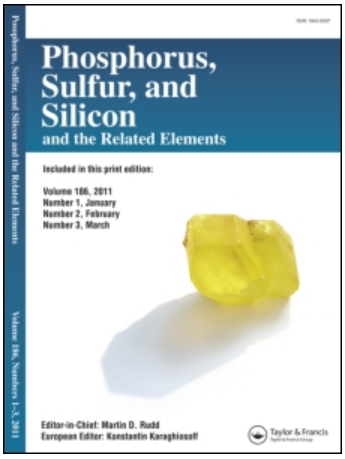

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Complexes of Tin(IV) Tetrachloride with 3-Formylpyridine Semicarbazone and Thiosemicarbazones

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COMPLEXES OF TIN(IV) TETRACHLORIDE WITH 3-FORMYLPYRIDINE SEMICARBAZONE AND THIOSEMICARBAZONES

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The reaction of tin(IV) tetrachloride with 3-formylpyridine semicarbazone and different 3-formylpyridine thiosemicarbazones produces [Sn(HL)CL$_3$][SnCl$_5$] where HL stands for the neutral ligand. The tin(IV) complexes were characterized using a variety of spectroscopic techniques. Coordination through the pyridine nitrogen occurs in all cases. Solvation studies in DMSO indicated that dissociation of the ligands and their complete replacement by solvent molecules occurs.

Keywords: 3-Formylpyridine; semicarbazones; thiosemicarbazones; tin(IV) tetrachloride

INTRODUCTION

In recent years there has been considerable interest in semicarbazones and thiosemicarbazones due to their wide range of biological applications.[1,2] The biological activity of these compounds was shown to be related to their complexing ability.[3] Metal complexes of semicarbazone and thiosemicarbazones derived from 2-formylpyridine have been extensively studied[4] but less attention has been given to the 3-formylpyridine analogues.

Tin displays a very interesting chemistry of its own and organotin complexes interact with biological systems in many different ways as antitumorals, bactericides, fungicides, and biocides.[5] In a previous work[6] researchers showed that the reaction of SnX_4 (X = Cl, Br, I) with

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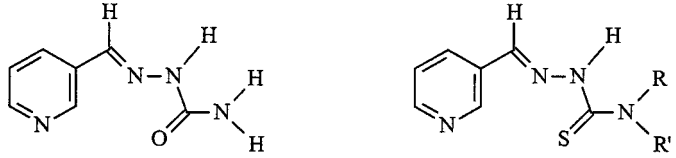

H3FPS H3FPT4RR'

FIGURE 1 Structure of 3-formylpyridine semicarbazone and 3-formylpyridine thiosemicarbazones.

2-fomylpyridine thiosemicarbazone (H2FPT) proceeds with deprotonation of the ligand and formation of octahedral $[Sn(2FPT)X_3]$ complexes. We now report the syntheses, characterization, and solvation studies of tin(IV) complexes of 3-formylpyridine semicarbazone (H3FPS) and nonsubstituted (H3FPT4DH) or N(4′)-substituted thiosemicarbazones (R = H and R′ = methyl, H3FPT4M; ethyl, H3FPT4E; Figure 1).

EXPERIMENTAL

The 3-formylpyridine thiosemicarbazones and 3-formylpyridine semicarbazone were prepared as described previously.[7,8] The metal complexes were obtained by refluxing EtOH solutions of the desired ligand with tin tetrachloride for 4 h in 2:1 ligand-to $SnCl_4$ molar ratio. The solids were washed with EtOH followed by diethylether and dried in vacuo. IR spectra were recorded on a Perkin Elmer 283B spectrometer using nujol mulls between CsI plates; NMR spectra were obtained with a Brucker DRX-400 Avance (400 MHz) spectrometer using d^6-DMSO as the solvent and TMS as internal reference. A YSI model 31 conductivity bridge was employed for molar conductivity measurements. ^{119}Sn NMR spectra were recorded at room temperature and were referred to external $Sn(CH_3)_3$. The thermogravimetric data were obtained under nitrogen at $10^{\circ}C\ min^{-1}$ in the 25–300°C range, using a Shimadzu TGA-50H analyser. Electronic spectra were acquired as dimethylsulfoxide (DMSO) solutions in 1 cm cells with a Hewlett Packard 8453 spectrometer. Mössbauer spectra were obtained from a constant acceleration spectrometer moving a $CaSnO_3$ source at room temperature. The samples were analysed at 85K. All spectra were computer-fitted assuming Lorentzian curves. The HPLC system consisted of a HRC-ODS C18 column (5 μm, 150×4.6 mm, Shimadzu), an LC-10AD auto sampler equipped with 20 μL loop injector and a SPD-10 UV-vis detector. Elution was performed with a system of water/dimethylsulfoxide/methanol (65:30:5, v/v/v) with flow rate of

