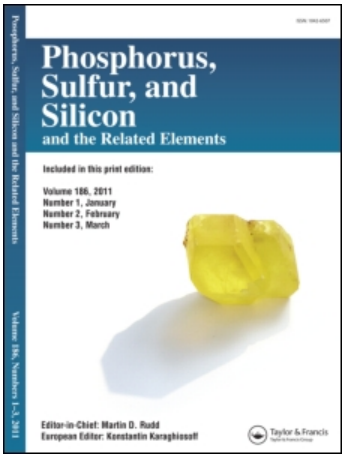

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Biologically Potent Azomethine Complexes of Palladium(II) and Platinum(II)

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Biologically Potent Azomethine Complexes of Palladium(II) and Platinum(II)

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The sulfur-nitrogen donor ligand, 1-acetylferrocenehydrazinecarbothioamide (L^1H) and oxygen-nitrogen donor ligand, 1-acetylferrocenehydrazinecarboxamide (L^2H) have been synthesized by condensation of 1-acetylferrocene with corresponding hydrazinecarbothioamide and hydrazinecarboxamide, respectively. The structure determination of palladium(II) and platinum(II) complexes was performed by elemental analysis, melting point determinations, conductivity measurements, molecular weight determinations, IR, ^1H NMR and UV spectral studies. Based on these studies the square planar environment around the metal atoms has been proposed. Studies were also conducted to assess the comparative growth- inhibiting potential of the synthesized complexes and the azomethines against a variety of fungal and bacterial strains.

Keywords Antimicrobial activity; hydrazinecarbothioamide and hydrazinecarboxamide; palladium(II) and Platinum(II) complexes; spectral studies

INTRODUCTION

In recent years, the chemistry of azomethines has become the focus of scientific attention on account of their industrial and biological relevance.[1] Metal complexes of these azomethines possess a wide spectrum of medicinal properties.[2] Sulfur-containing ligands show pronounced biological potency as antituberculosis,[3] antifungal,[4] antitumour,[5] and pest-averting properties.[6] They also function as analytical agents.[7–9]

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Nowadays, ferrocene and its derivatives are attracting much attention from the viewpoint of catalysis, organic synthesis, new materials as liquid crystals or polymers,[10] and in supramolecular chemistry.[11] They are chemically stable substances with low toxicity towards mammals and represent a potential source of iron for the organisms. Many reports[12] have shown that replacement of an aromatic group by ferrocenyl moiety in penicillines and cephalosporins improves their medicinal properties. Ferrocenylsemicarbazone has also been reported as antimicrobial agent.[13] It has been well established that certain platinum and palladium complexes[14] are of biological importance due to their carcinostatic activity and interest in biological chemistry.[15] These metals and their complexes are also useful as catalysts.[16] The complexes of palladium(II) with amino acids such as glycine, serine and glutamine have been reported to be active against certain tumours.[17] It is a well-established fact that carcinostatic action of drugs is due to their interaction with nuclear DNA.[18] Therefore, it was considered worthwhile to synthesize and characterize the complexes of Pd(II) and Pt(II) with two biologically active hydrazinecarbothioamide and hydrazinecarboxamide.

EXPERIMENTAL

Palladium and platinum salts, $PdCl_2$, and $PtCl_2$, as well as 1-acetylferrocene were purchased from Lobachemie and used as such. All the chemicals and solvents were dried and distilled before use.

Synthesis of the Ligands

The ligands 1-acetylferrocenehydrazinecarbothioamide[19](L^1H) and 1-acetylferrocenehydrazinecarboxamide[19] (L^2H) were prepared by the condensation of 1-acetylferrocene with hydrazinecarbothioamide and hydrazinecarboxamide (in presence of sodium acetate) in 1:1 molar ratio in ethanol. The reaction mixture was then refluxed over a water bath for 3–4 h and allowed to stand overnight. The products were recrystallized from the solvent ethanol and dried in vacuum. Their physicochemical properties and analytical data are given in Table I. The parent ligands exist in the tautomeric forms.(Figure 1).

