Synthesis and characterisation of metal complexes of orthovanillin thiosemicarbazone

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ABSTRACT

Six complexes of transition metals with 2 hydroxy 3 methoxy benzaldehyde (orthovanillin) thiosemicarbazone were synthesized and characterised by elemental analysis, (by CHNS Analyser and ICPAES) conductance and magnetic measurements, infrared and NMR spectral analysis and thermal analysis. Antibacterial activity tests, SHG measurements for non linear optical activity were made. Four complexes have the general formula [M(OVTSC)2X2] where M = Mn & Cd, OVTSC = Orthovanillin thiosemicarbazone. The copper complexes have the formula [Cu(IVTSC)X2 (H2O)2]. In all the complexes X = Cl,NO3. The presence of water in the copper complex is proved by thermal analysis. In all complexes the ligand co-ordinates to the metals bidendately.

Key words : Synthesis, Manganese (II) Chloride, Manganese (II) Nitrate, Copper (II) Chloride, Copper (II) Nitrate, Cadmium (II) Chloride and Cadmium (II) Nitrate complexes, Orthovanillin thiosemicarbazone or 2 hydroxy 3 methoxy thiosemicarbazone.

INTRODUCTION

Six complexes of Mn(II), Cu (II) and Cd (II) were prepared and characterised. Orthovanillin thiosemicarbazone (OVTSC) or 2-hydroxy 3-methoxy benzaldeyde thiosemicarbazone can be represented by the following structure:

Thiosemicarbazones can act as bidendate ligands similar to semicarbazones, with the exception that the former compounds use sulphur as one of the donor atoms in the place of oxygen as in semicarbazones. The complexes synthesised were characterised using infra red spectroscopy, elemental analysis (CHNS analyses as well as metal percentage analysis by ICPAES), conductance measurements, magnetic measurements and TG/DTG/DTA analyses. Antibacterial activity was tested in the light of the generally reported antibacterial activity of thio semi carbazones[1-4]. Second harmonic generation measurements of some of the complexes were done for non linear optical properties (NLO), NLO being important in telecommunication and information processing5-7, and orthovanillin being an isomer of vanillin which has NLO activity8.

MATERIAL AND METHODS

Experimental
Reagents

Chlorides and Nitrates of Mn (II), Cu (II), Cd (II) which were of 99.9% assay were used for the preparation of these complexes. The thiosemicarbazone was prepared by the condensation of thiosemicarbazide and orthovanillin, both of 99.9% purity, at a pH of 6.5.

Preparation of the ligand and complexes
Ligand

The ligand OVTSC was prepared by mixing equimolar methanolic solutions of thiosemicarbazide and orthovanillin in slightly acidic medium and refluxing for 2 hours. Ivory coloured crystals of the ligand separated out on cooling which was washed with water, filtered and dried.

Complexes

The transition metal complexes were prepared by warming the respective metal chloride or nitrate dissolved in methanol in an R.B flask fitted with a reflux condensor to which the prepared ivory crystals of orthovanillin thiosemicarbazone (2-hydroxy, 3-methoxy benzaldehyde) dissolved in methanol was added and mixed in the ratio 1 : 2 at a pH of 7.5 and refluxed for two hours. On cooling and evaporation crystalline complexes of various colours were formed.

Analyses and physical measurements

The ligand and complexes were analysed for their carbon, nitrogen, hydrogen and sulphur contents in a Vario EL III CHNS analyser. The metal contents of the complexes were analysed by ICPAES (Inductively Coupled Plasma Atomic Emission Spectroscopy) in an Iris Interprid II XSP model instrument. The 1H-NMR spectra of the ligands were recorded on a AMX 400 instrument.

Molar conductance values of the complexes in acetonitrile and nitro benzene were measured at room temperature using an Elico conductivity bridge (Type CM82T) equipped with a dip type cell having Pt electrodes (cell constant 1cm^{-1}). The FT - IR spectra of the ligand and complexes were recorded in KBr pellets on a Thermonicolet Avatar 370 D7G FT-IR Spectrophotometer in the range 4000-400 cm-1. Solubilities of the ligand and the complexes in various solvents were tested. The NLO activity (Second Harmonic Generation) of the ligand and complexes were measured in a Nd YAG Laser Spectra Physics DCR II instrument. The antibacterial activity of the ligand and complexes were studied on two bacterial strains, gram(-) E.coli ATCC 25922 and gram(+) S.coureus ATCC 25923.

