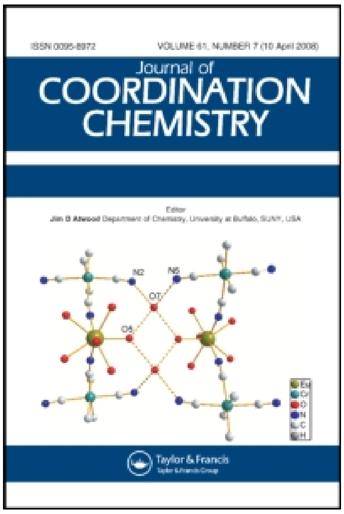

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THE SPECTRAL AND MAGNETIC PROPERTIES OF SOME CHLORO AND BROMO TRANSITION METAL COMPLEXES OF ISONICOTINIC ACID

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Complexes of isonicotinic acid have been prepared with the bromides and chlorides of cobalt(II), nickel(II) and copper(II) and also with the chlorides of manganese(II) and iron(II). These complexes have been characterized by analysis, vibrational and electronic spectra and magnetic moments. The compounds have octahedral polymeric structures.

INTRODUCTION

Isonicotinic acid is of biological origin, and can be produced by cell metabolism from isonicotinic acid hydrazide (isoniazid), a drug widely used in the treatment and prophylaxis of tuberculosis.[1] Isoniazid is, however, not without dangerous side effects, and an overdose can cause skin reaction, optic neuritis, convulsion, liver damage and psychotic reactions. Whether its chemical derivatives such as isonicotinic acid, or complexes of isoniazid itself, would have therapeutic effects without, or with lessened side effects, must await further research.

Several complexes of transition metals with isonicotinic acid have been previously prepared,[2–6] but only two compounds between a transition metal halide and this ligand have been reported in the literature.[5] This work describes the preparation, spectroscopic properties and magnetic measurements of some divalent metal halides with isonicotinic acid.

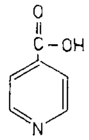

FIGURE 1 Isonicotinic acid (4-pyridine carboxylic acid).

EXPERIMENTAL

The manganese, cobalt, nickel and copper complexes were prepared by addition of a warm ethanolic solution of isonicotinic acid to a warm ethanolic solution of the metal halide in a 2 : 1 molar ratio. The precipitated complexes were washed with ethanol and ether and dried over calcium chloride.

A similar preparation was used for the iron compound with the exception that the preparation was carried out under dry nitrogen.

The complexes prepared by these methods are listed in Table I.

Magnetic susceptibility measurements were made by the Gouy method over the temperature range 300–100 K using a Newport variable temperature balance and as calibrant, $Hg[Co(SCN)_4]$. Each susceptibility value has been corrected for diamagnetism using Pascals constants.[7] The reciprocals of χ_m^{corr} plotted against the absolute temperature and the values of μ and θ in the Curie–Weiss equation, $\mu = 2.84[\chi_m^{corr}(T - \theta)]^{1/2}$ are obtained.[8] Electronic spectra were obtained on a Beckman ACTA MIV spectrophotometer. Infrared absorption spectra (KBr discs) were obtained with a Perkin–Elmer 257 Infrared Spectrophotometer. Far infrared spectra were obtained on a Beckman IR 720M interferometer using a polythene matrix to support the complexes.

RESULTS

The reaction of manganese(II) chloride with isonicotinic acid in ethanolic solution resulted in the formation of a complex of stoichiometry $Mn(INA)_2Cl_2$. No complex was formed when the reaction was repeated using manganese(II) bromide instead of manganese(II) chloride. The visible

TABLE I
Analysis of compounds and magnetic data

Compound	Colour	Metal (calculated)	Metal (found)	Halide (calculated)	Halide (found)	μ(BM)	θ
$Mn(INA)_2Cl_2$	Pale pink	14.77	14.72	19.06	19.01	6.39	20.10
$Fe(INA)_2Cl_2$	Red/brown	15.02	14.98	19.04	19.02	5.45	27.50
$Co(INA)_2Cl_2$	Lilac	15.67	15.62	18.85	18.80	5.53	16.80
$Co(INA)_2Br_2$	Blue	12.67	12.64	34.37	34.32	5.88	10.00
$Ni(INA)_2Cl_2$	Yellow/green	15.62	15.60	18.86	18.82	3.64	−26.00
$Ni(INA)_2Br_2$	Yellow	12.63	12.60	34.38	34.32	3.54	−11.40
$Cu(INA)_2Cl_2$	Blue/green	16.69	16.64	18.62	18.60	1.89	−3.45
$Cu(INA)_2Br_2$	Green	13.52	13.48	34.07	34.01	1.58	−15.90