Synthesis of Palladium Complexes

[Pd(L)$_2$] Type of Complexes

The methanolic solution of $PdCl_2$(3.35 mmol,0.68 g) was mixed with methanolic solution of ligands (3.32 mmol,2.32 g, and 2.42 g) in

TABLE I Analytical Data and Physical Characteristics of the Ligands and Their Corresponding Palladium(II) and Platinum(II) Complexes

Compound and empirical formula	Color M.P. (°C)	Yield (%)	Analysis (%) found/(calcd.)					Molecular weight Found/ (Calcd.)
			C	H	N	S	M	
L^1H	Light brown	—	51.26	5.22	13.76	10.60	—	314.32
($C_{13}H_{15}N_3SFe$)	172		(51.84)	(5.01)	(13.95)	(10.64)		(301.18)
L^2H	Brown	—	54.34	5.38	14.78	—	—	298.17
($C_{13}H_{15}N_3OFe$)	198		(54.76)	(5.30)	(14.73)			(285.12)
$[Pd(L^1H)_2]Cl_2$	Dark brown	72	40.19	3.59	10.85	8.34	13.22	785.93
($[Pd(C_{13}H_{15}N_3SFe)_2]Cl_2$)	234–237		(40.05)	(3.87)	(10.77)	(8.22)	(13.64)	(779.69)
$[Pd(L^1)_2]$	Brown	67	44.38	3.52	12.09	9.27	15.37	722.42
($[Pd(C_{13}H_{14}N_3SFe)_2]$)	212–215		(44.18)	(3.99)	(11.89)	(9.07)	(15.05)	(706.77)
$[Pd(L^2H)_2]Cl_2$	Dark brown	68	41.56	4.27	11.13	—	14.51	733.31
($[Pd(C_{13}H_{15}N_3OFe)_2]Cl_2$)	235–238		(41.77)	(4.04)	(11.24)		(14.23)	(747.58)
$[Pd(L^2)_2]$	Dark brown	71	45.96	4.27	12.68	—	15.72	681.92
($[Pd(C_{13}H_{14}N_3OFe)_2]$)	230–234		(46.28)	(4.18)	(12.45)		(15.77)	(674.65)
$[Pt(L^1H)_2]Cl_2$	Dark brown	64	35.86	3.24	9.17	7.18	22.37	856.14
($[Pt(C_{13}H_{15}N_3SFe)_2]Cl_2$)	260–263		(35.96)	(3.48)	(9.67)	(7.38)	(22.46)	(868.35)
$[Pt(L^1)_2]$	Brown	62	39.48	3.52	10.24	8.26	24.37	812.43
($[Pt(C_{13}H_{14}N_3SFe)_2]$)	272–275		(39.25)	(3.54)	(10.56)	(8.06)	(24.52)	(796.43)
$[Pt(L^2H)_2]Cl_2$	Dark brown	74	37.06	3.27	10.14	—	23.38	823.72
($[Pt(C_{13}H_{15}N_3OFe)_2]Cl_2$)	252–255		(37.34)	(3.61)	(10.04)		(23.32)	(836.23)
$[Pt(L^2)_2]$	Brown	70	40.34	3.27	11.68	—	25.79	777.72
$[Pt(C_{13}H_{14}N_3OFe)_2]$	265–268		(40.91)	(3.69)	(11.01)		(25.55)	(763.32)

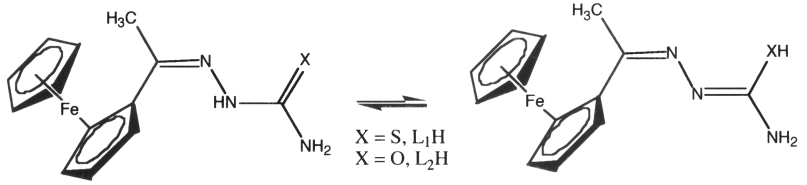

FIGURE 1

1:2 molar ratios. Aqueous NH_4OH was added drop wise to the reaction mixture until it was weakly alkaline (pH ca. 8.0). The mixture was then heated under reflux for about 1 h. On cooling, the complexes were separated out which were filtered and washed with methanol and dried in vacuum.

[Pd(LH)$_2$]Cl$_2$ Type of Complexes

The methanolic solution of $PdCl_2$ (3.15 mmol, 0.56 g) was mixed with methanolic solution of the ligands (3.02 mmol,0.91 g, and 2.75 g) in 1:2 molar ratios. The mixture was stirred on a magnetic stirrer for 2-3 hours in presence of few drops of concentrated HCl. The resulting products were recovered by filtration, washed with methanol and dried in vacuum.

