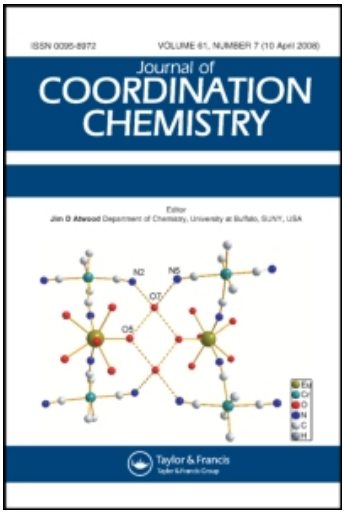

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

SOME METAL COMPLEXES WITH *N*-(2-PYRIDYL)THIOACETAMIDE AND *N*-(2-PYRIDYL)THIOBENZAMIDE

L. V. Sudha[a]; D. N. Sathyanarayana[a]
[a] Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore, India

To cite this Article Sudha, L. V. and Sathyanarayana, D. N.(1984) 'SOME METAL COMPLEXES WITH *N*-(2-PYRIDYL)THIOACETAMIDE AND *N*-(2-PYRIDYL)THIOBENZAMIDE', Journal of Coordination Chemistry, 13: 3, 207 — 214
To link to this Article: DOI: 10.1080/00958978408073869
URL: http://dx.doi.org/10.1080/00958978408073869

J. Coord. Chem., 1984, Vol. 13, pp. 207–214
0095-8972/84/1303-0207 $18.50/0

SOME METAL COMPLEXES WITH *N*-(2-PYRIDYL)THIOACETAMIDE AND *N*-(2-PYRIDYL)THIOBENZAMIDE

L.V. SUDHA and D.N. SATHYANARAYANA†
Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, India

(Received August 8, 1983; in final form December 1, 1983)

The Cu(II), Zn(II) and Cd(II) chloride and bromide complexes of *N*-2(2-pyridyl)thioacetamide and *N*-(2-pyridyl)thiobenzamide have been prepared. The infrared and ^{1}H and ^{13}C NMR spectra of the complexes and the free ligands have been analysed to determine the coordination sites. It was concluded that *N*-(2-pyridyl)thioacetamide behaves as a bidentate ligand, chelating to the metal *via* pyridine nitrogen and thionamide sulfur atoms while the other ligand, *N*-(2-pyridyl)thiobenzamide coordinates to the metal atom as a unidentate through the pyridine nitrogen atom. Conformations of the free ligands are discussed.

INTRODUCTION

Pyridine derivatives possessing the – N — C — S group have been reported to be biologically versatile compounds. Several pyridine thiourea derivatives have been characterized as prospective agents for antiviral chemotherapy.[1,2] In addition, pyridine derivatives with a suitable donor atom in the *ortho* position invariably possess a diverse coordination potential. A ligand of this type, namely *N*-(2-pyridyl)acetamide (NPA) has attracted much attention.[3–6] Work is presented here on spectroscopic and ligating properties of two new ligand systems namely, *N*-(2-pyridyl)thioacetamide (NPTA) and *N*-(2-pyridyl)thiobenzamide (NPTB). Further the ^{1}H and ^{13}C NMR and solution infrared spectra of the free ligands as well as their oxygen analogues have been obtained. An understanding of the coordination of toxic group IIB elements by sulfur-containing ligands is vital to the understanding of the way these toxic metals interact with such biologically relevant ligand system.[7]

EXPERIMENTAL

NPTA was synthesised in two stages. *N*-(2-pyridyl) acetamide (NPA) was prepared from 2-aminopyridine and acetic anhydride[3] [m.p. 66°; Lit. 66–67°]. NPA (0.13 mol) and P_2S_5 (0.18 mol) were refluxed in dry pyridine for 18–20 h. The mixture was cooled, poured into a large excess of water and treated with sodium bicarbonate. The compound was extracted with chloroform and purified by chromatography on silica gel using a hexane-benzene mixture as the eluent [m.p. 106–108°. Calcd. for NPTA: C 55.26, H 5.26, N 18.42%; Found C 55.1, H 5.3, N 18.3%].

