$[Ph_4Sb]^+$ cation are equivalent and the cation has a tetrahedral geometry (T_d symmetry).

Another strong band at 370 cm^{-1} is observed in compound I; it could be due to ν_3 vibration indicating the presence of tetrahedral geometry[10,11] of the anion $[FeCl_4]^-$. The occurrence of a band of medium intensity at 360 cm^{-1} in the spectrum of the compound (II) suggests that a tetrahedral tetrachloroferrate ion $[FeCl_4]^-$, instead of the dinuclear anion $[Fe_2Cl_9]^{3-}$, is present in the compound (II). Magnetic moment data of these compounds also suggest that in both the compounds the anion is similar. This is further confirmed by Mössbauer spectral study of both the compounds.

In the Mössbauer spectra of the compounds, the isomeric shift (δ) was observed in the range of 0.40-0.42 mm/sec at room temperature with respect to stainless steel which suggested the presence of tetrahedral high-spin iron complexes[12]. In the case of $R[Fe(III)Cl_4]$, the isomer shift of 0.4 mm/sec corresponds to $3d^5 4s^{0.40}$ configuration suggesting a 4s electron population of 0.41 (as calculated from M. O. theory)[13]. The quadrupole splitting ($\triangle Eq$) values are 0.6 and 0.65 mm/sec. Normally there should not have been any quadrupole interactions[14]. But in compounds having large cations, some quadrupole interactions are observed due to distortion in cubic symmetry[15,16]. In the cases of cations having tertiary groups, the splitting is large while in other cases it is small and therefore the distortion is also small.

Therefore, compound (II) should be represented by the formula $[(Ph_4Sb)(FeCl_4)]_2.Ph_4SbCl$ instead of $[Ph_4Sb]_3[Fe_2Cl_9]$..

PMR spectra of compounds I and II in DMSO-d_6 show peaks in the range δ 7.38-7.90. These peaks are complex multiplets and can be attributed to the protons of phenyl rings of tetraphenyl stibonium cations.

In the IR spectrum of the adduct $2FeCl_3.Ph_3SbCl_2$, the bands due to νSb-C(Ph) and phenyl ring vibrations did not shift to lower frequency on the formation of the adduct, whereas a band observed at 280 cm^{-1} due to ν(SB-Cl) vibrations shifted to lower frequency region indicating that the adduct is formed through chlorine bridges. The presence of another band at 360 cm^{-1} in the adduct $2FeCl_3Ph_3SbCl_2$ could be assigned to (Fe-Cl) terminal vibrations[17].

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Coordination Polymers of Cobalt(II), Nickel(II), Copper(II), Zinc(II) & Cadmium(II) with 1-Isonicotinoyl-4-allyl-3-thiosemicarbazide

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Polymeric coordination complexes of the type $(ML.2H_2O)_n$ where M = Co(II), Ni(II), Cu(II), Zn(II) or Cd(II); L = 1-isonicotinoyl 4-allyl-3-thiosemicarbazide; and n = degree of polymerization have been synthesized and characterized through analytical, infrared and reflectance spectral, magnetic and ESR spectral (in the case of the Cu complex) studies. The powdery and coloured complexes are insoluble in water and in common organic solvents. Infrared spectra show that the tetradentate ligand coordinates through the enolic oxygen, thioenolic sulphur and the nitrogen of C = N groups. The metal ion is the bridging unit between the donor sites of the ligand, and the polymeric chain grows through consecutive ligand-metal linkages. Electronic, magnetic moment and ESR data suggest octahedral geometry for the complexes.

FOLLOWING the discovery that complexation of isonicotinic acid hydrazide with Cu^{2+} ion enhances its antitubercular activity[1], complexes of thiocarbazide or thiosemicarbazide have received much attention[2,3]. Aggarwal *et al.*[4] have prepared a number of transition metal complexes of 1,4-substituted thiosemicarbazides. Preparation and characterization of coordination polymers of Co(II) Ni(II), Cu(II), Zn(II) and Cd(II) with 1-isonicotinoyl -4-allyl-3-thiosemicarbazide (INATS) are being reported in the present note.

Isonicotinic acid hydrazide (INH, Fluka), allylisothiocyanate (Fluka), ethanol, N,N-dimethylformamide (Siscochem), and metal acetate hydrates (BDH) were used as such.

Preparation of ligand — 1-Isonicotinoyl-4-allyl-3-thiosemicarbazide (INATS) was synthesized by the condensation of allylisothiocyanate with INH. Allylisothiocyanate (0.1 mol) dissolved in 25 ml ethanol was added dropwise with constant stirring to a solution of INH (0.1 mol) in 25 ml ethanol. On refluxing the mixture, a white solid was obtained, which was filtered, washed withe thanol and dried *in vacuo* over calcium chloride.

