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Co-ordination Compounds Derived from Isovaleric Acid Hydrazide

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Complexes of isovaleric acid hydrazide (IVH) with Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) salts have been prepared and characterised by their spectral and magnetic properties. The complexes are of the types $M(IVH)X_2{\cdot}H_2O$ *(M = Mn, Ni, Cu, Cd; X = Cl),* $Co(IVH)X_2{\cdot}\frac{1}{2}C_2H_5OH$ *(X = Cl, Br),* $Zn(IVH)Cl_2{\cdot}4H_2O$ $M(IVH_2Cl_2$ *(M = Co, Ni, Cu, Cd, Zn),* $Co(IVH)_2Br_2$ *and* $M(IVH)_3X_2{\cdot}H_2O$ *(M = Co, Ni, Cu; X = Cl, Br). In all the complexes, the ligand is unidentate and co-ordinated through the azomethine group.*

Introduction

The co-ordination chemistry of some acid hydrazides has been the subject of our previous communications. Thus we have shown that the acid hydrazides of simple aliphatic carboxylic acids up to isobutyric acid [1] and also cinnamic acid [2] form complexes with a variety of metal(II) cations from the first transition series. The mode of bonding of the acid hydrazide in such complexes has been a matter of some discussion. Thus some authors [3] claim to have prepared complexes in which the hydrazide is bonded via the oxygen of the carbonyl group while other authors favour bonding via the amino nitrogen atoms and the carbonyl group or via just the carbonyl group [4]. An alternative possible mode of bonding

TABLE I. Elemental Analyses and Electrical Conductance of IVH Complexes.

Compound	Colour	M.P. °C	Calc. (%)				Found				Molar conductance in DMF Λ_M ohm^{-1} mol^{-1} cm^2
			C	H	M	X	C	H	M	X	
$Co(IVH)Cl_2{\cdot}\frac{1}{2}C_2H_5OH$	deep blue	120	26.79	5.62	21.91	26.36	26.88	5.72	21.86	26.24	41
$Co(IVH)_2Cl_2$	pink	232	33.16	6.68	16.27	19.58	32.87	6.70	16.24	19.52	31
$Co(IVH)_3Cl_2{\cdot}H_2O$	violet	156	36.30	7.72	11.87	14.29	36.32	7.07	11.79	14.00	38
$Co(IVH)Br_2{\cdot}\frac{1}{2}C_2H_5OH$	deep blue	108	20.13	4.22	16.46	44.65	20.27	4.30	16.41	44.39	57
$Co(IVH)_2Br_2$	pink	238	26.63	5.36	13.07	35.43	26.78	5.44	12.53	35.99	42
$Co(IVH)_3Br_2{\cdot}H_2O$	pink	221	30.78	6.45			30.62	6.57			44
$Ni(IVH)Cl_2{\cdot}H_2O$	green	138	22.76	5.35	22.85	26.88	23.43	6.13	22.73	26.79	39
$Ni(IVH)_2Cl_2$	green	183	33.18	6.68	16.22	19.59	33.36	7.10	16.16	19.43	30
$Ni(IVH)_3{\cdot}Cl_2{\cdot}H_2O$	blue	236	36.31	7.71	11.83	14.29	36.00	7.84	11.74	14.16	31
$Ni(IVH)_3Br_2{\cdot}H_2O$	blue	227	30.79	6.55	10.03	27.32	30.54	6.95	9.46	27.15	28
$Cu(IVH)Cl_2{\cdot}H_2O$	green	169	22.40	5.25	26.40	23.65	22.75	4.62	26.01	23.36	30
$Cu(IVH)_2Cl_2$	green	92	32.75	6.60	18.87	19.33	31.97	6.43	18.75	18.92	36
$Cu(IVH)_3Cl_2{\cdot}H_2O$	blue	70	35.96	7.65	12.68	14.16	36.00	7.28	12.75	13.89	43
$Mn(IVH)Cl_2{\cdot}H_2O$	pale pink	200	21.60	5.80	19.76	25.50	21.32	5.14	19.27	25.59	46
$Mn(IVH)_2Cl_2{\cdot}H_2O$	pale pink	230	31.93	6.97	14.60	18.85	31.64	6.84	14.27	19.51	57
$Cd(IVH)Cl_2{\cdot}H_2O$	white	130	18.92	4.44	35.40	22.34	18.15	4.67	35.87	21.87	23
$Cd(IVH)_2Cl_2$	white	252	28.90	5.82	27.04	17.06	28.96	5.85	26.59	17.26	21
$Zn(IVH)Cl_2{\cdot}4H_2O$	white	106	18.51	6.21	20.14	21.85	18.31	6.06	20.68	22.21	26
$Zn(IVH)_2Cl_2$	white	142	29.68	6.97	17.73	19.23	29.47	6.78	18.30	19.20	34