NPTB was prepared in a similar fashion to NPTA starting from *N*-(2-pyridyl)benzamide, which was obtained by reacting *N*-(2-pyridyl)amine with benzoyl chloride according to the literature method[8] [m.p. 145–6°. Calcd. for NPTB: C 67.29, H 4.67, N 13.08%; Found C 67.1, H 4.7, N 12.7%].

† Author for correspondence

Ethanolic solutions of the metal halide and ligands were mixed in the mol ratio of 1:2 and the mixture was warmed on a water bath for 15 min. The solid which separated was washed with acetone followed by ether and dried in a vacuum desiccator.

Infrared spectra (4000–200 cm^{-1}) were measured in Nujol mull and KBr pellets by means of a Perkin-Elmer 597 spectrophotometer. The solution spectra using $CHCl_3$, CCl_4 and CS_2 as solvents were recorded in the 4000–200 cm^{-1} region using conventional cells with KBr windows of path length 0.2 to 0.5 mm. The Raman spectrum of NPTA was recorded on a SPEX Ramalog 6 instrument using an argon ion laser (excitation line 4880 A) with 100 mw power at the sample as a polycrystalline powder in a capillary tube. The NMR spectra were recorded on a Bruker WH 270 FT spectrometer system operating respectively at 270 and 67.89 MHz for proton and ^{13}carbon nuclei with TMS as the internal standard. Bulk susceptibility measurements were made at room temperature on a Gouy balance calibrated with $Hg[Co(CNS)_4]$.

RESULTS AND DISCUSSION

The analytical data (Table I) show that the complexes have the stoichiometry ML_2X_2. The reaction of copper(II) salts with excess ligand yields copper(I) complexes which are slowly oxidized on exposure to the atmosphere to copper(II) ones. The reaction of the ligand with excess copper(II) salt precipitates the copper(II) complexes. Room temperature magnetic moments of the copper(II) complexes are in the usual range, whereas the remaining complexes are diamagnetic. The complexes of Zn(II) and Hg(II) halides with NPTA quickly decompose to their sulfides, while for NPTB only Hg(II) complexes decompose. The metal complexes of NPTA and NPTB are soluble in dimethyl sulfoxide and insoluble in other common organic solvents.

An interesting aspect of the free ligands concerns the identification of their most stable conformation. From analogy with related amides and thioamides,[9] the four most probable planar conformations are those shown in Fig. 1.

In the *endo* form (A and B), the amide group has a *trans* configuration, while in the *exo* form (C and D), it has a *cis* configuration. The former conformation has been found to be more stable in secondary thionamides.[9] The ^{1}H and ^{13}C NMR spectra are used in an attempt to distinguish between the possible conformational modes. The ^{1}H NMR spectra of the free ligands were measured at different

TABLE I
Analytical Results

Complex	Colour	Found (Calcd) % C	H	M
$Cu(NPTA)_2Cl_2$	green	38.3(38.1)	3.6(3.4)	14.5(14.4)
$Cu(NPTA)_2Br_2$	green	33.6(33.5)	3.2(3.3)	12.7(12.3)
$Cd(NPTA)_2Cl_2$	dark yellow	34.5(34.1)	3.3(3.5)	23.1(22.7)
$Cd(NPTA)_2Br_2$	dark yellow	29.1(29.0)	2.9(2.9)	19.5(19.3)
$Cu(NPTB)_2Cl_2$	green	47.2(47.4)	3.3(3.2)	10.5(10.1)
$Cu(NPTB)_2Br_2$	green	37.7(37.5)	2.6(2.9)	8.4(8.2)
$Zn(NPTB)_2Cl_2$	yellow	47.1(47.0)	3.2(3.4)	10.7(10.6)
$Zn(NPTB)_2Br_2$	yellow	41.1(40.8)	2.9(3.2)	9.3(9.3)
$Cd(NPTB)_2Cl_2$	yellow	43.7(43.4)	3.0(2.9)	17.0(16.0)
$Cd(NPTB)_2Br_2$	yellow	38.5(38.2)	2.7(2.8)	15.0(14.7)