TABLE I Colors, Partial Elemental Analyses, and Molar Conductivities of Tin(IV) Complexes of 3-Formylpyridine Semicarbazone and 3-Formylpyridine Thiosemicarbazones

	Compound	Color	Found (calcd.) (%) C	H	N	M	Λ_M[a]
(1)	$[Sn(H3FPS)_3Cl_3][SnCl_5].EtOH$	White	26.00 (26.07)	2.85 (2.85)	15.86 (15.86)	22.30 (22.46)	90
(2)	$[Sn(H3FPT4DH)_3Cl_3][SnCl_5]$	Light yellow	23.90 (23.73)	2.23 (2.26)	15.62 (15.82)	22.07 (22.41)	92
(3)	$[Sn(H3FPT4M)_3Cl_3][SnCl_5]$	Yellow	25.66 (26.09)	3.41 (3.46)	15.01 (15.22)	21.09 (21.56)	90
(4)	$[Sn(H3FPT4E)_3Cl_3][SnCl_5]$	Yellow	28.40 (28.27)	3.09 (3.14)	14.44 (14.66)	20.38 (20.77)	80

[a] 10^{-3} mol/L em DMF.

1.0 mL/min. The system was piloted by the Class-LC10 software. Detection wavelength was set at 326 nm.

RESULTS AND DISCUSSION

Table I lists the colors, partial elemental analyses, and molar conductivities of the tin(IV) complexes. These data indicate the formation of $[Sn(HL)_3Cl_3][SnCl_5]$ complexes in all cases, which was confirmed by a variety of spectroscopic techniques (vide infra). The presence of crystallization ethanol in complex (1) was confirmed by thermogravimetric analyses, which shows a weight loss in the 80–140°C range (Found: 4.82; calcd.: 4.35%).

The infrared spectral bands, most useful for determining the ligands' mode of coordination are given in Table II. The ν(C=N) bands of the

TABLE II Infrared Spectra (cm^{-1}) of the Tin Complexes of 3-Formylpyridine Semicarbazone and the 3-Formylpyridine Thiosemicarbazones

Compound	ν(C=O)	ν(C=N)	ν(C=S)	ρ(py)	ν(Sn=N_{py})	ν(Sn=Cl)
H3FPS	1695 s	1600 s	—	595 m	—	—
(1)	1690 s	1590 s	—	650 m	255 w	275 s
H3FPT4DH	—	1585 s	805 s	592 m	—	—
(2)	—	1580 m	800 s	650 s	250 m	265 s
H3FPT4M	—	1590 m	800 m	610 m	—	—
(3)	—	1590 w	790 m	650 m	250 m	270 s
H3FPT4E	—	1590 m	780 m	610 m	—	—
(4)	—	1590 m	780 s	650 s	245 m	265 s

s = strong; m = medium; w = weak.

ligands at 1585–1600 cm^{-1} are not appreciably different in the spectra of the complexes, indicating that coordination of the azomethine nitrogen do not occur. Similarly, no change is observed for the ν(C=O) absorption of H3FoS and the ν(C=S) band of the thiosemicarbazones. However, the in-plane-deformation mode of pyridine at 592–610 cm^{-1} in the spectra of the ligands shift 40–65 cm^{-1} to higher frequencies in the complexes, indicating coordination of the heteroaromatic nitrogen. The absorptions at 245–255 cm^{-1} and at 265–270 cm^{-1} in the spectra of the complexes were assigned to Sn—N_{py}[9] and Sn—Cl[6] vibrations respectively.

