Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsrt19

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Version of record first published: 21 Aug 2006.

To cite this article: M. E. Khalifa, T. H. Rakha & M. M. Bekheit (1996): Ligational Behaviour of 1-Picolinoyl-4-phenyl-3-thiosemicarbazide (H_2PTS) Towards Some Transition Metal Ions, Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry, 26:7, 1149-1161

To link to this article: http://dx.doi.org/10.1080/00945719608004358

SYNTH. REACT. INORG. MET.-ORG. CHEM., 26(7), 1149–1161 (1996)

LIGATIONAL BEHAVIOUR OF 1-PICOLINOYL-4-PHENYL-3-THIOSEMICARBAZIDE (H_2PTS) TOWARDS SOME TRANSITION METAL IONS

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ABSTRACT

Complexes of 1-picolinoly-4-phenyl-3-thiosemicarbazide (H_2PTS) with Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II) and UO_2(VI) have been synthesized and characterized on the basis of elemental analyses, molar conductivities, magnetic moment and spectral (IR and visible) studies. IR spectral data show that H_2PTS behaves in a monoanionic bidentate or tetradentate and bianionic tetradentate manner. All complexes are non-electrolytes. An octahedral structure is proposed for the Cr(III), Mn(II), Fe(III), Co(II) and Ni(II) complexes, while a square-planar one is suggested for Cu(HPTS)Cl.H_2O and Cu(PTS) according to the data of magnetic and electronic spectral measurements.

INTRODUCTION

Metal complexes of thiosemicarbazides are of current interest due to their biological activity against smallpox, viral diseases and certain types of tumour[1,2]. Extensive investigations have been made on transition metal complexes of aromatic and aliphatic thiosemicarbazides[3-13]. Studies on metal complexes of (1-isonicotinoyl or 1-nicotinoyl)-4-phenyl-3-thiosemicarbazide have been reported[14,15]. As an extension of our previous work and in order to understand fully the diverse coordinating properties and reactivity of this important class of ligands, we now report the synthesis and structural studies of transition metal complexes formed by the interaction between metal chlorides or acetates and 1-picolinoyl-4-phenyl-3-thiosemicarbazide (Fig. 1)

EXPERIMENTAL

Reagents

All chemicals used are of BDH quality (British Drug, LTD, England).

Synthesis of the Ligand

1-Picolinoyl-4-phenyl-3-thiosemicarbazide (H_2PTS) was prepared by refluxing phenylisothiocyanate (13.6 mL, 0.1 mole) and picolinic acid hydrazide (13.7 mL, 0.1 mole) in absolute ethanol (60 mL) for 30 min. On cooling, yellow crystals were separated. The product was filtered off, washed, recrystallized from absolute ethanol and finally dried in a vacuum desiccator over anhydrous $CaCl_2$; yield 22 g (80%), m.p., 182°C.

Synthesis of Metal Chelates

The complexes $M(PTS).nH_2O$ (M = Cu(II), Zn(II) or Ni(II); n = 0 or 2) and $Co(HPTS)(AcO).2H_2O$ were prepared by adding a solution of (0.272 g, 1 mmole) of H_2PTS in 50 mL absolute ethanol to solution of 1 mmole of metal acetate in 25 mL bidistilled water. The mixture was heated under reflux for 0.5 hr. The $UO_2(PTS).2H_2O$ complex was prepared by the same method using uranyl acetate in absolute ethanol. The $Cd(HPTS)_2$ complex was prepared using 1 mmole of the cadmium acetate and 2 mmole of H_2PTS.