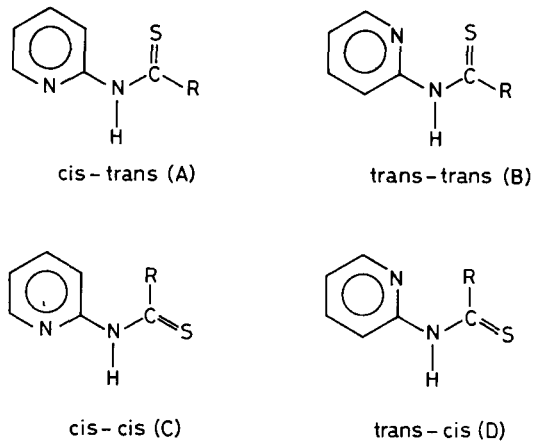

FIGURE 1 Planar conformations of NPTA and NPTB.

temperatures in $CDCl_3$ and DMSO-d_6. The chemical shift data are presented in Table II. The spectra of the oxygen analogues of the free ligands have also been measured. In Fig. 2, the ^1H NMR spectra of NPTA and its Cd(II) complex are shown.

The observed signal for the pyridyl H-3 proton is unusually broad at ambient probe temperatures due to the involvement of the amide proton in hydrogen-bonding with DMSO-d_6, which is well known to interact with amide protons.[10] In line with this expectation at higher probe temperatures (above 120°), the signal is

TABLE II
Proton Chemical Shifts (δ, ppm) of the Ligands, Their Oxygen Analogues and Complexes.

Compound	Solvent	Pyridyl					Phenyl			Methyl
		N-H	H-3	H-4	H-5	H-6				
NPA	$CDCl_3$	9.33	8.24	7.72	7.05	8.28				2.10
	DMSO-d_6	10.48	8.08	7.76	7.08	8.31				
NPB	$CDCl_3$	9.24	8.31	7.82	7.20	9.08	8.07	7.59	7.51	
	DMSO-d_6	10.81	8.21	7.86	7.18	8.40	8.05	7.60	7.52	
NPTA	$CDCl_3$	10.89	8.39	7.82	7.20	9.08				2.56
	DMSO-d_6	10.09	8.47	7.88	7.28	8.75				2.56
NPTB	$CDCl_3$	10.27	8.20	7.80	7.13	9.17	7.35	7.52	7.45	
	DMSO-d_6	12.13	8.32	7.92	7.33	8.56	7.33	7.52	7.45	
$Cd(NPTA)_2Cl_2$	DMSO-d_6	10.47	8.30	7.90	7.06	8.06				2.08
			6.83	7.76	6.92	7.09				
$Cd(NPTA)_2Br_2$	DMSO-d_6	10.47	8.29	7.78	7.08	8.06				2.09
			6.82	7.75	6.97	7.07				
$Zn(NPTB)_2Cl_2$	DMSO-d_6	12.1	8.29	7.92	7.33	8.51	7.33	7.53	7.45	
$Zn(NPTB)_2Br_2$	DMSO-d_6	12.1	8.29	7.92	7.33	8.51	7.33	7.53	7.45	
$Cd(NPTB)_2Cl_2$	DMSO-d_6	12.1	8.30	7.93	7.33	8.51	7.32	7.52	7.47	
$Cd(NPTB)_2Br_2$	DMSO-d_6	12.1	8.28	7.93	7.33	8.51	7.32	7.53	7.47	

