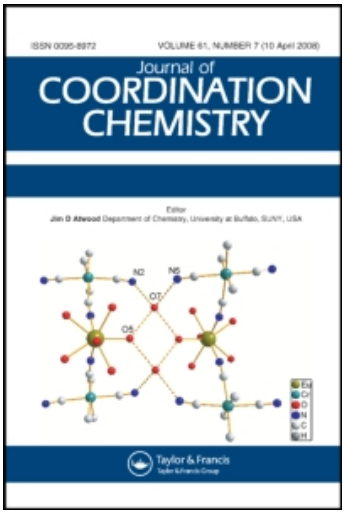

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Structural, spectroscopic, and biological aspects of SnN donor Schiff-base ligands and their chromium(III) complexes

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Structural, spectroscopic, and biological aspects of S∩N donor Schiff-base ligands and their chromium(III) complexes

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New chromium(III) complexes are synthesized by classical thermal and microwave (MW)-irradiated techniques. The Schiff bases 2-acetylfuran-*S*-benzyldithiocarbazate (L^1H), 2-acetylthiophene-*S*-benzyldithiocarbazate (L^2H), 2-acetylpyridine-*S*-benzyldithiocarbazate (L^3H), and 2-acetylnaphthalene-*S*-benzyldithiocarbazate (L^4H) were prepared by condensation of -*S*-benzyldithiocarbazate in ethanol with the respective ketones by using MW as well as conventional methods. The chromium(III) complexes have been prepared by mixing $CrCl_3 \cdot 6H_2O$ in 1 : 1 and 1 : 2 molar ratios with monofunctional bidentate ketimines. The structure of the ligands and their transition metal complexes were confirmed by elemental analysis, melting point determinations, molecular weight determinations, infrared (IR), electronic and electron paramagnetic resonance (EPR) spectral, and X-ray powder diffraction studies. On the basis of these studies it is clear that the ligands coordinated to the metal atom in a monobasic bidentate mode by S∩N donors. Thus, an octahedral environment around the chromium(III) has been proposed. The growth inhibiting potential of the ligands and complexes has been assessed against a variety of fungal and bacterial strains.

Keywords: Chromium(III) complexes; *S*-benzyldithiocarbazate; Spectral studies; Antimicrobial activity

1. Introduction

We are increasingly aware of the environmental impact of human activity and the need to develop cleaner and more energy-efficient technologies in chemical synthesis. Solvent-free reactions have played strategic roles in methodologies of organic as well as inorganic synthesis [1, 2]. Among the most promising pathways, microwave (MW)-assisted technique has been popularly used since 1986 for organic synthesis [3, 4] and for inorganic synthesis since 1989 [5]. Use of MW ovens in chemical synthesis and analysis has increasingly grown due to its ability to dramatically reduce reaction times, improve yield, and simplify procedures [6].

Resistance resulting from indiscriminate use of antibacterial and antifungal drugs both in humans and animals is a serious public health problem [7] and preparation of new antimicrobials with activity in low doses is extremely important. Schiff bases and

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their structural analogues as ligating compounds containing acyclic and cyclic imine C=N bonds are of importance in modern coordination chemistry [8]. Schiff bases are an important class of ligands due to their synthetic flexibility, selectivity, and sensitivity toward the central metal, structural similarities with natural biological substances, and also due to the presence of imine group (>C=N–) which is significant in elucidating the mechanism of transformation and racemization reactions in biological systems [9]. Schiff bases are easily prepared by condensation between aldehydes and imines. Stereogenic centers can be introduced in the synthetic design. Schiff bases coordinate with many different metal ions and stabilize various oxidation states and have numerous applications, e.g., anticancer, antibacterial, antiviral, antifungal, and other biological properties [10]. *S*-alkyl and *S*-benzyl esters of dithiocarbazic acids and their Schiff bases provide interesting series of ligands and most of them and their complexes are biologically active [11]. Dithiocarbazates exhibit significant antifungal, antiprotozoal, antibacterial, and anticancer activity [12]. Recently, an *in vitro* insulinomimetic potential of these compounds has been established [13]. Carcinostatic activities have been found for metal complexes of dithiocarbazic acid and the Schiff base derived from *S*-methyl ester [14]. Complexes of these ligand systems exhibit interesting metal–nitrogen and metal–sulfur bonding features with increased electron delocalization which may lead to improved biological activity [15].

Metal ions play a significant role in metabolic activity in the human body. Chromium has been determined to be an essential micronutrient for maintenance of normal glucose tolerance in animals. Chromium(III) acts as an antidiabetic agent [16]. Chromium(III) is safe and required in a proper dietary regimen of animals and humans [17].

We, therefore, synthesize and screen some new Cr(III) Schiff-base complexes of biologically potent ligands against a variety of pathogenic fungal and bacterial strains.

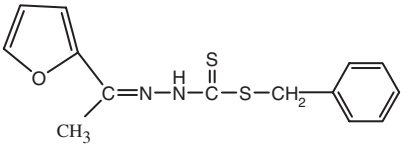
2. Experimental

The $CrCl_3 \cdot 6H_2O$ was purchased from Alfa Aesar. All reagents were dried and distilled before use. 2-Acetylfuran, 2-acetylthiophene, 2-acetylpyridine, and 2-acetylnaphthalene were purchased and used as received. *S*-benzyldithiocarbazate was prepared as described previously [18].