The complexes $M(HPTS)Cl.H_2O$ (M = Mn(II), Co(II), Cu(II), Zn(II) or Cd(II)) and $M(HPTS)Cl_2.nH_2O$ (M = Fe(III) or Cr(III); n = 0 or 2) were synthesized by mixing a solution of (0.272 g, 1 mmole) of H_2PTS in 50 mL absolute ethanol and a solution of 1 mmole of the metal chloride in 25 mL absolute ethanol. The mixture was heated under reflux for 0.5 hr. The $M(PTS).nH_2O$ complexes (M = Hg(II) or Mn(II); n = 0 or 2) were prepared by the same method in the presence of (0.82 g, 10 mmole) sodium acetate as a buffering agent. The products were filtered off,

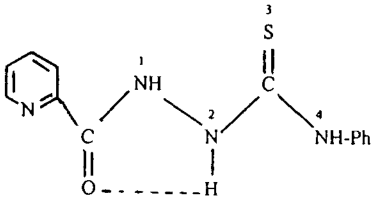


Fig. 1. Structure of the Ligand (H_2PTS)

washed several times with absolute ethanol followed by diethyl ether and finally dried in a vacuum desiccator over anhydrous $CaCl_2$.

Physical Measurements

The metal and chloride contents were analysed by standard methods[16]. Carbon and hydrogen were determined by the Microanalytical Unit of Mansoura University. Magnetic moments at 25°C were determined using a Gouy balance and $Hg[Co(SCN)_4]$ as a calibrant. Electronic spectra in DMSO were recorded on a Perkin-Elmer 3B spectrophotometer. IR spectra were obtained using a Perkin-Elmer 1430 spectrophotometer as Nujol mulls between CsI plates. Molar conductivities in DMSO at 25°C were measured using a Tacussel conductivity bridge type CD6NG.

RESULTS AND DISCUSSION

The physical data of the complexes together with the elemental analyses and conductivities are listed in Table I.

The formation of the complexes may be represented by the following equations:

$$M(AcO)_2 + H_2PTS \xrightarrow[\text{reflux 0.5 hr}]{\text{Aqueous ethanol}} M(PTS).nH_2O + 2AcOH \qquad (1)$$

[M = Cu(II), Zn(II) or Ni(II); n = 0 or 2]

$$Co(HPTS)(AcO).2H_2O + AcOH$$

$$UO_2(AcO)_2 + H_2PTS \xrightarrow[\text{reflux 0.5 hr}]{\text{Absolute ethanol}} UO_2(PTS).2H_2O + 2\,AcOH \qquad (2)$$

$$Cd(AcO)_2 + 2H_2PTS \xrightarrow[\text{reflux 0.5 hr}]{\text{Aqueous ethanol}} Cd(HPTS)_2 + 2\,AcOH \qquad (3)$$