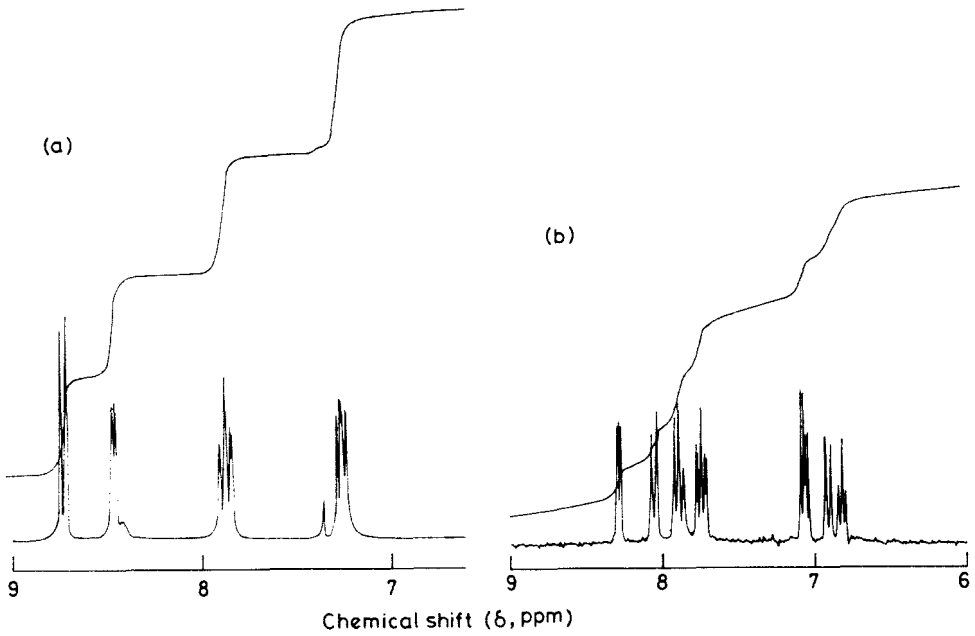

FIGURE 2 ^{1}H NMR spectra of (a) NPTA and (b) $Cd(NPTA)_2Cl_2$ in DMSO-d_6.

well resolved and further shows dependence on solvent dielectric. In the temperature range − 90° (in acetone-d_6) to + 120° (in DMSO-d_6), no new features were observed in the NMR spectra of the free ligands. The large deshielding effect of the H-3 resonance of the free ligands compared to that of 2-aminopyridine[11] indicates a restricted rotation around the $C_{ring} - N_{amide}$ bond of the ligands and also suggest that the molecules have a planar structure. It seems likely that the strong dipole-dipole interactions between the pyridine ring and the thioamido group stabilizes the *cis-trans* conformation (Fig. 1A).

^{1}H NMR spectral data for the complexes of NPTA and NPTB are compiled in Table II. The complexation shifts are the largest for the methyl and H-6 proton resonances of the NPTA molecule, suggesting the coordination of pyridine nitrogen and sulfur atoms. As expected, the pyridyl H-3 proton registers a significant upfield shift since it is no longer deshielded by the thiocarbonyl group in the *trans-trans* conformation of the complexed ligand (Fig. 1B). The magnitude of the shift (0.41 δ) is similar to that observed for the zinc complex of NPA.[4] The spectra of the NPTA complexes show two sets of signals of unequal intensities for the aromatic protons which suggests the presence of a mixture of *cis-* and *trans* isomers. Non-equivalence of the aromatic signals due to the pyridyl rings lying above and below the plane is ruled out from intensity considerations. On the other hand, in the spectra of the NPTB complexes only one set of aromatic proton signals occurs (Fig. 3). Other complexation shifts are negligible indicating the absence of coordination through sulfur.

The ^{13}C NMR spectral data for the ligands, their oxygen analogues and the complexes of NPTB are tabulated in Table III. Assignments in the ^{13}C NMR spectra were made from spectra obtained by the usual gated decoupling technique and literature data on related systems.[12] Owing to the poor solubility of the

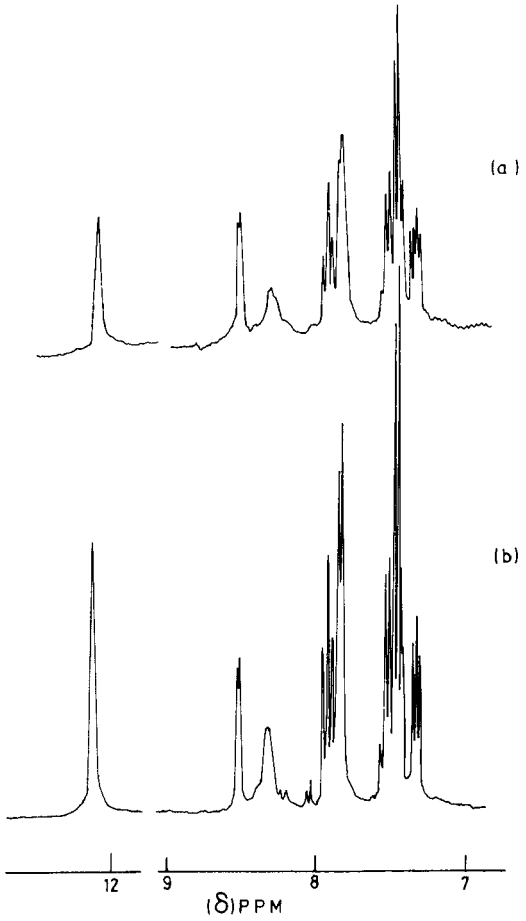

FIGURE 3 ^{1}H NMR spectra of (a) $Cd(NPTB)_2Cl_2$ and (b) NPTB in DMSO-d_6.

complexes of NPTA, their ^{13}C NMR spectra could not be obtained. In NPTB complexes, the C(=S) resonance, which should be most sensitive to coordination, does not change significantly. The largest complexation shift observed here is for the C-6 resonance of the pyridine ring. This leads us to conclude that the C=S group is not involved in coordination. This is consistent with the ^{1}H NMR results.