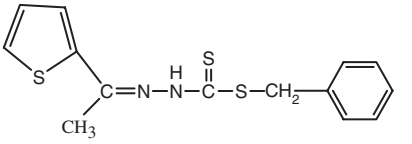
2.1. *Preparation of the ligands*

Two different routes were employed for synthesis of ligands.

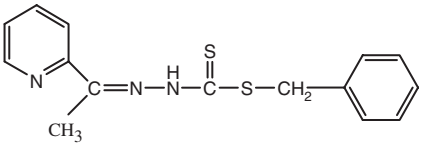
(1) In MW-assisted synthesis of the ligands, *S*-benzyldithiocarbazate of 2-acetylfuran, 2-acetylthiophene, 2-acetylpyridine, and 2-acetylnaphthalene were prepared by condensation of 2-acetylfuran (0.01 mol), 2-acetylthiophene (0.01 mol), 2-acetylpyridine (0.01 mol), and 2-acetylnaphthalene (0.01 mol) with *S*-benzyldithiocarbazate (0.01 mol) in 1 : 1 molar ratio using a beaker in a conventional MW oven by taking 2–5 mL alcohol as solvent. The reactions were completed in 4–7 min. The solution was then concentrated under reduced pressure, which on cooling gave white or brown precipitates, which were recrystallized twice in alcohol.



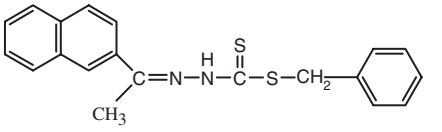
L^1H = 2-Acetylfuran-*S*-benzyldithiocarbazate



L^2H = 2-Acetylthiophene-*S*-benzyldithiocarbazate



L^3H = 2-Acetylpyridine-*S*-benzyldithiocarbazate



L^4H = 2-Acetylnaphthelene-*S*-benzyldithiocarbazate

Figure 1. Structure of the ligands.

Table 1. Comparison between conventional and MW methods of synthesis.

	Yield (%)		Solvent (mL)		Time	
Compound	Thermal	MW	Thermal	MW	Thermal (h)	MW (min)
L^1H	83	85	100	4	4	5
L^2H	82	88	100	3	4	6
L^3H	78	84	100	5	3.5	4.5
L^4H	86	93	100	4	3.5	8
$[Cr(L_1)Cl_2(H_2O)_2]$	73	81	45	2	17	8
$[Cr(L_1)_2ClH_2O]$	73	82	40	3	18	5
$[Cr(L_2)Cl_2(H_2O)_2]$	74	89	50	3	12	5
$[Cr(L_2)_2ClH_2O]$	77	86	50	2	13	5
$[Cr(L_3)Cl_2(H_2O)_2]$	69	82	40	3	15	3
$[Cr(L_3)_2ClH_2O]$	70	85	50	2	13	6
$[Cr(L_4)Cl_2(H_2O)_2]$	69	80	40	3	14	7
$[Cr(L_4)_2ClH_2O]$	70	82	50	2	17	4

(2) For comparison, the above ligands were also synthesized by a thermal method, where the starting materials were dissolved in ~100 mL of alcohol and the contents were refluxed for 4–5 h. The solution was then concentrated under reduced pressure, which on cooling gave brown crystalline precipitates, which were recrystallized twice in alcohol. The structures of ligands are shown in figure 1. A comparison between thermal method and MW method is given in table 1.

2.2. *Preparation of the complexes*

The complexes were also prepared by two different routes.

(1) In MW-assisted synthesis, the complexes were prepared by irradiating the reaction mixture of $CrCl_3 \cdot 6H_2O$ (0.001 mol) and respective ligand (0.001 and 0.002 mol)

in 1 : 1 and 1 : 2 molar ratios using NaOH in appropriate stoichiometric proportions in methanol. The products were recovered from the MW oven and dissolved in 2–5 mL of dry methanol, where sodium chloride precipitate formed during the course of the reaction was removed by filtration and the filtrate was concentrated under reduced pressure. The resulting compounds were washed and recrystallized with cyclohexane.

(2) These complexes were also synthesized by the thermal method and were completed in 14–18 h; the yield of product was also less than that obtained by the MW-assisted synthesis. In this method, the methanolic solution of $CrCl_3 \cdot 6H_2O$ (0.001 mol) was added to the methanolic solution of ligands (0.001 and 0.002 mol) in 1 : 1 and 1 : 2 molar ratios using NaOH in appropriate stoichiometric proportions. The resulting mixture was refluxed for 14–18 h; the sodium chloride precipitate formed during the course of the reaction was removed by filtration and the solvent was removed under reduced pressure. The product was dried in *vacuum*. The resulting compounds were washed and recrystallized with cyclohexane.