Table I. Analytical and Physical Data of H_2PTS and its Metal Complexes

Compound	Empirical formula (Formula weight)	Colour	M.P.*, °C	Yield ,% weight, g	% Calc. (Found)				A^{*}_{m} in DMSO ($ohm^{-1}cm^{2}$ mol^{-1})	μ_{eff} (BM)
					C	H	M	Cl		
H_2PTS	$H_{12}C_{13}N_4OS$ (272.331)	yellow	182	80(22.0)	57.3(57.5)	4.4(4.5)	-			
$Cr(HPTS)Cl_2.2H_2O$	$CrH_{15}C_{13}N_4O_3SCl_2$ (430.255)	brown	>300	50(0.22)	36.3(36.4)	3.5(3.6)	12.1(12.3)	16.5(16.7)	24	3.53
$Mn(HPTS)Cl.H_2O$	$MnH_{13}C_{13}N_4O_2SCl$ (379.729)	yellow	>300	45(0.18)	41.1(41.0)	3.5(3.4)	14.5(14.8)	9.3(9.6)	23	5.8
$Fe(HPTS)Cl_2$	$FeH_{11}C_{13}N_4OSCl_2$ (398.073)	black	>300	55(0.24)	39.2(39.1)	2.8(2.8)	14.0(14.2)	17.8(17.9)	28	6.1
$Co(HPTS)Cl.H_2O$	$CoH_{13}C_{13}N_4O_2SCl$ (383.719)	green	>300	50(0.20)	40.7(40.6)	3.4(3.5)	15.4(15.4)	9.2(9.0)	25	4.4
$Cu(HPTS)Cl.H_2O$	$CuH_{13}C_{13}N_4O_2SCl$ (388.329)	green	290	60(0.24)	40.2(40.1)	3.4(3.3)	16.4(16.1)	9.1(9.3)	24	1.66
$Zn(HPTS)Cl.H_2O$	$ZnH_{13}C_{13}N_4O_2SCl$ (390.159)	yellow	>300	55(0.23)	40.0(40.2)	3.4(3.3)	16.8(16.5)	9.1(9.3)	18	-
$Cd(HPTS)Cl.H_2O$	$CdH_{13}C_{13}N_4O_2SCl$ (437.189)	yellow	>300	60(0.27)	35.7(35.5)	3.0(2.9)	25.7(25.8)	8.1(8.2)	16	-
$Mn(PTS).2H_2O$	$MnH_{14}C_{13}N_4O_3S$ (361.287)	brown	>300	70(0.28)	43.2(43.1)	3.9(3.8)	15.2(15.3)	-	7	5.6
$Ni(PTS).2H_2O$	$NiH_{14}C_{13}N_4O_3S$ (365.057)	brown	>300	80(0.36)	42.8(42.6)	3.9(3.9)	16.1(16.4)	-	5	2.4
$Cu(PTS)$	$CuH_{10}C_{13}N_4OS$ (333.855)	green	>300	90(0.41)	46.8(46.7)	3.0(3.2)	19.0(19.1)	-	7	1.5
$Zn(PTS)$	$ZnH_{10}C_{13}N_4OS$ (335.685)	yellow	>300	85(0.39)	46.5(46.3)	3.0(3.1)	19.5(19.8)	-	4	-
$Hg(PTS)$	$HgH_{10}C_{13}N_4OS$ (470.905)	yellow	272	80(0.44)	33.2(33.1)	2.1(2.0)	42.6(42.3)	-	-	-
$UO_2(PTS)2H_2O$	$UH_{14}C_{13}N_4O_5S$ (576.377)	brown	280	85(0.56)	27.1(27.0)	2.5(2.3)	41.3(40.7)	-	3	-
$Co(HPTS)(AcO).2H_2O$	$CoH_{18}C_{15}N_4O_5S$ (425.331)	brown	>300	70(0.32)	42.4(42.1)	4.3(4.2)	13.9(13.8)	-	5	4.5
$Cd(HPTS)_2$	$CdH_{22}C_{26}N_8O_2S_2$ (655.046)	yellow	>300	65(0.50)	47.7(47.7)	3.4(3.2)	17.2(17.5)	-	3	-

* > 300 °C Decomposition

$$MCl_2 + H_2PTS \xrightarrow[\text{reflux 0.5 hr}]{\text{Absolute ethanol}} M(HPTS)Cl.H_2O \quad + HCl \qquad (4)$$

[M = Mn(II), Co(II), Cu(II), Zn(II) or Cd(II)]

$$MCl_3 + H_2PTS \xrightarrow[\text{reflux 0.5 hr}]{\text{Absolute ethanol}} M(HPTS)Cl_2.nH_2O + HCl \qquad (5)$$

[M = Fe(III) or Cr(III); n = 0 or 2)

$$MCl_2 + H_2PTS \xrightarrow[CH_3COONa + H_2O \atop \text{reflux 0.5 hr}]{\text{Absolute ethanol}} M(PTS).nH_2O \quad + 2HCl \qquad (6)$$

[M = Hg(II) or Mn(II); n = 0 or 2)

All the metal complexes are stable in air and insoluble in common organic solvents but soluble in dimethylformamide (DMF) and dimethylsulphoxide (DMSO). The molar conductivities in DMSO at 25°C (Table I) indicate a non-electrolytic nature for the complexes[17]. The high values of the molar conductivities for some complexes suggest partial dissociation in DMSO.

