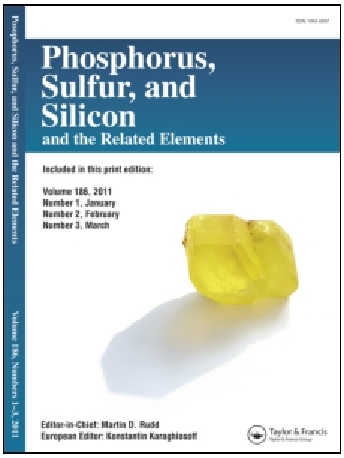


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Synthesis, Characterization, Antimicrobial Activities, and Structural Studies of Lanthanide (III) Complexes with 1-(4-Chlorophenyl)-3-(4-fluoro/hydroxyphenyl)prop-2-en-1-thiosemicarbazone

Chandra K. Oza[a]; Meenakshi Jain[a]; Neelima Jain[a]; Dinesh Verma[a]
[a] Centre of Advanced Studies, Department of Chemistry, University of Rajasthan, Jaipur, India

To cite this Article Oza, Chandra K. , Jain, Meenakshi , Jain, Neelima and Verma, Dinesh(2010) 'Synthesis, Characterization, Antimicrobial Activities, and Structural Studies of Lanthanide (III) Complexes with 1-(4-Chlorophenyl)-3-(4-fluoro/hydroxyphenyl)prop-2-en-1-thiosemicarbazone', Phosphorus, Sulfur, and Silicon and the Related Elements, 185: 2, 377 — 386

To link to this Article: DOI: 10.1080/10426500902797483

URL: http://dx.doi.org/10.1080/10426500902797483

Phosphorus, Sulfur, and Silicon, 185:377–386, 2010

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500902797483

SYNTHESIS, CHARACTERIZATION, ANTIMICROBIAL ACTIVITIES, AND STRUCTURAL STUDIES OF LANTHANIDE (III) COMPLEXES WITH 1-(4-CHLOROPHENYL)-3-(4-FLUORO/HYDROXYPHENYL)PROP-2-EN-1-THIOSEMICARBAZONE

Chandra K. Oza, Meenakshi Jain, Neelima Jain, and Dinesh Verma
Centre of Advanced Studies, Department of Chemistry, University of Rajasthan, Jaipur, India

Twelve coordinate lanthanide (III) complexes with the general composition [Ln $L_3X_n(H_2O)_n$] where Ln = Pr(III), Sm(III), Eu (III), Gd (III), Tb (III), Dy (III), X = Cl^{-1}, $NO_3{}^{-2}$, n = 2–7, and L is 1-(4-chlorophenyl)-3-(4-fluoro/hydroxyphenyl)prop-2-en-1-thiosemicarbazone have been prepared. The lanthanide complexes (5) were derived from the reaction between 1-(4-chlorophenyl)-3-(4-fluoro/hydroxyphenyl)prop-2-en-1-thiosemicarbazone (4) with an aqueous solution of lanthanide salt. Chalcone thiosemicarbazone ligand (4) was prepared by the reaction of [1-(4-chlorophenyl)-3-(4-fluoro/hydroxyphenyl)]prop-2-enone (chalcone) (3) with thiosemicarbazide in the presence of hot ethanol. All the lanthanide-ligand 1:3 complexes have been isolated in the solid state, are stable in air, and characterized on the basis of their elemental and spectral data.

Thiosemicarbazone ligands behave as bidentate ligands by coordinating through the sulfur of the isocyanide group and nitrogen of the cyanide residue. The probable structure for all the lanthanide complexes is also proposed. The chalcone thiosemicarbazone ligands and their lanthanide complexes have been screened for their antifungal and antibacterial studies. Some of the synthesized lanthanide complexes have shown enhanced activity compared with that of the free ligand.

Supplemental materials are available for this article. Go to the publisher's online edition of **Phosphorus, Sulfur, and Silicon and the Related Elements** ***to view the free supplemental file.***

Keywords Antimicrobial activities; 1-(4-chlorophenyl)-3-(4-fluoro/hydroxyphenyl)prop-2-en-1-thiosemicarbazone; lanthanide complexes; spectral studies

Received 4 June 2008; accepted 2 February 2009.

We would like to thank the late Prof. Vijai N. Pathak, Department of Chemistry, Centre of Advance Studies, University of Rajasthan, Jaipur, India, who was instrumental in our research work, and we extend our deepest warm regards to him. We express our sincere gratitude to Dr. K. P. Madhusudnan, Deputy Director and Head, SAIF, Central Drug Research Institute (CDRI), Lucknow, India, for elemental analyses and spectral (IR, NMR, and FAB mass) data, and also thanks to Prof. V. M. Rao, Department of Botany, University of Rajasthan, Jaipur, India, for biological activity. The authors are thankful to the Coordinator of Centre of Advanced Studies, Department of Chemistry, University of Rajasthan, for providing chemicals and other facilities.