Thermogravimetric (TG), derivative thermogravimetric (DTG) and differential thermal analysis (DTA) curves of the samples were obtained from a Perkin Elmer Diamond simultaneous TG/DTA analyser. A constant heating rate of 100C/min and sample mass of 2 mg to 12mg were employed in all the thermogravimetric experiments with the ligand and complexes. Samples were taken in ceramic crucibles for thermal analysis and all experiments were conducted under flowing nitrogen (99.9% pure) atmosphere with a flow rate of 100ml/minute.

RESULTS AND DISCUSSION

The condensation of the aldehydic oxygen and the -NH2 group of thiosemi carbazide in acid medium yeilded the ligand OVTSC with structure represented in figure - 1, which is in agreement with the elemental percentages (Table - 1). IR spectral data are presented in table - 2 and 1H-NMR spectrum of OVTSC in CD3OD was taken. 1H-NMR has 2 peaks at 3.3 ppm and 4.85 ppm, which are singlets, due to the solvent. One at 3.85 ppm is due to the protons on OCH$_3$. The peak at 8.38 ppm is due to the proton on OH of the aryl ring. One doublet at 6.9 ppm due to the H adjacent to OCH3 (aryl), one triplet due to H, meta to the aryl OCH3 and an another doublet at 7.4 ppm due to H, para to aryl OCH3. These assignments are compatible to the structure of the ligand shown in figure 1.

The elemental percentages of the complexes tabulated in table 1 are in good agreement with their suggested formulae and their proposed structures [figures 2(a) & 2(b)].

All the 6 complexes of IVTSC are non-hygroscopic solids of various colours (Table 1), soluble or sparingly soluble in dimethyl formamide, acetonitrile, hot HCl and H2SO4 but insoluble in methanol, ethanol and water.

Molar Conductance

All the complexes are non-electrolytes as is evident from the values of their conductances, which are less than 120 ohm^{-1} cm$_2$ mol^{-1} measured in acetonitrile and less than 20 ohm^{-1} cm^2 mol^{-1} in nitrobenzene which are the minimum values of conductance in these solvents[9] for a 1:1complex. The values are tabulated in table - 1.

Table 1: Analytical data Transition metal complexes of 2-Hydroxy-3-Methoxy Benzaldehyde Thiosemicarbazone, (Ortho vanilin or OVTSC)

Complex/ligand	Colour	Mol. wt	Metal%	Carbon%	Hydrogen%	Nitrogen %	Sulphur%	Conductance ohm⁻¹ cm⁻¹ mol⁻¹	
								Acetonitrite	Nitrobenzene
OVTSC	Ivory	225 (225)*	-	47.80 (48.00)	4.90 (4.88)	18.80 (18.6)	14.15 (14.2)		
[Mn(OVTSC)$_2$Cl$_2$]	Orange red	576 (575.9)	9.45 (9.54)	37.35 (37.50)	3.86 (3.82)	14.57 (14.50)	11.05 (11.11)	3.1	1.2
[Mn(OVTSC)$_2$(NO$_3$)$_2$]	Orange red	629 (628.9)	8.80 (8.72)	34.40 (34.30)	3.57 (3.49)	17.60 (14.80)	10.12 (10.17)	3.0	1.3
[Cu(OVTSC)Cl$_2$]2H$_2$O	Black	396.00 (395.54)	16.20 (16.03)	27.45 (27.30)	3.90 (3.79)	10.70 (10.62)	8.10 (8.09)	2.0	1.1
[Mn(OVTSC)$_2$(NO$_3$)$_2$]2H$_2$O	Black	412 (412.54)	15.60 (15.4)	26.26 (26.18)	2.77 (2.67)	16.40 (16.96)	7.82 (7.76)	2.0	1.4
[Cd(OVTSC)$_2$Cl$_2$]	Yellow	635.00 (633.40)	17.80 (17.74)	34.20 (34.10)	3.53 (3.47)	13.19 (13.26)	10.19 (10.10)	1.0	1.5
[Cd(OVTSC)$_2$(NO$_3$)$_2$]	Lime Yellow	685.00 (686.40)	16.40 (16.37)	31.57 (31.47)	3.27 (3.20)	16.39 (16.39)	9.40 (9.32)	1.0	1.3

