Inorganica Chimica Acta, 141 (1988) 179–183

Synthesis and Characterization of Complexes of (4-Methoxybenzaldehyde)-4-phenyl-3-thiosemicarbazone

PRAKASH M. M. S. KINTHADA*

Department of Chemistry, University of Alberta, Edmonton, T6G 2G5, Canada

L. D. PRABHAKAR and D. VENKATA REDDY

Department of Chemistry, Sri krishnadevaraya University, Anantapur, 515003, India

(Received March 31, 1987)

Abstract

Some hitherto unknown complexes of 4-methoxybenzaldehyde-4-phenyl-3-thiosemicarbazone (MBPT) with certain transition metal ions have been synthesized and characterized by spectral, magnetic, thermal, and conductance studies. All complexes except the mercury complex are hydrated, crystalline powders decomposed by mineral acids. IR spectral data suggests the coordination through the nitrogen and sulphur atoms. The electronic spectra indicate that Au(III), Os(VIII), Ru(III), Rh(III), Pd(II), Cu(II) and Ag(I) complexes are square planar. The high molar conductance value of the copper chelate suggests that the complex is a 1:1 electrolyte, whereas all other complexes are non electrolytes.

Introduction

The thiosemicarbazide and thiosemicarbazone compounds have gained special attention due to their activity against protozoa [1], influenza [2], smallpox [3] and certain kinds of tumours [4, 5]. Since Domagks original discovery [6] of their antitubercular activity the number of papers on the pharmacology of these compounds has increased dramatically. A large number of thiosemicarbazones have been evaluated for their antimalarial, antitumour and antibacterial activity because of their useful chemotherapeutic properties [7]. In cancer treatment it has been shown that the metal chelates are more potent than chelating agents [8, 9]. Thiosemicarbazones have been found to be more effective in reducing tissue iron levels than the deferroxamine, which is used for removing excess iron accumulated in tissues of patients with Cooleys anemia [10]. They have been employed as chelating agents for (technetium-99) labelling proteins [11]. A thorough survey of the literature reveals that only a few reports have appeared on the synthesis and characterization of transition metal complexes of phenylthiosemicarbazones [12–15]. Hence we report in this paper, the synthesis and characterization of transition metal complexes of 4-methoxybenzaldehyde-4-phenyl-3-thiosemicarbazone (MBPT).

Experimental

Apparatus

Elemental analyses (C, H and N) were carried out in the Analytical Division, Regional Research Laboratories, Hydrabad, India. IR spectra were recorded in KBr pellets on a Perkin-Elmer 983G infrared spectrophotometer. NMR spectra were recorded on a Perkin-Elmer EM-390 MHZ spectrometer. A Pye Unicam SP-100 UV–Vis spectrophotometer was used for recording ultraviolet and visible spectra. TG and DTA studies were done on an ULVAC SINKU RIKURA 1500 thermal analyser at the Indian Institute of Sciences at Bangalore, India. Magnetic susceptibilities were determined at room temperature, on a Guoy balance, using mercurytetrathiocyanato cobaltate(II), as a magnetic standard. Molar conductivities were determined by a systronics direct reading conductivity bridge provided with conventional dip type blacked electrodes.

Synthesis and Characterization of MBPT

A solution prepared by dissolving 0.835 g of 4-phenyl-3-thiosemicarbazide in 50 ml methanol and 2 ml of glacial acetic acid was added dropwise to a solution of 4-methoxybenzaldehyde (0.68 g) in 50 ml while stirring. A white product that quickly separated was recrystallized in methanol. Melting point (m.p.) 182–184 °C. Identification of the product was based on elemental analysis, IR and NMR data as described earlier [16, 17].

---

*Author to whom correspondence should be addressed.

0020-1693/88/$3.50

Synthesis of Metal Complexes of MBPT

Au(III)–MBPT complex

To 30 ml of Au(III) solution (5×10^{-2} M) in methanol was added 1×10^{-2} M MBPT solution in methanol and the mixture refluxed for about 30 min. The yellow solid that separated was filtered and washed with water. The precipitate was dried under reduced pressure over P_4O_{10} for 24 h (yield 60%).

Pt(IV)–MBPT complex

30 ml of Pt(IV) solution (5.5×10^{-3} M) in methanol was added dropwise to MBPT solution in methanol (1×10^{-2} M) and the mixture was refluxed for about one hour. The yellow solid that separated was filtered and washed with water. The precipitate was dried over P_4O_{10} for about 24 h.

