Synthesis and Characterization of Novel Methyl 2-(1,7,7-Tri methylbicyclo[2.2.1]hept-2-yieldene)hydrazinecarbodithioate Schiff Bases Derived From Methylhydrazine carbodithioate And Their Bi(III) And Ag(II) Complexes

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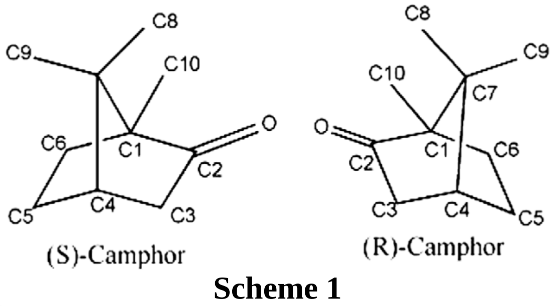
Abstract

Novel bidentate Schiff bases having nitrogen-sulphur donor sequence was synthesized from condensation of racemate camphor, (R)-camphor and (S)-camphor with Methyl hydrazinecarbodithioate (SMDTC). Its metal complexes were also prepared through the reaction of these ligands with silver and bismuth salts. All complexes were characterized by elemental analyses and various physico-chemical techniques. These Schiff bases behaved as uninegatively charged bidentate ligands and coordinated to the metal ions via β-nitrogen and thiolate sulphur atoms. The NS Schiff bases formed complexes of general formula, $[M(NS)_2]$ or $[M(NS)_2.H_2O]$ where M is Bi^{III} or Ag^{I}, the expected geometry is octahedral for Bi(III) complexes while Ag(I) is expected to oxidized to Ag(II) forming square planner complexes.

Keywords: Methyl hydrazinecarbodithioate, Schiff Base, Silver, Bismuth Complexes

Introduction:

Natural chiral drugs (e.g., morphine, cocaine, and atropine) usually exist as single stereoisomers due to their formation by enzymatic reactions whereas synthetic 'chiral' drugs are made by chemical reactions and usually exist as racemates [1]. Drug stereoisomerism is a recognized issue having research, clinical and regulatory implications as differences are observed in the pharmacodynamic and pharmacokinetic properties of the enantiomers of chiral molecules [2]. Camphor (1,7,7-trimethyl-bicyclo[2.2.1] hepta-2-one) is cyclic and has a ketone structure, existing in two enantiomeric forms: the (R)- and (S)-camphor (Scheme 1) [3].



Scheme 1

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Dithiocarbazate, NH_2NHCS_2 and its substituted derivatives have been synthesized and investigated, due to the presence of both hard nitrogen and soft sulphur donor atoms, they readily coordinate with a wide range of transition or non-transition metal ions yielding stable and intensely coloured metal complexes [4]. Metal ions are also known to accelerate drug action. The efficacy of a therapeutic agent is known to be enhanced upon coordination with a metal ion [5].

Compounds of Bi(III) have applications in diverse areas including medicine, materials, organic synthesis, and catalysis [6]. Several Bi(III) complexes showed selective activities against bacteria, thus, the primary role of the ligands is to transport the bismuth into susceptible microbes [7].

Camphor, which is used commercially as an insect repellent, can also be used as a preservative in pharmaceuticals and cosmetics (Miyazawa and Miyamoto)[8].

Materials and Methods:

Materials:

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

Methods:

Preparation of Methyl hydrazinecarbodithioate

Methyl hydrazinecarbodithioate (SMDTC) was synthesized as reported in Trafder (Tarafder et al., 2002)[9] and Yaseen (Yaseen et al., 2012) [10]

General preparation of the Schiff Bases

SMDTC (0.02 mol) was dissolved in methanol (40 ml). To this solution stoichiometric amount of , *R*-camphor and *S*-camphor, in methanol (25 ml) was added. Hydrobromic acid (0.02 mol) is also added to the mixture. The mixture was heated while being stirred. The precipitate was filtered and dried over silica gel [7, 11, 12].

General Preparation of the metal complexes

Metal salt (0.01 mol) dissolved in boiling water (25 ml) was mixed with a solution of the appropriate Schiff base (0.02mol) in ethanol (40 ml) and the resulting mixture was heated on a water bath for half an hour. On standing overnight, the mixture yielded crystalline complexes which were filtered off, washed with ethanol and dried in a desiccator over anhydrous silica gel, overnight. Yield:. 65% for Bi(III) complexes and 75% for Ag(II) complexes [8, 13-15].