2.3. *Physical measurements and analytical method*

Both sets of the ligands and complexes were subjected to various physicochemical measurements. The molecular weights were determined by the Rast camphor method [19]. The metal contents were analyzed gravimetrically. Sulfur and nitrogen were determined by Messenger's [20] and Kjeldahl's methods [21], respectively. Carbon and hydrogen analyses were performed at the Central Drug Research Institute (CDRI), Lucknow. Infrared spectra were recorded on a Nicolet Magna FTIR-550 spectrophotometer using KBr pellets. Electronic spectra were recorded on a Varian–Cary/5E spectrophotometer at SAIF, IIT Madras, Chennai. Electron paramagnetic resonance (EPR) spectra of the complexes were monitored on a Varian E-4X band spectrometer at SAIF, IIT Madras, Chennai.

2.4. *Antimicrobial studies*

2.4.1. Antifungal studies. Bioefficacies of the compounds synthesized by thermal and MW methods were checked *in vitro*. The *in vitro* antifungal activities of the ligands and their complexes have been evaluated against three pathogenic fungi, *Candida albicans*, *Aspergillus niger*, and *Fusarium oxysporum* by the agar plate technique [22]. The potato dextrose agar (PDA) medium was prepared in the laboratory to maintain fungal growth. For PDA preparation, 20 g potato was extracted with distilled water (100 mL) at 100°C for 1 h and filtered by cotton filter. The potato juice was then mixed with 2 g dextrose and 1.5 g agar and finally the pH of the prepared PDA media was adjusted to 7. Solutions of the test compounds in methanol at 100 and 200 ppm were prepared and then mixed with the medium. The medium was then poured into Petri plates and spores of fungi were placed on the medium with the help of inoculum's needle. These Petri plates were wrapped in polythene bags containing a few drops of alcohol and were placed in an incubator at 25 ± 2°C. The activity was determined after 96 h of incubation at room temperature (25°C). Controls were also run and three replicates were used in each case. The linear growth of fungus was obtained by measuring the

diameter of the fungal colony after 4 days and the percentage inhibition was calculated as $100 \times (C-T)/C$, where C is the diameter of the fungus colony in the control plate after 96 h and T the diameter of the fungal colony in the test plates after the same period. The antifungal screening data of compounds were compared with the standard (Flucanazone).

2.4.2. Antibacterial screening. *In vitro* antibacterial screening is generally performed by disk diffusion method [23] for primary selection of the compounds as therapeutic agents. The antibacterial activity of the ligands and their chromium complexes were evaluated against four bacteria including Gram-positive (*Bacillus subtilis* and *Staphylococcus aureus*) and Gram-negative (*Escherichia coli* and *Pseudomonas aeruginosa*). The nutrient agar medium having composition of peptone 5 g, beef extract 5 g, NaCl 5 g, agar-agar 20 g, and distilled water 1000 mL was pipetted into the Petri dish. When it solidified, 5 mL of warm-seeded agar was applied. The seeded agar was prepared by cooling the molten agar to 40°C and then adding 10 mL of bacterial suspension. The compounds were dissolved in methanol in 500 and 1000 ppm concentrations. Paper disks of Whatman No. 1 filter paper measuring diameter of 5 mm were soaked in these solutions of varied concentrations. The disks were dried and placed on the medium previously seeded with organisms in Petri plates at suitable distance. The Petri plates were stored in an incubator at 28 ± 2°C for 24 h. The diameters of the zone of inhibition produced by the compounds were compared with the standard antibiotic (Streptomycin). The zone of inhibition thus formed around each disk containing the test compounds was measured accurately in millimeter.

2.4.3. Determination of minimum inhibitory concentration. Minimum inhibitory concentration (MIC) is the lowest concentration of test agent that inhibited visible growth of bacteria after 18 h incubation at 37°C. The determination of the MIC involves a semi-quantitative test procedure, which gives an approximation to the least concentration of an antimicrobial needed to prevent microbial growth. The MIC was determined by the liquid dilution method [24]. Stock solutions of Cr(III) complexes with 10–50 mg mL^{-1} concentrations were prepared with aqueous methanol. Inoculum of the overnight culture was prepared. In a series of tubes, 1 mL each of Cr(III) complex solutions with different concentrations were taken and 0.4 mL of the inoculum was added to each tube. Further, 3.5 mL of sterile water was added to each of the test tubes. These test tubes were incubated for 24 h and observed for the presence of turbidity. The absorbance of the suspension of the inoculum was observed with spectrophotometer at 555 nm. The end result of the test was the minimum concentration of antimicrobial (test materials), which gave a clear solution, for example, no visual growth [25, 26].

3. Results and discussion

Reactions of $CrCl_3 \cdot 6H_2O$ with the ligands and a stoichiometric amount of NaOH were carried out in 1 : 1 and 1 : 2 molar ratios in methanol. The successive replacement of chloride resulted in $[CrCl_2(L)(H_2O)_2]$ and $[(CrCl(L)_2(H_2O)]$. The overall reaction of 1 : 1

and 1 : 2 complexes are as follows:

$$CrCl_3 \cdot 6H_2O + LH + NaOH \xrightarrow[MeOH]{1:1} [CrCl_2(L)(H_2O)_2] + NaCl + 5H_2O \quad (1)$$

$$CrCl_3 \cdot 6H_2O + 2LH + 2NaOH \xrightarrow[MeOH]{1:2} [CrCl(L)_2(H_2O)] + 2NaCl + 7H_2O \quad (2)$$

The physical properties and analytical data of the ligands and their metal complexes, synthesized by MW technique as well as conventional method, are listed in "Supplementary material" and table 2. As indicated in table 1, the yield of MW-assisted synthesized complexes is more and the time utilized is less compared to conventionally synthesized ligands and complexes. All the chromium complexes are dark green, stable at ambient temperature, slightly soluble in ethanol and methanol, and highly soluble in dimethylformamide (DMF) and dimethyl sulfoxide (DMSO). Molecular weight determinations indicate their monomeric nature.