Infrared Spectra

The most important IR assignments in the spectrum of the free ligand as well as the bonding sites have been determined by a careful comparison of both the ligand and its metal complexes (Table II) and by considering our previous work[3-13]. The IR spectrum (Nujol mull) of 1-picolinoyl-4-phenyl-3-thiosemicarbazide (H_2PTS) shows bands in the 3100-3310 cm^{-1} region assigned to the stretching vibration of NH groups. The strong band at 1658 cm^{-1} is attributed to the $\nu(C=O)$ vibration. The medium intensity band at 995 cm^{-1} is assigned to the $\nu(N-N)$ vibration. The two bands at 705 and 1240 cm^{-1} are assigned to $\nu(C=S)$ and a combination of $\nu(C=S)$ and $\nu(CN)$, respectively. No bands exist above 3500 cm^{-1} or in the 2500-2600 cm^{-1} region which would be due to $\nu(OH)$ and $\nu(SH)$[18] vibrations, respectively. The absence of these bands indicates the presence of H_2PTS in the thione form. Two weak broad bands at ca. 2200 and ca. 1950 cm^{-1} are assigned to the stretching and bending vibrations of (N-H...O). This may suggest the presence of intramolecular hydrogen bonding[19], as shown in Fig. 1.

The IR spectra of the complexes $Cr(HPTS)Cl_2.2H_2O$, $Co(HPTS)(AcO).2H_2O$ and $Cd(HPTS)_2$ show that H_2PTS behaves as a mononegative bidentate ligand coordinating via the NH group and the

Table II. Infrared Spctra of H_2PTS and its Metal Complexs

Compound	ν(C=0)	ν(CS+ν(CN) & ν(C=S)		ν(S-C=N)	ν(O-C=N)	ν(N-N)	ν(C-S)	ν(C-O)
H_2PTS	1658	1240	705	-	-	995	-	-
$Cr(HPTS)Cl_2.2H_2O$	-	1230	715	-	1580	1005	-	1190
$Mn(HPTS)Cl.H_2O$	1635	-	-	1615	-	1020	630	-
$Fe(HPTS)Cl_2$	1635	-	-	1615	-	1020	630	-
$Co(HPTS)Cl.H_2O$	1635	-	-	1610	-	1020	630	-
$Cu(HPTS)Cl.H_2O$	1652	-	-	1615	-	1020	645	-
$Zn(HPTS)Cl.H_2O$	1640	-	-	1615	-	1020	630	-
$Cd(HPTS)Cl.H_2O$	1645	-	-	1610	-	1015	625	-
$Mn(PTS).2H_2O$	-	-	-	1625	1600	1015	635	1180
$Ni(PTS).2H_2O$	-	-	-	1615	1590	1015	635	1175
$Cu(PTS)$	-	-	-	1620	1590	1020	645	1180
$Zn(PTS)$	-	-	-	1615	1590	1015	635	1180
$Hg(PTS)$	-	-	-	1620	1595	1005	650	1180
$UO_2(PTS).2H_2O$	-	-	-	1625	1575	1005	640	1170
$Co(HPTS)(AcO).2H_2O$	-	1230	710	-	1590	1015	-	1195
$Cd(HPTS)_2$	-	1225	715	-	1585	1015	-	1180

enolic carbonyl oxygen (=C-OH) with the displacement of the hydrogen atom from the latter group, forming a five-membered ring including the metal atom. This mode of chelation (Fig. 2) is supported by the following evidence: (i) the disappearance of ν(C=O) with the appearance of new bands in the 1580 - 1590 cm^{-1} and 1180 - 1195 cm^{-1} regions assigned to ν(O-C=N)[20] and ν(C-O)[21], respectively; (ii) ν(N-N) shifts to a higher wave number; (iii) the appearance of new bands in the regions 500-480 and 450-440 cm^{-1} and at 280 cm^{-1} assigned to ν(M-O)[22], ν(M-N)[23] and ν(Cr-Cl)[24], respectively. The Co(HPTS)(AcO).2H_2O complex shows two bands at 1535 and 1415 cm^{-1} assignable to $\nu(\text{C-O})_{as}$ and $\nu(\text{C-O})_{s}$ bands of the acetate group. The difference (120 cm^{-1}) between these two bands indicates a bridging or bidentate bonding for the acetate group[25].