TABLE III
^{13}Chemical Shifts (δ, ppm) of the Ligands, Their Oxygen Analogues and Metal Complexes.

Compound	C=O/S	C-2	C-3	C-4	C-5	C-6	$-CH_3$	*o*-	*m*-	*p*-
NPA	169.30	152.25	113.53	137.92	119.13	147.82	23.90			
NPB	169.98	152.18	114.77	138.05	119.73	147.81		127.94	128.32	130.85
NPTA	200.64	152.28	116.35	137.49	121.40	148.22	35.68			
NPTB	198.81	152.62	118.52	137.58	121.80	148.46		127.45	127.88	130.88
$Zn(NPTB)_2Cl_2$	198.71	152.62	118.60	137.61	121.80	147.80		127.45	127.85	130.88
$Zn(NPTB)_2Br_2$	198.71	152.62	118.60	137.61	121.80	147.80		127.45	127.85	130.88
$Cd(NPTB)_2Cl_2$	198.71	152.64	118.57	137.70	121.77	147.80		127.41	127.88	130.89
$Cd(NPTB)_2Br_2$	198.71	152.64	118.57	137.70	121.77	147.80		127.41	127.88	130.88

TABLE IV
Infrared Spectral Data (cm^{-1}) in the N-H Stretching Region.

Compound	Nujol mull	$CHCl_3$
NPA	3280 mb	3420 s, 3260 b, 3200 w
NPB	3185 s	3400 s, 3200 mb
NPTA	3160 s	3360 s, 3200 mb, 3220 sh
NPTB	3160 s	3360 s, 3200 mb, 3160 sh

The N-H stretching frequencies of the ligands and their oxygen analogues are given in Table IV. The position and character of the ν(N-H) band is indicative of the formation of N-H . . . S/O bonds in the solid. The in and out of plane N-H bending vibrations are assigned respectively at 1540 and 860 cm^{-1} in NPTA, consistent with an observed shift to 1290 and 640 cm^{-1} respectively on *N*-deuterium labelling. The in-plane N-H bending mode of NPTA is in the same region as that of *N*-methylthioacetamide[13] (1537 cm^{-1}), which has a *trans* -CSNH- grouping. The out of plane N-H bending mode which is found over the wide range 600-850 cm^{-1} in secondary thioamides and thioureas[14] occurs at 690 cm^{-1} in *N*-methylthioacetamide.[13]

Direct information on pyridine *N*-coordination would be obtained from the displacements to higher wave numbers upon complexation of the following bands[15,16] arising from (i) a coupled mode of C=N and C=C stretching (1600 cm^{-1}), (ii) in-plane C-H bending (1135 cm^{-1}), (iii) ring breathing (1000 cm^{-1}) and (iv) out of plane ring deformation (635 cm^{-1}). The data summarized in Table V demonstrates the coordiantion of NPTA and NPTB through the pyridine nitrogen atom.

Among the other bands, the ν(N-H) is nearly unaffected in the complexes. This signifies that the ligand is not bonded to the metal through the amide nitrogen atom. The shifts in ν(N-H) result from a combination of factors including electronic changes within the molecule upon coordination as well as hydrogen-bonding effects. The thioamide bands which show most significant changes upon coordintion are the I and II bands. The thioamide I band has major contributions from C=S stretching. Recent work[14] shows that more realistic assignments of the ν(C=S) vibrations should involve the 800–550 cm^{-1} range. Medium intensity infrared bands near 740 cm^{-1} are assigned to C=S stretching in the free ligands. The corresponding band in the Raman spectrum of NPTA is observed as a strong line. The thioamide I band exhibits negative shifts ranging from 15 to 25 cm^{-1} in the spectra of the NPTA complexes and remains nearly stationary in the NPTB complexes. The complexation shift for the thioamide II band arising from a coupled mode of δ(NH) + ν(CN) is much larger (50 cm^{-1}) for complexes of NPTA but is marginal for complexes of NPTB. These observations are consistent with the coordination of metal through sulfur for complexes of NPTA and the absence of coordination through sulfur for NPTB complexes.