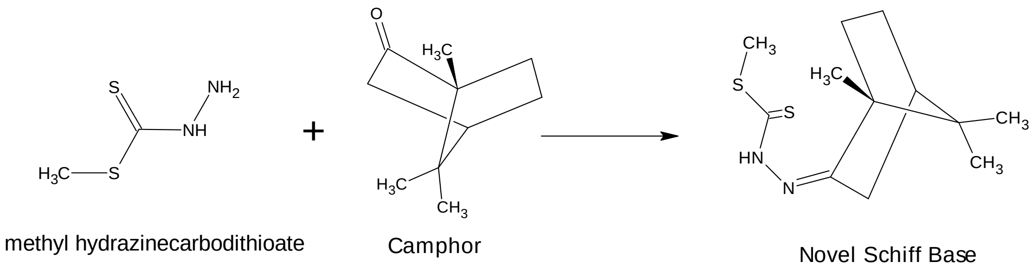
Physical Measurements and Elemental Analysis

Melting points were determined by using a Barn Stead Electrothermal Digital Melting Apparatus Model 9100. The analyses for carbon, hydrogen, nitrogen and sulphur were carried out using a LECO CHNS-932 instrument. The IR spectra as KBr discs were recorded on a Perkin-Elmer FT IR 1750X spectrophotometer (4000-400 cm^{-1}). Metal determinations were carried out using a Perkin-Elmer Plasma 1000 Emission Spectrometer. The molar conductance of 10^{-3} M solutions of the metal complexes in DMSO were measured at 29°C using a Jenway 4310 conductivity meter and a dip-type cell with a 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 (1000-200 nm).

Results and Discussion:

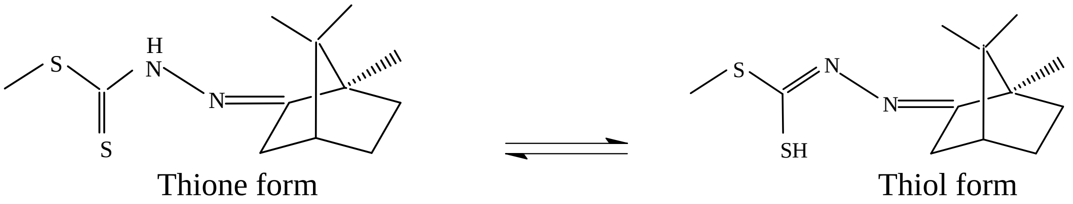
Methyl hydrazine carbodithioate used with racemate camphor, R-camphor and S-camphor to form Schiff base Methyl 2-(1,7,7-Trimethylbicyclo[2.2.1]hept-2-

yieldene) hydrazinecarbodithioate as in the equation (Scheme 2).



Scheme (2) Synthesis of Methyl 2-(1,7,7-Trimethylbicyclo[2.2.1]hept-2-yieldene) hydrazinecarbodithioate

The synthesized Schiff bases contain the thioamide function –NH-C(S)SR and therefore, in principle, each can exhibit thione-thiol tautomerism as shown in (Scheme 3). Metal complexes were synthesized using silver(I) nitrate and bismuth(III) nitrate pentahydrate salts. Metal complexes of Schiff bases were prepared in the presence of potassium hydroxide. The Schiff bases can quickly form the thiolate anions in solution [16, 17]. This enhances the nucleophilicity of the ligand thus affording bidentate uninegative chelation with metal ions [18], this will lead to oxidize silver(I) to silver(II).



Scheme(3): Thione thiol tautomerizm

In the presence of metal ions, the Schiff base is rapidly converted into the thiol tautomeric form thereby facilitating the formation of metal complexes with the deprotonated ligand [15].