Pd(II)–MBPT complex

To 30 ml of Pd(II) solution (5.5×10^{-3} M) in methanol was added 30 ml of MBPT solution (1×10^{-2} M) in methanol and the contents were refluxed for about 30 min. The yellow solid that separated was filtered off and washed with water. The precipitate was dried over P_4O_{10} for about 24 h (yield 75%).

Os(VIII)–MBPT complex

30 ml of MBPT solution (3×10^{-1} M) was added dropwise to 60 ml of metal solution (5×10^{-2} M) in methanol and the mixture was refluxed for 30 min. The resulting solution was concentrated to half the volume. The solid that resulted was washed with water. The precipitate obtained was dried over P_4O_{10} (yield 60%).

Ru(III)–MBPT complex

25 ml of a 2×10^{-1} M solution of the ligand in methanol was added dropwise to 60 ml of metal solution (5×10^{-2} M) in methanol and the mixture was refluxed for about 3 hours. The resultant brown solid that separated was washed with water and dried under vacuum for 24 h over P_4O_{10} (yield 70%).

Rh(III)–MBPT complex

30 ml of a 2×10^{-1} M solution of the ligand in methanol was added dropwise to 60 ml of metal solution (5×10^{-2} M) in methanol and the mixture was refluxed for about 30 min. The red complex that resulted was filtered, washed with water, and dried under vacuum for 24 h over P_4O_{10} (yield 75%).

Cu(II)–MBPT complex

40 ml of the ligand solution (2×10^{-2} M) in methanol was added dropwise to a hot solution of curic acetate (2×10^{-2} M) in 50 ml methanol and the mixture was refluxed for 30 min. The resulting solution was concentrated to half the volume. The green solid that separated was washed with water and dried under reduced pressure for 24 h (yield 50%).

Ni(II)–MBPT complex

To 50 ml of nickel ammonium sulphate solution (1×10^{-2} M) in methanol was added 50 ml of hot solution of MBPT (1×10^{-2} M) in methanol and the mixture was refluxed for 30 min. The grey–brown product that separated was filtered, washed with methanol and dried under vacuum for 20 h over P_4O_{10} (yield 80%).

Co(II)–MBPT complex

A hot solution of MBPT (5×10^{-2} M) in 50 ml methanol was added dropwise to 50 ml cobalt nitrate solution (5×10^{-2} M) and the mixture was refluxed for 1 h. The resultant brown solution was concentrated. The solid that separated was filtered off and washed with water. The brown precipitate obtained was dried over P_4O_{10} under vacuum for 24 h (yield 80%).

Ag(I)–MBPT complex

30 ml of MBPT solution (5×10^{-3} M) in methanol was added to a hot solution of 30 ml of silver nitrate (1×10^{-2} M) in methanol. The contents were refluxed for 2 h. The resultant brown solution was concentrated to half the volume. The grey coloured solid that separated was filtered, washed with water and dried over P_4O_{10} (yield 50%).

Hg(II)–MBPT complex

50 ml of MBPT solution (2×10^{-2} M) in methanol was added dropwise to a solution of mercuric chloride (5×10^{-2} M) in methanol and the mixture was refluxed for 30 min. The yellow solid that separated was filtered and dried over P_4O_{10} for about 10 h (yield 80%).

Physical Properties

Physical properties of the complexes are given in Table I.

Chemical Analysis

Compleximetric titration methods using EDTA [18] were employed for the estimation of copper and nickel in the respective solid complexes. Au(III) was determined by the hydroquinone method [18]. The amount of palladium in the Pd(II)-MBPT complex was determined gravimetrically using dimethylglyoxime as a precipitating agent [18]. Platinum in the complex was determined by pyrolysis of the solid chelate at 600 °C and weighing the residue obtained as platinum metal.

The analysis of the complexes is given in Table II.