*Calculated values are given in paranthesis

Table 2: IR specstral assignments of 2-Hydroxy-3-methoxy Benzaldehyde Thiosemi carbazone (Orhovanillin or OVTSC) and its transition metal complexes

Compound	νOH	νN-H	νPh-H	νC-H	νC=N	δNH$_2$	νPh	νC=S	νNO$_2$	νC-N	νN-N	νM-N
OVTSC	3560w	3461vs 3343s	3167m	2975w	1635m	1580s	1538s 1483s 1453s	1185		1263	1059	
[Mn(OVTSC)$_2$Cl$_2$]	3568w	3447m 3339m	3173w	2980w	1605vs	1575m	1521s 1474s 1450s	1174w		12257s	1063s	460w
[Mn(OVTSC)$_2$(NO$_3$)$_2$]	3569	3460s	3166m	2981w	1605s 3343m	1568m	1538s	1165w	1430s 1309s 1050m	1272s	1063s	460w
[Cu(OVTSC)Cl$_2$]2H$_2$O	3568w	3489w 3340m	3172w	2998w	1605vs	2589s	1546s 1503s 1443s	1171m		1242s	1084m	477w
[Mn(OVTSC)$_2$(NO$_3$)$_2$]2H$_2$O	3568w	3489w 3341m	3173w	3000w	1608vs	1589s	1545s 1502s 1440s	1170m	1410s 1310m 1050m	1240s	1085m	477w
[Cd(OVTSC)$_2$Cl$_2$]	3569w	3460s 3343w	3168m	2970w	1600vs	1575m	1536s 1490m 1452s	1160m		1263m	1080m	460w
[Cd(OVTSC)$_2$(NO$_3$)$_2$]	3569w	3460s 3340s	3168m	2960w	1609vs	1570w	1537s 1488m 1452vs	1154m	1431m 1312m 1050m	1240s	1080m	460w

Magnetic Measurements

The magnetic susceptibility of the various complexes of orthovanillin thiosemicarbazone was determined at room temperature using a field strength of 5 KOe in a VSM. The chloride salt complex of Cu (II) showed a value of 1.9 BM and 2.0 BM for the nitrate salt complex of Cu (II). The experimental value obtained is compatible for a d9

Table 3: Measured SHG efficiency of IVTSC and its transition metal complexes

Sample	SHG signal	Efficiency	
	at 1.3mJ/pulse	with respect to KDP	with respect to urea
KDP	63	1.000	0.1260
Urea	500	7.9365	1.0000
OVTSC	1.8	0.02857	3.6×10^{-3}
$[Cd(OVTSC)_2Cl_2]$	4	0.06349	8×10^{-3}
$[Cd(OVTSC)_2(NO_3)_2]$	5	0.7937	0.0100

Table 3: OVTSC and Transition metal complexes - TG/DATA Data

Compound	$T_1°C$	$T_3°C$	$T_r°C$	Mass Loss%	DTA $T_8°C$
OVTSC	220	233	340	47	Endo 234 Exo 250
$[Mn(OVTSC)_2Cl_2]$	325	373	400	30.3	Endo 372 Exo 382
$[Mn(OVTSC)_2(NO_3)_2]$	220	235	340	27.8	Endo 230 Exo 250
$[Cu(OVTSC)Cl_2]2H_2O$	220	228	380	36.6	Endo 230 Exo 260
$[Mn(OVTSC)_2(NO_3)_2]2H_2O$	150	265	370	35	Endo 280 Exo 336
$[Cd(OVTSC)_2Cl_2]$	200	216	370	33.3	Endo 212 Exo 220
$[Cd(OVTSC)_2(NO_3)_2]$	190	213	350	27.3	Endo 215 Exo 223