Synthesis of Platinum Complexes

[Pt(L)$_2$] Type of Complexes

These complexes were prepared by dissolving $PtCl_2$(2.70 mmol,0.72 g) in 1:1 mixture of water and ethanol and then adding an ethanolic solution of the ligands (5.41 mmol,1.63 g, and 1.46 g) to this solution in 1:2 molar ratios. Aqueous NH_4OH was added dropwise to the reaction mixture until it was weakly alkaline (pH ca. 8.0). The reaction mixture was heated under reflux for about 1 h. On cooling, the complexes were separated out which were filtered and washed with ethanol and dried in vacuum.

[Pt(LH)$_2$]Cl$_2$ Type of Complexes

The 1:1, water, ethanol solution of $PtCl_2$(2.59 mmol,0.69 g) was mixed with an ethanolic solution of the ligands (3.32 mmol,1.57 g, and 1.03 g) in 1:2 molar ratios. The mixture was stirred on a magnetic stirrer for 2–3 h in presence of few drops of concentrated HCl. The resulting products were recovered by filtration, washed with ethanol and dried in vacuum.

The physicochemical properties and analytical data of these complexes are given in Table I.

Antifungal Activity

The antifungal activity was evaluated against *Fusarium oxysporum* and *Aspergillus niger* by the agar plate method[20] using Czapek's agar medium having the composition, glucose 20 g, starch 20 g, agar-agar 20 g, and distil water 1000 mL. To this medium was added requisite amount of the compounds after being dissolved in dimethylformamide so as to get a certain concentration(50,100, and 200 ppm). The medium then was poured into petri plates and the 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 30 ± 2^{o}C. The controls were also run and three replicates were used in each case. The linear growth of the fungus was recorded by measuring the diameter of the fungal colony after 96h and the percentage inhibition was calculated by Eq. (1):

$$\% \text{ Inhibition} = (C - T)100/C, \tag{1}$$

where C and T are the diameters of the fungal colony in the control and the test plates, respectively.

Antibacterial Activity

Antibacterial activity was tested against *Escherichia coli* and *Staphylococcus aureus* using the paper disc plate method.[21] The nutrient agar medium (peptone, beef extract, NaCl, agar-agar, and distil water) and 5-mm diameter paper discs (Whatman filter paper No. 1) were used. The compounds were dissolved in methanol for obtaining the concentration of 500 and 1000 ppm. The filter paper discs were soaked in these solutions, dried and then placed in the petri plates previously seeded with the test organisms. The plates were incubated for 24 h at $28 \pm 2^{\circ}$C and inhibition zone around each disc was measured.

Physical Measurements and Analytical Methods

Molecular weights were determined by the Rast Camphor method. Conductivity measurements were made with a Systronics model 305 conductivity bridge. IR spectra of the ligands and their complexes were recorded with the help of Nicolet-Megna FT-IR 550 spectrophotometer using KBr pellets. The electronic spectra were recorded on a Varian-Cary/2390 spectrophotometer at RSIC, I.I.T., Chennai. ^{1}H NMR spectra were recorded on a Hitachi Perkin Elmer spectrometer in DMSO-d_6 at 300 MHz using TMS as the internal standard at Delhi University, New

Delhi. Pd(II) and Pt(II) were estimated gravimetrically. Carbon and hydrogen analyses were performed at the CDRI, Lucknow. Nitrogen was determined by the Kjeldahl's method and sulfur was estimated by the Messenger's method.[22]

RESULTS AND DISCUSSION

The reactions of 1-acetylferrocenehydrazinecarbothioamide (L^1H) and 1-acetylferrocenehydrazinecarboxamide (L^2H) with $PdCl_2$ and $PtCl_2$ have been carried out in 1:2 molar ratios in ethanol and in 1:1 water and ethanol solutions, respectively. The metal chloride interacts with the ligands in presence of few drops of concentrated HCl to form complexes of the type $[M(LH)_2]Cl_2$. However, complexes of the $[M(L)_2]$ type were obtained when reactions were carried out in the presence of aqueous ammonium hydroxide.

$$MCl_2 + 2LH \rightarrow M(LH)_2]Cl_2$$

$$MCl_2 + 2LH + NH_4OH \rightarrow [M(L)_2] + 2NH_4Cl + 2H_2O, \qquad (2)$$

Where M = Pd(II) and Pt(II); and LH is the ligand molecule.

The reactions proceed easily and all the complexes are soluble in DMSO, DMF and $CHCl_3$. The molar conductance values of 10^{-3}M solutions of $[M(L)_2]$ type of complexes lie in the range 10–15 $ohm^{-1}cm^2mol^{-1}$in dry DMF indicating their nonelectrolytic behavior. However, the $[M(LH)_2]Cl_2$ type of complexes are 1:2 electrolytes, with conductance values of 205–228 ohm^{-1} cm^2 mol^{-1}. The complexes are monomers as revealed by their molecular weight determinations.

