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Complexes of Phenyl- and *p*-Chloro-Phenylthiopyruvic Acids with Some Bivalent Metals. Part I

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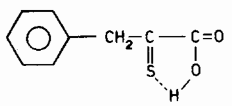
Neutral bischelates of bivalent nickel(II), cobalt(II), copper(II) and palladium(II) with phenylthiopyruvic acid (PTAH) and p*-chlorophenylthiopyruvic acid (*p*-ClPTAH) of the formula ML_2nH_2O (where L = PTA and* p*-ClPTA; M = Co and Ni, n = 2; M = Cu, n = 1; M = Pd, n = 0) are described. The i.r., U.V. and magnetic susceptibilities of complexes are reported. The magnetic moment values of Ni(II), Cu(II) complexes are normal but those of Co(II) complexes are anomalous. The i.r. spectra indicate the coordination of ligands through thione sulphur and one of the carboxylate oxygens by deprotonation of OH.*

Introduction

The coordination complexes of oxygen and sulphur donor ligands have received considerable interest due to their various physiological properties. The formation and structure of complexes of thioglycolic acid, thiodiglycolic acids and related ligands have been investigated [1–10]. Except for a preliminary communication by us [11] nothing is known about the complexing behaviour of phenylthiopyruvic acid (PTAH) and substituted phenylthiopyruvic acids.



(PTAH)

In the present communication we are reporting the complexes of PTAH and *p*-ClPTAH with bivalent nickel, cobalt, copper and palladium.

Experimental

Phenylthiopyruvic and *p*-chlorophenylthiopyruvic acid were prepared by the cleavage of benzylidinerhodanine and *p*-chlorobenzylidinerhodanine by 8% sodium hydroxide solution [12, 13].

Preparation of Metal Complexes

An aqueous ethanolic solution of metal chloride or acetate (0.06 mol in 30 ml 50% ethanol) was added slowly to an ethanolic solution of the ligand (0.1 mol), when a deep brown or orange coloured solution resulted. From the resulting solution the complex was separated by diluting it by adding a large volume of water. In the case of Pd(II), a reddish brown complex separated immediately when 1% aqueous solution of Pd(II) chloride was treated with an ethanolic solution of ligand (less than 1:2 molar proportion). The precipitates were digested on a steam bath, filtered, washed thoroughly with water and dried over $CaCl_2$ in a desiccator.

Magnetic susceptibility, electrical conductance and U.V. absorption or reflectance spectra of the complexes were determined as reported earlier [14]. The i.r. spectra of the complexes were recorded in the range 4000–200 cm^{-1} in KBr disc as Nujol mull on a 621 Perkin Elmer I.R. Spectrophotometer at B.H.U. Banaras.

Results and Discussion

From the analytical results of the complexes (Table I) it is found that Ni(II), Co(II), Cu(II) and Pd(II) form stable bischelate complexes of the general formula $M(PTA/p\text{-}ClPTA)_2 \cdot nH_2O$ (M = Co and Ni, n = 2; M = Cu, n = 1; M = Pd, n = 0). The complexes are almost insoluble in water but fairly soluble in methanol, ethanol, DMF *etc.* The DMF solutions of the complexes were found to be non conducting, indicating them to be non-ionic.

The hydrated complexes do not lose water molecules below 90 °C but above 100 °C they gradually do so and become anhydrous above 150–60 °C and complexes are converted into brownish-black tarry masses, which indicates that water molecules are either coordinated or strongly held up in crystal lattices. Except for Pd(II) complexes, which are diamagnetic, the others are paramagnetic and their magnetic moment values are given in Table I. The magnetic moment values of Ni(II) complexes are found to be 2.90–2.95 B.M. at room temperature, which are similar to those of reported spin free octahedral Ni(II) complexes [15, 16]. The Cu(II) complexes exhibit magnetic moment values of 2.14

TABLE I. Analytical Results, Magnetic Moment at 304 °K and Molar Electrical Conductance Value of DMF Solution of Complexes at 30 °C.[a]

