

Distorted Octahedral S-Methyl 2-(2-Oxoindolin-3-Ylidene)hydrazinecarbodithioate (SMISA) Tridentate Schiff Base Complex of Co(II): Synthesis, Characterization and Structural Studies

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Schiff base ligand S-methyl 2-(2-oxoindolin-3-ylidene)hydrazinecarbodithioate, SMISA (**1**) obtained by condensation of S-methyldithiocarbamate with isatin has been used to synthesize a cobalt(II) complex, namely Co(SMISA)₂-DMSO (**2**). The metal complex (**2**) was formed by reacting Schiff base (**1**) with cobalt(II) acetate tetrahydrate. These compounds have been characterized by a variety of physico-chemical techniques including FT-IR spectroscopy, elemental analysis, magnetic susceptibility, UV-Vis spectroscopy, molar conductivity, ICP-AES analysis, and single-crystal X-ray diffraction. The crystal structure analysis of the bis-ligand cobalt(II) complex, Co(SMISA)₂-DMSO (**2**) revealed that the central Co(II) ion was six coordinate with a distorted octahedral geometry. The X-ray result also showed that the ligand in the thione form was transformed into the thiol form upon coordination to Co(II) ion. The Schiff base acted as a monoanionic tridentate NOS (nitrogen-oxygen-sulphur) chelating agent, coordinating the Co(II) metal center via azomethine nitrogen atoms (N7 and N23), thiolate sulphur atoms (S2 and S18), and carbonylic oxygen atoms of the isatin moiety (O13 and O26).

Key words: Cobalt(II); dithiocarbamate; crystal structure; octahedral; solvated

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Schiff base is one of the most important class of compounds in medicinal and pharmaceutical fields [1–3]. This class of compounds plays a vital role in the development of coordination chemistry and can readily form stable complexes with most transition metals [4–6]. Schiff bases derived from S-alkyl/aryl esters of dithiocarbamic acids and their transition metal complexes are among the most widely studied compounds due to their interesting physico-chemical and potentially beneficial chemotherapeutic properties [7–9]. However, only limited studies have reported on dithiocarbamate Schiff bases with nitrogen, oxygen, and sulphur (NOS) donor sequences derived from isatins [10]. The interest of studying dithiocarbamate Schiff bases containing NOS donors came from their significant antifungal, antibacterial, and anticancer activities [10–12]. In addition, the presence of both hard and soft donor groups in one ligand increases the coordination ability towards the hard as well as soft acidic metals [13]. It is worthwhile to carry out the study of new various NOS chelating ligands and their metal complexes to supplement available information towards the effort in elucidating the selectivity pattern of compounds. Therefore, as part of our ongoing study on Schiff bases derived from dithiocarbamates, we report herein, the synthesis and crystallographic analysis of dimethylsulfoxide (DMSO)-

solvated cobalt(II) (**2**), derived by equimolar condensation of S-methyldithiocarbamate with isatin.

MATERIALS AND METHODS

Elemental CHNS analyses were carried out using LECO CHNS-932. The IR spectra as KBr pellets were recorded using Perkin-Elmer FTIR 1750X spectrophotometer (4000–400 cm⁻¹). The molar conductance of 10⁻³ M solutions of Co(SMISA)₂ in DMSO complex was measured at 29°C using Jenway 4310 conductivity meter and a dip-type cell with a platinised electrode. Magnetic susceptibility at room temperature was measured using Sherwood Scientific MSB-AUTO magnetic susceptibility balance. The UV-Vis spectra were recorded on Shimadzu UV-2501 PC Recording Spectrophotometer (1000–200 nm). A metal determination was carried out using Perkin-Elmer Plasma 1000 Emission Spectrometer.

1. Preparation of SMISA (1)

SMISA (**1**) was synthesized following a previously reported study [14]. S-methyldithiocarbamate, SMDTC (1.22 g, 0.01 mol) was dissolved in hot ethanol (35 mL) and an equimolar amount of isatin (1.47 g, 0.01 mol) was added to this solution. The mixture was heated and stirred for 15 minutes and allowed to stand for 20 minutes. The dark orange product was filtered, washed with cold

ethanol, and recrystallized from ethanol (2.0 g; 80%); m.p. 225-227°C. Selected IR data (KBr pellet, cm^{-1}) 3180 (C=O); 1620 (C=N); 1138 (N-N); 1070 (C=S).