Table (1): physical properties of the synthesized compounds

Compound	Colour	Melting Point (± °C)	Found (Calc.)				
			%C	**%H**	**%N**	**%S**	**%M**
SMDTC	White	80.0	19.84 (19.66)	5.09 (4.95)	23.01 (22.92)	52.71 (52.47)	-
RACSM	Pale yellow	161.0	57.64 (57.21)	7.45 (7.86)	11.58 (10.92)	28.99 (25.01)	-
RCSM Schiff base	Pale yellow	160.0	60.44 (56.21)	6.91 (7.86)	10.15 (10.92)	22.97 (25.01)	-
SCSM Schiff base	Pale yellow	160.2	51.96 (56.21)	7.19 (7.86)	15.88 (10.92)	18.78 (25.01)	-
RACSM $Bi[(NS)_2.NO_3.H_2O]$	White	188.0 Decomposed	32.76 (35.86)	5.28 (5.52)	8.44 (8.71)	21.66 (15.96)	28.14 (26.00)
RCSM $Bi[(NS)_2\cdot NO_3.H_2O]$	White	183.0 Decomposed	28.68 (35.86)	4.69 (5.52)	10.07 (8.71)	18.87 (15.96)	31.65 (26.00)
SCSM $Bi[(NS)_2\cdot NO_3.H_2O]$	White	179.0 Decomposed	31.05 (35.86)	5.14 (5.52)	11.21 (8.71)	20.15 (15.96)	28.58 (26.00)
RACSM $Ag(NS)_2$	Dark brown	188.0 Decomposed	43.63 (46.29)	5.94 (6.80)	8.11 (9.00)	17.66 (20.60)	15.37 (17.32)
RCSM $Ag(NS)_2$	Dark brown	188.0 Decomposed	41.75 (46.29)	5.01 (6.80)	7.52 (9.00)	15.84 (20.60)	19.57 (17.32)
SCSM $Ag(NS)_2$	Dark brown	189.0 Decomposed	44.04 (46.29)	4.20 (6.80)	11.78 (9.00)	24.15 (20.60)	14.20 (17.32)

NOTE:

RACSM Schiff base = Schiff base of racemate camphor with SMDTC

RCSM Schiff base = Schiff base of R-camphor with SMDTC

SCSM Schiff base = Schiff base of S-camphor with SMDTC

RACSM $Bi[(NS)_2\cdot NO_3.H_2O]$ = Bismuth complex of RACSM Schiff base

RCSM $Bi[(NS)_2\cdot NO_3.H_2O]$ = Bismuth complex of RCSM Schiff base

SCSM $Bi[(NS)_2\cdot NO_3.H_2O]$ = Bismuth complex of SCSM Schiff base

RACSM $Ag(NS)_2$ = Silver complex of RACSM Schiff base

RCSM $Ag(NS)_2$ = Silver complex of RCSM Schiff base

SCSM $Ag(NS)_2$ = Silver complex of SCSM Schiff base

The Schiff bases and all the metal complexes were characterized using various analyses. The abbreviations used for the Schiff bases and metal complexes are listed in (Table 1) along with their CHNS, metal content and physical properties, the results are compared to the calculated values. The ICP-AES measurements shows that all the prepared metal complexes have 1:2 metal to ligand ratio and the results agreed with the suggested formula.

Fourier Transform Infrared Spectroscopy

The IR spectra of free ligands in solid state (Table 2) showed only N–H peak at 3155 cm^{-1} and 3176 cm^{-1} these bands disappeared in the IR spectra of metal complexes suggesting that the proton on the β-nitrogen atom is lost upon complex formation with the metal ion[19-22]. No S–H stretching appeared at *ca*. 2564 cm^{-1}, indicating that the Schiff base existed not in thiol form. It is also indicating coordination through the thiolate anions[23].

The synthesized Schiff base showed strong bands at *ca.*1661 cm^{-1} attributed to the ν(C=N) stretching to free ligands. The spectra of metal complexes to ν(C=N) stretching bands were shifted to lower frequencies, they are 1617 cm-1 to 1630 cm-1 this could be due to the lowering of the C=N bond order as a result of the metal-nitrogen bond formation [18]. A band of 1054 cm-1 appeared in the IR spectra of free ligands is assigned as the ν(C=S). This band disappeared in the spectra of metal complexes, supporting the change in the nature of the C=S bond on coordination of Schiff base through the sulphur atom [11]. The disappearance of the ν(C=S) band indicated that the complexation reaction took place when the Schiff base was in the thiol form.

IR spectrum of Schiff base possessed a peak at 1032 cm-1 which was assigned to the ν(N–N) absorption. This band shifted to lower frequencies in the IR spectrum of metal complexes indicating coordination of the azomethine nitrogen to the central metal atom [24].

For the metal complex, RACSM Bi[(NS)2·NO3H2O], RCSM Bi[(NS)2NO3H2O] and SCSM Bi[(NS)2NO3H2O] three bands were appeared at 1374, 1368 and 1379 cm-1 respectively indicating the coordination of nitrate group (NO3-) as ONO2 to the bismuth metal ion [25]. Also a medium sharp band which appeared at (774 cm-1) indicates the presence of H2O as aqua molecule of the structure. [25].