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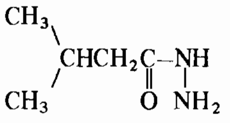
TABLE II. Spectral and Magnetic Properties of IVH Complexes.

Compound	Magnetic moment μ_{eff} (BM)	Electronic Spectra (in $cm^{-1} \times 10^3$)	
		Ligand Field Bands	Charge-transfer
$Co(IVH)Cl_2 \cdot \frac{1}{2}C_2H_5OH$	4.53	5.2, 6.0, 14.6, 15.8, 18.4	27.3
$Co(IVH)_2Cl_2$	4.69	8.1, 14.9, 15.7, 18.9	27.9, 39.6
$Co(IVH)_3Cl_2 \cdot H_2O$	5.08	8.6, 14.6, 15.6, 18.7, 19.8	27.3
$Co(IVH)Br_2 \cdot \frac{1}{2}C_2H_5OH$	4.62	6.1, 14.9, 18.2(sh)	25.1
$Co(IVH)_2Br_2$	4.83	8.8, 14.9, 16.1, 17.5, 18.8, 19.9	35.6
$Co(IVH)_3Br_2 \cdot H_2O$	4.93	9.1, 14.9, 18.9, 19.7, 39.7	39.7
$Ni(IVH)Cl_2 \cdot H_2O$	2.75	9.3, 14.9, 24.8	
$Ni(IVH)_2Cl_2$	3.33	9.5, 14.6, 25.0	
$Ni(IVH)_3Cl_2 \cdot H_2O$	3.01	10.3, 11.2, 16.2, 17.2, 27.6	41.2
$Ni(IVH)_3Br_2 \cdot H_2O$	3.14	10.2, 16.4, 27.7	37.0
$Cu(IVH)Cl_2 \cdot H_2O$	2.02	14.6	27.6
$Cu(IVH)_2Cl_2$	1.97	12.5	27.1
$Cu(IVH)_3Cl_3 \cdot H_2O$	1.85	12.8	28.3, 40.2, 41.3
$Mn(IVH)Cl_2 \cdot H_2O$	6.35		
$Mn(IVH)_2Cl_2 \cdot H_2O$	6.09		
$Cd(IVH)Cl_2 \cdot H_2O$	diamag.		
$Cd(IVH)_2Cl_2$	diamag.		
$Zn(IVH)Cl_2 \cdot 4H_2O$	diamag.		
$Zn(IVH)_2Cl_2$	diamag.		

is via the imide nitrogen atom and this is preferred by Ahmed and co-workers [5]. We here report our findings on the previously unstudied ligand, isovaleric acid hydrazide.

Results and Discussion

Isovaleric acid hydrazide can be represented by the following tautomeric forms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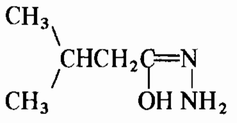
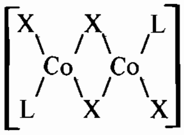