Address correspondence to Chandra K. Oza, Centre of Advanced Studies, Department of Chemistry, University of Rajasthan, Jaipur 302 004, India. E-mail: drneelimajain@yahoo.com

INTRODUCTION

The chemistry of chalcone thiosemicarbazones, hydrazones, and their allied derivatives has aroused great interest due to their diverse pharmaceutical activities, i.e., their use as anticholinesterase,[1] antibacterial,[2–5] antifungal,[4] antimalarial,[2,6–8] antileukemic,[8,9] antituberculosis,[10] antimicrobial,[11–13] and antiproliferative[14] agents. Some of them have shown biological activities[15,16] and were found to possess increased activity when they were administered as corresponding metal complexes.[17–19] A significant correlation between the chelating properties and antitumor activity of some heterocyclic aldehydic thiosemicarbazones in animal systems were also reported.[20–22] Extensive studies on some substituted 1-benzoyl-4-phenylthiosemicarbazide metal ion complexes were also reported.[23] Encouraged by these observations, we report in this article the synthesis and antimicrobial activities of 12 new lanthanide complexes of 1-(4-chlorophenyl)-3-(4-fluoro/hydroxyphenyl)prop-2-en-1-thiosemicarbazone.

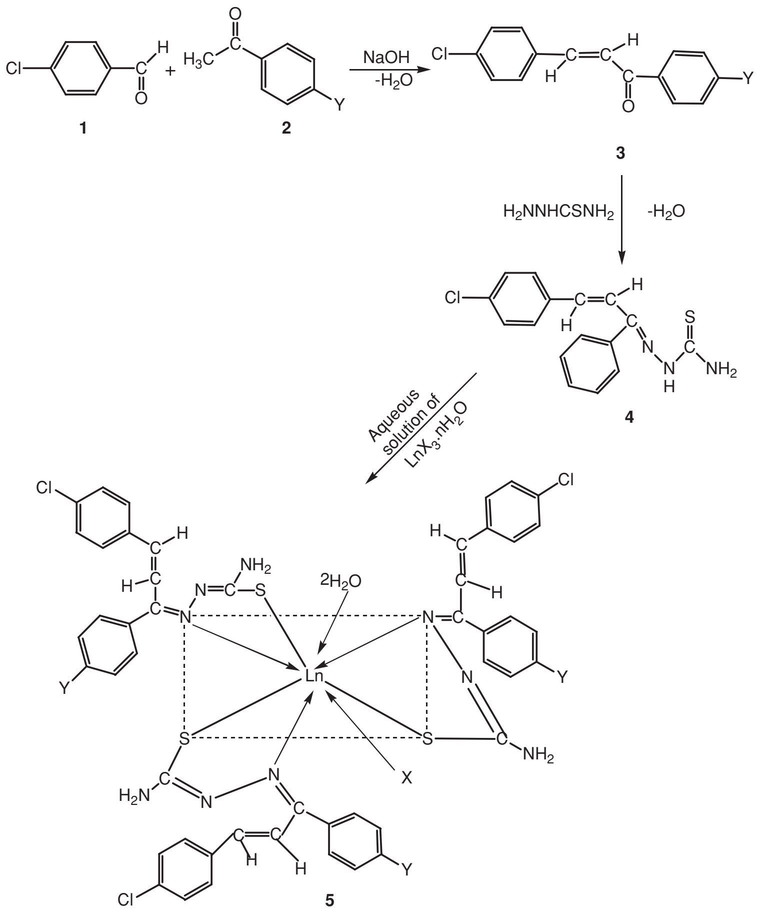
RESULTS AND DISCUSSION

Synthesis

[1-(4-Chlorophenyl)-3-(4-fluoro/hydroxyphenyl)prop-2-enone] (chalcones) (**3**) were prepared by the method of Joshi and Jauhar.[23] 1-(4-Chlorophenyl)-3-(4-fluoro/hydroxy phenyl)prop-2-enones were then treated with thiosemicarbazide in hot ethanolic solution by Campaigne and Archer's method.[24] A solution of 1-(4-chlorophenyl)-3-(4-fluoro/hydroxyphenyl)prop-2-en-1-thiosemicarbazone was treated with an aqueous solution of lanthanide salt Ln = Pr(III), Sm(III), Eu(III), Gd(III), Tb(III), and Dy(III) in a 3:1 molar ratio with stirring to afford tris[1-(4-fluoro/hydroxyphenyl)-3-(4-chlorophenyl)prop-2-en-1-thiosemicarbazone]praseodymium/samarium/europium/gadolinium/terbium/dysprosium (III) (**5a–l**) (Scheme 1). The structure of the synthesized lanthanide complexes was established on the basis of their IR, ^{1}H NMR, and FAB mass spectral studies. Physical and analytical data of chalcone thiosemicarbazone ligands and their lanthanide complexes **4** and **5** are given in Tables I and II, respectively. The spectral data of synthesized chalcone thiosemicarbazone ligands (**4**) and their lanthanide complexes (**5a–l**) are given in Table III. Major mass fragments along with their relative intensities and *m/z* values of lanthanide complexes are given in Table IV S (available online in the Supplemental Materials).