The ^{119}Sn Mössbauer spectra of all complexes were fitted by supposing the existence of two tin sites, in agreement with the proposed formulations. Moreover, the similarity among all the spectra suggests coordination by the pyridine nitrogen in all cases The spectrum of $[Sn(H3FPT4DH)_3Cl_3][SnCl_5]$ is shown in Figure 2. The isomer shift (δ) and quadrupole splitting (Δ) were found in the range of $\delta = 0.48$–$0.50\ mms^{-1}$; $\Delta = 0$ for the first site and $\delta = 0.43$–$0.44\ mms^{-1}$; $\Delta = 0.86$–$0.96\ mms^{-1}$ for the second site. The first site was attributed to the complex and the second to the $SnCl_5^-$ counter ion. The parameters obtained for the first site are in agreement with those obtained previously ($\delta = 0.58\ mms^{-1}$; $\Delta = 0\ mm\ s^{-1}$) for $[SnCl_3(2FPT)]$.[6]

Tables III and IV list all the ^{1}H and ^{13}C NMR assignments for the tin complexes. The ^{1}H resonances were assigned based on chemical

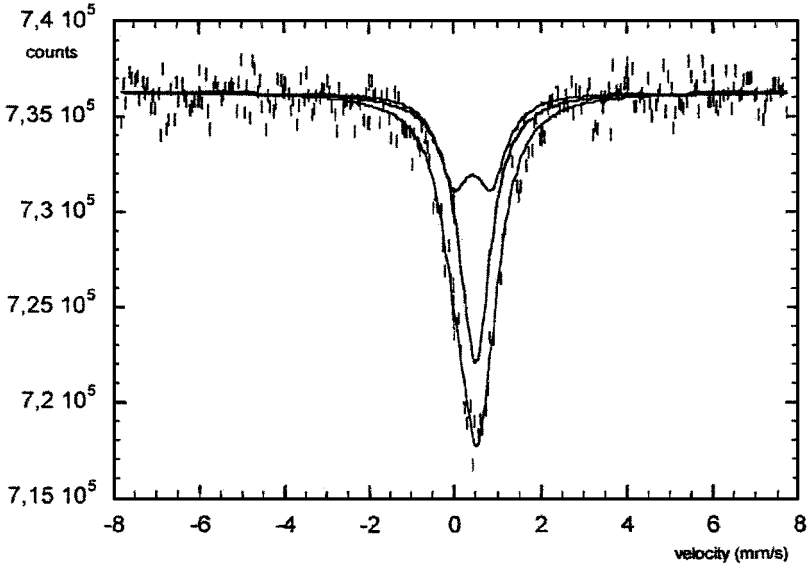

FIGURE 2 ^{119}Sn Mössbauer spectrum of $[Sn(H3FPT4DH)_3Cl_3][SnCl_5]$.

TABLE III ^{1}H NMR Spectral Assignments (δ) of Tin(IV) Complexes $[Sn(H3FPS)_3Cl_3][SnCl_5]$ (1), $[Sn(H3FPT4DH)_3Cl_3][SnCl_5]$ (2), $[Sn(H3FPT4M)_3Cl_3][SnCl_5]$ (3), and $[Sn(H3FPT4E)_3Cl_3][SnCl_5]$ (4) (d^6-DMSO)

Compound	(1)	(2)	(3)	(4)
N(2′)H	10.82 (s)	11.89 (s)	11.91 (s)	11.85 (s)
H(2)	9.28 (s)	9.41 (d)	9.29 (d)	9.33 (d)
		$J_{2-4} = 1.45$	$J_{2-4} = 1.40$	$J_{2-4} = 1.40$
H(4)	8.83 (dt)	8.93 (dt)	8.83–8.79[b]	8.88 (dt)
	$J_{4-5} = 8.05$	$J_{4-5} = 8.17$		$J_{4-5} = 8.20$
		$J_{4-6} = 1.45$		$J_{4-6} = 1.40$
		$J_{4-2} = 1.45$		$J_{4-2} = 1.40$
H(6)	8.76 (dd)	8.84 (dd)	8.83–8.79[b]	8.82 (dd)
	$J_{6-5} = 5.43$	$J_{5-6} = 5.54$		$J_{5-6} = 5.60$
		$J_{6-4} = 1.45$		$J_{6-4} = 1.40$
H(5)	7.98 (dd)	8.03 (dd)	7.94 (dd)	7.99 (dd)
	$J_{5-4} = 8.05$	$J_{5-4} = 8.17$	$J_{5-4} = 8.05$	$J_{5-4} = 8.20$
	$J_{5-6} = 5.43$	$J_{5-6} = 5.54$	$J_{5-6} = 5.50$	$J_{5-6} = 5.60$
H(7)	7.97 (s)	8.16 (s)	8.13 (s)	8.15 (s)
N(4′)HR[a]	6.79 (s)	8.48 (s)	8.88 (q)	8.95 (t)
		8.46 (s)	$J_{H-Me} = 4.58$	$J_{H-Et} = 6.70$
CH_2	—	—	—	3.62 (m)
				$J_{Et-H} = 6.70$
CH_3	—	—	3.04 (d)	1.17 (t)
			$J_{Me-H} = 4.58$	$J_{Me-Et} = 6.70$

J coupling constants in Hz.