In the complexes studied both NMR and IR data indicate that the metals are coordinated to NPTA through both sulfur and pyridine nitrogen atoms, whereas in the other ligand, NPTB is bonded only through the latter coordiantion site. The non-participation of sulfur in coordination in this case may be attributed to the weakening of the donor ability of sulfur through extensive conjugation in NPTB. Finally, the molar conductivities for the Zn(II) and Cd(II) complexes in dimethyl sulfoxide solutions (0.001 M) range from 7.0 to 12.0 $ohm^{-1}\ cm^2\ mol^{-1}$, indicating the coordinated nature of the halide ion.

TABLE V
Important Infrared Bands (cm^{-1}).

Compound	Pyridine bands				Thioamide bands			
	ν(C=C) + ν(C=N)	δ(C-H)	ring breathing	ring def. (o.p)	ν(N-H)	II band	I band	δ(C=S)
NPTA	1605	1135	1045	617	3160	1572	740	540
$Cu(NPTA)_2Cl_2$	1630	1150	1060	635	3140	1620	710	525
$Cu(NPTA)_2Br_2$	1635	1160	1060	640		1620	725	530
$Cd(NPTA)_2Cl_2$	1628	1160	1060	630		1620	728	520
$Cd(NPTA)_2Br_2$	1627	1158	1065	630		1625	728	520
NPTB	1605	1150	1050	618	3160	1585	745	510
$Cu(NPTB)_2Cl_2$	1620	1165	1070	620	3160	1590	740	540
$Cu(NPTB)_2Br_2$	1620	1160	1070	630		1595	745	540
$Zn(NPTB)_2Cl_2$	1630	1165	1070	640	3160	1595	740	
$Zn(NPTB)_2Br_2$	1600	1170	1060	640	3160	1600	740	510
$Cd(NPTB)_2Cl_2$	1620	1160	1060	630	3160	1595	740	510
$Cd(NPTB)_2Br_2$	1620	1165	1075	628	3160	1600	740	510

REFERENCES

1. A. Galabov, L. Shindarov, G. Vassilev and R. Vassileva, *Chemotherapy*, **17,** 161 (1972).
2. R.S. Srivastava, *Inorg. Chim. Acta*, **55,** L71 (1981).
3. M. Nonoyama, S. Tomita and K. Yamasaki, *Inorg. Chim. Acta*, **12,** 33 (1975).
4. J. Bould and B.J. Brisdon, *Inorg. Chim. Acta*, **19,** 159 (1976).
5. C. Airoldi, F.S. Dias, G.F. De Sa and J.G. Espinola, *J. Inorg. Nucl. Chem.*, **40,** 1537 (1978).
6. M. Sekizaki, Acta Crystallogr., **B29,** 327 (1973); and references therein.
7. A.J. Carty, *A. C. S. Symp. Ser.*, **82,** 339 (1978).
8. S.I. Lure, *Zhur. Obs. Ch. Chei. Khim.*, **20,** 195 (1950); C.A. **44,** 5880.
9. W.E. Stewart and T.H. Siddall, *Chem. Rev.*, **70,** 517 (1970).
10. L.A. LaPlanche and M.T. Rogers, *J. Amer. Chem. Soc.*, **86,** 337 (1964).
11. R.F.C. Brown, L. Radom, S. Sternhell and I.D. Rae, *Can. J. Chem.*, **46,** 2577 (1968).
12. L. Stefanaik, *Org. Mag. Reson.*, **12,** 379 (1979).
13. I. Suzuki, *Bull. Chem. Soc. Jpn.*, **35,** 1456 (1962).
14. K.R.G. Devi, D.N. Sathyanarayana and S. Manogaran, *Spectrochim. Acta*, **37A,** 633 (1981) and references therein.
15. B.F. Little and G.J. Long, *Inorg. Chem.*, **17,** 3401 (1978).
16. S. Burman and D.N. Sathyanarayana, *J. Coord. Chem.*, **11,** 219 (1982).