} = 9.94$ Hz, $J_{\alpha\beta} = 15.8$ Hz)	6.94 (d, 2H, $J_{\alpha\beta} = 15.8$ Hz)	2.50 (s, 6H)	8.25 (d, 2H, $J_{1\alpha} = 8.23$ Hz)

s: singlet; d: doublet; m: multiplet.

Table 6. UV-Vis spectral data of the ligand and its complexes.

Compounds	I	II	III	$\varepsilon_{\lambda\mathrm{I}}$ ($\times 10^4$)	$\varepsilon_{\lambda\mathrm{II}}$ ($\times 10^4$)	$\varepsilon_{\lambda\mathrm{III}}$ ($\times 10^4$)
HCSmz	294.3	353.5	–	0.61	2.21	–
$Co(CSmz)_2$	328.5	413.9	–	1.71	0.96	
$Ni(CSmz)_2$	327.5	411.3	486.0	1.49	1.10	0.50
$Cu(CSmz)_2$	330.5	387.0	–	2.54	2.30	–
$Zn(CSmz)_2$	326.0	386.0	–	1.39	2.20	–
$Cd(CSmz)_2$	322.8	381.5	–	1.18	2.19	–
$Hg(CSmz)_2$	313.9	369.0	–	1.20	2.15	–

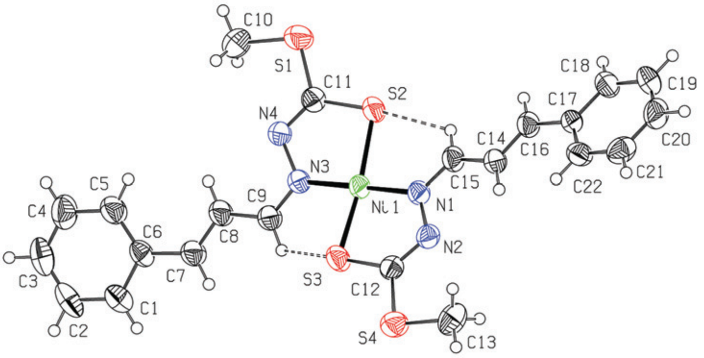


Figure 1. ORTEP3 view of $Ni(CSmz)_2$ (50% probability ellipsoids); dash shows the intramolecular C–H···S hydrogen bonds.

shown in "Supplementary material". The complex has a *trans*-configuration, as for other complexes [42]. The Ni is coordinated – in a slightly distorted square-plane – by two azomethine nitrogens of N2 and N4 and sulfurs S2 and S3 after tautomerism of thiotone to thioenol and deprotonation. The Ni(II) deviates from the square plane 0.088 Å; angles N2–Ni1–N3 and S2–Ni1–S3 are 177.35(8)° and 172.29(3)°, respectively. The Ni is in the plane of S–C–N–N in one ligand deviating 0.447 Å from the other; the dihedral angle between the two planes is 159.0°.

Tautomerism of the dithiocarbazate to its iminothiolate form is proved by increasing the C=S double bond length and decreasing the C–S single bond length, forming an extended conjugated system. The bond length of either C11–S2 [1.720(2) Å] or C12–S3 [1.724(2) Å] is shorter than a single bond of C–S [1.82 Å] but longer than the double bond of C=S [1.62 Å]; that of either N1–N2 [1.413(2) Å] or N8–N9 [1.413(2) Å] is also shorter than N–N single bond [1.45 Å]; and that of either C9–N3 [1.295(2) Å] or C10–N9 [1.301(3) Å] is also longer than C=N double bond [1.40 Å]. The phenyl ring forms a dihedral angle of 8.81(5)° with the metal coordination plane and the very small dihedral angle indicates high electron delocalization in the π-system of the Schiff bases, in agreement with other reported results [17].

In $Ni(CSmz)_2$, the two azomethine nitrogens of C9 and C15 are intramolecular hydrogen-bond donors *via* H9 and H15 to S3 and S2 with distances C9···S3 3.043(2) Å and C15···S2 3.124(2) Å and angles of C9–H9···S3 112.6° and C15–H15···S2

Table 7. Hydrogen bonds of $Ni(CSmz)_2$ (Å, °).

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠DHA
C9–H9···S3	0.93	2.56	3.043(2)	112.6
C15–H15···S2	0.93	2.52	3.124(2)	123.1
C19–H19···$S3^{i}$	0.93	2.96	3.802(3)	151.1
C13–H13A···$S2^{ii}$	0.96	2.84	3.640(3)	141.4

Symmetry code: ^{i} ½ + x, 3/2 − y, −½ + z; ^{ii} −½ + x, 3/2 − y, ½ + z.