INATS is insoluble in water, methanol, ethanol, benzene, chloroform, but soluble in boiling ethanol and in dimethylformamide. The purity of the compound was checked by determining the melting point (200-202°) which corresponds to literature value[5].

Preparation of the complexes — INATS (2.36g) dissolved in DMF (30 ml) was added to the metal salt solution [2.49g of $Co(CH_3COO)_2.4H_2O$, 2.49g of $Ni(CH_3COO)_2.4H_2O$, 2.00g of $Cu(CH_3COO)_2.H_2O$, 2.19g of $Zn(CH_3COO)_2.2H_2O$, or 2.66g of $Cd(CH_3COO)_2.2H_2O$, dissolved in minimum amount of water followed by the addition of excess DMF slowly with constant stirring and solution refluxed for 2 hr. A dark coloured mass separated which was filtered, washed with hot dimethylformamide and finally with diethyl ether and dried at 100°C.

The complexes are insoluble in water and in common organic solvents, their insolubility being due to their polymeric nature[6-8].

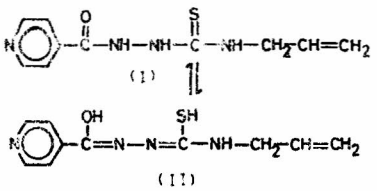
The metal contents were determined by titration against EDTA after decomposing the complexes with fuming nitric acid. C, H and N were estimated by usual microanalytical methods. Analytical data are shown in Table 1.

Infrared and electronic spectral measurements were made as described earlier[6-8]. Magnetic susceptibility measurements were done by Faraday's method at room temperature (298 K). In the case of the Cu(II) complex, magnetic measurements down to 85.8K were made using a liquid nitrogen cryostat, a temperature variation and control unit and EMCO Digital Microvoltmeter EE 214.

Derivatives of ESR spectrum were recorded using the powder form of the complex on a Varian V-4500-10 ESR spectrometer.

TABLE 1 — ANALYTICAL DATA OF THE COMPLEXES

Empirical formula	Colour	Found (calc.), %			
		Metal	C	H	N
INATS (H_2L)	White	—	51.25 (50.84)	5.78 (5.08)	23.10 (23.72)
$CoL.2H_2O$	Reddish-brown	17.80 (17.86)	36.25 (36.48)	4.05 (4.25)	16.94 (17.02)
$NiL.2H_2O$	Brown	17.80 (17.85)	36.43 (36.50)	4.17 (4.25)	17.10 (17.03)
$CuL.2H_2O$	Black	19.00 (19.05)	36.00 (36.97)	4.25 (4.19)	16.70 (16.78)
$ZnL.2H_2O$	Yellow	19.30 (19.49)	35.68 (35.78)	4.10 (4.17)	16.50 (16.69)
$CdL.2H_2O$	Yellow	29.27 (29.39)	31.24 (31.28)	3.50 (3.66)	14.62 (14.64)



The analytical data (Table 1) agree with general formula $ML.2H_2O$ (where M = metal ion, L = $C_{10}H_{10}N_4OS$).

The IR spectrum (band positions in cm^{-1}) of INATS shows a strong band at 3260 assigned to NH stretching. The thione and keto groups, both having protons adjacent to them, are relatively unstable in the monomeric form and usually tend to undergo enethiolization[9] and enolization. In the present case, however, strong bands at 1670, 1545, 1460, 1150 and 820 are observed due to $\nu C=O$ three bands due to $\nu N-C=S$[10] and $\delta N-C=S$ modes respectively. No bands due to S-H[10] and OH stretching modes are observed near 2570 and 3400 respectively. This indicates that in solid state the molecule remains in thione and keto form. However, in solution these forms are likely to be in equilibrium with the thiol and enol tautomeric forms (I and II). A comparision of the spectra of ligand and complexes shows that the above mentioned ligand bands are not present in the spectra of complexes; instead some new bands in the regions 1640-1655, 1560-1570, 1505-1520, 1360-1380 and 600-660 are observed which may be due to $\nu O-C = N$ and $\nu S-C=N$[11], $\nu N-C=N$ and $\nu C=N-N$[11,13], νCNH, $\nu C-O$ and $\nu C-S$ [10,16] respectively. The presence of these bands in the complexes shows that N^4H is not involved in enethiolization. The bands in the region 580-520, 485-450 and 315-310 are due to $\nu M-O$ $\nu M-N$[14,15] and $\nu M-S$ respectively.

All the compounds show bands in the reported ranges, 1605-1600, 1420-1410, 1000-980, and 1070-1080, due to 4-substituted pyridine[10] ring vibration; this indicates that nitrogen of the pyridine ring is not involved in complexation.