Electronic Spectra

The electronic spectra of the ligands and their complexes were recorded in distilled DMSO. The spectra of both the ligands L^1H and L^2H show a broad band at 375–382 nm which can be assigned to the n-π^* transitions of the azomethine group, which undergoes a blue shift in the complexes due to the polarization within the >C=N chromophore caused by the metal-ligand interaction. The K bands, π-π^* transitions of the ligands are observed at 292–317 nm, which undergoes a red shift in the complexes. This shift can be attributed due to the overlap of the central metal d-orbital with the p-orbital of the donor atom which causes an increase in conjugation in the ligand and thus lowers the π-π^* energy.[23] The broad absorption band at 416 nm in the ligands is assigned to the charge transfer from the metal to either the non-bonding or antibonding orbitals of the cyclopentadienyl rings. This band remains almost at

TABLE II Electronic Spectral Data(nm) of the Palladium(II) and Platinum(II) Complexes

Complex	Transition	nm
$[Pd(L^1H)_2]Cl_2$	$^1A_{1g} \rightarrow {}^1A_{2g}$ (ν_1)	470
	$^1A_{1g} \rightarrow {}^1B_{1g}$ (ν_2)	410
	$^1A_{1g} \rightarrow {}^1E_{1g}$ (ν_3)	390
$[Pd(L^1)_2]$	$^1A_{1g} \rightarrow {}^1A_{2g}$ (ν_1)	472
	$^1A_{1g} \rightarrow {}^1B_{1g}$ (ν_2)	412
	$^1A_{1g} \rightarrow {}^1E_{1g}$ (ν_3)	394
$[Pt(L^2H)_2]Cl_2$	$^1A_{1g} \rightarrow {}^1A_{2g}$ (ν_1)	540
	$^1A_{1g} \rightarrow {}^1B_{1g}$ (ν_2)	460
	$^1A_{1g} \rightarrow {}^1E_{1g}$ (ν_3)	357
$[Pt(L^2)_2]$	$^1A_{1g} \rightarrow {}^1A_{2g}$ (ν_1)	544
	$^1A_{1g} \rightarrow {}^1B_{1g}$ (ν_2)	463
	$^1A_{1g} \rightarrow {}^1E_{1g}$ (ν_3)	371

the same position in the complexes. The spectra of the complexes also show three bands due to three d-d spin allowed transitions. These are corresponding to the transitions from the three lower lying d orbitals to the empty d^2_{x-y} orbital. The ground state is $^1A_{1g}$ and excited states corresponding to the above transitions are $^1A_{2g}$, $^1B_{1g}$, and $^1E_{1g}$ in order of increasing energy. Three d-d transition bands are observed in the regions 540–472, 410–463, and 357–394 nm. These bands are attributed to $^1A_{1g} \rightarrow {}^1A_{2g}$, $^1A_{1g} \rightarrow {}^1B_{1g}$ and to $^1A_{1g} \rightarrow {}^1E_{1g}$ transitions, respectively. The electronic spectra indicate the square planar geometry[24] of the complexes (Table II).

I.R. Spectra

The IR spectra of the free ligands L^1H and L^2H display absorption bands at 3130–3420, 1610–1620, 1580–1615, 1046/1700, and 960–975 cm^{-1} and are assigned to ν(NH), ν(C=N), δ(NH), ν(C=S)/ν(C=O), and v(N-N), respectively.[25] The characteristic bands of the ferrocenyl group appear at 3080, 1449, 1110, 827, and 479 cm^{-1} arising from ν(CH), ν(C=C), δ(-CH), π(CH) and (Fe-ring), respectively.[25] The ν(N-H), δ(N-H) and ν(C=S)/v(C=O) absorption bands are absent in the complexes indicating ligand enolization followed by deprotonation during the complex formation. A sharp band at 1610–1620 cm^{-1} due to ν(C=N) is shifted to the lower frequency (15 cm^{-1}) in the complexes. The band at 3130–3420 cm^{-1} due to $-NH_2$ remains at the same position in the complexes suggesting that the amino group is not taking part in chelation. The appearance of the non-ligand bands further support the bonding of the ligands to the metals through the nitrogen, sulfur and