IR Spectra

The IR spectra of 1-(4-chlorophenyl)-3-(4-fluoro/hydroxyphenyl)prop-2-enone (chalcones) (**3**) showed absorption bands at 1680 cm^{-1}, which is attributed to $>$C=O stretching vibration. In the IR spectra of 1-(4-chlorophenyl)-3-(4-fluoro/hydroxyphenyl) prop-2-en-1-thiosemicarbazone (**4**), a $>$C=O absorption band at 1680 cm^{-1} disappeared and new absorption bands appeared in the region 3304–3420 cm^{-1}, 3150–3300 cm^{-1}, and 1175–1180 cm^{-1} due to $-NH_2$ absorption, $>$N−H absorption, and $>$C=S stretching vibration, respectively. The IR spectra of lanthanide complexes of tris[1-(4-chlorophenyl)-3-(4-fluoro/hydroxyphenyl)prop-2-en-1-thiosemicarbazone] (**5**) exhibited $-NH_2$ absorption in the region 3392–3440 cm^{-1}, which remains unaltered, indicating non-involvement of nitrogen of $-NH_2$ group on coordination with lanthanide ions in complexation reactions, but slight displacement of these frequencies is due to increased



	X	Y	Ln		X	Y	Ln
5a	NO_3	F	Pr	5g	NO_3	OH	Pr
5b	Cl	F	Sm	5h	Cl	OH	Sm
5c	NO_3	F	Eu	5i	NO_3	OH	Eu
5d	Cl	F	Gd	5j	Cl	OH	Gd
5e	NO_3	F	Tb	5k	NO_3	OH	Tb
5f	NO_3	F	Dy	5l	NO_3	OH	Dy

Scheme 1

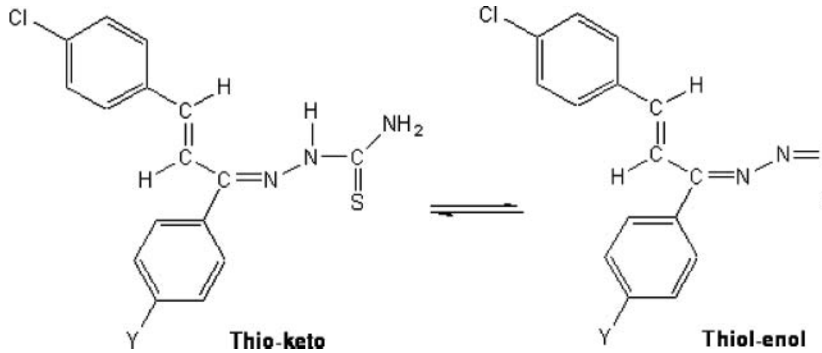
positive charge on the nitrogen atom arising because of donation of an electron pair from sulfur of thioamide moiety, which is involved in chelation. A sharp >N—H absorption in the range of 3150–3300 cm^{-1} disappeared, indicating possible deprotonation on the β-nitrogen after complexation with the lanthanide ion. This band undergoes a negative shift by ~35 cm^{-1} in the lanthanide complexes, and this shift is the consequence of drainage of an electron of the terminal N atom of (=N—N=) moiety, indicating the coordination of at least one of the —N— groups to the central lanthanide ion. A very strong >C=N

Table I Physical data of 1-(4-chlorophenyl)-3-(4-fluoro/hydroxyphenyl)prop-2-en-1-thiosemicarbazone(**4**)

Compd. No.	Y	Color	Mp °C	Yield	Molecular formula
4a	F	Yellow	>156	92	$C_{16}H_{13}N_3ClFS$
4b	OH	Yellow	>180	74	$C_{16}H_{14}N_3ClS$

absorption was observed in the range of 1594–1642 cm^{-1} of the free azomethine group in the ligand shifts to the lower frequency side (~5–8 cm^{-1}) in the spectra of complex indicating the coordination of the azomethine nitrogen to the lanthanide atom. The strong (N—N) absorption in the range of 835–843 cm^{-1} in the ligand experiences a positive shift by ~10–15 cm^{-1} upon complexation, which confirms the involvement of one N atom (=N—N=) group in the bonding.

The IR spectra of these complexes do not display the S—H mode at about 2600 cm^{-1}, indicating that in the solid state, these ligands remain in thio-keto form (Scheme 2).



Scheme 2

However, upon lanthanide complex formation, all these bands disappear, showing the bonding of sulfur to the lanthanide atom by the loss of thiolic protons of ligands. A new absorption band in the lanthanide complexes at 477–499 cm^{-1} assigned to Ln—N confirms the lanthanide nitrogen bond in the complexes. The appearance of a new Ln—S absorption band occurs in the range of 320–340 cm^{-1}.