2. Preparation of Co(SMISA)₂·DMSO complex (2)

A solution of cobalt(II) acetate tetrahydrate (1.0 mmol in 95% ethanol, 5 mL) was mixed with SMISA (1) (2.0 mmol in hot 95% ethanol, 10 mL) and stirred while being heated for 20 minutes. The resultant solution was cooled and the solid formed was filtered and dried over a silica gel. Recrystallization from dimethylsulfoxide yielded the DMSO solvate Co(II) complex (2) as light dark green crystals (0.42 g; 75%); m.p. > 300°C. Anal. Calc. for C₂₂H₂₂CoN₆O₃S₅ requires: C, 41.44; H, 3.48; N, 13.18; S, 25.14; Co, 9.24. Found: C, 41.18; H, 3.46; N, 13.14; S, 25.04; Co, 9.21%. Selected IR data (KBr pellet, cm^{-1}) 3387 (C=O); 1606 (C=N); 1048 (N-N); 992 (C-S). UV-Vis spectrum [λ_{max} , DMSO, nm (Log ϵ mol⁻¹ l cm⁻¹)] 269(4.18), 320sh, 388(4.30), 453(4.36), 550sh, 906(1.53). $\mu_{\text{eff}} = 4.37$ B.M. The synthetic reaction for the preparation of compounds (1) and (2) is shown in Scheme 1.

3. X-ray structure determination of Co(SMISA)₂·DMSO (2)

A selected single crystal was mounted on a glass fibre using perfluoropolyether oil and cooled rapidly to 150 K in a stream of cold N₂ using Oxford Cryosystems CRYOSTREAM unit. Diffraction data were measured using Enraf-Nonius Kappa CCD diffractometer (graphite-monochromatic Mo K α radiation, $\lambda = 0.71073\text{\AA}$). Intensity data were processed using DENZO-SMN package [15]. The crystal structure was solved using the direct-methods program SIR92 [16], which located all

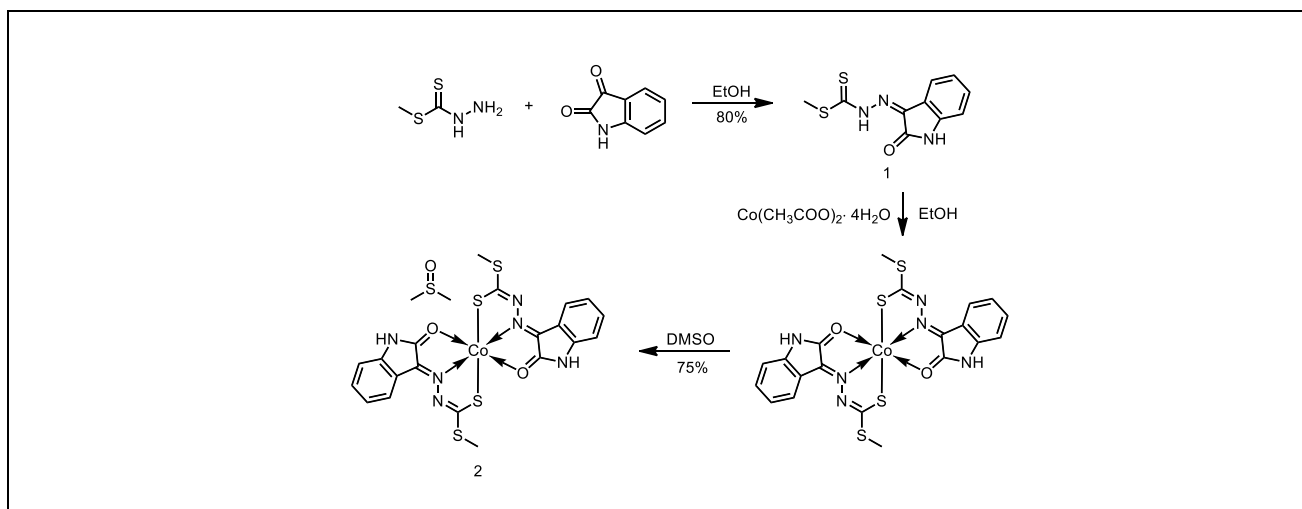
non-hydrogen atoms. Subsequent full-matrix least-squares refinement of F² was carried out using CRYSTALS Program Suite [17]. Coordinates and anisotropic thermal parameters of all non-hydrogen atoms were refined. Hydrogen atoms were positioned geometrically after each refinement cycle. Refinement converged satisfactorily to give good R and R_w values with the best minimum and maximum residual electron density.