TABLE II
Electronic spectra (cm^{-1})

Transition Element	Compound	d-d Transitions		
		$^6A_{1g} \to {}^4T_{1g}(G)$	$^6A_{1g} \to {}^4T_{2g}(G)$	$^6A_{1g} \to {}^4E_g(G), {}^4A_{1g}(G)$
Manganese	$Mn(INA)_2Cl_2$	16,660	20,840	23,260
			$^5T_{2g} \to {}^5Eg$	
Iron	$Fe(INA)_2Cl_2$		10,210	
		$^4T_{1g}(F) \to {}^4T_{2g}(F)$		$^4T_{1g}(F) \to {}^4A_{2g}(F)$
Cobalt	$Co(INA)_2Cl_2$	8,333		18,870
	$Co(INA)_2Br_2$	9,170		17,390
		$^3A_{2g}(F) \to {}^3T_{2g}(F)$	$^3A_{2g}(F) \to {}^3T_{1g}(F)$	$^3A_{2g}(F) \to {}^3T_{1g}(P)$
Nickel	$Ni(INA)_2Cl_2$	8,405	14,190	26,670
	$Ni(INA)_2Br_2$	8,212	13,700	26,540
			$^2Eg \to {}^2T_{2g}$	
Copper	$Cu(INA)_2Cl_2$		14,290	
	$Cu(INA)_2Br_2$		14,080	

reflectance spectra of bisisonicotinic acid manganese(II) chloride (Table II) would suggest that the compound has an octahedral structure.[9] The weak bands observed are assigned to the transitions $^6A_{1g} \to {}^4T_{1g}(G)$; $^6A_{1g} \to {}^4T_{2g}(G)$; $^6A_{1g} \to {}^4E_g(G)$, $^4A_{1g}(G)$. The magnetic moment for the compound is 6.39BM. This is greater than the spin only value (high spin d^5 configuration, $S = 5/2$) which is normally observed for manganese(II) compounds. It is suggested that the variation of the magnetic moment with temperature (Table I) is due to some antiferromagnetic interaction in the compound.[9] The compound obeys the Curie–Weiss law with a positive value for θ. The far infrared spectrum (Table III) also supports an octahedral configuration for this compound.[10]

The compound of stoichiometry $Fe(INA)_2Cl_2$ was formed between iron(II) chloride and isonicotinic acid in ethanolic solution. No complex was formed for iron(II) bromide. The preparation was carried out in a dry nitrogen atmosphere. The visible reflectance spectrum of bisisonicotinic acid iron(II) chloride exhibits a broad absorption band at 10210 cm^{-1} (Table II) which is assigned to the transition $^5T_{2g} \to {}^5E_g$. The compound has a magnetic moment (Table I) which agrees with an octahedral structure and obeys the Curie–Weiss law with a positive value of θ. The magnetic moment varies with temperature as expected for a T ground state term. This is due to the fact that the T term ground state is split by spin-orbit coupling to produce levels whose energy differences are of the order of the Boltzmann factor, kT.

TABLE III
Infrared spectra (4000 – 50 cm^{-1})

Compound	ν(O–H)	ν(C–O)	δ(O–H)	Ring Vibrations	ν(C=O)	ν(M–X)	ν(M–N)
INA	3360,3180	1410	1327	1595,1545	1620	–	–
$Mn(INA)_2Cl_2$	3215,3145	1415	1340	1560,1490	1590	238,144	400
$Fe(INA)_2Cl_2$	ca 2940	1415	1298	1610,1555	1690	250,185	390
$Co(INA)_2Cl_2$	ca 2940	1415	1295	1610,1555	1685	242,208	304
$Co(INA)_2Br_2$	ca 2940	1410	1296	1610,1568	1660	252	296
$Ni(INA)_2Cl_2$	ca 2940	1415	1300	1612,1560	1690	210,185	305
$Ni(INA)_2Br_2$	ca 2940	1414	1295	1612,1555	1690	205	304
$Cu(INA)_2Cl_2$	ca 2940	1415	1295	1615,1555	1685	233,197	298
$Cu(INA)_2Br_2$	ca 2940	1416	1295	1615,1555	1690	236,188	304