3.1. *UV spectra*

The electronic spectra of the complexes were recorded in DMSO. Three transitions are expected for Cr(III) complexes and are observed. Bands at 15,344–17,490, 21,110–23,385, and 30,050–33,980 cm^{-1} are due to $^4A_{2g} \rightarrow {}^4T_{2g}(\nu_1)$, $^4A_{2g} \rightarrow {}^4T_{1g}(\nu_2)$, and $^4A_{2g} \rightarrow {}^4T_{1g}(P)(\nu_3)$ transitions, respectively, suggesting an octahedral geometry around Cr^{3+} [27]. Various ligand field parameters like Dq, *B*, and β have been calculated and given in table 3. Energy of the first spin allowed transition [$^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$] directly gives the value of 10Dq. Electronic repulsion parameter is expressed in terms of Racah parameter and "*B*" has been evaluated during these studies. The nephelauxetic ratio β indicates that the complexes have appreciable covalent character.

3.2. *ESR spectra and magnetic moment*

The electron spin resonance (ESR) spectra of 1 : 1 and 1 : 2 chromium(III) complexes synthesized by different routes were recorded at room temperature. These consist of a single broad peak in each case and from which the Lande splitting factor ("*g*" values) has been calculated and given in table 4. The *g* values lie in the range 1.9783–1.9831 with g_{iso} (2.04), which are characteristic of octahedral geometry [28]. The room temperature magnetic moment for $[Cr(L_1)_2ClH_2O]$ is slightly less than required. The observed magnetic moment value of ~3.74 BM and the electronic spectra of $[Cr(L_1)_2ClH_2O]$ support the octahedral structure of the complexes [29].

3.3. *IR spectra*

The significant IR bands of the ligands and their metal complexes along with their tentative assignments, reported in "Supplemental material", are used to establish the mode of coordination of bidentate ligands toward the metal. IR spectra of the ligands display a strong band at 3250–3200 cm^{-1} due to ν(NH) vibrations, absent in spectra of

Table 2. Analytical data and physical properties of the ligands and their complexes synthesized by MW method.

Compound	Color	Melting point (°C)	Found (calculated) (%)					Molar mass found (calculated)	Magnetic moment (μ)
			C	H	N	S	M		
L^1H	Light brown	140	57.74 (57.90)	4.75 (4.80)	9.66 (9.64)	22.90 (22.08)	–	298.16 (290.45)	–
L^2H	White	102	55.00 (54.89)	4.45 (4.60)	9.56 (9.14)	31.44 (31.40)	–	299.59 (306.32)	–
L^3H	Brown	148	59.60 (59.77)	4.96 (5.01)	13.81 (13.94)	21.38 (21.27)	–	295.95 (301.42)	–
L^4H	Brown	118	68.46 (68.53)	5.15 (5.17)	8.00 (7.99)	18.39 (18.29)	–	356.84 (350.50)	–
$[Cr(L_1)Cl_2(H_2O)_2]$	Green	160	37.42 (37.50)	3.80 (3.82)	6.36 (6.24)	14.00 (14.30)	11.55 (11.59)	443.98 (448.33)	3.73
$[Cr(L_1)_2ClH_2O]$	Green	175	49.24 (49.14)	4.10 (4.12)	8.04 (8.18)	18.65 (18.74)	7.77 (7.59)	680.84 (684.25)	3.74
$[Cr(L_2)Cl_2(H_2O)_2]$	Green	80	35.89 (36.20)	3.68 (3.69)	5.21 (5.03)	20.64 (20.71)	11.24 (11.19)	460.54 (464.39)	3.70
$[Cr(L_2)_2ClH_2O]$	Green	100	47.15 (46.93)	3.90 (3.93)	7.77 (7.82)	26.70 (26.85)	7.54 (7.25)	703.58 (716.38)	3.74
$[Cr(L_3)Cl_2(H_2O)_2]$	Green	120	39.55 (39.22)	3.93 (3.94)	8.61 (9.14)	13.91 (13.96)	11.26 (11.31)	449.91 (459.35)	3.74
$[Cr(L_3)_2ClH_2O]$	Green	130	50.62 (51.01)	4.20 (4.28)	11.94 (11.89)	18.54 (18.15)	7.36 (7.36)	699.68 (706.31)	3.75
$[Cr(L_4)Cl_2(H_2O)_2]$	Green	110	46.06 (45.75)	2.64 (2.71)	4.93 (4.81)	16.31 (16.17)	11.23 (11.01)	447.80 (452.11)	3.74
$[Cr(L_4)_2ClH_2O]$	Green	145	61.88 (61.59)	3.00 (3.11)	5.10 (5.24)	14.19 (14.21)	5.82 (5.99)	770.70 (777.15)	3.77

Table 3. Electronic spectral data (cm^{-1}) of the chromium(III) complexes synthesized through thermal and MW methods.