Compound	Colour	μ_{eff} (B.M.)		% C	% H	% S	% M	λ_m Ohm^{-1} cm^2
[$Co(PTA)_2(H_2O)_2$]	Dark Brown	3.51	Found:	47.72	3.17	14.18	13.06	7
			Reqd.:	47.68	3.11	14.11	13.00	
[$Co(p\text{-}ClPTA)_2(H_2O)_2$]	Dark Brown	3.20	Found:	41.46	3.01	12.35	11.25	3
			Reqd.:	41.32	3.10	12.26	11.28	
[$Ni(PTA)_2(H_2O)_2$]	Dark Grey	2.90	Found:	47.27	4.55	14.20	12.99	4
			Reqd.:	47.71	4.45	14.12	12.95	
[$Ni(p\text{-}ClPTA)_2(H_2O)_2$]	Grey	2.95	Found:	47.63	3.61	14.08	12.99	3
			Reqd.:	47.71	3.56	14.12	12.95	
[$Cu(PTA)_2$]H_2O	Dull Brown	2.14	Found:	49.36	3.25	14.65	14.46	5
			Reqd.:	49.15	3.17	14.55	14.38	
[$Cu(p\text{-}ClPTA)_2$]H_2O	Dull Brown	2.09	Found:	42.67	2.65	12.60	12.50	4
			Reqd.:	42.48	2.77	12.48	12.57	
[$Pd(PTA)_2$]	Reddish Brown	Dia.	Found:	46.40	3.07	13.71	22.98	–
			Reqd.:	46.48	3.03	13.76	22.94	
[$Pd(p\text{-}ClPTA)_2$]	Reddish Brown	Dia.	Found:	40.42	2.31	11.96	19.93	–
			Reqd.:	40.49	2.27	11.99	19.97	

[a]PTAH = Phenylthiopyruvic acid; *p*-ClPTAH = *p*-chlorophenylthiopyruvic acid.

B.M. for $Cu(PTA)_2H_2O$ and 2.09 B.M. for $Cu(p\text{-}ClPTA)_2H_2O$, which fall in the range of tetrahedral Cu(II) complexes [17, 18]. Cobalt(II) complexes exhibit anomalous magnetic moment values at room temperature (Table I) of *ca.* 3.51 B.M. for $Co(PTA)_2(H_2O)_2$ and 3.20 B.M. for $Co(p\text{-}ClPTA)_2(H_2O)_2$. Of various possible qualitative interpretations for the anomalous magnetic behaviour of Co(II) complexes, Stoufer *et al.* [19, 20] suggested that the only convincing explanation involves a model in which there is a distribution of magnetic ions among two or more low lying electronic levels which contribute different amounts of spin and orbital angular moment to the magnetic moment value. Stoufer *et al.* [20] have verified these hypotheses by calculating the paramagnetic susceptibilities as a function of temperature and measuring the actual susceptbility values of such complexes in the temperature range 100–400 K. In the present investigation, the authors could not measure magnetic susceptibility values at various temperatures due to lack of facility. However, from observed room temperature magnetic moment values of complexes which do not fall in the range of spin paired six coordinated octahedral and four coordinated planar Co(II) complexes, an octahedral environment in the vicinity of cross over point from low spin to high spin ground level is suggested.

The electronic absorption spectra of the complexes are of little significance for elucidation of structure in the present case. The complexes exhibit intense charge transfer absorptions near 400 nm, which probably obscure the weak d–d transition expected for octahedral Co(II) and Ni(II) complexes. Phenylthiopyruvic acid displays intense absorption bands at 220, 280 nm due to intraligand transition which shift to higher wavelength in the complexes by 5–15 nm. In case of *p*-chlorophenylthiopyruvic acid two intense intraligand transitions are observed at 230 and 315 nm, and these also suffer a blue shift by 5–45 nm which indicates the coordination of ligand molecule through metal atoms. However, the solid reflectance spectra of complexes exhibit weak and broad bands between 400 and 1000 nm. The position of bands and their tentative assignments are given in Table II. $Ni(PTA)_2(H_2O)_2$ displays two weak and broad bands at 570 and 825 nm arising from transitions $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$, and $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ respectively. The third broad absorption observed near 380 nm is assigned to a combination of ligand to metal charge transfer plus $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transition arising from octahedral envoronment of Ni(II) ions. Similarly $Ni(p\text{-}ClPTA)_2(H_2O)_2$ displays weak diffused reflectance bands characteristic of octahedral nickel(II) complexes [21]. From the 10Dq value of Ni(II) complexes it appears that the position of the ligand occurs in the strong end of spectrochemical series. The solid reflectance spectrum of $Co(PTA)_2(H_2O)_2$ also exhibits a very weak band at 480 and a shoulder near 550 nm attributed to $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ and $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ transitions in a octahedral field [22]. The solid reflectance spectrum of Cu(II) phenylthiopyruvate exhibits a very broad and