TABLE I. Physical Properties of the Solid Complexes of MBPT

Complex	Colour of the chelate	State	Solubility
Gold(III)	yellow	crystalline powder	methanol, DMF, DMSO
Platinum(IV)	yellow	crystalline powder	methanol, DMF, DMSO
Palladium(II)	yellow	crystalline powder	methanol, DMF, DMSO
Osmium(VIII)	black	crystalline powder	methanol, DMF DMSO
Ruthenium(III)	yellow	crystalline powder	methanol, DMF, DMSO
Rhodium(III)	dark brown	crystalline powder	methanol, DMF, DMSO
Copper(II)	green	crystalline powder	methanol DMF, DMSO
Cobalt(II)	brown	crystalline powder	methanol, DMF DMSO
Nickel(II)	grey–green	crystalline powder	methanol, DMF, DMSO
Silver(I)	grey	crystalline powder	methanol, DMF DMSO
Mercury(II)	yellow	crystalline powder	methanol DMF, DMSO

Results and Discussion

IR Spectra

The infrared spectra and their spectral assignments are presented in Table III. The IR spectral data suggests that in all complexes coordination occurs through the azomethine nitrogen and thioketosulphur atom. The band at 1610 cm^{-1}, corresponding to the azomethine nitrogen atom is lowered indicating the coordination of the azomethine nitrogen atom [19]. The bands at 1075, 1025, 835 and 745 cm^{-1} assigned to the ν(C=S) band are shifted towards a lower frequency indicating the sulphur coordination [20]. The absence of a band due to the SH stretching mode near 2570 cm^{-1} suggests that in the solid state the molecule remains in the thione form. The palladium(II) and osmium(VIII) complexes show a shift corresponding to ν(NH), in addition to the shift due to azomethine nitrogen, and thioketosulphur coordination, indicating the deprotonation of the ligand. Coordination through the nitrogen atom is further substantiated by the appearance of new bands in the far IR region corresponding to M–N and M–S bonds.

TABLE II. Elemental Analysis

Complex	Carbon (%)		Hydrogen (%)		Nitrogen (%)		Sulphur (%)		Metal (%)	
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
$[(AuLCl_3)_2]\cdot 2H_2O$	29.60	29.49	2.82	2.78	6.92	6.84	5.28	5.21	32.30	32.22
$[PdL]\cdot H_2O]$	43.94	43.88	4.18	4.02	10.26	10.18	7.83	7.76	25.98	25.86
$[PtCl_4L]\cdot H_2O$	28.11	28.04	2.67	2.49	6.56	6.39	5.01	4.92	30.47	30.42
$[RuL_2Cl_3]\cdot 4H_2O$	40.35	42.28	4.59	4.53	9.96	9.84	7.54	7.41	11.89	11.86
$[RhL_2Cl_3]\cdot 2H_2O$	44.12	44.06	4.19	4.08	10.30	10.31	7.86	7.74	12.61	12.55
$[OsO_3L_2]\cdot 4H_2O$	40.89	40.76	4.31	4.25	9.54	9.44	7.27	7.24	21.60	21.79
$[CuL_2(OAc)]OAc\cdot 2H_2O$	45.34	45.24	4.31	4.29	10.58	10.46	8.07	7.92	8.00	7.95
$[CoL_2(NO_3)_2]\cdot H_2O$	46.67	46.59	4.18	4.13	14.60	14.53	8.31	8.22	7.64	7.59
$[NiL_2SO_4]\cdot 2H_2O$	47.29	47.21	2.51	2.42	11.04	10.91	12.64	12.54	7.71	7.62
$[AgLNO_3]\cdot H_2O$	38.05	37.94	3.62	3.51	11.84	11.76	6.77	6.68	22.62	22.56
$[HgL_2Cl_2]$	42.75	42.63	3.59	3.50	9.98	9.85	7.61	7.54	23.82	23.78

TABLE III. Infrared Spectral Bands of MBPT and Metal Complexes

MBPT	$[CuL_2(OAc)]OAc\cdot 2H_2O$	$[NiL_2SO_4]\cdot 2H_2O$	$[CoL_2(NO_3)_2]\cdot H_2O$	$[AgLNO_3]H_2O$	$[HgL_2Cl_2]$	Assignment
3320(s)	3320(s)	3320(s)	3340(s)	3320(s)	3320(s)	ν(NH)
1610(s)	1600(s)	1595(s)	1600(s)	1570(ms)	1600(s)	ν(C=N)
1510(s)	1500(s)	1500(s)	1510(s)	1515(s)	1510(s)	ν(CN)
1075(s)	–	1055(s)	1075(s)	1070(br)		ν(C=S)
1025(s)	1025(s)	1025(s)	1020(s)	1020(s)		
835(s)	835(s)	820(s)	825(s)	820(s)	825(s)	
740(s)	700(s)	740(s)	730(s)	740(s)	740(s)	
	490(s)	420(s)	520(s)	410(s)	435(s)	M–N
	410(s)	390(s)	420(s)	300(s)	385(s)	M–S
					275(s)	M–Cl