Compound	Transitions	Spectral bands cm^{-1} (nm)	$10D_q$	B^o	$\beta = B/B^o$	$\varepsilon = A/cl$ (L/mol L^{-1})
$[Cr(L_1)Cl_2(H_2O)_2]$	$^4A_{2g}(F) \rightarrow 4T_{2g}(F)$	17,100 (584)	1710	574	0.62	5.999×10^3
	$^4A_{2g}(F) \rightarrow 4T_{1g}(F)$	22,990 (434)				5.872×10^3
	$^4A_{2g}(F) \rightarrow 4T_{1g}(P)$	33,000 (303)				2.677×10^3
$[Cr(L_1)_2ClH_2O]$	$^4A_{2g}(F) \rightarrow 4T_{2g}(F)$	16,510 (605)	1651	566	0.61	5.987×10^3
	$^4A_{2g}(F) \rightarrow 4T_{1g}(F)$	22,368 (467)				5.892×10^3
	$^4A_{2g}(F) \rightarrow 4T_{1g}(P)$	32,250 (310)				3.614×10^3
$[Cr(L_2)Cl_2(H_2O)_2]$	$^4A_{2g}(F) \rightarrow 4T_{2g}(F)$	16,970 (589)	1697	589	0.64	2.932×10^3
	$^4A_{2g}(F) \rightarrow 4T_{1g}(F)$	22,488 (425)				1.956×10^3
	$^4A_{2g}(F) \rightarrow 4T_{1g}(P)$	32,600 (306)				1.938×10^3
$[Cr(L_2)_2ClH_2O]$	$^4A_{2g}(F) \rightarrow 4T_{2g}(F)$	15,344 (651)	1534	840	0.91	944×10^3
	$^4A_{2g}(F) \rightarrow 4T_{1g}(F)$	22,952 (435)				878×10^3
	$^4A_{2g}(F) \rightarrow 4T_{1g}(P)$	33,980 (294)				441×10^3
$[Cr(L_3)Cl_2(H_2O)_2]$	$^4A_{2g}(F) \rightarrow 4T_{2g}(F)$	17,226 (580)	1722	428	0.46	5.997×10^3
	$^4A_{2g}(F) \rightarrow 4T_{1g}(F)$	21,885 (456)				5.131×10^3
	$^4A_{2g}(F) \rightarrow 4T_{1g}(P)$	32,970 (303)				1.517×10^3
$[Cr(L_3)_2ClH_2O]$	$^4A_{2g}(F) \rightarrow 4T_{2g}(F)$	15,856 (630)	1585	499	0.54	5.980×10^3
	$^4A_{2g}(F) \rightarrow 4T_{1g}(F)$	21,110 (473)				5.716×10^3
	$^4A_{2g}(F) \rightarrow 4T_{1g}(P)$	30,050 (332)				2.921×10^3
$[Cr(L_4)Cl_2(H_2O)_2]$	$^4A_{2g}(F) \rightarrow 4T_{2g}(F)$	16,000 (625)	1600	664	0.72	5.879×10^3
	$^4A_{2g}(F) \rightarrow 4T_{1g}(F)$	22,580 (442)				5.611×10^3
	$^4A_{2g}(F) \rightarrow 4T_{1g}(P)$	32,660 (306)				1.472×10^3
$[Cr(L_4)_2ClH_2O]$	$^4A_{2g}(F) \rightarrow 4T_{2g}(F)$	17,490 (571)	1749	563	0.61	5.996×10^3
	$^4A_{2g}(F) \rightarrow 4T_{1g}(F)$	23,385 (427)				4.422×10^3
	$^4A_{2g}(F) \rightarrow 4T_{1g}(P)$	33,846 (295)				2.303×10^3

B, complex and B^o, free ion (918).

Table 4. ESR spectral data of the chromium(III) complexes synthesized through thermal and MW methods.

Compound	Medium wave frequency (GHz)	H_0	g^{II} value	T (°C)
$[Cr(L_1)_2ClH_2O]$	9.38	3379.01	1.9831	25
$[Cr(L_2)Cl_2(H_2O)_2]$	9.38	3375.02	1.9856	25
$[Cr(L_3)Cl_2(H_2O)_2]$	9.38	3388.81	1.9783	25
$[Cr(L_4)_2ClH_2O]$	9.38	3380.93	1.9833	25

the complexes. A sharp and strong band at 1625–1615 cm^{-1} is due to the azomethine of the ligands. IR spectra of the complexes showed a shift to lower wave numbers of 15–25 cm^{-1}. Strong bands at 1050–1100 cm^{-1} in all the ligands, attributed to ν(C=S) moiety, shifted to lower frequency upon coordination. In spectra of Cr(III) complexes a band is observed at 850–875 cm^{-1} which may be attributed to coordinated water. A broad band around 3430–3455 cm^{-1} may be due to ν(O–H) of water. These data, on comparison with the spectra of the ligands, suggest that the azomethine nitrogen and thiolic sulfur are involved in coordination with Cr(III). The far IR spectra of these metal complexes exhibited new bands, which are not present in spectra of the ligands. The single band observed from 310 to 320 cm^{-1} is due to ν(Cr–CI), suggesting thereby that the complexes have a *trans* structure [30]. Bands at 415–460 and 330–356 cm^{-1} are