TABLE II. The Electronic and Absorption Spectra of Complexes.

Compound	Medium	Ligand Absorption (nm)	Charge Transfer (nm)	d–d Transition (nm)	Assignment
PTAH	Ethanol	220, 280	–	–	
p-ClPTAH	Ethanol	230, 315	–	–	
$[Cu(PTA)_2]H_2O$	Ethanol	255	345	–	
	Solid	–	400	650–720	
$[Cu(p\text{-}ClPTA)_2]H_2O$	Ethanol	225, 270	350	–	
	Solid	–	410	680–750	
$[Ni(PTA)_2(H_2O)_2]$	Ethanol	280	–	–	
	Solid	–	380	380	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$
				575	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$
				825	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$
$[Ni(p\text{-}ClPTA)_2(H_2O)_2]$	Ethanol	225, 228	370	–	
	Solid	–	400	400	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$
				570	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$
				880	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$
$[Co(PTA)_2(H_2O)_2]$	Ethanol	220, 265	–	–	
	Solid	–	410	480 sh	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
				550	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$
$[Co(p\text{-}ClPTA)_2(H_2O)_2]$	Solid	–	425	475	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
				570	$^4T_{1g(F)} \rightarrow {}^4A_{2g}(F)$
				650–750	Due to tetragonal species

TABLE III. I.R. Vibrations of Ligands and Their Metal Complexes.[a]

Compound	$\nu_{as}(COO)$	$\nu_s(COO)$	$\nu(C{=}S) + \nu(C–O)$	$\nu(C{=}S)$	$\nu(M–O)$	$\nu(M–S)$
PTAH	1650 s	1400 s	1250 m	875 s	–	–
$[Cu(PTA)_2]H_2O$	1677 s	1442 s	1204 m 1180 m	855 m	515 m	417 w
$[Ni(PTA)_2(H_2O)_2]$	1680 s	1484 s	1200 m 1175 m	850 w	465 w	338 w
$[Co(PTA)_2(H_2O)_2]$	1696 s	1442 s	1200 m 1180 m	850 m	511 m	408 m
p-ClPTAH	1652 s	1408 s	1250 m	875 s	–	–
$[Cu(p\text{-}ClPTAH)_2]H_2O$	1675 s	1483 s	1195 m 1175 m	822 sh	446 m	430 w, 383 w
$[Ni(p\text{-}ClPTA)_2(H_2O)_2]$	1675 s	1483 s	–	812 s	625 w	–
$[Co(p\text{-}ClPTA)_2(H_2O)_2]$	1672 s	1479 s	1175 m	812 s	612 w	426 m
$[Pd(p\text{-}ClPTA)_2]$	1683 s	1483 s	1196 w 1175 w	841 s	450 m	375 w

[a] s = strong; m = medium; w = weak; sh = sharp.

asymmetric band at 650–750 nm whose energy is less than that in octahedral and planar Cu(II) complexes. Thus, it appears that Cu(II) ions are surrounded by a tetrahedral or distorted tetrahedral arrangement of ligand molecules.