Also, H_2PTS acts as a mononegative bidentate ligand in Cu(HPTS)Cl.H_2O, coordinating via the $\overset{1}{\mathrm{N}}$H group and the thiol sulphur atom with loss of the proton from the latter group. This mode of complexation (Fig. 3) is confirmed by the following: (i) the disappearance of ν(C=S) with the appearance of new bands due to ν(S-C=N)[20] and ν(C-S)[26] ; (ii) ν(C=O) remains more or less at the same position ; (iii) the appearance of new bands at 415, 345 and 295 cm^{-1} assignable to ν(Cu-N)[23], ν(Cu-S)[27] and ν(Cu-Cl)[24], respectively.

In M(PTS).nH_2O [M = Cu(II), Zn(II), Hg(II), Mn(II), Ni(II) and UO_2^{2+}; n = 0 or 2], H_2PTS behaves as a binegative tetradentate ligand, coordinating through the enolic carbonyl oxygen and the nitrogen of the $\overset{2}{\mathrm{N}}$H group from one end, and the thiol sulphur atom and the nitrogen atom of the $\overset{1}{\mathrm{N}}$H group from the other, with the loss of both protons from the enolized carbonyl and thiol groups. Geometrical factors prevent the coordination of all the donors to a single metal ion, which must, therefore, act as a bridging unit between two metal centres, giving a polymeric structure as shown in Fig. 4. This mode of complexation is suggested by the following evidence: (i) the disappearance of the ν(C=O) and ν(C=S) bands ; (ii) the appearance of new bands due to ν(O-C=N) and ν(S-C=N)[20], ν(C-O)[21] and ν(C-S)[26] and (iii) the appearance of new bands in the regions 495-460, 450-410 and 340-310 cm^{-1} assignable to ν(M-O)[22], ν(M-N)[23] and ν(M-S)[27], respectively.

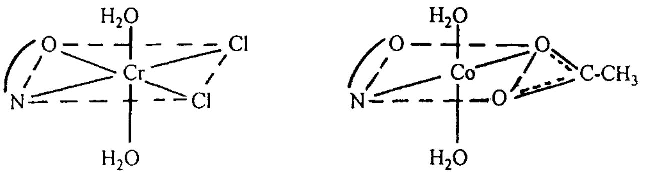


Fig. 2. Structures of the Complexes Cr(HPTS)Cl_2.$2H_2O$ and Co(HPTS)(AcO).$2H_2O$

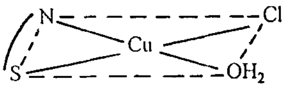
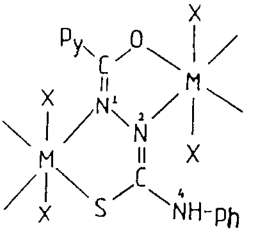


Fig. 3. Structure of the Cu(HPTS)Cl.H_2O Complex



M = Cu(II), Zn(II), Hg(II); X = 0) or
M = Mn(II), Ni(II) and UO_2^{2+}; X = H_2O

Fig. 4. Structure of the Complexes M(PTS).nH_2O

Finally, H_2PTS can also act as mononegative tetradentate ligand coordinating through the carbonyl oxygen and the nitrogen atom of the ^{2}NH group from one end and the thiol sulphur atom and the nitrogen atom of the ^{1}NH group on the other, with loss of the proton from the thiol group as shown in Fig. 5. This behaviour is found in the case of the complexes M(HPTS)Cl.H_2O [M = Mn(II), Co(II), Zn(II) and Cd(II)] and Fe(HPTS)Cl_2. This mode of complexation is supported by the following observations: (i) ν(C=O) shifts to lower wave number; (ii) the

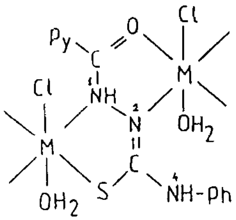


Fig. 5. Structure of the Complexes M(HPTS)Cl.H_2O

disappearance of ν(C=S) with the appearance of new bands due to ν(S-C=N)[20] and ν(C-S)[26] and (iii) the appearance of new bands in the regions 515-485, 430-405, 350-335 and 290-260 cm^{-1}, assignable to ν(M-O)[22], ν(M-N)[23], ν(M-S)[27] and ν(M-Cl)[24], respectively.