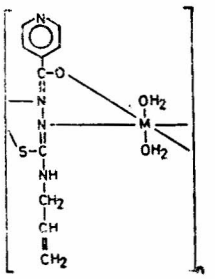
The presence of water within the coordination sphere is supported by the presence of bands in the region 3440-3400, 1640-1610 and 960-955 in the spectra of the complexes due to OH stretching, HOH deformation and H_2O rocking modes respectively.

Thus, INATS behaves as tetradentate, coordinating through the thiol sulphur atom and the nitrogen atom on one end and enolic oxygen atom and nitrogen atom on the other. Steric factors prevent the coordination of all the donors to a single metal ion, which therefore acts as bridging unit between the donor sites of the ligand, and thus the polymeric chain grows through consecutive INATS-metal linkages (III).

In the electronic spectrum of Co(II) complex, the ν_2 band cannot be seen clearly and has to be, calculated. The ν_2 transition is a two electron transition ($t_{2g}^5\ e_g^2 \longrightarrow t_{2g}^3\ e_g^4$), thus having a much lower oscillator strength than the other two bands.

TABLE 2 — ELECTRONIC SPECTRA, MAGNETIC MOMENT AND VARIOUS LIGAND FIELD PARAMETERS

Metal ion	Temp. (K)	μ_{eff} (B.M.)	Band (cm^{-1})	Assignment	$10Dq$ (cm^{-1})	ν_2/ν_1	B' (cm^{-1})	β	β(%)
			10417	$^4T_{1g}(F) \longrightarrow {}^4T_{2g}(F)$					
Co(II)	298	4.81	22197	$^4T_{1g}(F) \longrightarrow {}^4A_{2g}(F)$	11780	2.12	947	0.975	2.47
			23256	$^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$					
			10204	$^3A_{2g} \longrightarrow {}^3T_{2g}$					
Ni(II)	298	2.84	16394	$^3A_{2g} \longrightarrow {}^3T_{1g}(F)$	1 0204	1.6	916	0.860	14.00
			27778	$^3A_{2g} \longrightarrow {}^3T_{1g}(P)$					
			10000	$^2B_{1g} \longrightarrow {}^2A_{1g}$					
Cu(II)	298	2.01	10869	$^2B_{1g} \longrightarrow {}^2B_{2g}$		..	..	..	..
	199.2	1.90	11363	$^2B_{1g} \longrightarrow {}^2E_g$	...				
	151.8	1.89							
	101.5	1.85							
	87.7	1.99							
	85.8	1.97							



(III)

Due to its weakness and its proximity to the strong ν_3 and ν_2 transitions, it is obscured. In the case of Ni(II) complex[17], $10Dq$ (ν_1) is not high and thus the ligand produces a weak ligand field. The ligand field parameters and assignments (Table 2) are consistent with octahedral stereochemistry of Co(II) and Ni(II) ions. A broad envelope which can be resolved into three bands is seen in the case of Cu(II)[17] complex. The Jahn-Teller effect causes splitting of the $^2E_g \longrightarrow {}^2T_{2g}$ band. Distortion of D_{4h} symmetry removes the degeneracy of E_g, and further splitting of the E_g (B_{1g}, A_{1g}) and T_{2g} (B_{2g}, E_g) level occurs. Procter *et al.*[18] have suggested three possible energy level sequences due to increasing distortion. Since the separation in the present case is not large, the bands are assigned in terms of weakly distorted octahedral Cu(II) complexes. The magnetic moments of 4.81, 2.84 and 2.01 B.M. are observed for octahedral Co(II), Ni(II) and Cu(II) complexes respectively.

In the case of Cu(II) complex, the magnetic moment was found to be nearly temperature-independent showing that the individual copper(II) ions are well separated from each other and that no spin-spin interaction can occur[19].

The ESR spectrum of the Cu(II) complex consists of a single comparatively broad line at g values 2.11-2.24. It is found that $g_{\parallel} > g_{\perp}$. These features are in agreement with those observed by Lancaster and coworkers[20] for a Cu(II) complex and interpreted as pseudoisotropic arising from the exchange interaction between crystallographically non-equivalent Cu^{2+} ions and the weak hyperfine splitting. μ_{eff} values were also determined by substituting g, $g_{\parallel}$ and $g_{\perp}$ values obtained from ESR spectra for monomeric copper (II) complexes[21] in the following equation,

$$\mu_{eff}^2 = \frac{g_{\parallel}^2}{4} + \frac{g_{\perp}^2}{2} + \frac{3kT}{\lambda_0} (g-2)$$

The values obtained are consistent with those observed by magnetic susceptibility measurements.