II

The infrared spectrum of this ligand indicates that it exists largely in the keto form (I); it shows $\nu(CO)$ at 1683 cm^{-1} and no bands above 3320 cm^{-1} which would be expected for the enol form (II). The complexes of this ligand which have been isolated from ethanolic solution are listed in Table I. They are insoluble in non-polar organic solvents but dissolve in dimethylformamide (DMF) and dimethylsulphoxide. Molar conductivities in DMF at 25 °C (Table I) indicate [6] these complexes to be non-electrolytes in this solvent. The infrared spectra of the complexes are all very similar; they show a broad band around 3400 cm^{-1} (irrespective of whether or not they contain water) which we attribute to $\nu(OH)$ and lack a band in the 1650–1750 cm^{-1} region attributable to $\nu(CO)$ from the ligand. A new band appears however in the complexes at around 1595 cm^{-1} (with minor variations from complex to complex) which we attribute to $\nu(C{=}N)$. It is thus apparent that these complexes contain the ligand bonded in the enol form (II). The N–N stretching frequency in the free ligand we believe to be the band at 1087 cm^{-1}; this band is shifted to 1105 cm^{-1} in the complexes – a shift compatible with coordination of the ligand via one of the nitrogen atoms. A similar small increase in $\nu(N{-}N)$ occurs in hydrazine complexes which contain unidentate hydrazine while a much larger increase is found in complexes containing bidentate hydrazine [7]. The bands at 1632, 1321 and 1159 cm^{-1} assigned to $\beta(NH_2)$ and $\delta(NH_2)$ in the free ligand remain largely unchanged in the complexes suggesting that the NH_2 group is not taking part in co-ordination. The band at 1017 cm^{-1} in the ligand which is assigned to $\delta(NH)$ [8] however is not present in the spectra of the complexes; bands at 1045 and 920 cm^{-1} however appear and these are assigned to ν_{as} (–C–O) and ν_s (–C–O–) respectively. Strong evidence for the presence of a free –OH group in the co-ordinated ligand comes from the proton magnetic resonance spectra of solutions of the diamagnetic complexes in d_6-DMSO. In for example, solutions of $Cd(IVH)_2Cl_2$, the –OH proton signal at 10.05 ppm downfield from TMS disappears upon addition of D_2O. We thus believe all of the complexes to contain unidentate IVH bonded via the azomethine nitrogen atom.

The electronic spectra and magnetic data on the complexes (Table II) show that cobalt forms both tetrahedral and octahedral complexes with IVH. Thus the compounds $Co(IVH)X_2 \cdot \frac{1}{2}C_2H_5OH$ (X = Cl or Br) have magnetic moments in the range normally found for tetrahedral cobalt(II) complexes and show the $^4A_2 \rightarrow {}^4T_1(F)$ and $^4A_2 \rightarrow {}^4T_1(P)$ transitions in the 6000 and 15,000 cm^{-1} region as expected. The only difference in the i.r. spectra of the two complexes lies in the far i.r. where the chloride complex shows a broad band centred around 280 cm^{-1} which we attribute to ν(Co–Cl); only a weak band at 240 cm^{-1} is found in the bromide complex, this may be ν(Co–Br). The most likely structure for these compounds is a halogen bridged tetrahedral dimer:



$\cdot C_2H_5OH$

Such a structure is compatible with the spectroscopic evidence – only the terminal ν(Co–X) being found since the bridging ν(Co–X) is known to occur below 200 cm^{-1} [9]. Hemi-ethanolates have been found in other cobalt(II) systems, *e.g.* $Co(MeMeNHS)_2Br_2 \cdot \frac{1}{2}C_2H_5OH$ (MeMeNHS = 1-(isopropylidene)thiosemicarbazide) but no structures proposed [10]. Nitratotetrakis(2-methylimidazole)cobalt(II) nitrate–0.5 ethanol has been shown [11] to contain disordered ethanol in the lattice.

The other cobalt complexes in Table II have magnetic moments and electronic spectra characteristic of octahedral cobalt(II) complexes: the 8–9,000 cm^{-1} band being the $^4T_{1g} \rightarrow {}^4T_{2g}$, the band around 15,000 cm^{-1} being the $^4T_{1g} \rightarrow {}^4A_{2g}$ and that in the 18–19,000 cm^{-1} being the $^4T_{1g} \rightarrow {}^4T_{1g}(P)$ transition. The complexes $Co(IVH)_2X_2$ (X = Cl or Br) show only one band (other than ligand bands) below 500 cm^{-1} and since this is at 255 cm^{-1} for both compounds it is evident that this is likely to be ν(Co–N). A polymeric structure with halogen bridging as found in *e.g.* $Co(py)_2Cl_2$ [7] is thus proposed for these complexes. The other cobalt complexes, $Co(IVH)_3X_2 \cdot H_2O$, show a broad band centred on 3420 cm^{-1} in the i.r. which is not present in $Co(IVH)_2X_2$ and they may have monomeric structures with a co-ordinated water molecule, two halide ions, and three unidentate IVH ligands. The fact that the water molecule is not removed when the complex is dried *in vacuo* over phosphorus pentoxide lends further support for the presence of the water molecule in the co-ordination sphere.