The appearance of a broad band at 3285–3520 cm^{-1} in the spectra of all lanthanide complexes is associated with coordinated and/or lattice water molecules supported from mass spectral data. These lanthanide complexes also show new bands at 1385–1399 cm^{-1} and 356–362 cm^{-1}, which may be assigned to NO_3 and Ln—Cl absorptions, proving the presence of NO_3^- and Cl^- as a free ion.[25]

^{1}H NMR Spectra

The ^{1}H NMR spectra of 1-(4-chlorophenyl)-3-(4-fluoro/hydroxyphenyl)prop-2-en-1-thiosemicarbazone (**4a**) showed an additional broad signal at δ 3.07 ppm (2H), a sharp singlet at δ 10.31 ppm (1H), and a multiplet at δ 6.82–7.12 ppm (12H) assigned to the $-NH_2$ proton, —NH proton, and aromatic protons, respectively. The two olefinic protons constitute an AB pattern and appeared as a pair of doublets. The doublet appeared at δ 5.42–6.03 ppm

Table II Physical and analytical data of tris[1-(4-chlorophenyl)-3-(4-fluoro/hydroxyphenyl)prop-2-en-1-thiosemicarbazone] lanthanide (III) (**5**)

							Elemental analyses Found (Calc.)					
Compd. No.	X	Y	Color	Mp (°C)	Yield (%)	Molecular formula	C	H	N	S	Ln	ueeff. B.M.
5a	NO_3	F	Brown	>217	84	$[Pr(C_{48}H_{36}Cl_3F_3N_9S_3)(7H_2O)(2NO_3)]$	41.52	3.60	11.10	6.92	10.16	2.51
						$[PrC_{48}H_{50}Cl_3F_3N_{11}O_{13}S_3]$	(41.50)	(3.58)	(11.09)	(6.90)	(10.15)	
5b	Cl	F	Brown	>225	91	$[Sm(C_{48}H_{36}Cl_3F_3N_9S_3)]\ (5H_2O)$	46.60	3.72	10.19	7.76	12.13	2.55
						$[SmC_{48}H_{46}Cl_3F_3N_9O_5S_3]$	(46.59)	(3.70)	(10.18)	(7.75)	(12.12)	
5c	NO_3	F	Brown	>205	88	$[Eu(C_{48}H_{36}Cl_3F_3N_9S_3)\ (2H_2O)(3NO_3)]$	42.04	2.91	12.26	7.00	11.09	
						$(Eu_{48}H_{40}Cl_3F_3N_{12}O_{11}S_3]$	(42.03)	(2.90)	(12.25)	(7.02)	(11.05)	
5d	Cl	F	Brown	>232	92	$[Gd(C_{48}H_{36}Cl_3F_3N_9S_3)(4H_2O)]$	47.02	3.59	10.28	7.83	12.81	7.33
						$[GdC_{48}H_{44}Cl_3F_3N_9O_4S_3]$	(47.01)	(3.58)	(10.25)	(7.80)	(12.80)	
5e	NO_3	F	Brown	>227	87	$[Tb(C_{48}H_{36}Cl_3F_3N_9S_3)(2H_2O)(3NO_3)]$	44.96	3.12	13.11	7.49	12.41	3.51
						$[TbC_{48}H_{40}Cl_3F_3N_{12}O_{11}S_3]$	(44.95)	(3.10)	(13.10)	(7.45)	(12.39)	
5f	NO_3	F	Brown	>235	86	$[Dy(C_{48}H_{36}Cl_3F_3N_9S_3)(5H_2O)(3NO_3)]$	40.16	3.20	11.71	6.69	11.29	2.51
						$[DyC_{48}H_{46}Cl_3F_3N_{12}O_{14}S_3]$	(40.14)	(3.18)	(11.69)	(6.65)	(11.25)	
5g	NO_3	OH	Brown	>242	87	$[Pr(C_{48}H_{39}Cl_3N_9O_3S_3)(2H_2O)(3NO_3)]$	42.57	3.17	12.41	7.09	10.42	
						$[PrC_{48}H_{43}Cl_3N_{12}O_{14}S_3]$	(42.55)	(3.15)	(12.40)	(7.05)	(10.40)	
5h	Cl	OH	Brown	>210	87	$[Sm(C_{48}H_{39}Cl_3N_9O_3S_3)(3H_2O)]$	48.24	3.76	10.55	8.04	12.56	
						$[SmC_{48}H_{45}Cl_3N_9O_6S_3]$	(48.22)	(3.75)	(10.53)	(8.02)	(12.54)	
5i	NO_3	OH	Brown	>227	88	$[Eu(C_{48}H_{39}Cl_3N_9O_3S_3)(H_2O)]$	49.65	3.53	10.86	8.27	13.10	
						$[EuC_{48}H_{41}Cl_3N_9O_4S_3]$	(49.62)	(3.52)	(10.84)	(8.25)	(13.08)	
5j	Cl	OH	Brown	>222	86	$[Gd(C_{48}H_{39}Cl_3N_9O_3S_3)(4H_2O)]$	47.25	3.85	10.33	7.87	12.87	
						$[GdC_{48}H_{47}Cl_3N_9O_7S_3]$	(47.22)	(3.82)	(10.32)	(7.85)	(12.85)	
5k	NO_3	OH	Brown	>208	89	$[Tb(C_{48}H_{39}Cl_3N_9O_3S_3)(2H_2O)(3NO_3)]$	40.33	3.01	11.76	6.72	11.13	
						$[TbC_{48}H_{43}Cl_3N_{12}O_{14}S_3]$	(40.30)	(3.00)	(11.75)	(6.70)	(11.11)	
5l	NO_3	OH	Brown	>232	85	$[Dy(C_{48}H_{39}Cl_3N_9O_3S_3)(5H_2O)(3NO_3)]$	42.01	3.57	12.25	7.00	11.81	
						$[DyC_{48}H_{49}Cl_3N_{12}O_{17}S_3]$	(42.01)	(3.55)	(12.22)	(7.01)	(11.80)	