Suggested structures for chromium complexes

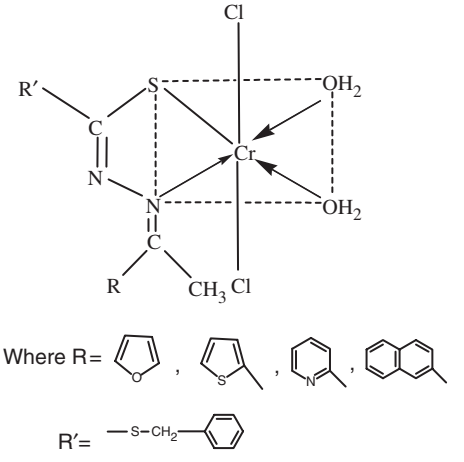


Figure 2. 1 : 1 complex.

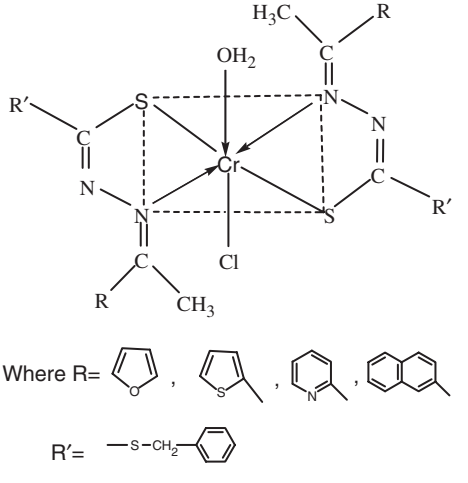


Figure 3. 1 : 2 complex.

assigned to $\nu(Cr \leftarrow N)$ and $\nu(Cr–S)$ [31], thus supporting bonding through the azomethine nitrogen and thiolic sulfur.

The above data suggest that the ligands are bidentate toward the metal ion. On the basis of magnetic measurement, IR and electronic spectral data with an octahedral environment around the metal atom has been proposed and structures are shown in figures 2 and 3.

3.4. *X-ray structure determination*

The possible lattice dynamics of the finely powdered product, $[CrCl_2(L^1)(H_2O)_2]$, has been deduced on the basis of X-ray powder diffraction. The observed interplanar

Table 5. Antibacterial screening data for the ligand and their complexes synthesized through thermal and MW methods.

	Antibacterial activity: diameter (mm) of inhibition zone after 24 h (concentration in ppm)							
	E. coli		*P. aeruginosa*		*B. subtilis*		*S. aureus*	
Compound	500	1000	500	1000	500	1000	500	1000
L^1H	8.0 ± 0.04	9.0 ± 0.02	7.0 ± 0.12	9.0 ± 0.05	6.0 ± 0.18	7.0 ± 0.03	10.0 ± 0.03	10.0 ± 0.08
L^2H	8.7 ± 0.02	9.0 ± 0.03	7.0 ± 0.06	8.0 ± 0.02	6.0 ± 0.06	9.0 ± 0.04	9.0 ± 0.05	9.0 ± 0.04
L^3H	7.0 ± 0.02	8.0 ± 0.16	7.0 ± 0.05	8.0 ± 0.03	5.0 ± 0.01	7.1 ± 0.03	8.0 ± 0.02	8.0 ± 0.03
L^4H	7.0 ± 0.04	9.3 ± 0.10	6.0 ± 0.08	9.0 ± 0.04	5.0 ± 0.04	8.0 ± 0.01	9.9 ± 0.03	11.0 ± 0.12
$[Cr(L_1)Cl_2(H_2O)_2]$	11.0 ± 0.03	14.0 ± 0.07	10.0 ± 0.03	12.0 ± 0.03	9.0 ± 0.06	14.0 ± 0.02	13.0 ± 0.04	17.0 ± 0.15
$[Cr(L_1)_2ClH_2O]$	13.0 ± 0.08	15.0 ± 0.06	14.0 ± 0.04	17.0 ± 0.02	11.0 ± 0.08	17.0 ± 0.03	14.0 ± 0.03	18.0 ± 0.04
$[Cr(L_2)Cl_2(H_2O)_2]$	13.5 ± 0.04	14.0 ± 0.09	12.0 ± 0.06	17.0 ± 0.03	12.0 ± 0.02	14.0 ± 0.02	14.0 ± 0.09	19.0 ± 0.03
$[Cr(L_2)_2ClH_2O]$	13.8 ± 0.05	16.0 ± 0.14	13.0 ± 0.04	19.0 ± 0.05	13.0 ± 0.11	15.0 ± 0.08	15.0 ± 0.03	19.0 ± 0.04
$[Cr(L_3)Cl_2(H_2O)_2]$	10.7 ± 0.04	17.0 ± 0.04	14.0 ± 0.03	18.0 ± 0.14	9.0 ± 0.10	13.0 ± 0.04	12.0 ± 0.18	18.0 ± 0.04
$[Cr(L_3)_2ClH_2O]$	11.0 ± 0.03	19.0 ± 0.02	17.0 ± 0.04	19.0 ± 0.07	10.0 ± 0.05	16.0 ± 0.03	15.0 ± 0.04	19.0 ± 0.03
$[Cr(L_4)Cl_2(H_2O)_2]$	12.0 ± 0.04	16.0 ± 0.05	10.0 ± 0.06	19.2 ± 0.03	10.0 ± 0.09	12.0 ± 0.04	15.0 ± 0.03	20.0 ± 0.04
$[Cr(L_4)_2ClH_2O]$	13.0 ± 0.09	18.5 ± 0.03	11.0 ± 0.04	19.5 ± 0.07	13.0 ± 0.05	13.7 ± 0.04	16.0 ± 0.03	21.0 ± 0.05
Streptomycin	17.6 ± 0.05	19.2 ± 0.01	18.0 ± 0.01	20.0 ± 0.03	17.0 ± 0.01	22.0 ± 0.03	18.6.0 ± 0.05	22.0 ± 0.02