Table 4: Kinetic parameters for the decomposition of OVTSC and its transition metal complexes using coats-Redfern equation

Compound	E kJ/mol	A sec^{-1}	r
OVTSC	98.5	2.82×10^7	0.9910
$[Mn(OVTSC)_2Cl_2]$	97.1	8.207×10^{33}	0.9926
$[Mn(OVTSC)_2(NO_3)_2]$	82.3	3.27×10^6	0.9932
$[Cu(OVTSC)Cl_2]2H_2O$	109.70	1.41×10^8	0.9907
$[Mn(OVTSC)_2(NO_3)_2]2H_2O$	50.9	2.57×10^2	0.9962
$[Cd(OVTSC)_2Cl_2]$	99.0	6.17×10^7	0.9909
$[Cd(OVTSC)_2(NO_3)_2]$	103.9	3.28×10^8	0.9956

configurational octahedral geometry10 that abides by the suggested formula of the complex, [Cu (OVTSC)X2(H$_2$O)$_2$].

The Mn (II) complex, [Mn (OVTSC)2 Cl2], shows a magnetic moment of 1.78 BM and [Mn (OVTSC)2 (NO3)2] shows a value 1.8 BM . An octahedral geometry, may be suggested.

Infra Red Spectra

The prominent IR spectral bands of OVTSC and its various transition metal complexes along with their assignments are presented in table 2.

The stretch, v N-H, of the amide and imide group of OVTSC shows strong absorptions at 3461 cm^{-1} and 3343 cm^{-1} in the spectrum. These values are seen retained as almost the same in the complexes of Mn, Cu and Cd, indicating the absence of co-ordination through the amide and imide group nitrogen atoms.

The v C = S mode is seen strongly absorbed at 1185 cm-1 in the ligand while its transition metal complexes show absorptions shifted to values 1174m., 1165m, 1171m, 1170m, 1160m and 1154m cm-1 in Mn (chloride), Mn (nitrate) Cu (chloride), Cu(nitrate), Cd (chloride) and Cd (nitrate) respectively. The down shift of this value from the ligand is due to the co-ordination of the thiocarbonyl sulphur to the transition metal ion in the complexes.

The azomethine nitrogen of the free ligand due to v C = N shows a strong absorption at 1635 cm-1. This is seen to suffer a lower shift to values of 1605s, 1600s, 1605s, 1608s, 1600s and 1609s cm-1 in the complexes of Mn (chloride), Mn (nitrate), Cu(chloride), Cu(Nitrate), Cd (chloride) and Cd (nitrate) respectively. This change can be attributed to the co-ordination of the azomethine nitrogen of the ligand to the transition metal ions. Chelation of the nitrogen to the metal ion brings about such lowering of IR bands12, 13. The spectrum of the ligand and complexes show strong absorption at 1580 cm^{-1}. This is assignable to the bending mode, d NH2, vibrations.
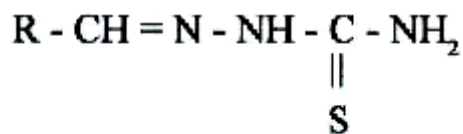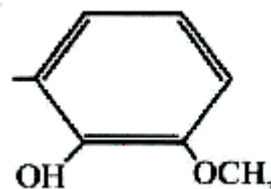