The uranyl complex exhibits three bands at 920, 830 and 250 cm^{-1} assigned to ν_3, ν_1 and ν_4 vibrations, respectively, of the dioxouranium ion[28]. The force constant (F) of ν(U=O) is calculated by the method of McGlynn et al.[29], the F_{UO} value is 6.99 mdyne $Å^{-1}$. The U-O bond distance is calculated with the help of the equation[30]:

$$R_{U\text{-}O} = 1.08\, F^{-1/3} + 1.17$$

The U-O bond distance is 1.735 Å and falls in the usual region as reported earlier[31].

All the hydrated complexes are thermally stable up to ca. 150°C which may indicate the presence of water molecule(s) in the inner sphere.

Magnetic and Electronic Spectral Studies

The electronic spectrum of Cr(HPTS)Cl_2.$2H_2O$ exhibits two strong absorption bands at 21277 (ν_1) and 26316 cm^{-1} (ν_2) attributable to $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1) and $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ (ν_2) transitions[32], respectively, in an octahedral environment around the Cr(III) ion. The magnetic moment (3.53 BM) can be taken as additional evidence for the octahedral configuration.

The electronic spectrum of $Fe(HPTS)Cl_2$ shows two bands at 21740 and 29410 cm^{-1} assignable to $^6A_{1g} \rightarrow {}^4T_{2g}(G)$ and $^6A_{1g} \rightarrow {}^4T_{2g}(D)$ transitions[33], respectively. The magnetic moment value (6.1 BM) for this complex indicates that it is of the spin-free octahedral type.

The μ_{eff} values (5.6-5.8 BM) for the manganese(II) compounds are as expected for high-spin $3d^5$ systems. The electronic spectrum of $Mn(HPTS)Cl.H_2O$ displays very weak absorption bands and it is difficult to assign them to definite transitions[34]. The electronic spectrum of $Mn(PTS).2H_2O$ shows one broad band at 14706 cm^{-1} attributable to the $^6A_{1g} \rightarrow {}^4T_{1g}(G)$ transition[34] for an octahedral structure around Mn(II) ion. The other characteristic bands for d-d transitions are difficult to be recognized in this complex.

In the spectra of the Co(II) complexes, the two broad bands at <u>ca</u>. 15400 and <u>ca</u>. 22200 cm^{-1} are assigned to $^4T_{1g} \rightarrow {}^4A_{2g}$ and $^4T_{1g} \rightarrow {}^4T_{1g}(P)$ transitions[33], respectively. Also, the values of the magnetic moment (4.4-4.5 BM) are in good agreement with those reported for an octahedral structure.

The electronic spectrum of $Ni(PTS).2H_2O$ shows two bands at 16130 and 22220 cm^{-1} assignable to $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transitions[33], respectively. Also, the value of μ_{eff} (2.4 BM) is additional evidence for an octahedral structure.

The electronic spectra of the Cu(II) complexes give one broad band with a maximum in the 14290-15150 cm^{-1} range due to the $^2B_{1g} \rightarrow {}^2A_{1g}$ transition in a square-planar geometry[35]. The band at 27020 cm^{-1} in the electronic spectrum of $Cu(HPTS)Cl.H_2O$ may be assigned to Cl→Cu charge transfer[36]. Also, the values of μ_{eff} (1.50-1.66 BM) lie within the range of Cu(II) ions.

Finally, the UV spectrum of the uranyl complex shows a band at 26670 cm^{-1} assigned to the $^1\Sigma_g^+ \rightarrow {}^2\pi_u$ transition for dioxouranium (VI)[37].

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Received: 16 October 1995
Accepted: 27 March 1996
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