RESULTS AND DISCUSSION

1. Physical and Spectroscopic Characterization of Co(SMISA)₂·DMSO complex (2)

The IR spectrum of the free ligand exhibited a (C=S) band at 1070 cm^{-1} . The disappearance of this band along with the appearance of a new (C-S) band at 992 cm^{-1} in the spectrum of the complex suggested that complexation occurred through its thiolate sulphur atoms. The presence of (C=N), (N-N), and (C=O) bands at 1606 cm^{-1} , 1048 cm^{-1} , and 1672 cm^{-1} respectively indicated the coordination of the Schiff base to metal ions via azomethine nitrogen, thiolate sulphur, and carbonylic oxygen atoms [18]. These bands shifted to lower wavenumbers upon coordination to metal ions [19].

The UV-Vis spectrum of the complex exhibited a strong band at 453 nm, which could be assigned to S atom to Co(II) charge transfer, indicating that Co(II) ions were coordinated to sulphur through the thiolate sulphur atoms [20]. It also displayed three *d-d* transition bands, which was consistent with a high-spin six-coordinate distorted octahedral field [21,22]. These bands could be assigned to ⁴T_{1g}(F)→⁴T_{2g}(F)(ν_1) at 906 nm, ⁴T_{1g}(F)→⁴A_{2g}(ν_2) at 550 nm, and ⁴T_{1g}→⁴T_{1g}(P)(ν_3) at 320 nm.



Scheme 1. Synthesis of SMISA (1) and Co(SMISA)₂·DMSO complex (2).

The magnetic susceptibility value of complex (2) at room temperature obtained was 4.37 B.M (Table 1). It has been reported that the normal range for octahedral Co(II) complexes is 4.3–5.2 B.M [23]. The magnetic susceptibility value obtained indicated that the Co(II) complex was in an octahedral environment with high-spin configuration [23]. The magnetic susceptibility value of the complex was also indicative of three unpaired electrons per cobalt(II) ion, suggesting consistency with the octahedral environment [24,25]. The complex was found to be non-electrolyte in DMSO.

2. Single X-Ray Characterization of Co(SMISA)₂·DMSO (2)

The summary of crystal data and structure refinement parameters of the bis-ligand cobalt(II) complex is shown in Table 2, while the ORTEP diagram is presented in Figure 1. The asymmetric unit of the title compound comprised of a unit of cobalt complex and DMSO solvent of crystallisation. The central cobalt atom was tri-coordinated by the uninegatively charged tridentate ligand through the azomethine nitrogen atoms N7 and N23,

Table 1. Electronic spectra, magnetic susceptibility, and molar conductance data

Compound	UV-Vis spectra (λ_{\max} , nm) ^a	μ_{eff} (B.M)	Ref.
Co(SMISA) ₂ ·DMSO (2)	269 (4.18), 320 sh, 388 (4.30), 453 (4.36), 550 sh, 906 (1.53)	4.37	This work
Co(isasme) ₂ ·DMF	267 (4.80), 320 sh, 350 sh, 444 (4.42), 740 sh, in DMF	4.30	14

^aLog ϵ (mol⁻¹ l cm⁻¹) are in parentheses

Table 2. Summary of crystal data and structure refinement parameters for [Co(SMISA)₂·DMSO (2)]

Chemical formula	C ₂₂ H ₂₂ Co ₁ N ₆ O ₃ S ₅
Formula weight	637.72
Crystal class	Monoclinic
Space group	<i>P</i> 21/n
<i>a</i> (Å)	10.1278(2)
<i>b</i> (Å)	13.5311(3)
<i>c</i> (Å)	19.7780(4)
α (°)	90
β (°)	103.5643(10)
γ (°)	90
<i>V</i> (Å³)	2634.78(10)
<i>Z</i>	4
Mo Kα (Å)	0.7107
T (K)	150
ρ_{calc} (mg m⁻³)	1.608
μ (mm⁻¹)	1.086
Crystal dimension (mm)	0.12 × 0.14 × 0.16
F (000)	1308
Theta range for data collection (°)	5 to 27
Limiting indices	(-13 ≤ <i>h</i> ≤ 13) (-17 ≤ <i>k</i> ≤ 17) (-25 ≤ <i>l</i> ≤ 25)
Reflections collected/unique	11775 / 5958 [R(int) = 0.0048]
Maximum & minimum transmission	0.88 , 0.86
Data/restraints/parameters	5958 / 0 / 334
Goodness-of-fit on F²	0.861
Minimum & maximum residual electron density (e Å⁻³)	-1.16 , 1.29
R, R_w (%)	4.1 , 9.0

