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Complexes of Ni(II), Cu(II), Zn(II), Pd(II) and Cd(II) with 1-Salicylidene-4-Pyrrolidino Thiosemicarbazone

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Complexes of Ni(II), Cu(II), Zn(II), Pd(II) and Cd(II) with 1-salicylidene-4-pyrrolidino thiosemicarbazone (H_2-sptsc) of general formulae [M(H-sptsc)$_2$], M(sptsc) . nH_2O and [M(sptsc)py] ($M = Ni^{2+}$, Cu^{2+}, Zn^{2+}, Pd^{2+}, or Cd^{2+}; n = 0 or 1) have been prepared and characterised by elemental analyses, molar conductance, magnetic susceptibility, infrared and electronic spectral measurements.

INTRODUCTION

The coordination chemistry of thiosemicarbazides and thiosemicarbazones has created much interest due to their antibacterial[1, 2], antitubercular[3, 4], and antitumour[5–8] activities and has been reviewed[9, 10] recently. From the survey of existing literature, it appears that the complexing behaviour of 1-salicylidene-4-pyrrolidino thiosemicarbazone (H_2-sptsc) has not been investigated hitherto. The present investigation describes the complexation of the ligand (H_2-sptsc) with Ni(II), Cu(II), Zn(II), Pd(II) and Cd(II) ions. The ligand (Fig.1) can exist in the keto and enol forms and act as monoprotic and biprotic tridentate chelating agent depending upon pH values.

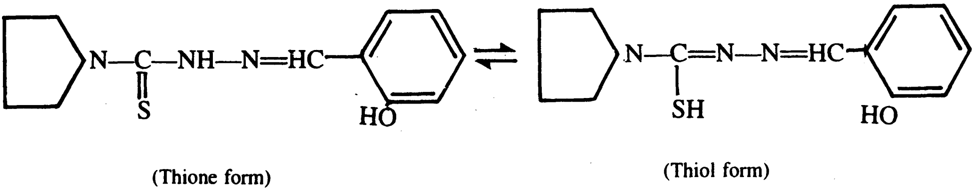

Fig. 1

EXPERIMENTAL

The ligand (H_2-sptsc) was prepared by condensation of 4-pyrrolidino thiosemicarbazide[11] and salicylaldehyde in 50% ethanol. The cream white product was recrystallised in ethanol and its m. p. was found to be 224°C (Found: C = 57.42%, H = 6.11%, N = 16.58%, S = 12.58%, Calcd for $C_{12}H_{15}N_3OS$: C = 57.81%, H = 6.05%, N = 16.85%, S = 12.86%)

Preparation of [M(H-sptsc)$_2$]: An aqueous ethanolic solutions of metal chlorides (0.005 M in 40 mL) and ligand (0.01 M in 50 mL) were mixed and

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refluxed on a steam bath for 1/2 h when a solid mass separted out. The products were filtered, washed with ethanol and dried in vaccum desiccator over anhydrous $CaCl_2$.

Preparation of M(sptsc).nH$_2$O (n = 0 or 1): An aqueous ethanolic solution of metal chlorides (0.005 M in 50 mL) was treated with ethanolic solution of ligand (0.005M in 50 mL) with constant stirring and the pH of resulting mixture was raised to 7–8 by adding dilute NH_4OH solution when solid complexes separated out immediately. The product was digested on a steam bath for 20 min, filtered, washed with ethanol and dried as usual.