The nickel complexes have electronic spectra and magnetic moments clearly characterising them as octahedral. The mono- and bis-ligand complexes $Ni(IVH)Cl_2 \cdot H_2O$ and $Ni(IVH)_2Cl_2$ are most probably polymeric with halogen bridges; they show i.r. bands in the 240–250 cm^{-1} region but no other absorptions below 500 cm^{-1}. Absorptions at 246, 258 and 235 cm^{-1} in the halogen-bridged $Ni(py)_2Cl_2$ have been variously ascribed to ν(Ni–Cl) [12] and ν(Ni–N) [13] and we are unable to assign the absorptions in our complexes with certainty. The electronic transitions from the $^3A_{2g}$ to the $^3T_{2g}$, $^3T_{1g}$ and $^3T_{1g}(P)$ terms increase in energy in going from the mono to the tris ligand complexes indicating that in the environment of the nickel atoms the number of nitrogen ligands increases. No splitting of the bands due to tetragonality is observed for the mono and bis complexes but the tris-ligand complex $Ni(IVH)_3Cl_2 \cdot H_2O$ shows a splitting in both ν_1 and ν_2. The electronic spectra of the copper(II) complexes rule out a tetrahedral environment and are typical of the spectra of tetragonal copper(II) complexes; the magnetic moments confirm that no reduction to copper(I) or anomalous magnetic behaviour is occuring.

The manganese(II) complexes show ν(Mn–Cl) at 242 cm^{-1} ($Mn(IVH)Cl_2 \cdot H_2O$) and 239 cm^{-1} ($Mn(IVH)_2Cl_2 \cdot H_2O$) in the region typically found for six co-ordinate complexes of the type MnL_2Cl_2; tetrahedral complexes of this formula have ν(M–Cl) around 310 cm^{-1} [13]. The zinc complexes have a broad absorption band from 300 to 260 cm^{-1}, while in the cadmium complexes there is a broad rising absorption below 240 cm^{-1}, the zinc complexes may therefore be tetrahedral.

Experimental

Physical Measurements

Molar conductances were measured using a Philips PR 9500 conductivity bridge. Magnetic moments were determined by the Gouy method at room temperature. Electronic spectra were measured on solid compounds by reflectance using a Unicam SP 700C spectrophotometer fitted with the standard attachment. Infrared spectra were measured over the range 4000–200 cm^{-1} using CsI plates on a Perkin-Elmer 557 instrument and proton magnetic resonance spectra on a Perkin-Elmer R12B (60 MHz) spectrometer. Analytical methods were as previously described in [1].

Preparation of Isovaleric Acid Hydrazide and Its Complexes

IVH was prepared as described earlier [14]. The complexes of manganese(II), zinc(II) and cadmium(II) were prepared using ethanolic solutions of the hydrated metal chlorides, adding an equimolar amount of IVH (for the 1:1 complexes) or a 2:1 mol ratio of ligand to metal (for the 2:1 complexes) and heating the mixture under reflux. The complexes crystallised on cooling the solution; they were filtered off, washed with diethyl ether and dried in a vacuum desiccator over silica gel. No tris-ligand complexes could be isolated from these solutions by using an excess *i.e.* greater than 3:1 mole ratio, of the ligand.

The cobalt(II), nickel(II) and copper(II) complexes were prepared using ethanolic solutions of the hydrated metal halides, adding the ligand in a 1:1, 2:1 or 3:1 mole ratio (for the mono- bis- and tris-complexes) and heating the mixture on a water bath until only a small volume remained. The complexes, which were isolated by adding dry diethyl ether, crystallised upon scratching the mixture; they were filtered off, washed with dry diethyl ether and dried over phosphorus pentoxide.

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