Anionic Spectra

The IR spectra of complexes of Au(III), Pt(VI), Pd(II), Ru(III), Rh(III) and Hg(II) show bands in the far IR region corresponding to ν(M–Cl) bonds. The nitrate group has D_{3h} symmetry in the free ion and IR active vibrations (three); ν_2(A), 831; ν_3(E), 1390, ν_4(E), 790 cm^{-1}. The symmetry becomes C_{2v} with six IR vibrations; ν_4(B$_I$), 1530–1480; ν_1(A$_1$), 1290; ν_2(A$_1$), 1030; ν_5(B$_2$), 810; ν_3(A$_1$), 740 and ν_6(B$_1$), 731 cm^{-1}, owing to mono or bicoordination to the metal. The spectra of the Ag(I) and Co(II) complexes show bands at 1500 and 1260 cm^{-1} corresponding to the coordinated nitrate group, and the band at 1380 cm^{-1} typical for the ionic nitrate group is absent. Coordination of the nitrate group is further supported by conductance studies. Sharp peaks at 1170 and 780 cm^{-1} in the Ni(II) complex correspond to the bidentate sulphate group. In the copper complex a peak at 1550 cm^{-1} which is absent in the ligand is attributed to the ν_{ass} mode of the acetate group.

Electronic Spectra

The electronic spectra of the Pt(IV) complex displays bands in the regions 30 000, 32 000, and 38 480 cm^{-1} which may be assigned to the transitions $^1A_{2g} \rightarrow {}^1A_{2g}$; $^1A_{1g} \rightarrow {}^1B_{1g}$ and $^1A_{1g} \rightarrow {}^1E_{1g}$ respectively in the square planar field. From the electronic spectra it is observed that the platinum(IV) complex exhibits only two transitions in the ultraviolet range at 38 460 and 29 410 cm^{-1} corresponding to $^1A_{1g} \rightarrow {}^1E_{1g}$ and $^1A_{1g} \rightarrow {}^3A_{2g}$ respectively indicating the square planar nature of the complex [21].

In the square planar complexes of palladium(II), two energy level sequences [22, 23] *viz.* $d_{z^2} < d_{xz} < d_{yz} < d_{xy} < d_{x^2-y^2}$ and $d_{xz} < d_{yz} < d_{z^2} < d_{xy} < d_{x^2-y^2}$ have been suggested. The former has recently been studied by X-ray and polarized single crystal spectral studies [24] of the palladium ions $[PdCl_4]^{2-}$ and $[PdBr_4]^{2-}$. Three spin allowed d–d transitions from the three lower lying d levels to the empty $d_{x^2-y^2}$ orbitals are predicted on the basis of this sequence. Accordingly the bands observed in the regions 16 000–23 500; 23 500–28 500; 28 500–35 000 cm^{-1} may be assigned to the transitions $^1A_{1g} \rightarrow {}^1A_{2g}$, $^1B_{1g} \rightarrow {}^1B_{1g}$ and $^1A_{1g} \rightarrow {}^1E_{1g}$, respectively. The peaks observed for the palladium(II) complex at 22 200, 27 700 and 37 037 cm^{-1} support the square planar geometry. Bands around 30 000 and 37 100 cm^{-1} in the osmium complex appear to be charge transfer in origin [25].

The electronic spectral bands of the ruthenium(III) complex in the regions 16 800 and 29 400 cm^{-1} may be assigned to the transitions $^2T_{2g} \rightarrow {}^2A_{2g}$ and π- - -$t_{2g}\pi^*$) respectively in the octahedral field [26], in addition to the main charge transfer band at 35 700 cm^{-1}. The rhodium(III) complex displays a charge transfer band at 3300 cm^{-1}, a shoulder at 28 570 cm^{-1} (regarded as $^1A_{1g} \rightarrow {}^1T_{1g}$) and a band at 25 400 cm^{-1} corresponding to the first spin allowed $^1A_{1g} \rightarrow {}^1T_{1g}$ as a result of low symmetry splittings, in the distorted octahedral structure.