Table III Spectral data of [1-(4-chlorophenyl)-3-(4-fluoro/hydroxyphenyl)-prop-2-en-1-thiosemicarbazone] **(4)** and their lanthanide complexes **(5)**

Compound no.	IR (KBr)ν_{max} cm^{-1}	^1H NMR ($CDCl_3$) δ ppm	FAB mass m/z
4a	3420 (NH_2 str.), 3300 (NH str.), 1180 (>C=S str.), 3062 (aromatic C−H str.), 2700 (aliphatic C−H str.), 1605 (>C=N str.), 1482 (>C=C< str.), 545 (C−Cl str.), 1140 (C−F str.), 835 (N−N str.)	3.07 (s, NH_2, 2H), 10.31 (S, NH, 2H), 6.82–7.92 (m, ArH, 12H), merged (2H, −CH=CH−)	M^++1; 334/336; M^+; 333/335 (isotopic cluster) (mp) > 156
4b	3304 (NH_2 str.), 3150 (NH str.), 1175 (>C=S str.), 3050 (OH str.), 3060 (aromatic C−H str.), 1600 (>C=N str.), 2975 (aliphatic C−H str.), 1470 (>C=C< str.), 540 (C−Cl str.), 842 (N−N str.)	2.87 (S, NH_2, 2H), 10.62 (S, NH, 2H), 6.89–7.94 (m, ArH, 12H), 7.41 (S, OH, 1H), merged (−CH=CH−, 2H)	M^++1; 332/334, M^+; 331/333 (isotopic cluster) (mp)>180
5a	3392 (NH_2 str.), 1110 (−C−S str.), 3052 (aromatic C−H str.), 1606 (aliphatic C−H str.), 1600 (>C=N str.), 1474 (>C=C< str.), 838 (N−N str.), 728 (C−Cl str.), 444 (Pr−N str.), 1320 (Pr−S str.)	3.07 (S, NH_2, 6H), 6.92–7.92 (m, ArH, 36H), merged (−CH = CH−, 6H)	M^++1; 1388/1390 M^+; 1387 / 1389 (isotopic cluster) (mp)>217
5b	3407 (NH_2 str.), 1109 (C−S str.), 3027 (aromatic C−H str.), 1602 (aliphatic C−H str.), 1594 (>C=N str.), 1475 (>C=C< str.), 721 (C−Cl str.), 1142 (C−F str.), 835 (N−N str.), 494 (Sm−N str.), 1325 (Sm−S str.)	3.12 (S, NH_2, 6H), 7.02–7.03 (m, ArH, 36H), merged (−CH=CH−, 6H)	M^++1; 1237/1239, M^+; 1236/1238 (isotopic cluster) (mp)>225
5c	3415 (NH_2 str.), 1116 (C−S str.), 3029 (aromatic C−H str.), 1604 (aliphatic C−H str.), 1592 (>C=N str.), 1472 (>C=C< str.), 742 (C−Cl str.), 1145 (C−F str.), 837 (N−N str.), 499 (Eu−N str.), 345 (Eu−S str.)	3.08 (S, NH_2, 6H), 7.04–7.08 (m, ArH, 36H), merged, −CH=CH−, 6H	M^++1; 1371/1373 M^+; 1370/1372 (isotopic cluster) (mp)>205
5d	3396 (NH_2 str.), 1140 (C−S str.), 3030 (aromatic C−H str.), 1608 (aliphatic C−H str.), 1600 (>C=N str.), 1477 (>C=C< str.), 752 (C−Cl str.), 1148 (C−F str.), 847 (N−N str.), 473 (Gd−N str.), 348 (Gd−S str.)	3.10 (S, NH_2, 6H), 7.08–8.02 (m, ArH, 36H), merged (−CH=CH−, 6H)	M^++1; 1226/1228 M^+; 1225/1227 (isotopic cluster) (mp)>232
5e	3418 (NH_2 str.), 1109 (C−S str.), 3032 (aromatic C−H str.), 1610 (aliphatic C−H str.), 1612 (>C=N str.), 1482 (>C=C< str.), 748 (C−Cl str.), 1150 (C−F str.), 840 (N−N str.), 482 (Tb−N str.), 340 (Tb−S str.)	2.92 (S, NH_2, 6H), 7.23–8.34 (m, ArH, 36H), merged (−CH=CH−, 6H)	M^++1; 1282/1284 M^+; 1281/1283 (isotopic cluster) (mp)>227
5f	3400 (NH_2 str.), 1110 (C−S str.), 3036 (aromatic C−H str.), 1612 (aliphatic C−H str.), 1615 (>C=N str.), 1484 (>C=C< str.), 745 (C−Cl str.), 1158 (C−F str.), 843 (N−N str.), 485 (Dy−N str.), 348 (Dy−S) str.	2.92 (S, NH_2, 6H), 7.43–8.94 (m, ArH, 36 H), merged (−CH=CH−, 6H)	M^++1; 1435/1437 M^+; 1434/1436 (isotopic cluster) (mp)>235