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Organophosphonic Acids as Complexones : Part I — Complexes of 1-Hydroxyethylidenediphosphonic Acid with Manganese (II), Nickel (II), Copper(II), Zinc (II), Cadmium (II) & Lead (II)

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Complexes of Mn(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) with 1-hydroxyethylidenediphosphonic acid, having 2:1 stoichiometry, have been prepared in aqueous medium. Their IR and electronic spectral, and magnetic moment data are reported.

IN recent years, considerable interest has been shown in the study of 1-hydroxyethylidenediphosphonic acid (HEDP, H_4L) and its salts due to their use[1] in medicine, electroplating, etching solutions, prevention of scale formation and as detergents and disinfectants. Survey of literature shows that though work has been done on stability constants of various complexes of HEDP[2-4], little effort has been made to isolate and characterize the complexes[5-9]. In view of this, we have synthesized and characterized Mn(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) complexes of HEDP and results are reported here.

HEDP was obtained from M/s Aquapharm Chemical Co. and its purity ascertained by chemical analysis. Metal acetates (BDH, AR) were used as such.

Preparation of metal derivatives of HEDP — HEDP (0.01 mol) was dissolved in water and neutralised with NH_4OH. It was then added dropwise, with constant stirring, to an aqueous solution of the metal acetate (0.02 mol) when immediate precipitation occurred. The precipitates were filtered and washed with distilled water and then with acetone. The precipitates were dried in air and finally *in vacuo* to a constant weight.

IR spectra were run in nujol (600-4000 cm^{-1}) on a Beckman IR-20 spectrophotometer. Diffuse reflectance spectra were recorded in the region 200–1200 nm on a Unicam SP700 spectrophotometer fitted with a standard reflectance accessory. MgO was used as the reference. Magnetic measurements were made on a Guoy balance.

The analytical data (Table 1) show that the compounds are of the general formula $M_2L.xH_2O$. They are insoluble in water and common organic solvents which suggests that they are probably polymeric in nature.

TABLE 1 — ANALYTICAL AND MAGNETIC MOMENT DATA OF THE COMPLEXES

Compound	Colour	Found (Calc.), % M	Found (Calc.), % P	μ_{eff}(B.M.) at 308°K
$Mn_2L.2H_2O$	Pale-pink	30.5 (31.6)	18.7 (17.8)	3.72
$Ni_2L.6H_2O$	Light-green	26.06 (27.4)	14.25 (14.5)	2.46
$Cu_2L.4H_2O$	Light-blue	31.5 (31.6)	15.3 (15.4)	1.49
$Zn_2L.3H_2O$	White	32.0 (33.8)	15.5 (16.03)	—
Cd_2L	White	—	14.2 (14.4)	—
$Pb_2L.2H_2O$	White	—	9.01 (9.5)	—

TABLE 2 — PRINCIPAL BANDS (cm^{-1}) IN THE INFRARED SPECTRA OF HEDP AND ITS METAL DERIVATIVES

	δ COH	νP=O	νO-H
HEDP	1035	1170(br), 1204(br)	3500, 3300
Mn(II)	1050	1130	3280
Ni(II)	1060	1100	3200
Cu(II)	1060	1110	3200
Zn(II)	1090(br)	—	3300
Cd(II)	1050	1120	—
Pb(II)	1060	1080	3300

Infrared spectrum of solid HEDP (Table 2) is characterized by intense absorption in the range 1170-1204 cm^{-1} which is assigned to $\nu P=O$ mode of phosphoryl group. The splitting of this band is reported to be due to hydrogen bonding with the alcoholic group[10]. In the spectra of solid metal derivatives of HEDP, this band shifts to 1060–1100 cm^{-1} (Table 2) owing to displacement of π-electron density during coordination with the metal. Similar observations have been reported by earlier workers in the case of complexes with rare earth elements[11].

Free HEDP shows a medium intensity band at 1035 cm^{-1}, which is assigned to δ COH mode. In the spectra of chelates, this band is displaced to higher frequencies, probably due to coordination of the metal with alcoholic group without the loss of hydrogen. This coordination is also confirmed by the change in νOH, as has also been observed by earlier workers in the case of lanthanum compounds[11].

Manganese (II) hydroxyethylidenediphosphonate dihydrate ($Mn_2L.2H_2O$) — A distinction between tetrahedral and octahedral forms of Mn(II) can be made unambiguously only from a measurement of extinction coefficients. Since Mn(II) complex is insoluble in common organic solvents, extinction coefficients could not be calculated and hence specific assignment of stereochemistry is not possible in this case. The complex shows absorption bands at 43,480; 39,220; 30,300; 22,220 and 15,380 cm^{-1}.