the thiolate sulphur atoms S2 and S18, and the carbonylic oxygen atoms of the isatin moiety, O13 and O26. Both nitrogen atoms (N7 and N23) of the two ligands were coordinated at opposite positions. The coordination geometry around Co could be best described as distorted octahedral, in which the ligand coordinated to the metal in a tridentate manner (NOS) forming four five-membered chelate rings. The ligands were in a meridional configuration with S and O atoms *cis* to each other (coordination angles of 97.62° and 89.67°) and N atoms *trans* (coordination angle of 171.61°).

The relevant bond distances and angles are given in **Table 3**. The Co-S bonds were relatively long with 2.401(8) Å and 2.414(9) Å compared to 2.19 Å–2.20 Å values in typical cobalt(II) octahedral species [26]. The Co-N distances of 2.056(2) Å and 2.061(2) Å were normal,

which were within the range found in the literature [14,27]. However, the Co-O bonds, 2.266(2) Å and 2.254(2) Å, were fairly long and larger than the sum of the Pauling covalent radii, 2.05 Å. The lengthening of the Co-O distances, as found in 1-methylisatin 3-thiosemicarbazone and triazole complexes [26,28], was determined by the rigidity of the isatin moiety, which affected the geometry of the chelation ring. The N6-N7 and N22-N23 distances of 1.375(3) Å and 1.379(3) Å were in the normal range of about 1.36–1.38 Å [14,23,24]. The C3-S2 and C3-N6 bond lengths in the complex were 1.722(3) Å and 1.317(4)Å, while the C19-S18 and C19-N22 bond lengths were 1.731(3) Å and 1.320(3) Å, respectively. These distances were longer than those observed for analogous free ligands [10,12] and in good agreement with the thiolate character of the dithiocarbazate ligand in the complex.

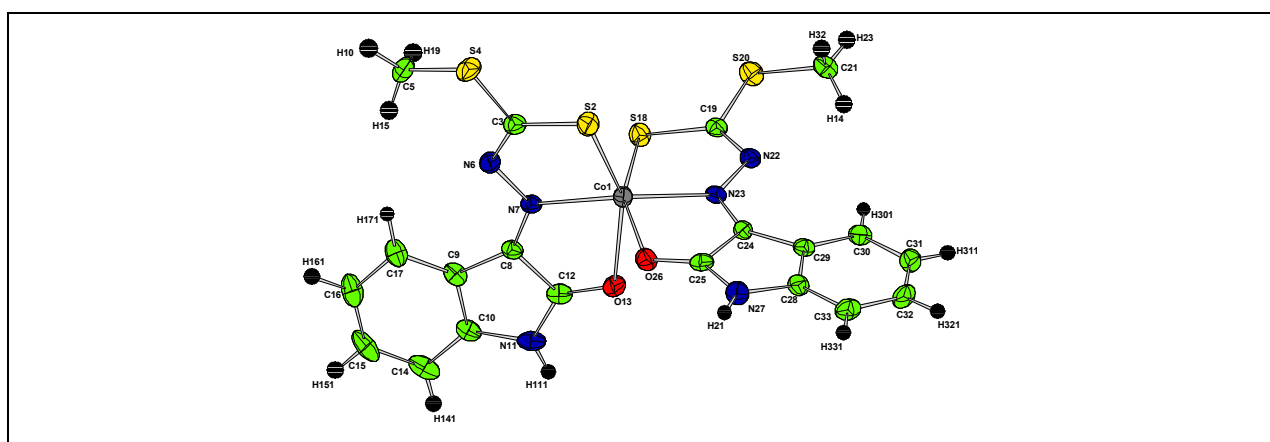


Figure 1. ORTEP diagram and atom numbering scheme of Co(SMISA)₂·DMSO (**2**) complex. The DMSO molecule is omitted for clarity