The copper(II) complex shows peaks in the electronic spectrum at 14 860 and 19 120 cm^{-1} corresponding to the d–d transitions [27, 28] and two bands at 29 400 cm^{-1} assignable to L → M charge transfer. On the basis of the electronic spectrum, a square planar geometry is proposed for the complex. Low spin cobalt(II) complexes have been characterized by a weak band around 8500 cm^{-1} and a more intense band around 1800 cm^{-1} [29]. Under an octahedral field the 2G term for the free ion splits into ^2E_g, $^2T_{1g}$ and $^2A_{1g}$ components in increasing order of energy. The bands observed at 16 000 and 20 000 cm^{-1} are assigned to the transitions $^2A_{1g}$ ground term to the higher energy $^2A_{2g}$ and ^2E_g states, the split components of the excited $^2T_{1g}$ term respectively. The higher energy intense band is attributed to a M–L(π^*) charge transfer transition. The nickel(II) complex shows bands at 35 700 and 155 500 cm^{-1} ($^3A_{2g} \rightarrow {}^1T_{1g}$) and another peak at 27 020 cm^{-1} ($^3A_{2g} \rightarrow {}^3T_{1g}$(P)) indicating the octahedral nature of the complex. The mercury complex is diamagnetic as expected and hence shows no bands in the visible region. Since the silver complex has the metal ion with a d^{10} electronic configuration, no bands are observed in the visible region [31].

Conductance Measurements

The conductance data are presented in Table IV. The high molar conductance value for the copper chelate suggests that the complex is a 1:1 electrolyte. The IR spectra and magnetic measurements are consistent with the structures proposed.

TABLE IV. Conductance and Magnetic Susceptibility Data

Complex	Solvent	Conductance	μ_{eff}
$[(AuLCl_3)_2]\cdot 2H_2O$	DMF	38.46	diamagnetic
$[(PdL)\cdot H_2O]$	DMF	26.34	diamagnetic
$[PtCl_4L)\cdot H_2O]$	DMF		diamagnetic
$[RuL_2Cl_3]\cdot 4H_2O$	DMF	6.25	2.24
$[RhL_2Cl_3]\cdot 2H_2O$	DMF	10.20	diamagnetic
$[OsO_3L_2]\cdot 4H_2O$	DMF	15.5	diamagnetic
$[CuL_2(OAc)]OAc\cdot 2H_2O$	DMF	90.00	1.74
$[CoL_2(NO_3)_2]\cdot H_2O$	DMF	14.46	1.90
$[NiL_2SO_4]\cdot 2H_2O$	DMF	9.52	2.62
$[AgLNO_3]\cdot H_2O$	DMF		diamagnetic
$[HgL_2Cl_2]$	DMF		diamagnetic

Magnetic Measurements

The μ_{eff} of the complexes are presented in Table IV. Gold(III), platinum(IV), palladium(II), rhodium(III), osmium(VIII) and mercury(II) complexes are diamagnetic. The room temperature magnetic moment values for ruthenium(III), copper(II) and cobalt(II) complexes indicate the presence of one unpaired electron whereas the nickel chelate has two unpaired electrons.

Thermal Analysis

In the present investigations on the thermal behaviour of the metal complexes of MBPT it is observed that all complexes except the mercury complex are hydrated. The platinum, palladium, cobalt and silver complexes are monohydrates. Rhodium and nickel are dihydrates whereas osmium and ruthenium complexes have four water molecules. The experimental amount of water in the chelates determined from the weight loss in the thermogram approaches the theoretical weight amount calculated for mono, di, and quadrihydrates. The residues from the thermogravimetric runs of the compounds were weighed and compared to the weight that would be obtained if the residue were a metal and was found to be in good agreement with the theoretical value.

Acknowledgements

The authors thank the Council of Scientific and Industrial Research, New Delhi, for awarding senior research fellowships to two of the authors (K.M.M.S.P. and L.D.P.). Thanks are due to Mr P. Ravi Prasad, Regional Research Laboratories, Hydrabad, India, for his help in elemental analysis. Mr R. Mani of the Indian Institute of Technology, Madras, India, is thanked for his help in electronic and infrared spectra.

References

1 *U.S. Patent 3 382 266* (1968) to K. Butler.