TABLE IV ^{13}C NMR Spectral Assignments (δ) of Tin(IV) Complexes $[Sn(H3FPS)_3Cl_3][SnCl_5]$ (1), $[Sn(H3FPT4DH)_3Cl_3][SnCl_5]$ (2), $[Sn(H3FPT4M)_3Cl_3][SnCl_5]$ (3), and $[Sn(H3FPT4E)_3Cl_3][SnCl_5]$ (4) (d^6-DMSO)

Compound	(1)	(2)	(3)	(4)
C═S	—	178.65	178.08	177.15
C═O	156.56	—	—	—
C(6)	141.45	142.25	144.06	142.69
C(2)	141.35	141.25	142.91	141.27
C═N	133.37	136.08	136.15	135.90
C(4)	140.29	141.509	139.593	141.608
C(3)	134.385	133.55	132.89	133.58
C(5)	126.88	126.49	125.84	126.56
CH_2	—	—	—	38.48
CH_3	—	—	30.79	14.41

J coupling constants in Hz.

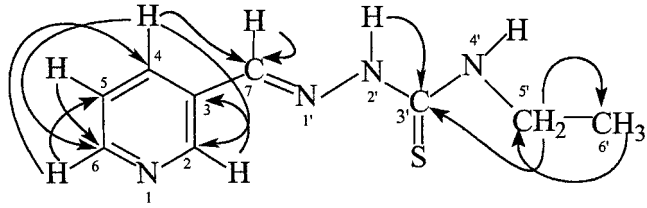

FIGURE 2 $^{1}H/^{13}$ C couplings observed in the HMBC sepctrum of $[Sn(H3FPT4E)_3Cl_3][SnCl_5]$.

shifts, multiplicities and coupling constants. The carbon type (C, CH) was determined by using DEPT135 experiments. The assignments of the protonated carbons were made by 2-D heteronuclear-correlated experiments (HMQC) using delay values which correspond to $^{1}J(C,H)$. The non protonated carbons C=N, C=O, C3 of 3-formylpyridine semicarbazone and thiosemicarbazones were determined using delays in the 2D HMBC experiment to emphasize the long range coupling, either $^{2}J(C,H)$ or $^{3}J(C,H)$ between the carbons and protons. The heteronuclear long range interaction between C=O or C=S and N(2′)-H; C(7)=N and N(2′)-H, H(2), H(4); C(3) and H(2), H(5), H(7) observed in the HMBC spectra were also used to confirm the assignments of these carbons. Figure 3 shows the $^{1}H/^{13}C$ couplings and Figure 4 the HMBC spectrum of $[Sn(H3FPT4DH)_3Cl_3][SnCl_5].0.5EtOH$.

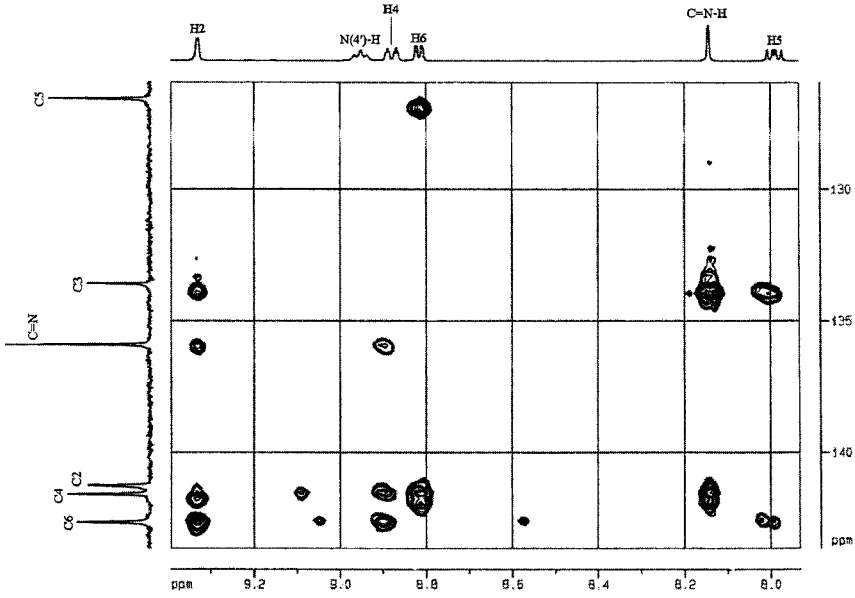

FIGURE 3 HMBC spectrum of $[Sn(H3FPT4E)_3Cl_3][SnCl_5]$.