5g	3400 (NH$_2$ str.), 1111 (C−S str.), 3050 (OH str.), 3036 (aromatic C−H str.), 1615 (aliphatic C−H str.), 1615 (>C=N str.), 1485 (>C=C< str.), 748 (C−Cl str.), 1152 (C−F str.), 840 (N−N str.), 486 (Pr−N str.), 340 (Pr−S str.)	3.07 (S, NH$_2$, 6H), 7.04–7.92 (m, ArH, 36H), 8.01 (S, OH, 3H), 5.92 (d, CH=$\overset{\alpha}{\dot{\mathrm{C}}}$H−C=N, 3H), 7.44 (d, $\overset{\beta}{\dot{\mathrm{C}}}$H=CH−C=N, 3H)	M$^+$+1; 1354/1356 M$^+$; 1353/1355 (isotopic cluster) (mp)>242
5h	3420 (NH$_2$ str.), 1116 (C−S str.), 3052 (OH str.), 3038 (aromatic C−H str.), 1620 (aliphatic C−H str.), 1615 (>C=N str.), 1488 (>C=C< str.), 750 (C−Cl str.), 1158 (C−F str.), 840 (N−N str.), 496 (Sm−N str.), 340 (Sm−S str.)	3.10 (S, NH$_2$, 6H), 7.03–7.39 (m, ArH, 36H), 8.25 (S, OH, 3H), merged (−CH=CH−, 6H)	M$^+$+1; 1195/1197 M$^+$; 1194/1196 (isotopic cluster) (mp)>210
5i	3440 (NH$_2$ str.), 1120 (C−S str.), 3058 (OH str.), 3038 (aromatic C−H str.), 1625 (aliphatic C−H str.), 1635 (>C=N str.), 1489 (>C=C< str.), 754 (C−Cl str.), 1160 (C−F str.), 840 (N−N str.), 492 (Eu−N str.), 340 (Eu−S str.)	3.72 (S, NH$_2$, 6H), 7.04–7.50 (m, ArH, 36H), 8.28 (S, OH, 3H), merged (−CH=CH−, 6H)	M$^+$+1; 1161/1163 M$^+$; 1160/1162 (isotopic cluster) (mp)>227
5j	3448 (NH$_2$ str.), 1124 (C−S str.), 3060 (OH str.), 3040 (aromatic C−H str.), 1628 (aliphatic C−H str.), 1638 (>C=N str.), 1488 (>C=C< str.), 756 (C−Cl str.), 1162 (C−F str.), 835 (N−N str.), 481 (Gd−N str.), 320 (Gd−S str.)	3.74 (S, NH$_2$, 6H), 7.02–7.59 (m, ArH, 36H), 8.30 (S, OH, 3H), 5.81 (d, CH=$\overset{\alpha}{\dot{\mathrm{C}}}$H−C=N, 3H), 7.41 (d, $\overset{\beta}{\dot{\mathrm{C}}}$H=CH−C=N, 3H)	M$^+$+1; 1220/1222 M$^+$; 1219/1221 (isotopic cluster) (mp)>222
5k	3415 (NH$_2$ str.), 1120 (C−S str.), 3065 (OH str.), 3042 (aromatic C−H str.), 1625 (aliphatic C−H str.), 1640 (>C=N str.), 1489 (>C=C< str.), 757 (C−Cl str.), 1164 (C−F str.), 838 (N−N str.), 487 (Tb−N str.), 322 (Tb−S str.)	3.12 (S, NH$_2$, 6H), 7.05–7.92 (m, ArH, 36H), 8.42 (S, OH, 3H), 5.92 (d, CH=$\overset{\alpha}{\dot{\mathrm{C}}}$H−C=N, 3H), 7.52 (d, $\overset{\beta}{\dot{\mathrm{C}}}$H=CH−C=N, 3H)	M$^+$+1; 1372/1374 M$^+$; 1371/1373 (isotopic cluster) (mp)>232
5l	3418 (NH$_2$ str.), 1127 (C−S str.), 3071 (OH str.), 3042 (aromatic C−H str.), 1628 (aliphatic C−H str.), 1642 (>C=N str.), 1487 (>C=C str.), 752 (C−Cl str.), 1165 (C−F str.), 837 (N−N str.), 473 (Dy−N str.), 330 (Dy−S str.)	3.12 (S, NH$_2$, 6H), 7.03–7.95 (m, ArH, 36H), 8.45 (S, OH, 3H), 6.01 (d, CH=$\overset{\alpha}{\dot{\mathrm{C}}}$H−C=N, 3H), 7.64 (d, $\overset{\beta}{\dot{\mathrm{C}}}$H=CH−C=N, 3H)	M$^+$+1; 1429/1431 M$^+$; 1428/1430 (isotopic cluster) (mp)>208