Table 3. Selected bond lengths (Å) and bond angles (°) for Co(SMISA)₂·DMSO (**2**)

Bond lengths		Bond angles	
C3-S2	1.722(3)	S2-Co1-N7	79.57(7)
C3-S4	1.743(3)	S18-Co1-N23	79.83(7)
C19-S18	1.731(3)	N7-Co1-O13	77.72(8)
C19-S20	1.741(3)	N23-Co1-O26	77.97(8)
C3-N6	1.317(4)	S2-Co1-S18	101.50(3)
C19-N22	1.320(3)	S2-Co1-O13	151.51(6)
N6-N7	1.375(3)	S2-Co1-O26	89.67(5)
N22-N23	1.379(3)	S18-Co1-O26	157.35(5)
C8-N7	1.278(3)	N23-Co1-S2	108.13(7)
C24-N23	1.300(3)	N7-Co1-S18	95.57(7)
Co1-S2	2.401(8)	N7-Co1-N23	171.61(9)
Co1-S18	2.414(9)	N7-Co1-O13	77.72(8)
Co1-O13	2.266(2)	N7-Co1-O26	105.88(8)
Co1-O26	2.254(2)	O13-Co1-O26	80.29(7)
Co1-N7	2.056(2)	O13-Co1-S18	97.62(6)
Co1-N23	2.061(2)		

Table 4. Comparison of crystal systems, space groups, and coordinate bond distances (Å) in six coordinate Co(II)N₂O₂S₂ complexes.^a

	Crystal system	Space group	Ref.
[Co(SMISA) ₂ ·DMSO](2)	Monoclinic	P2 ₁ /n	This work
[Co(isasme) ₂ ·DMF]	Triclinic	P-1	[14]
[Co(edbbh)]	Monoclinic	C 2/c	[27]

Bond Type			
Co-S	Co-N	Co-O	
2.401(8)	2.056(2)	2.266(2)	This work
2.414(9)	2.061(2)	2.254(2)	This work
2.414(1)	2.054(3)	2.334(3)	[14]
2.403(1)	2.065(3)	2.261(3)	[14]
2.338(1)	2.112(3)	2.287(3)	[27]
2.338(1)	2.132(3)	2.320(3)	[27]

^aisasme/SMISA = deprotonated form of the Schiff base, S-methyl 2-(2-oxoindolin-3-ylidene)hydrazinecarbodithioate; edbbh = 2,2'-ethylenedioxybis-(benzylidenehydrazono)]-3,3'-diphenylbis(2-thiapropanethiolato-S).

The C-N bond distances of the complex of trichelated ligands were typical for double bond Schiff base compounds [29]. The C-S bond distances of 1.722(3) Å and 1.731(3) Å indicated single bond character, which supported the suggestion that the complex formation involved the ligand in its thiol form.

The relevant bond distances and angles are given in **Table 3**.

For comparison, cobalt coordinate bond distances reported in the related work are shown in **Table 4** [14,30]. The bond distances in the cobalt(II) complexes were comparable with the differences (shorter Co-O distances obtained in this work).

The dihedral angles between the two metal chelate rings [Co1-N23-C24-C25-O26] and [Co1-S18-C19-N22-N23]; [Co1-N7-C8-C12-O13] and [Co1-S2-C3-N6-N7] were 5.69° and 14.37° respectively, which further supported the distorted octahedral structure of the complex. The two rings of isatin moiety (five- and six-membered) [C24-C25-N27-C28-C29] and [C28-C29-C30-C31-C32-C33]; [C8-C9-C10-N11-C12] and [C9-C10-C14-C15-C16-C17] were essentially planar with the dihedral angles between the mean planes being 2.23° and 1.65°, respectively. The conjugation system of the moieties was influenced by the coordination system with the metal as shown by the slight bond lengthening compared with the similar uncomplexed ligands in SMMISA and SM5CIISA [12,31].

CONCLUSION

The synthesis, characterization, and structural studies of the bis-ligand cobalt(II) DMSO solvated complex of the isatin Schiff base of S-methyldithiocarbamate (SMISA) have been described. The crystal structure showed that the central cobalt atom was hexa-coordinated and has a distorted octahedral geometry with the Schiff base

coordinated to the metal ion as uninegatively charged tridentate ligand through the azomethine nitrogen atoms, thiolate sulphur atoms, and carbonylic oxygen atoms of the isatin moiety.

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