In the ^{1}H NMR spectra of the ligands the resonance for the N(2′)H in the range $\delta = 10.53$–11.62 (data not shown) is consistent with hydrogen bonding to DMSO[10] In the complexes the signal for N(2′)-H is found at $\delta = 10.82$–11.91, indicating a greater acidity of this hydrogen, probably due to electron donation from the ligands to the metal center. Upon complexation the signals of all other hydrogens shift to higher frequencies due to this same effect. The C=O signal at $\delta = 156.78$ in the spectrum of H3FPS is essentially unchanged, $\delta = 156.56$, in complex (1), suggesting that the carbonyl oxygen is not involved in complexation. The C=S resonances of the free thiosemicarbazones in the $\delta = 176.82$–178.23 range shift to $\delta = 177.15$–178.65 in the spectra of complexes (2–4). As in the previous case the small shift indicates that the sulfur is not coordinated to the metal. On the other hand C(2) and C(6) shift from $\delta = 147.36$–148.66 and $\delta = 148.86$–150.20, respectively, in the free ligands to $\delta = 141.25$–142.91 and $\delta = 142.25$–144.06, respectively, in the complexes, indicating coordination of the pyridine ring. Also, C(4) shifts from $\delta = 133.19$–135.04 in the ligands to $\delta = 139.59$–141.61 in the tin(IV) complexes, as a consequence of the pyridine coordination. C(3) and C(5) undergo smaller shifts upon coordination, because of their meta position relative to the heteroaromatic nitrogen. The C(7)=N signals at $\delta = 136.41$–139.12 in the ligands shift to $\delta = 133.37$–136.15 in the complexes, due to the extended conjugation involving the ring and the imine group. For all complexes, the ^{1}H and ^{13}C NMR signals 4 h after dissolution exhibit no shift relative to their position in the free ligands, indicating dissociation and substitution of the ligands by solvent molecules.

The ^{119}Sn spectra of the complexes in DMSO show two signals at ca. $\delta = -631$ and $\delta = -674$, indicating the presence of two different tin(IV) species in solution, which are attributed to the complex and the $SnCl_5^-$ counter ion respectively. The spectrum of NH_4SnCl_5 recorded in DMSO shows the same signals, suggesting again the presence of two tin sites. The literature reports[12] the occurrence of an exchange reaction between $SnCl_5^-$ and $SnCl_4$. In this case, we may ascribe the signals to two hexacoordinated tin species obtained by solvation of $SnCl_5^-$ and $SnCl_4$. In fact, the close position of the NMR signals indicates that the two species have the same coordination number (six) and could be obtained by complexation of one DMSO molecule to $SnCl_5^-$ and two DMSO molecules to $SnCl_4$. Other authors[11] observed a signal at ca. $\delta = -460$ for $SnCl_5^-$ in a noncoordinating solvent, which moves upfield to ca. $\delta = -638$ on addition of dibutylether (DBE) and formation of a hexacoordinated tin species [$SnCl_5$(DBE)]. By analogy, the signals in the complex were attributed to the hexacoordinated [$Sn(HL)_3Cl_3$] and [$SnCl_5$(DMSO)].