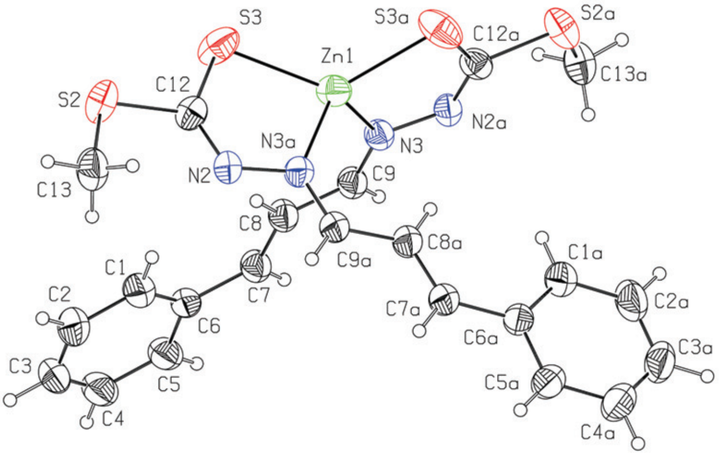


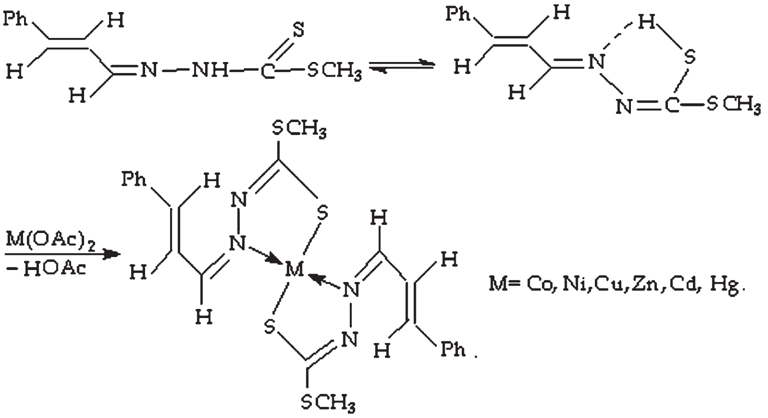
Figure 2. ORTEP3 view of $Zn(CSMz)_2$ showing 30% probability ellipsoids.

123.1° (table 7). The two intramolecular C–H···S hydrogen bonds make the two coordinated five-membered rings coplanar.

In molecular packing of $Ni(CSmz)_2$, two molecules are linked into $R_2^2(14)$ [43] centrosymmetric dimer by two C–H···S hydrogen bonds, *via* methyl C13 at (x, y, z) acting as donor to S2 in the molecule at $(1-x, 2-y, -z)$ and so generating an inversion. The molecule at (x, y, z) is made into a C(7) [44] zig-zag chain by C19–H19···S3 hydrogen bond *via* phenyl atom C19 at (x, y, z) acting as hydrogen-bond donor to S3 at $(1/2+x, 3/2-y, -1/2+z)$. They form a band running parallel to the (202) plane (Supplementary material).

3.5.2. Crystal structure of $Zn(CSmz)_2$.

Compared with $Ni(CSmz)_2$, $Zn(CSmz)_2$ differs in its molecular structure (figure 2) and packing. Although the two ligands also undergo tautomerism of thiotone to thioenol, and deprotonation and chelate Zn(II) by two nitrogens of azomethine and two sulfurs of thioenol, the central Zn forms distorted tetrahedral geometry with N–Zn–N, N–Zn–S, and S–Zn–S angles between 86.45(5)° and 127.97(5)°. The ligands coordinated with Zn are more co-planar than with Ni because Zn, S3, C12, S2, N2, N3a, C9a, C8a, C7a, C6a, C5a, C4a, C3a, C2a, and C1a form a large π-conjugation system (atom deviations from the plane are −0.1238(2), 0.0580(9), 0.057(2), 0.0978(8), 0.0249(18), −0.0249(18), −0.007(2), −0.016(2), 0.026(2), −0.014(2),



Scheme 1. Coordination of the ligand with metal ions.

0.029(3), 0.005(3), –0.011(3), –0.006(3), and 0.005(3) Å, respectively). The dihedral angle of the two planes is *ca* 80.3°. Such a configuration has been found in the literature [17].

The most striking difference in the supramolecular aggregation of $Zn(CSmz)_2$ is that two molecules are linked into a dimer *via* four intermolecular $C–H\cdots\pi/Cg$ (centroid of phenyl ring) interactions and there is no intramolecular or intermolecular hydrogen bonding. Every C9 of azomethine in every ligand is a hydrogen-bond donor to near Cg forming $C(9)–H(9)\cdots\pi/Cg$ (3.793(2) Å, 161°) (table 1) and four $C–H\cdots\pi$ hydrogen bonds combine two molecules into a block. In every crystal cell there are six pairs of the dimer (Supplementary material).

4. Conclusion

A Schiff base and six metal complexes were synthesized and characterized. The ligand exists only in thiotone form in solid state, but it can tautomerize from the form of thiotone to thioenol in chloroform. After tautomerism of thiotone to thioenol and deprotonation, the two ligands chelate to the central metal by two nitrogens of azomethine and two sulfurs of thioenol (scheme 1). $Ni(CSmz)_2$ exhibits a slightly distorted square-planar *trans*-configuration and $Zn(CSmz)_2$ is distorted tetrahedral. In the solid state, molecules are stabilized by intramolecular or intermolecular $C–H\cdots S$ or $C–H\cdots\pi$ hydrogen bonds.

Supplementary material

Full crystallographic data (CCDC No. 687813 for the complex of $Ni(NS)_2$ and CCDC No. 687814 for $Zn(NS)_2$) have been deposited at the Cambridge Crystallographic Database Centre and are available on request from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; Email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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