TABLE-1

ANALYTICAL DATA AND MAGNETIC MOMENT VALUES OF COMPLEXES

Compound	Colour	% Analysis, Found (Calcd.)				$\mu_{eff.}$
		C	H	N	M	
[Ni(H–sptsc)$_2$]	Yellowish green	52.24	5.31	15.38	10.48	3.42
		(51.90)	(5.06)	(15.13)	(10.57)	
[Cu(H–sptsc)$_2$]	Greenish yellow	51.25	5.42	14.48	11.02	1.86
		(51.46)	(5.02)	(14.99)	(11.35)	
[Zn(H–sptsc)$_2$]	Colourless	51.48	5.30	14.38	11.87	Dia
		(51.23)	(5.00)	(14.95)	(11.63)	
[Pd(H–sptsc)$_2$]	Orange yellow	48.12	4.98	13.68	16.94	Dia
		(47.80)	(4.66)	(13.93)	(17.65)	
[Cd(H–sptsc)$_2$]	Colourless	47.64	4.85	13.52	18.16	Dia
		(47.33)	(4.61)	(13.79)	(18.46)	
[Ni(sptsc)·H_2O]	Brownish yellow	44.25	4.80	13.14	18.02	1.45
		(44.48)	(4.67)	(12.96)	(18.12)	
[Cu(sptsc)]	Brown	46.05	4.52	13.42	20.13	1.67
		(46.36)	(4.21)	(13.51)	(20.44)	
[Zn(sptsc)·H_2O]	Colourless	43.82	4.87	12.88	19.58	Dia
		(43.58)	(4.57)	(12.70)	(19.77)	
[Pd(sptsc)·H_2O]	Yellowish brown	38.63	4.32	11.42	28.41	Dia
		(38.77)	(4.07)	(11.30)	(28.63)	
[Cd(sptsc)·H_2O]	Colourless	38.42	4.25	11.28	29.94	Dia
		(38.16)	(4.00)	(11.12)	(29.76)	
[Ni(sptsc)py]	Yellow	52.87	4.96	14.38	15.39	Dia
		(53.03)	(4.73)	(14.55)	(15.25)	
[Cu(sptsc)py]	Grey	52.12	4.83	14.20	16.45	1.92
		(52.35)	(4.67)	(14.36)	(16.29)	
[Zn(sptsc)py]	Colourless	52.32	4.78	14.15	16.89	Dia
		(52.08)	(4.64)	(14.29)	(16.68)	
[Pd(sptsc)py]	Cream yellow	46.93	4.35	12.68	24.32	Dia
		(47.15)	(4.20)	(12.93)	(24.57)	
[Cd(sptsc)py]	Colourless	46.38	4.32	12.56	26.12	Dia
		(46.51)	(4.16)	(12.76)	(25.60)	

Preparation of [M(sptsc)py]: An aqueous ethanolic solution of metal chlorides (0.005 M in 40 mL) was treated with 5 mL pyridine and the resulting mixture was added to hot ethanolic solution of ligand (0.005 M in 40 mL) when the solid complexes separated immediately. The product was digested on a steam bath for 1/2 h and allowed to stand at room temperature overnight. The solid complexes were filtered, washed with water containing pyridine and dried in a desiccator over fused KOH.

The analytical results of complexes and their molar conductance and magnetic moment values are given in Table-1. The magnetic susceptibilities, electrical conductance values, IR and electronic spectra of complexes were recorded as reported previously[12].

RESULTS AND DISCUSSION

The analytical data (Table-1) indicate that the ligand (H_2-sptsc) behaves as monoprotic as well as biprotic molecule and forms both bisligated and monoligated complexes, [M(H-sptsc)$_2$], M(sptsc) . nH_2O and base adducts [M(sptsc)py)] with bivalent metal ions. The aquo complexes have poor solubilities in organic solvents but the other complexes are fairly soluble in DMF and dioxane. In DMF the complexes are almost non-conducting [8–20 Ω^{-1} cm^2 mol^{-1}] indicating their non-ionic nature. TG analysis shows that the hydrated complexes do not lose water molecule below 140°C. This suggests that water molecule is either coordinated or strongly held up in crystal lattices.

As expected Zn(II), Pd(II) and Cd(II) complexes are diamagnetic. Excepting [Ni(sptsc)py], all other Ni(II) and Cu(II) complexes are paramagnetic. The diamagnetism of Pd(II) and base adduct Ni(II) complexes indicate their square planar geometry. [Ni(H-sptsc)$_2$] shows magnetic moment value of 3.42 B.M. which occurs in the range of octahedral complexes. The aquo complex, Ni(sptsc). H_2O shows magnetic moment value of 1.45 B.M. The sub-normal magnetic moment value of this complex may be explained by assuming the complex to be polymeric having mixed stereochemistry[13] with one nickel atom possessing 0_h symmetry and the other D_{4h} symmetry in the unit cell. The formation of polymeric species is supported by its poor solubility in organic solvents. Cu(II) complexes, [Cu(H-sptsc)$_2$] and [Cu(sptsc)py] display normal magnetic moment value (1.86–1.92 B.M.) at room temperature but [Cu(sptsc)] shows sub-normal value (1.67 B.M.). The lowering of magnetic moment value is attributed to partial metal-metal bonding in the oxygen bridged dimeric structure[14] of the complex.