Table (2): Infrared data for Schiff bases and their metal complexes

Compound	**Bands (cm^{-1})**				
	ν(N–H)	**ν(C=N)**	**ν(C=S)**	**ν(N–N)**	**ν(CSS)**
RACSM Schiff base	3155	1662	1054	1032	1006
RCSM Schiff base	3171	1661	1053	1032	1006
SCSM Schiff base	3176	1662	1053	1032	1006
RACSM $Bi[(NS)_2 NO_3 H_2O]$	-	1618	-	985	942
RCSM $Bi[(NS)_2 NO_3 H_2O]$	-	1618	-	986	942
SCSM $Bi[(NS)_2 NO_3 H_2O]$	-	1617	-	986	942
RACSM $Ag(NS)_2$	-	1629	-	989	958
RCSM $Ag(NS)_2$	-	1630	-	992	958
SCSM $Ag(NS)_2$	-	1630	-	990	958

UV-Vis Spectrophotometry

The electron adsorption spectra of the metal complexes were recorded at room temperature using DMSO as solvent. The compounds displayed UV/Vis bands in the region 200 nm to 400 nm. The data are shown in (Table 3). Generally, the electronic spectra of the Schiff bases showed two bands ranging from 279 nm to 310 nm. The bands above 400 nm were mostly observed as shoulder peaks and were broad and less intense. The band that appeared in the range 279–285 nm in the Schiff bases assigned to the localized electronic transition of the benzenoid system of the compounds due to its higher energy, lower wavelength, and higher molar absorptivity [26]. Bands 279–285 nm can be ascribed to the π–π^* transitions of the benzenoid system of the compounds, while bands 306-310 nm ascribed n–π^* transition which involves the nonbonding electrons of the azomethine nitrogen atom [27].

The spectra of all the metal complexes showed intra-ligand bands arising from π–π^* and n–π^* electronic transitions at 266 to 275 nm and 312 to 390 nm respectively Only RACSM $Bi[(NS)_2 NO_3 H_2O]$ shows LMCT at 405 nm that arises due to the S to M(II) interaction [28, 29].

Table (3): Uv/Vis Data for Schiff Bases and Their Metal Complexes

Schiff base	λ_{max} (cm^{-1})	Metal complex	λ_{max} (cm^{-1})
RACSM Schiff base	281 (17378), 310(5623)	RACSM $Bi[(NS)_2 NO_3 H_2O]$	372(9772), 390(3981) 405(2818)
		RACSM $Ag(NS)_2$	275(11220), 312(20417)
RCSM Schiff base	285(11748), 308(2884)	RCSM $Bi[(NS)_2 NO_3 H_2O]$	374(13182), 382(15488)
		RCSM $Ag(NS)_2$	266(16595)
SCSM Schiff base	279(25703), 306(26302)	SCSM $Bi[(NS)_2 NO_3 H_2O]$	362(3162), 379(1584)
		SCSM $Ag(NS)_2$	272(16218)

Nuclear Magnetic Resonance (NMR) Spectroscopy Analysis

The methyl carbon adjacent to the sulphur atom gave signal at δ 52.77 ppm while the thione carbon and the azomethine carbon gave peaks at δ 197.37 ppm and δ168.06 ppm respectively. These peaks appeared more downfield due to the deshielding effect from the neighbouring electronegative atoms. Peaks at δ 39.17 – δ 39.61 ppm was apparently due to the chemical shift of the DMSO solvent. The methyl proton that is attached to the sulphur atom occurred as a singlet at δ 2.35 ppm. While the peak which is assigned to the highly deshielded N–H group that is adjacent to the azomethine nitrogen and thione carbon is appeared at δ 11.87 ppm.

The appearance of N–H signal at δ 11.57 ppm in the 1H NMR spectra and the absence of any peak at ~δ 4.00 ppm due to the S–H proton have once again supported that the Schiff base remained in their thione form in DMSO. The presence of N–H signal at ~12 ppm in the 1H NMR spectrum was also indicated that the secondary N-H proton was probably intermolecularly hydrogen bonded with a thione sulphur of another molecule or the N–H proton participated in the hydrogen bonding with the DMSO solvent [14].

A singlet at approximately δ 4.00 ppm which is attributed to the S–H proton is not observed in the 1H NMR spectrum of the Schiff base in DMSO. The Schiff base is in the thione form in both solid and solution.

Molar conductivity and Magnetic Susceptibility

The molar conductance data below 30 ΛM (Ω-1 cm2 mol-1) indicated that all complexes were non- electrolytes, suggesting that the two molecules of Schiff bases were covalently bonded with the metal ions [18]. The non-electrolytic nature of the complexes indicates that these ligands are coordinated to the metal ions as uninegatively charged species [18].