Table 6. Antifungal screening data for the ligands and their complexes synthesized through thermal and MW methods.

	Antifungal activity: percentage inhibition after 96 h (concentration in ppm)					
	C. albicans		*A. niger*		*F. oxysporum*	
Compound	100	200	100	200	100	200
L^1H	42.0 ± 0.4	47.0 ± 0.6	45.0 ± 0.6	48.0 ± 0.2	39.0 ± 0.2	43.0 ± 0.4
L^2H	34.0 ± 0.9	44.0 ± 0.6	38.0 ± 0.6	42.0 ± 0.1	32.0 ± 0.2	40.0 ± 0.2
L^3H	51.0 ± 0.4	56.0 ± 0.8	32.0 ± 0.6	40.0 ± 0.1	52.0 ± 0.2	57.0 ± 0.2
L^4H	40.0 ± 0.3	50.0 ± 1.1	41.0 ± 0.3	50.0 ± 0.4	36.0 ± 0.2	45.0 ± 0.2
$[Cr(L_1)Cl_2(H_2O)_2]$	59.0 ± 0.4	65.0 ± 0.4	55.0 ± 1.5	61.0 ± 1.4	50.0 ± 0.4	65.0 ± 0.2
$[Cr(L_1)_2ClH_2O]$	60.0 ± 0.2	78.0 ± 0.5	50.0 ± 0.6	64.0 ± 0.1	53.0 ± 0.2	63.0 ± 0.3
$[Cr(L_2)Cl_2(H_2O)_2]$	50.0 ± 0.8	66.0 ± 0.7	49.0 ± 0.5	55.0 ± 1.4	44.0 ± 0.7	50.0 ± 0.4
$[Cr(L_2)_2ClH_2O]$	49.0 ± 0.5	52.0 ± 0.7	59.0 ± 0.3	67.0 ± 0.6	55.0 ± 0.4	60.0 ± 0.6
$[Cr(L_3)Cl_2(H_2O)_2]$	78.0 ± 0.6	80.0 ± 0.5	72.0 ± 0.5	75.0 ± 0.5	79.0 ± 0.3	83.0 ± 0.3
$[Cr(L_3)_2ClH_2O]$	69.0 ± 0.5	77.0 ± 0.7	63.0 ± 0.2	68.0 ± 0.4	84.0 ± 0.6	89.0 ± 0.7
$[Cr(L_4)Cl_2(H_2O)_2]$	61.0 ± 0.4	67.0 ± 0.3	50.0 ± 0.2	57.0 ± 0.2	71.0 ± 0.2	77.0 ± 0.5
$[Cr(L_4)_2ClH_2O]$	60.0 ± 1.1	65.0 ± 0.3	54.0 ± 0.3	59.0 ± 0.5	69.0 ± 0.6	73.0 ± 0.4
Flucanazone	95.0 ± 0.8	10.0 ± 0.9	98 ± 1	10 ± 1	10 ± 1	10 ± 1

spacing values (“*d*” in Å) have been measured from the diffractogram of the compound and the Miller indices *h*, *k*, and *l* have been assigned to each *d* value and 2-θ angles are reported. The results show that the compound belongs to “orthorhombic” crystal system having unit cell parameters as $a = 9.05$, $b = 17.15$, $c = 21.15$, maximum deviation of $2\theta = 0.046$ and $\alpha = 90$, $\beta = 90$, and $\gamma = 90$ at wavelength = 1.93728. We have tried to isolate single crystal of a chromium(III) complex suitable for X-ray diffraction study, but could not succeed. However, Byun and Han [32] have recently reported the single crystal structure of a six-coordinate chromium(III) complex in which the bidentate ligand adopts the most stereochemically favorable octahedral orientation.

3.5. *Antimicrobial assay*

The ligands and their chromium complexes synthesized through thermal and MW methods were evaluated for antimicrobial activity against four bacteria, *E. coli*, *P. aeruginosa*, *B. subtilis*, and *S. aureus* and three fungi, *C. albicans*, *A. niger*, and *F. oxysporum*. The results, summarized in tables 5 and 6, were compared with those of the standard drug Streptomycin for bacteria and Flucanazole for fungi. All the ligands and their Cr(III) complexes were sensitive against all the fungal and bacterial strains. The antimicrobial screening data indicate that the metal complexes are more potent antimicrobial agents than the free ligands.