The electronic spectrum of ligand (H_2-sptsc) displays absorption bands at 230, 280 and 360 nm attributed to $\sigma \rightarrow \sigma^*$; $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. These bands are little affected in metal complexes. The spectrum of [Ni(H-sptsc)$_2$] in dioxane displays a medium band at 430 nm attributed to ligand field transition $^1A_{1g} \rightarrow {}^1B_{1g}$ in square planar field[15]. But the solid reflectance spectrum of this complex is quite different from that of solution spectrum and shows three weak bands at 410, 630 and 840 nm assigned to $^3A_{2g} \rightarrow {}^3T_{1g}$ (P), $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) and $^3A_{2g} \rightarrow {}^3T_{2g}$ transitions similar to octahedral complexes[16]. The absence of these bands in solution with respect to solid reflectance bands and appreance of a band at 430 nm may be due to transformation of octahedral complex into square planar species in solution. The diamagnetism of [Ni(H-sptsc)$_2$] in pyridine solution also supports the conversion of octahedral form to square planar species in solution[17]. The absorption spectra of [Ni(sptsc)B] (B = H_2O or py) in dioxane or pyridine show ligand field band at 410–420 nm attributed to ${}^1A_{1g} \rightarrow {}^1B_{1g}$ transition in square planar field[15]. In case of greenish yellow Cu(II) complex, $[Cu(H\text{-}sptsc)_2]$, a broad shoulder near 735 nm is observed which may be assigned to ${}^2E_g \rightarrow {}^2T_{2g}$ transition in distorted octahedral field[18]. The monoligated Cu(II) complex, [Cu(sptsc)] and its base adduct [Cu(sptsc)py] show ligand field bands at 630, 670 and 730 nm attributed to ${}^2B_{1g} \rightarrow {}^2A_{1g}$, ${}^2B_{1g} \rightarrow {}^2E_g$ and ${}^2B_{1g} \rightarrow {}^2B_{2g}$ transitions in square planar field[19]. Palladium(II) complexes show ligand field absorption at 410–425 nm attributed to ${}^1A_{1g} \rightarrow {}^1B_{1g}$ transition in planar field[20].

The IR spectrum of ligand shows a medium band at 3230 cm^{-1} assigned to NH stretch and a medium broad band at 3060 cm^{-1} to hydrogen bonded phenolic OH stretching vibration[21]. The absence of band in the region 2400–2600 cm^{-1} indicates that the ligand exists in thione form. In monoligated complexes both NH and OH stretch disappear indicating that ligand coordinates in dianionic form. The hydrated complexes M(sptsc) · H_2O show a broad band at about 3400 cm^{-1} attributed to νOH of water molecule. In addition these complexes show a medium band at about 840 cm^{-1} assigned to rocking mode of coordinated H_2O molecule[22]. In bisligated complexes only ν(OH) disappears and ν(NH) appears at 3225 ± 5 cm^{-1} indicating the deprotonation of phenolic (OH) only and mono anionic nature of lignad molecule in acidic medium.

A strong band observed at 1608 cm^{-1} in free ligand asigned to ν(C═N) mode shifts to lower frequency at 1590 ± 5 cm^{-1} in complexes and sometimes observed as very strong broad in hydrated complexes due to mixing of $\delta(H_2O)$ and ν(C═C) vibrations. The shifting of ν(C═N) to lower frequency[23] suggests coordination of azomethine nitrogen atom to metal ions. The free ligand displays four thioamide bands[24] at 1540, 1380, 1160 and 950 cm^{-1}. The shift of band positions and intensity change of bands indicate the bonding of the ligand molecule in complexes. The thioamide band IV (major contribution of ν(C═S) observed at 950 cm^{-1} disappears[25] in M(sptsc) · nH_2O and [M(sptsc)py] and a new band is observed at 700 ± 10 cm^{-1}. This indicates coordination of (C═S) sulphur atom by deprotonation in the thiol form. This band is not affected appreciably in bisligated Zn(II), Cd(II) or Pd(II) complexes $[M(H\text{-}sptsc)_2]$ indicating the non-coordination of thione sulphur atom and bidentate nature of ligand molecule. On the other hand, this band shifts to lower frequencies by 50–60 cm^{-1} in bisligated Cu(II) and Ni(II) complexes, $[M(H\text{-}sptsc)_2]$ suggesting the coordination of thione sulphur atom to the metal ions and tridentate nature of ligand molecule. In metal pyridine complexes, [M(sptsc)py], the bands due to (νC = C + νC ≐ N) vibrations couple with ligand vibration while pyridine ring breathing mode is observed at *ca.* 1090 cm^{-1} shows red shift. The additional bands observed at about 660 cm^{-1} and *ca.* 440 cm^{-1} in far IR spectra assigned to in-and out-of plane deformation vibrations of the pyridine ring are an indication of coordination[26] of pyridine to the metal ions.

In the far IR region the complexes display two to three bands in the region 500–450, 400–350 and 340–300 cm^{-1} assignable to (M—O) (M—N) and (M—S) stretching vibrations[24], respectively. The complexes, $[M(H\text{-}sptsc)_2]$ ($M = Zn^{2+}$,

Pd^{2+} or Cd^{2+}) do not display distinct band in the region 350–300 cm^{-1} indicating the absence of sulphur coordination in these complexes.

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