with coupling constant ($J = 9.0$ Hz) due to the α proton ($-CH=CH-C=N$), and a doublet appeared at δ 7.84–7.92 ppm with coupling constant ($J = 9.0$ Hz) due to the β proton ($-CH=CH-C=N$). This strong downfield shift of these protons is due to an extended conjugation with aromatic protons. The high value of the coupling constant suggests trans geometry across the double bond. ^{1}H NMR spectra of compounds **5a–l** revealed the singlet at δ 3.07–3.13 ppm (6H), a sharp double doublet at δ 6.80–7.84 (6H) ppm with coupling constant 6.0–6.4 Hz ($CH-CH-C=N$), and the doublet in the region δ 6.16–7.25 (6H) ppm with coupling constant 6.0–6.3 Hz due to ($CH = CH-C=N$) proton and a singlet at δ 8.01–8.58 (3H) ppm due to $-NH_2$ protons, olefinic protons, and –OH protons, respectively. ^{1}H NMR spectra of lanthanide complex **5** exhibited multiplets due to aromatic protons in the range of δ 7.01–7.97 (36H) ppm. The lattice and coordinated water molecules were observed at δ 4.23–4.10 ppm and δ 4.39–4.48 ppm, respectively. All other NMR spectral data are given in Table III.

The molar conductance of the complexes in nitrobenzene (10^{-3}m mol) indicates that they are essentially non-electrolytes. The magnetic moments of the complexes at room temperature (Table II) show little deviation from the Van Vleck values, indicating the non-participation of the **4f** electrons in bond formation in these complexes. The magnetic moments of these complexes are within the predicted range.[26,27]

Electronic Spectra

The electronic spectra of the complexes in the visible region indicate a shift of the bands. The magnitude of nephelauxetic effect is dependent on the change in electronic repulsion parameter. The nephelauxetic ratio (β), percentage covalency parameter ($\delta\%$), bonding parameter ($b^{1/2}$), and the angular covalency (η) values, respectively, are 0.9797–0.9818, 0.9998–2.0823, 0.0092–0.0104, and 0.009207–0.010406.

The values are less than one, and the positive values of% and bonding between the metal and ligands are covalent.[28,29]

Fast Atom Bombardment (FAB) Mass Spectra

All FAB mass spectra of synthesized lanthanide complexes exhibited M^++1 peak due to transfer of proton matrix. Lanthanide complexes **5a** exhibited (M^++1) peak at *m/z* 1388/1390 of relative intensity of 13.23% and molecular ion peak (M^+) at *m/z* 1387/1389 of relative intensity 14.89%. Lanthanide complex **5a** exhibited a base peak at *m/z* 391 (100.0%)/393 (100.0%) corresponding to the molecular formula.

Lanthanide complex **5i** exhibited (M^++1) peak at *m/z* at 1161 (15.0%)/1163 (5.0%) and molecular ion peak (M^+) at m/z 1160 (20.0%)/1162 (10.0%). FAB mass spectra of lanthanide complexes **5** exhibited (M+1) peak and (M^+) peak. Details are given in Table IV S (available online in the Supplementary Materials).

EXPERIMENTAL

Melting points were determined in open glass capillaries and are uncorrected (Tempo melting point apparatus). The purity of the synthesized lanthanide complexes was checked by thin layer chromatography (TLC) on silica gel in various non-aqueous solvent systems. IR spectra were recorded in KBr on a Perkin Elmer 557 spectrometer, PMR spectra were recorded in $CDCl_3$ on a Brucker spectrometer (200 MHz) using tetramethylsilane (TMS) as an internal reference, and FAB mass spectra were recorded on Jeol SX-102 (FAB) spectrometer. Electronic spectra were recorded on a Elico CL-54, and magnetic moments of the complexes were determined by the Gouy method at room temperature. The conductance measurements were carried out in nitrobenzene medium (-10^{-3}M) by a Systronics 303 conductivity meter.

Different 1-(4-chlorophenyl)-3-(4-fluoro/hydroxyphenyl)prop-2-enone (chalcones) were prepared by the method proposed by Joshi and Jauhar,[23] and 1-(4-chlorophenyl)-3-(4-fluoro/hydroxyphenyl)prop-2-en-1-thiosemicarbazones were prepared by another method given by Campaigne and Archer.[24]

Tris[1-(4-chlorophenyl)-3-(4-fluoro/hydroxyphenyl)prop-2-en-1-thiosemicarbazone]lanthanide (III) Complexes (5a–l): Tris[1-(4-chlorophenyl)-3-(4-hydroxyphenyl)prop-2-en-1-thiosemicarbazone]europium (III) (5i)

1-(4-Chlorophenyl)-3-(4-hydroxyphenyl) prop-2-en-1-thiosemicarbazone (3 mmol, 0.84 g) was dissolved in ethanol (20 mL) taken in 100 mL round bottomed flask and heated on a water bath. This hot solution was stirred with an aqueous solution of lanthanide salt $Eu(NO_3)_3$ $5H_2O$ (1 mmol, 0.428 g) in dropping funnel in 3:1 molar ratio. The resulting mixture thus obtained was refluxed on a water bath for 2 h and left overnight to yield the dark brown crystalline lanthanide complex, which was filtered off under suction and repeatedly washed several times with water (4 × 50 mL) until the filtrate became colorless. The solid was washed with diethylether and dried over anhydrous $CaCl_2$ in a vacuum desiccator. The complexes were found to be amorphous colored lanthanide complexes, stable at room temperature, and soluble in $CDCl_3$. Yield 1.02 g (88%) **5i**, mp >227°C. All other lanthanide complexes (**5a–l**) were prepared using the same procedure and are given in Table II along with their characteristics and analytical data.