2 N. N. Orlova, V. A. Aksenova, V. A. Selidovkin, N. S. Bogdanova and G. N. Pershin, *Russ. Pharmacol. Toxicol.*, 348 (1968).

3 D. J. Bauer, L. S. Vincent, C. H. Kempe and A. W. Downe, *Lancet, 2,* 494 (1963).

4 G. H. Petering, H. S. Burkik and G. E. Underwood, *Cancer Res., 64,* 367 (1964); R. W. Broeckman, J. R. Thomson, M. J. Bell and H. E. Skipper, *Cancer Res., 16,* 167 (1956).

5 E. C. Moore, B. A. Booth, K. C. Agarwal and A. C. Sartorelli, *Biochemistry, 9,* 4492 (1970).

6 G. Domagk, R. Behenich, F. Mierrsch and H. Schmidt, *Naturwissenschaften, 33,* 315 (1946).

7 D. L. Klayman, J. F. Bertosevich, J. P. Scovill and J. Bruce, *J. Med. Chem., 26,* 35 (1983), and refs. therein.

8 J. A. Gim and H. G. Petering, *Cancer Res., 27,* 1278 (1967).

9 H. G. Petering and G. J. Van Giessen, 'The Biochemistry Chowdaray, *Anal. Lett.*, in press.
208.

10 H. S. Waxman and E. B. Brown, *Prog. Hermatol., 6,* 338 (1969); A. W. Nienhius, *J. Am. Med. Assoc., 237,* 1926 (1977).

11 Y. Arano, A. Yokoyama, Y. Magata, H. Saji, K. Horiwchi and K. Torizuka, *Int. J. Nucl. Med. Biol., 12,* 6 425 (1986).

12 R. C. Agarwal and R. B. S. Yadav, *Indian J. Chem., 15,* 50 (1977).

13 S. Ghosh, P. B. Ray, M. S. Mitra and T. Banik, *J. Indian Chem. Soc., 58,* 533 (1981)

14 S. K. Jain, B. S. Garg and Y. K. Bhoon, *Transition Met. Chem., 11,* 89 (1986).

15 S. K. Jain, B. S. Garg, Y. K. Bhoon, J. P. Scovill and D. K. Klayman, *Spectrochim. Acta, 24,* 407 (1985); R. P. Gupta, B. N Yadav, K. Srivastava and K. Ashutosh, *Proc. Ind. Acad. Sci., 94,* 475 (1985).

16 K. M. M. S. Prakash, L. D. Prabhakar and M. C. Chowdary, *Analyst., 111,* 1301 (1986).

17 K. M. M. S. Prakash, L. D. Prabhakar and M. C. Chowdary, *Anal. Lett.*, in press.

18 A. I. Vogel, 'A Textbook of Quantitative Inorganic Analysis., 3rd edn., Longmand, London, 1969.

19 B. D. Sharma and J. C. Bailer, *J. Am. Chem. Soc., 77,* 5476 (1955); N. K. Dutta and N. C. Chakdar, *J. Inorg. Chem., 39,* 2183 (1977).

20 M. C. Jain and P. C. Jain, *J. Inorg. Nucl. Chem., 39,* 2183 (1977).

21 M. P. Toetia, J. N. Gurtu and V. B. Rana, *Indian J. Chem., 20A,* 520 (1981).

22 J. Chatt, G. A. Gamlen and L. E. Orgell, *J. Chem. Soc., 486 (1958).*

23 H. B. Gray and C. J. Ballhausen, *J. Am. Chem. Soc., 75,* 2543 (1963).

24 R. N. Rush, D. S. Martin and R. G. Legrand, *Inorg. Chem.*, 14 (1975).

25 B. N. Figgis, 'Introduction to Ligand Fields', Wiley, New York, 1976.

26 K. W. Fung, and Johnson, *Inorg. Chem., 10,* 1347 (1971).

27 J. Jorgenson, *Inorg. Nucl. Chem., 24,* 1571 (1962).

28 M. J. M Campbell, *Coord. Chem. Rev., 15,* 311 (1975).

29 J. Chakrabarthy and B. Sahoo, *Indian J. Chem., 20A,* 431 (1981).

30 A. K. Rana and J. R. Shaw, *Indian J. Chem., 21A,* 929 (1982).

31 K. S. Arulsamy, R. F. N. Ashok and U. C. Agarwala, *Indian J. Chem., 23A,* 127 (1984).