Temperature thus has a direct effect on the population of the levels. The far infrared spectra (Table III) would agree with an octahedral environment for this compound.[10]

The complexes of cobalt(II) have stoichiometry $Co(INA)_2X_2$ and have been previously reported along with their visible spectra in the literature.[5] The visible spectra are characteristic of cobalt(II) in an octahedral environment.[10] The observed transitions are $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$; $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$; $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$. In an octahedral field, the ground state, $^4T_{1g}$ is orbitally degenerate and this results in an orbital angular momentum contribution to the magnetic moment. This comes from the fact that the $^4T_1$ and $^4T_2$ states are split into four states one of which in each state has the same symmetry as the $^4A_2$ ground state. Thus these levels mix and there is a sharing of properties with the result that a certain amount of orbital angular momentum is introduced into the ground state and hence an orbital contribution to the magnetic moment. The magnetic moment then lies between the spin only value, $\mu = [4S(S+1)]^{1/2} = 3.88$BM and the spin-orbital value, $\mu = [4S(S+1) + L(L+1)]^{1/2} = 5.2$BM, the actual value of L depending on the strength of the crystal field. The values for the magnetic moments of the compounds (Table I) are higher than the experimental values which normally lie in the range of 4.7 – 5.2BM for the cobalt(II) ion in an octahedral environment. This suggests an orbital contribution which is greater than that normally observed for cobalt(II) in an octahedral environment. The presence of the T ground state term is shown by the variation of the magnetic moment with temperature over the temperature range of 300–100 K. The compounds show a satisfactory dependence on the Curie–Weiss law with positive values of θ. The far infrared spectra (Table III) also support an octahedral configuration for the compounds.[10]

The nickel(II) ion forms compounds of stoichiometry $Ni(INA)_2X_2$ with isonicotinic acid in ethanolic solution. The visible reflectance spectra of the compounds (Table II) resemble those normally found for nickel(II) in an octahedral environment.[10] The observed transitions are the spin allowed transitions $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$; $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$; $^3A_{2g}(F) \rightarrow {}^3T_{2g}(P)$. The prediction of an octahedral structure for these compounds is further supported by the fact that the compounds have temperature independent magnetic moments (Table I) in the range 2.8–3.2BM. However, the temperature dependence of the susceptibility would suggest anti-ferromagnetic interaction in these compounds. The compounds obey the Curie–Weiss law with negative values of θ. The far infrared spectra also support an octahedral configuration for these compounds.[10]

The complexes of copper(II) were quite stable and showed no tendency to undergo reduction to copper(I). The magnetic moments of the complexes (Table I) would suggest an octahedral or square planar environment for the copper(II). Thus the evidence for structional assignment is from spectral data. The compounds $Cu(INA)_2Cl_2$ and $Cu(INA)_2Br_2$ each show a broad absorption band at 14290 cm^{-1} and 14080 cm^{-1} respectively (Table II).

This suggests an octahedral environment for the copper atom since square planar copper(II) compounds show bands of near equal intensity at about 15000 cm^{-1} – 18000 cm^{-1}.[11-13]. The observed bands are assigned to the transition $^2E_g \rightarrow {}^2T_{2g}$. The broadness of the bands is due to Jahn-Teller distortion which results from an odd number of electrons in the E_g orbitals.[14] The magnetic moment for the $Cu(INA)_2Cl_2$ compound is close to the spin only value expected for copper(II) compounds while the magnetic moment of the $Cu(INA)_2Br_2$ compound is a great deal less than the spin only value. This indicates some copper–copper magnetic interaction in the bromide compound.[15] The compounds obey the

Curie–Weiss law with negative values of θ. The far infrared spectra (Table III) also support an octahedral configuration of these compounds.[10]