Antibacterial and Antifungal Activities

Representative chalcone thiosemicarbazone ligands and their lanthanide complexes were screened for their antibacterial activity against Gram-negative bacteria *E. coli* and Gram-positive bacteria *S. aureus* at 100, 200, 500, and 1000 ppm concentrations. (See the Supplemental Materials online, Tables VS and VIS).

REFERENCES

1. S. S. Tiwari, A. K. Sengupta, and J. Kumari, *J. Indian Chem. Soc.*, **L1,** 402 (1974).
2. D. L. Klayman, J. P. Scovill, J. F. Bartosevich, C. J. Mason, and T. S. Griffin, U. S. US 4, 317, 776 (Cl. 260–244.4; CO7D211/24), 02 Mar 1982, Appl. 4, 247, 04 Jan 1979; 7 pp; *Chem. Abstr.*, **96,** 199538S (1982).
3. A. S. Dobek, D. L. Klayman, E. T. Dickson Jr., J. P. Scovill, and E. C. Tramont, *Antimicrob. Agents Chemother.*, **18**(1)**,** 27 (1980).
4. B. J. A. Jeragh and A. El-Dissouky, *J. Coord. Chem.*, **58**(12/15)**,** 1029 (2005).
5. N. Siddiqui and O. Singh, *Indian J. Pharma. Sci.*, **65**(4)**,** 423 (2003).
6. D. L. Klayman, J. P. Scovill, J. F. Bartosevich, and C. J. Mason, *J. Med. Chem.*, **22**(11)**,** 1367 (1979).
7. D. L. Klayman, J. P. Scovill, J. F. Bartosevich, and J. Bruce, *J. Med. Chem.*, **26**(1)**,** 35 (1983).

8. J. P. Scovill, D. L. Klayman, and C. F. Franchino, *J. Med. Chem.*, **25**(10)**,** 1261 (1982).
9. D. L. Klayman, J. P. Scovill, C. J. Mason, J. F. Bartosevich, J. Bruce, and A. J. Lin, *Arzneim-Forsch. Drug Res.*, **33**(7)**,** 909 (1983).
10. F. M. Collins, D. L. Klayman, and N. E. Morrison, *Am. Rev. Respir. Dis.*, **125**(1)**,** 58 (1982).
11. M. B. Halli and Z. S. S. Qureshi, *Metal-Org. Nano-Metal Chem.*, **34**(10)**,** 1755 (2004).
12. G. Domagk et al., *Naturwissenschaften*, **33**, 315 (1946).
13. D. B. Lovejoy and D. R. Richardson, *Blood*, **100**(2)**,** 666 (2002).
14. N. Ergenc, E. Ilhan, and G. Otuk, *Pharmazie*, **47**(1)**,** 59 (1992).
15. M. Baldini, M. Belicchi-Ferrari, F. Bisceglie, G. Pelosi, S. Pinelli, and P. Tarasconi, *Inorg. Chem.*, **42**(6)**,** 2049 (2003).
16. D. R. Williams, *Chem. Rev.*, **72**(3)**,** 203 (1972).
17. A. Furst and R. T. Haro, *Progr. Exp. Tumor Res.*, **12,** 102 (1969).
18. F. P. Dwyer, E. Mayhew, E. M. F. Roe, and A. Shulman, *Brit. J. Cancer*, **19**(1)**,** 195 (1965).
19. F. A. French, E. J. Blanz Jr., S. C. Shaddin, and R. W. Brockman, *J. Med. Chem.*, **17**(2)**,** 172 (1974).
20. K. C. Agrawal, A. J. Lin, B. A. Booth, J. R. Wheaton, and A. C. Sartorelli, *J. Med. Chem.*, **17**(6)**,** 631 (1974).
21. J. A. Crim, H. H. Buskirk, and H. G. Petering, *Cancer Res.*, **27**(1)**,** 1109 (1967).
22. A. A. El-Asmy, *J. Chim. Chem. Soc.*, **35**(1)**,** 29 (1988).
23. K. C. Joshi and A. K. Jauhar, *Indian J. Chem.*, **4**(6)**,** 277 (1966).
24. E. Campaigne and W. L. Archer, *J. Am. Chem. Soc.*, **74,** 5801 (1952).
25. M. D.Gutierrez, R. Lopez, M. A. Romero, and J. M. Salas, *Can. J. Chem.*, **66,** 249 (1988).
26. J. H. Vanvleck and A. Frank, *Phys. Rev.*, **34,** 1494, 1625 (1929).
27. M. Shrivastava and G. S. Pandey, *Indian J. Chem.*, **27**(A)**,** 447 (1988).
28. (a) K. K. Dahiya and N. K. Kaushik, *Indian J. Chem.*, **27**(A)**,** 449 (1988); (b) T. R. Rao, I. A. Khan, and R. C. Agarwal *J. Indian Chem. Soc.*, **63,** 380 (1986).
29. S. Ghosh and B. Pradhan *J. Indian Chem. Soc.*, **72,** 818 (1995).
30. M. C. Bryant, *Antibiotics and Their Laboratory Control* (Butterworth, London, 1968).