TABLE III ^{1}H NMR Spectral Data (δ ppm) of the Ligands and Their Complexes

Compound	-NH_2	-NH	-C_5H_5	-CH_3
L^1H	2.62	8.80	4.28	2.52
L^2H	2.80	8.32	4.22	2.28
$[Pd(L^1H)_2]Cl_2$	2.61	8.75	4.25	2.43
$[Pd(L^1)_2]$	2.60	—	4.23	2.40
$[Pd(L^2H)_2]Cl_2$	2.75	8.30	4.23	2.23
$[Pd(L^2)_2]$	2.73	—	4.21	2.24
$[Pt(L^1H)_2]Cl_2$	2.61	8.76	4.26	2.49
$[Pt(L^1)_2]$	2.60	—	4.24	2.45

oxygen atoms. However, no ν(M-Cl) band is observed in the spectra of $[M(LH)_2]Cl_2$ type of complexes, suggesting that chloride is ionic in these complexes.

^{1}H NMR Spectra

The ^{1}H NMR spectra of the free ligands and their metal complexes were recorded in DMSO-d_6. The spectral data of the ligands L^1H and L^2H exhibit a broad signal due to the -NH proton which disappears in the complexes of the type $[M(L)_2]$. The absence of this signal in these complexes suggest that this proton has been lost via thioenolization and ketoenolization of >C═S and >C═O groups and coordination of sulfur and oxygen to the metal atoms, respectively, has taken place. The signals observed at δ 2.52 and 2.28 ppm in the ligands L^1H and L^2H are due to the methyl protons of (H_3C-C═N) group. The downfield shift in this group in the spectra of the complexes substantiates the coordination of the azomethine nitrogen to the metal atoms. The -NH_2 group gives singlet at δ 2.60 – 2.80 ppm in the free ligands, as well as in the complexes. It shows that -NH_2 group is not taking part in the complexation(Table III).

Antimicrobial Screening

The growing interest in biochemical applications and demand of better fungicides and bactericides have prompted us to screen all the synthesized complexes with their ligands. The antifungal activity was evaluated against *Fusarium oxysporum* and *Aspergillus niger* by the agar plate method (Table IV). The antibacterial activity was evaluated by the paper disc method. Antibacterial activity was evaluated against *Escherichia coli* and *Staphylococcus aureus* (Table V). It has been

TABLE IV Fungicidal Screening Data of the Ligands and Their Complexes

	Inhibition % after 96 h					
	Fusarium oxysporium (conc. in ppm)			*Aspergillus niger* (conc. in ppm)		
Compound	50	100	200	50	100	200
L^1H	74	80	86	83	88	92
L^2H	71	77	82	77	84	87
$[Pd(L^1H)_2]Cl_2$	79	85	91	88	91	96
$[Pd(L^1)_2]$	77	84	89	85	89	93
$[Pd(L^2H)_2]Cl_2$	76	80	87	81	89	90
$[Pd(L^2)_2]$	74	79	84	79	85	89
$[Pt(L^1H)_2]Cl_2$	78	83	89	86	90	94
$[Pt(L^1)_2]$	75	81	87	83	89	92
$[Pt(L^2H)_2]Cl_2$	76	79	86	80	88	89
$[Pt(L^2)_2]$	73	78	84	78	84	88
Bavistin	84	98	100	90	96	100

Margin error is 0.5–1%.

observed that all the complexes showed good antimicrobial activities than their parent ligands. The enhanced activities of the metal complex compared to the free ligand can be ascribed to the increased lipophilic nature of these complexes arising due to the chelation. It

TABLE V Bactericidal Screening Data of the Ligands and Their Complexes

	Diameter of inhibition zone (mm) after 24 h			
	Escherichia coli (conc. in ppm)		*Staphylococcus aureus* (conc. in ppm)	
Compound	500	1000	500	1000
L^1H	7	8	8	10
L^2H	5	7	7	9
$[Pd(L^1H)_2]Cl_2$	10	11	12	14
$[Pd(L^1)_2]$	9	10	10	12
$[Pd(L^2H)_2]Cl_2$	8	10	11	12
$[Pd(L^2)_2]$	7	9	9	11
$[Pt(L^1H)_2]Cl_2$	9	10	12	13
$[Pt(L^1)_2]$	8	9	10	11
$[Pt(L^2H)_2]Cl_2$	7	9	11	12
$[Pt(L^2)_2]$	6	8	9	11
Streptomycin	16	18	15	18

Margin error is 0.5–2%.

is also noted that sulfur containing ligand, as well as its complexes, are more active than their oxygen containing counterparts. It is natural to hypothesize that more lipophilic compounds are more active simply because they enter the lipid layers of the cell membranes more rapidly.