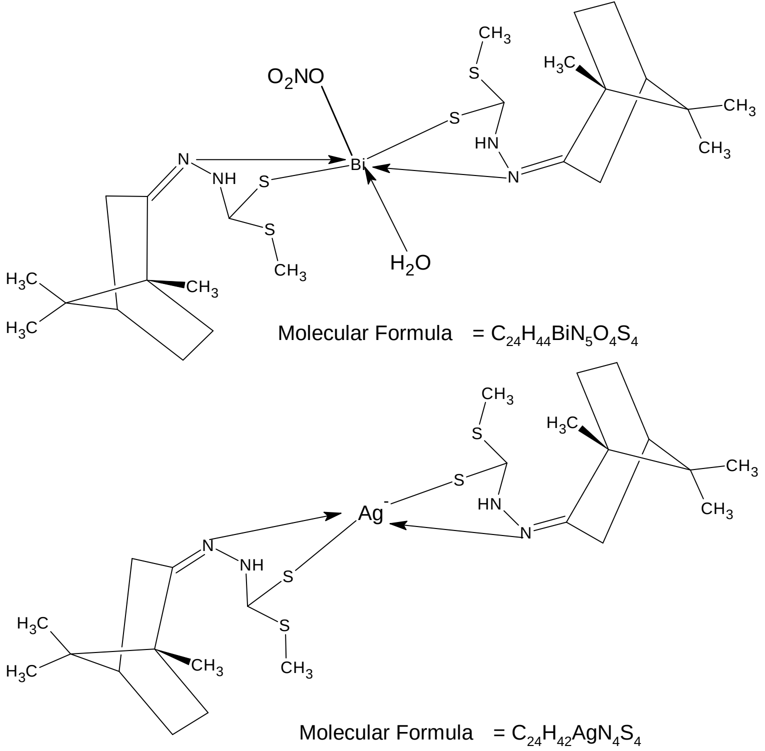
At room temperature, magnetic susceptibility measurements showed that all the Ag(II) complexes are paramagnetic. All silver(II) complexes are expected to have four coordinated complexes and to exhibit square planar structure. The magnetic susceptibility for Bi(III) complexes were not conducted because bismuth is a non-transition metal and the magnetic susceptibility of its complexes cannot be detected by the instrument. (Table 4) shows the values of conductivity and magnetic susceptibility consequently.

Table (4): Magnetic moments, Conductivity and Suggested Structures for Complexes in (10^{-3} M) DMSO solvent.

Complex	**Magnetic moment μeff. (B.M.)**	**Conductivity μS.cm^{-1}**	**Suggested structure**
RACSM Bi[$(NS)_2$ NO_3 H_2O]	N/A	1.20	Octahedral
RCSM Bi[$(NS)_2$ NO_3 H_2O]	N/A	3.76	Octahedral
SCSM Bi[$(NS)_2$ NO_3 H_2O]	N/A	5.32	Octahedral
RACSM Ag$(NS)_2$	1.21	0.15	Square planar
RCSM Ag$(NS)_2$	1.83	0.29	Square planar
SCSM Ag$(NS)_2$	1.92	0.87	Square planar

Note: N/A – Not Applicable

The expected structures of the new metal complexes are shown in scheme 4.



Scheme 4: Proposed structures of Bi(III) and Ag(II) complexes

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تخليق وتشخيص مثيل 2-(7,7,1 – ثلاثي مثيل ثنائي حلقي (2.2.1) سداسي – 2- يلدين) هيدرازين كاربودي ثايويت قواعد شف الجديدة والمشتقة من مثيل هيدرازين كاربوداي ثايويت ومعقداتها للبزموث (III) والفضة (II)

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الخلاصة

تم تحضير قواعد شف ثنائية جديدة والحاوية على ذرات النتروجين والكبريت المانحة من تكاثف الكافور الراسيمي (ر-كامفور) و (س-كامفور) مع مثيل هايدرازين كاربوداي ثايويت (SMDTC). لقد تم تحضير معقداتها الفلزية من تفاعل الليكاندات مع املاح الفضة والبزموث. تم تشخيص كافة المعقدات باستخدام وسائل التحليل والتقنيات الفيزيائية- الكيميائية. قواعد شف تسلك سلوك اليكاندات الثنائية المانحة والاحادية الشحنة السالبة وتتناسق مع الايونات الفلزية من خلال البيتا نايتروجين وذرة الكبريت الثايولوية. قواعد شف النايتروجينية الكبريتية تكون معقدات ذات الصيغة العامة $[M(NS)_2]$ or $[M(NS)_2.H_2O]$ حيث يمثل M اما Ag^I او Bi^{III} . الشكل الهندسي المتوقع هو ثماني السطوح لمعقدات البزموث بينما يتوقع لايون الفضة الاحادي ان يتاكسد الى ايون الفضة الثنائي Ag(II) ليكون معقدات رباعية السطوح