DISCUSSION

The stoichiometry of the compounds prepared show that the maximum number of isonicotinic acid molecules present in any one compound is two. Without X-ray analysis, no definite structures can be described. However spectroscopic and magnetic data enable one to predict possible structures. The magnetic moments (Table I), visible spectra (Table II) and far infrared spectra (Table III) suggest that the compounds have octahedral structures. The infrared spectrum of the solid free ligand is almost identical to those of the complexes in the region 2000–650 cm^{-1} (Table III). With the exception of the bisisonicotinic acid manganese (II) chloride the γ(C=O) and γ(O–H) bands of the isonicotinic acid molecule undergo a change to higher frequency in the complexes being studied. This would suggest that the carbonyl oxygen of the isonicotinic acid is not involved in coordination in these compounds.[16,17] For these complexes the infrared spectrum shows a change to higher frequency of the bands due to ring vibrations of the pyridine ring, thus suggesting that coordination takes place through the nitrogen in the pyridine ring. The bands corresponding to γ(M–Cl) and γ(M–Br) vibrations in the low frequency infrared spectra are consistent with similar modes in halogen bridged polymeric octahedral structures in the solid state.[18]

It is thus postulated that the structure of the complexes is a chain of metal atoms bonded to halogens with isonicotinic acid molecules above and below the plane of the metal-halogen chain. It is further postulated that the isonicotinic acid molecules are bonded to the metal atom through the lone pair of electrons on the nitrogen atom in the pyridine ring while being joined to each other by hydrogen bonding between the carbonyl groups. It is also suggested that alternate pairs of isonicotinic acid molecules lie above and below the plane of the metal halogen chain with one member of each pair bonded to the same metal. Previous research work with nicotinic acid and nicotinamide[10] suggests that hydrogen bonding exists between the carbonyl groups of adjacent paired ligands, and it is suggested that a similar phenomenon is exhibited

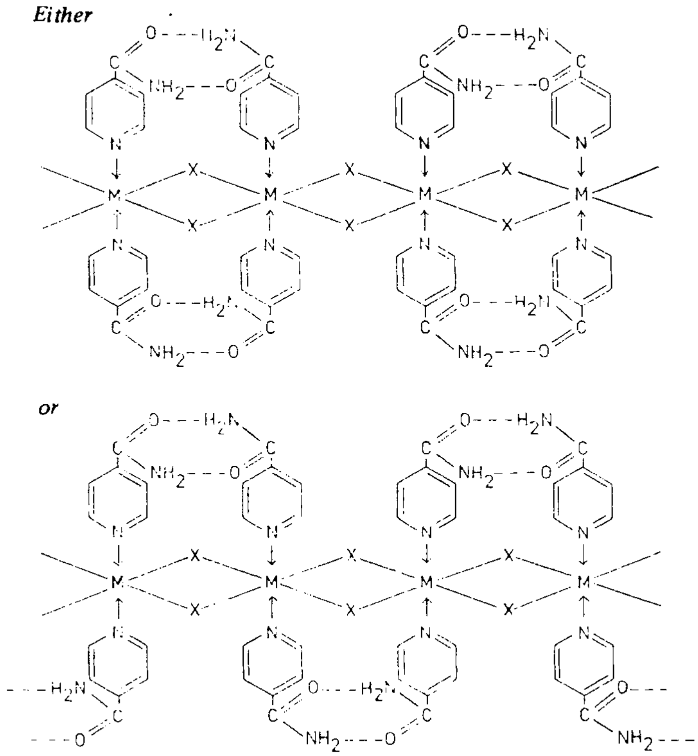

FIGURE 2

in the complexes of isonicotinic acid. In the work on nicotinic acid and nicotinamide, it was possible to postulate this by comparing the infrared spectra in the region 4000–650 cm^{-1} for the dimeric solid form on a KBr disc with the monomeric form in tetrachloromethane solution, of the free ligand; infrared spectra of the complexes showed a shift in band wavelengths which would be consistent with hydrogen bonding. Unfortunately, the extreme insolubility of isonicotinic acid in tetrachloromethane rendered it impossible to make the same direct comparison in this instance, but it is reasonable to infer that hydrogen bonding also exists in the isonicotinic acid complexes. Fig. 2.

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