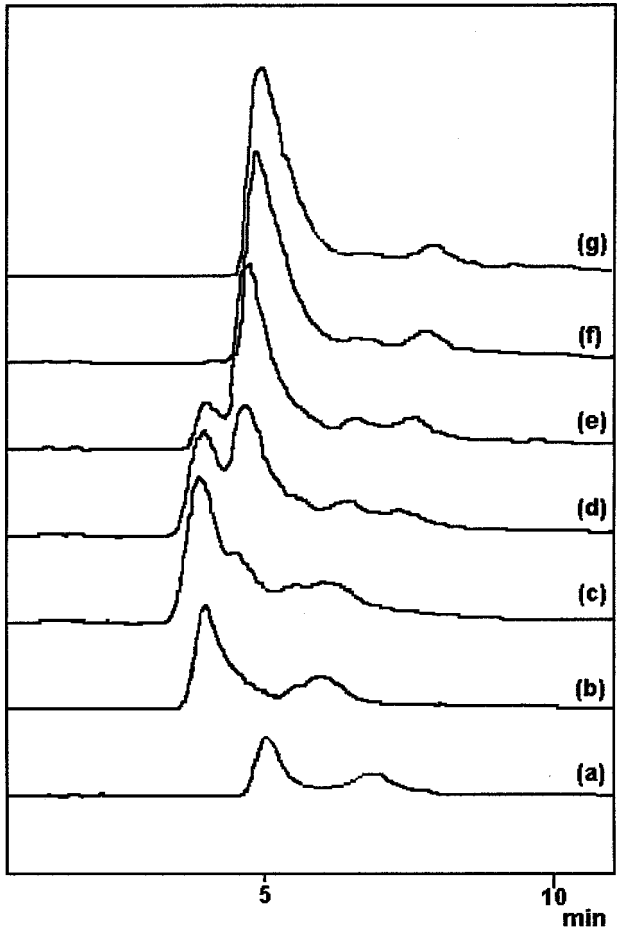

FIGURE 4 HMBC chromatogram of (a) H3FTP4DH, (b) $[Sn(H3FPT4DH)_3Cl_3][SnCl_5]$, (c) 60 min after injection, (d) 2 h after injection, (e) 3 h after injection, (f) 3.5 h after injection and (g) 4 h after injection.

The solvation of $[Sn(H3FPT4DH)_3Cl_3][SnCl_5]$ was monitored with time by HPLC at the absorption maximum (326 nm) (see Figure 5). The electronic spectrum of $NH_4[SnCl_5]$, recorded in DMSO for comparison, shows an absorption at 325 nm. H3FPT4DH displays two peaks at 5.0 and 6.8 min, probably due to the presence of the thione and thiol forms of the ligand. The chromatogram of the complex after 10 min presents peaks at 3.9, 5.6, and 5.9 min. As the time passes the peak at 3.9 min gradually vanishes with the concomitant appearance of those of the ligand. The other peaks are probably due to intermediate species.

After 4 h the thiosemicarbazone's chromatogram is recovered with, in addition, a peak at 7.9 min, attributed to a species resultant from the solvation of the tin salt obtained upon the release of the three thiosemicarbazone molecules. A similar behavior was observed for the all other complexes.

CONCLUSION

In conclusion, 3-formylpyridine semicarbazone and N(4′)-substituted or non substituted 3-formylpyridine thiosemicarbazones form $[Sn(HL)_3Cl_3][SnCl_5]$ complexes in which the ligands coordinate through the pyridine nitrogen. In DMSO solvolyses occurs with complete substitution of the semicarbazone or the thiosemicarbazones by the solvent after 4 h.

REFERENCES

[1] D. X. West, S. B. Padhye, and P. S. Sonawane, *Struct. Bond.*, **76,** 1 (1991).
[2] N. Fahmi and R. V. Singh, *J. Indian Chem. Soc.*, **73,** 257 (1996).
[3] J. Valdes-Martinez, A. Sierra-Romero, C. Alvarez-Toledano, R. A. Toscano, and H. Garcia-Tapia, *J. Organomet. Chem.*, **352,** 321 (1983).
[4] W. E. Antholine and F. Taketa, *J. Inorg. Biochem.*, **20,** 69 (1984).
[5] D. Kovala-Demertzi, P. Tauridou, U. Russo, and M. Gielen, *Inorgânica Chim. Acta*, **239,** 177 (1995).
[6] R. Barbieri, H. Beraldo, C. A. L. Filgueiras, A. Abras, J. F. Nixon, and P. B. Hitchcock, *Inorganica Chim. Acta*, **206,** 169 (1993).
[7] H. Beraldo, W. Nacif, and D. X. West, *Spectrochim. Acta A*, (2001).
[8] H. Beraldo, R. Lima, L. R. Teixeira, A. A. Moura, and D. X. West, *J. Molec. Struct.*, **553,** 43 (2000).
[9] J. S. Casas, A. Castiñeras, A. Sánchez, J. Sordo, A. Vasquez-Lopez, M. C. Rodriguez-Argüelles, and U. Russo, *Inorgânica Chim. Acta*, **221,** 61 (1994).
[10] R. Lima, L. R. Teixeira, T. G. Carneiro, and H. Beraldo, *J. Braz. Chem. Soc.*, **10,** 184 (1999).
[11] H. Katayama, M. Kamigaito, and M. Sawamoto, *Macromolecules*, **31,** 4703 (1998).