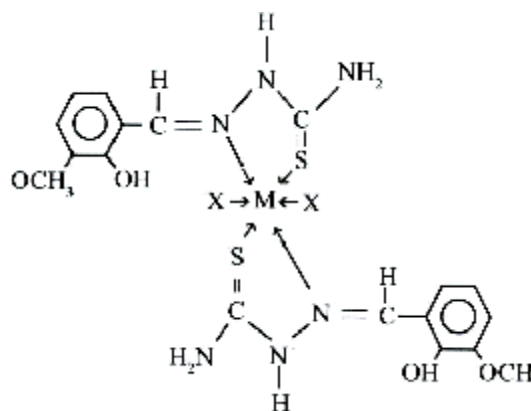**Fig. 1: Isovanillin Thisemicarbazone**

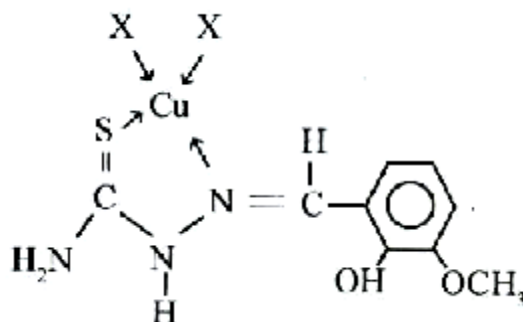**Fig. 2(a): Proposed structure of OVTSC complexes where M = Mn & Cd, X = Cl, NO$_3$**

Fig. 2(b): Proposed structure of OVTSC copper complexes where X = Cl, NO$_3$

Stretching vibrations of the phenyl ring of the ligand (*v* - Ph) account for strong absorptions at 1545 cm-1, 1490cm-1 and 1450 cm-1 in the free as well as the co-ordinated ligand.

The phenyl *v* C - H mode causes absorption at and around 3165 cm^{-1} in the free ligand and the metal co-ordinated ones. The *v* C - N mode of vibration absorbs frequencies of 1260 cm^{-1} in the non-co-ordinated and co-ordinated ligand. The *v* O-H mode due to the hydroxy group in the benzene ring of OVTSC and its transition metal co-ordination complexes show an absorption at *v* 3560 cm^{-1}. The unchanged values of absorptions due to various groups in the free and co-ordinated ligands provide ample evidence for absence of co-ordination through these groups.

The complexes of nitrate salts of transition metals in this series with OVTSC also bear unidendately co-ordinated nitrate ion to to the transition metal ion as inferred from nitrate ion absorptions around 1440, 1308 and 1058 cm-1 due to *v*4, *v*1, *v*3 modes respectively.

NLO activity (SHG)

SHG intensities of the powdered form of the ligand and its complexes with only cadmium were measured since complexes of manganese and copper were intense coloured and had to be avoided. KDP and urea in powder form were used as reference compounds.

The SHG signals are tabulated in Table 3 It is seen that the ligand has low efficiency as compared to the two references, urea and KDP. However its efficiency is seen to increase on complexation.

Anti bacterial Activity Tests

The antimicrobial activity was studied adopting the agar diffusion method. Gentamycin disc was used as the positive control. Sterile paper disc was asceptically impregnated with methanol and processed as for the test sample, which was the negative control.

None of the samples showed antimicrobial activity. The strains of bacteria used here viz., gram negative *E.coli* ATCC 25922 and gram positive *S. aureus* ATCC 25923 are seen to overcome any activity of the ligand and its complexes that tend to destroy them.

Thermal Analysis

The kinetic analysis of all thermal data obtained was done using the non mechanistic equation derived by Coats and Red Fern14. The order parameter 'n' was evaluated for the decompositional reactions using the same equation by an iteration method. Linear plots of ln[g(a)/T2] versus 1/T were drawn by the method of least squares. Linear curves were drawn for different values of 'n' ranging from 0 to 3, in increments of 0.05. The value of 'n' which gave the best fit value, was chosen as the order parameter for the particular reaction. The values of activation energy, E, and pre exponential factor, A, from the slope and intercept respectively of the linear plots of the left handside of the kinetic equation versus 1/T.

From the TG/DTG15/DTA curves of OVTSC and its complexes show that the mass loss occuring due to the decomposition, from 1800C to 4000C has only one distinct and reproducible stage (Table 3). The copper complexes showed mass loss due to water lost. The stability as well as the decomposition pattern of the complexes vary with the metal involved. The thermal stability of the ligand OVTSC is seen to increase on complexation generally. The kinetic parameters of the compounds studied are given in Table - 4. The highest correlation was obtained for the kinetic plot with order parameter n = 2 or closely matching to 2 in all cases. Hence the order parameter 'n' was taken as 2 for the calculation of kinetic parameters. The values of correlation coefficients for the kinetic plots found as high as 1, prove the validity of the method adopted for kinetic analysis.

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