CONCLUSION

On the basis of the analytical data and spectral studies, it has been observed that the ligands coordinated to the metal atoms in a monobasic bidentate manner and thus possess square planar geometry. The complexes showed better antimicrobial activities as compared to the parent ligands. The compounds also inhibit the growth of fungi and bacteria to a greater extent as the concentration is increased.

REFERENCES

[1] M. K. Biyala, N. Fahmi, and R. V. Singh, *Indian J. Chem. A*, **43,** 2536 (2004).
[2] M. K. Biyala, N. Fahmi, and R. V. Singh, *Main Group Met. Chem.,* **27**(3), 181 (2004).
[3] N. C. Kasuga, K. Sekino, M. Ishikawa, A. Honda, M. Yokoyama, S. Nakano, N. Shimada, C. Koumo, and K. Nomiya, *J. Inorg. Biochem.,* **96,** 298 (2003).
[4] K. Dey, B. Bikash, and S. Sarkar, *Indian J. Chem. A,* **43,** 773 (2004).
[5] S. K. S. Gupta, O. P. Pandey, A. Bhatt, V. Srivastava, and K. N. Mishra, *Indian J. Chem. A,* **41,** 1421 (2002).
[6] M. Jain, S. Maanju, and R. V. Singh, *Appli. Organometal. Chem.,* **18,** 471 (2004).
[7] N. C. Kasuga, K. Sekino, C. Koumo, N. Simada, M. Ishikawa, and K. Nomiya, *J. Inorg. Biochem.,* **84,** 55 (2000).
[8] J. Garcia-Tojal, J. Luis Pizarro, A. Garcia-Orad, A. Rocia Peroz Sanz, M. Ugalde, A. Alwarez Dia Z., J. Luis Serra, M. Isabel Arriortua, and T. Roji, *J. Inorg. Biochem.,* **86,** 627 (2001).
[9] R. B. Singh and H. Ishi, *Critical Rev. Anal. Chem.,* **22,** 381(1991).
[10] A. Togni and T. Hayashi,*Homogenous Catalysis, Organic Synthesis, Material Science* (VCH, Weinheim, Germany, 1995).
[11] A. E. Kaifer and J. De Mendoza, *Comprehensive Supramolecular Chemistry*, J. L. Atwood, J. E. D. Davies, D .D. MacNicol, and F. Vogtlee, Eds. (Elsevier, Oxford, 1996), Vol. 1, p. 701.
[12] E. I. Edwards, R. Epton, and G. Marr, *J. Organomet. Chem.,* **85,** C23 (1975).
[13] M. A. Metwally and F. A. Amer, *J. Indian Chem. Soc.,* **LXV,** 51 (1988).
[14] S. Kirchner, A. Maurer, and D. Dragulesku, *J. Clin. Hematol. Ocnol.,* **7,** 293 (1977).
[15] M. K. Biyala, N. Fahmi, and R. V. Singh, *Indian J. Chem.,* **45A,** 1999 (2006).
[16] P. A. Chaloner, *Coord. Chem. Rev.*, **72,** 1 (1986).
[17] M. A. Ali and S. E. Livingstone,*Coord. Chem. Rev.*, **13,** 101 (1974).
[18] B. Rosenberg, *Biochemie,* **60,** 859 (1978).
[19] A. O. Baghlaf, K. Banaser, H.Y. Hashem, A. Albishary, and M. Ishaq, *Trans. Met. Chem.,* **21,** 16 (1996).

[20] R. V. Singh and A. Chaudhary, *J. Inorg. Biochem.,* **98,** 1712 (2004).
[21] M. Jain, D. Kumar, and R.V. Singh, *Main Group Met. Chem.,* **26**(2), 99 (2003).
[22] J. T. Makode and A. S. Aswar, *Indian J. Chem. A,* **43,** 2120 (2004).
[23] Z. Gang and C. Yuan, *Trans. Met. Chem.,* **19,** 218 (1994).
[24] A. Garg and J. P. Tandon, *Synth. React. Inorg. Met.-Org. Chem.,* **18,** 705 (1998).
[25] M. Jain, P. Nagpal, and R.V. Singh, *Main Group Met. Chem.,* **25,** 615 (2002).