3.6. *Minimum inhibitory concentration*

MIC values calculated for the ligands and their chromium(III) complexes as shown in table 7 indicated that the ligands and their metal complexes were active in inhibiting the growth of the tested organisms between 15 and 40 MIC ($mg\,mL^{-1}$) against selected bacteria and fungi.

Table 7. MIC ($mg\,mL^{-1}$) of the ligands and their complexes synthesized through thermal and MW methods.

Compound	*E. coli*	*P. aeruginosa*	*B. subtilis*	*S. aureus*	*C. albicans*	*A. niger*	*F. oxysporum*
L^1H	25.0 ± 0.1	26.0 ± 0.2	34.0 ± 0.1	28.0 ± 0.2	24.0 ± 0.6	32.0 ± 0.1	39.0 ± 0.2
L^2H	21.0 ± 0.2	32.0 ± 0.2	25.0 ± 0.2	24.0 ± 0.2	36.0 ± 0.4	40.0 ± 0.1	30.0 ± 0.2
L^3H	24.0 ± 0.2	33.0 ± 0.2	23.0 ± 0.1	31.0 ± 0.2	34.0 ± 0.1	27.0 ± 0.4	25.0 ± 0.2
L^4H	37.0 ± 0.2	32.0 ± 0.2	35.0 ± 0.1	34.0 ± 0.1	36.0 ± 0.2	31.0 ± 0.2	30.0 ± 0.2
$[Cr(L_1)Cl_2(H_2O)_2]$	18.0 ± 0.2	16.0 ± 0.1	20.0 ± 0.2	21.0 ± 0.1	15.0 ± 0.1	17.0 ± 0.1	26.0 ± 0.2
$[Cr(L_1)_2ClH_2O]$	19.0 ± 0.2	16.0 ± 0.1	21.0 ± 0.1	18.0 ± 0.3	12.0 ± 0.1	16.0 ± 0.1	20.0 ± 0.2
$[Cr(L_2)Cl_2(H_2O)_2]$	19.0 ± 0.1	24.0 ± 0.2	19.0 ± 0.2	19.0 ± 0.1	12.0 ± 0.2	15.0 ± 0.2	22.0 ± 0.2
$[Cr(L_2)_2ClH_2O]$	16.0 ± 0.1	17.0 ± 0.1	10.0 ± 0.0	16.0 ± 0.1	16.0 ± 0.1	21.0 ± 0.1	15.0 ± 0.2
$[Cr(L_3)Cl_2(H_2O)_2]$	13.0 ± 0.2	17.0 ± 0.2	23.0 ± 0.1	15.0 ± 0.2	15.0 ± 0.2	15.0 ± 0.2	19.0 ± 0.1
$[Cr(L_3)_2ClH_2O]$	16.0 ± 0.2	25.0 ± 0.2	17.0 ± 0.2	31.0 ± 0.3	15.0 ± 0.2	16.0 ± 0.2	18.0 ± 0.2
$[Cr(L_4)Cl_2(H_2O)_2]$	15.0 ± 0.2	24.0 ± 0.2	20.0 ± 0.2	22.0 ± 0.1	15.0 ± 0.2	15.0 ± 0.1	21.0 ± 0.2
$[Cr(L_4)_2ClH_2O]$	30.0 ± 0.6	14.0 ± 0.3	24.0 ± 0.3	16.0 ± 0.1	18.0 ± 0.1	23.0 ± 0.4	14.0 ± 0.2

The biological activity of the ligands exhibited a marked enhancement on coordination with the metal ions against all the test bacterial/fungal strains, which shows that metal chelates are more active than the ligands [33–35]. Increase in concentration of the compounds increases the activity.

A review of the literature indicated that a large number of Schiff bases and their metal complexes have been tested for antimicrobial activity against microorganisms. In most tests, the complexes showed higher inhibitory activity than the ligands proving their potential usefulness as broad-spectrum antimicrobial agents [36]. The antimicrobial activity of Schiff-base ligand and its chromium(III) complex was evaluated by Badwaik and Aswar [37] indicating that the metal complex has higher activity than the free ligand against the same organism under identical experimental conditions. The increased antimicrobial activity of complexes than free ligands has been attributed to chelation theory [38].

4. Conclusions

MW irradiation is an efficient and environmentally benign method to accomplish inorganic synthesis to afford products in higher yields in shorter reaction periods. The ligands and their chromium complexes synthesized through thermal as well as MW methods were used for analyzing their physicochemical properties and antimicrobial activity. The results indicate that all the ligands behave as monofunctional bidentate. Chromium complexes synthesized in 1 : 1 and 1 : 2 molar ratios with monofunctional bidentate ligands were six-coordinate. Antimicrobial activity of the complexes and ligands showed that the Cr(III) complexes are more active than the parent ligands.

Supplementary material

The related data to ESR and X-ray powder diffraction will be provided from the authors on request.

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