The important infrared bands of the ligands and their complexes in KBr disc are recorded in Table III. It is found that PTAH and *p*-ClPTAH exhibit strong and broad hydrogen bonded OH frequency near 2800–2550 cm^{-1}, which disappears in their metal complexes indicating the coordination of the ligand through carboxyl OH by deprotonation. The ν_{as}(COO) and ν_s(COO) of free PTAH observed at 1650 and 1400 cm^{-1} as strong bands shift to higher frequency by 30–50 cm^{-1} in their complexes. A detailed investigation of carboxylate complexes has shown similar results [24]. A strong and broad band observed at 1250 cm^{-1} in free ligand is attributed to a combination of ν(CO) and ν(C=S) vibrations. This band splits on coordination and shifts to lower frequency and is observed as a weak band near 1200 and 1180 cm^{-1}. A medium and broad ν(C=S) frequency observed at 875 cm^{-1} in the ligands shifts to lower frequencies in the complexes (Table III). It indicates that the thiocarbonyl sulphur is involved in coordination. The new bands observed in the spectra of metal complexes have been tentatively assigned to M–O and M–S bands (Table III). The range of metal sulphur vibration has been observed between 315–418 cm^{-1} in various complexes [25] as has been observed in the present investigation.

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References

1 C. Fernando and H. Freiser, *J. Am. Chem. Soc., 80,* 4928 (1958).
2 D. L. Leussing. R. E. Laramy and G. S. Alberts, *J. Chem. Soc., 82,* 4826 (1960).
3 J. Podlaha and S. Podlahova, *Inorg. Chim. Acta, 4,* 521 (1970).
4 J. Podlaha and J. Podlahova, *Inorg. Chim. Acta, 4,* 549 (1970).
5 S. E. Livingstone, R. A. Plowmann and J. Sorenson, *J. Proc. Roy. Soc. New South Wales, 84,* 28 (1950).
6 S. E. Livingstone and R. A. Plowmann, *J. Proc. Roy. Soc. New South Wales, 85,* 116 (1951).
7 D. Pettil Leslei and C. Sherington, *J. Chem. Soc. A, 12,* 3078 (1968).
8 M. B. Mishra, S. C. Sinha and H. L. Nigam, *Indian J. Chem., 5,* 649 (1967).
9 A. N. Kumar, H. L. Nigam and M. Katyal, *J. Pract. Chem., 33,* 107 (1966).
10 P. C. Shrivastava, K. B. Pandey and H. L. Nigam, *J. Inorg. Nucl. Chem., 35,* 3611 (1973).
11 E. B. Singh, J. O. Shrivastava, S. N. Chaubey and L. K. Mishra, *Proc. Indian Sc. Cong. Association* (1976).
12 P. N. Bhargava and M. P. Kulyadi, *Vigyan Parisad Anusandhan Patrika,* No. 1, 29–32 (1958).
13 N. Campbell and J. E. Mekail, *J. Chem. Soc.,* 1251 (1948).
14 S. P. Ghosh and L. K. Mishra, *Inorg. Chim. Acta, 7,* 545 (1973).
15 R. S. Nyholm and B. N. Figgis, *Prog. Inorg. Chem. (Ed. F. A. Cotton),* 6, p. 41 (1964).
16 W. Byers, A. B. P. Lever and R. V. Parish, *Inorg. Chem., 7,* 1835 (1968).
17 F. M. Ditri and Alexander I. Popov, *Inorg. Chem., 6,* 597 (1967).
18 M. Kato, H. B. Jonassen and J. C. Fanning, *Chem. Rev., 64,* 99 (1964).
19 R. C. Stoufer, D. W. Smith, E. A. Clevenger and T. E. Norris, *Inorg. Chem., 5,* 1169 (1966).
20 D. L. Williams, Darvin W. Smith and R. C. Stoufer, *Inorg. Chem., 6,* 590 (1967).
21 C. K. Jϕrgensen, *Acta Chem. Scand., 9,* 1362 (1955).
22 A. B. P. Lever and D. Ogden, *J. Chem. Soc. A,* 2041 (1967).
23 J. Ferguson and B. O. West, *J. Chem. Soc.,* 1569 (1966).
24 K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Complexes", Wiley, London, p. 197 (1963).
25 M. Akbar Ali, S. E. Livingstone and D. J. Phillips, *Inorg. Chim. Acta, 5,* 119 (1971).