

in spite of the fact that it contains a hydroxyl group at C₃ adjacent to carbonyl group.

The R_f values, colour with the spray reagent and colour in the UV light are given in Table I.

TABLE I

Substance	R _f	Colour observed	Fluorescence in UV light
2-hydroxy 1 : 4 Naphthaquinone	0.84	LY	BL
Chrysophanol	0.76	LY	LB
Emodin	0.64	LY	LB
Mono-methyl ether of Phycion	0.11	P	P
Phycion 1-O-arabino glucoside	0.68	P	P
Taxifoline	0.78	Y	LB
Taxifoline galactoside	0.73	Y	LB
5, 7 dihydroxy flavanone	0.57	Y	LB
Kaempferol	0.83	Y	LB
Quercetin	0.78	Y	DB
Rhamnetin	0.80	Y	DB
5, 7 dihydroxy flavone	0.67	LY	LY
5, 3' dihydroxy 7, 4' dimethoxy flavonol	0.52	LY	LB
5, 7', 4' trihydroxy 3, 6, 3' trimethoxy flavonol	0.61	LY	LY
5, 7 dihydroxy 4' methoxy flavone	0.50	Y	LB
5 hydroxy 7, 3', 4' trimethoxy flavone	0.43	Y	LB
7 hydroxy flavone	0.00	—	BL
Avicularin	0.70	Y	LB
Quercitrin	0.82	Y	LB
Rutin	0.56	Y	LB
Penta methyl quercetin	0.71	—	BL
3', 4', 5, 7 tetra methoxy quercetin	0.88	—	BL
5 hydroxy 7', 3', 4' trimethoxy flavonol	0.38	LY	LY

LY = light yellow; LB = light brown; DB = dark brown; BL = bluish; P = pink.

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SYNTHESIS AND STRUCTURAL STUDIES OF MALONYL AND SUCCINYL DIHYDRAZIDE COMPLEXES OF SOME FIRST ROW TRANSITION METAL IONS

ALTHOUGH there are a few papers¹⁻⁴ on the synthesis and structural studies of transition metal complexes of malonyl dihydrazide (MDH) and succinyl dihydrazide (SDH), yet there is disagreement among the various investigators regarding the composition of complexes formed and bonding sites of the ligands utilized therein. We have undertaken in continuation of our previous work⁵, the synthesis and structural investigations of the complexes of Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) with the above dihydrazides and the results of these studies are reported in this note.

Preparation and Analysis of the Complexes

The complexes were prepared by mixing together cold/hot ethanolic solutions of the metal salts and ligand in 1 : 1 and/or 1 : 2 molar ratios. All the complexes precipitated immediately except [Ni(MDH)₂Cl₂].2H₂O and [Ni(SDH)₂Cl₂].2H₂O which were kept overnight to get the filterable precipitate. All the complexes thus obtained were filtered, washed with ethanol, ether and finally dried at room temperature. Experimental details pertaining to the analysis of the complexes, molar conductance, magnetic susceptibility, i.r. and electronic spectral measurements were the same as described in our earlier papers⁶.

MDH and SDH react with metal(II) chlorides and nickel(II) nitrate to yield the complexes of the empirical compositions MCl₂, ML₂Cl₂, [NiL₂Cl₂].2H₂O and [NiL₂(H₂O)₂](NO₃)₂ where M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) and L = MDH and SDH. The complexes are insoluble in common organic solvents but the chloride complexes are slightly soluble in cold or hot DMSO. Most of the complexes melt in temperature range 131-238° and some decompose in the temperature range 148-241° but a few complexes do not melt or decompose up to 250°. The loss of water molecules in 100-115° temperature range in hydrated nickel(II) chloride complexes and in 140-160° temperature range in hydrated nickel(II) nitrate complexes shows that the water molecules are in lattice⁶ in the former complexes and coordinated⁶

in the latter. The molar conductances of the chloride complexes lying in the range $1.33\text{--}6.80\text{ ohm}^{-1}\text{ cm}^2/\text{mole}$ indicate their non-ionic nature⁷.

The magnetic moments⁸ of CoLCl_2 (4.65–4.69 B.M.) and CoL_2Cl_2 (4.98–5.00 B.M.) complexes indicate tetrahedral geometry for the former complexes and spin-free octahedral geometry for the latter. The μ_{eff} values of Ni(II) complexes (2.91–3.20 B.M.) and of Fe(II) complexes (5.45–5.50 B.M.) are consistent with spin-free octahedral geometry while those of Mn(II) (5.90–6.05 B.M.) and Cu(II) (1.85–2.08 B.M.) complexes⁹ correspond to five and one unpaired electrons respectively.

The d-d bands observed in the visible spectra in $10810\text{--}11110\text{ cm}^{-1}$ region with iron(II) complexes¹⁰, in $8330\text{--}8700$, $15380\text{--}16000$ and $19050\text{--}20000\text{ cm}^{-1}$ regions with 1:2 Co(II) complexes¹¹, in $8890\text{--}10260$, $14810\text{--}17040$ and $24690\text{--}28570\text{ cm}^{-1}$ in the regions with nickel(II) complexes¹² and in the $12400\text{--}16000\text{ cm}^{-1}$ region with Cu(II) complexes are consistent with the octahedral geometry for these complexes. However, the appearance of only two bands in $4800\text{--}4810$ and $\sim 14390\text{ cm}^{-1}$ regions in 1:1 Co(II) complexes¹³ shows them to be tetrahedral. The octahedral geometry¹⁴ for nickel(II) complex is further confirmed by ν_2/ν_1 ratio lying in the range $1.62\text{--}1.66$. The broadness of the band in the case of copper(II) complexes is indicative of the distorted octahedral geometry¹² of these complexes.

The various ligand field parameters such as $10Dq$, B' , β , β^2 and LFSE have been calculated¹⁵ and are found to lie in the region $2736\text{--}16000\text{ cm}^{-1}$, $682\text{--}988\text{ cm}^{-1}$, $0.705\text{--}0.935$, $6.44\text{--}29.47\%$ and $39.10\text{--}146.70\text{ kJ/mole}$ respectively. The values of $10Dq$ suggest a place between water and ammonia for the ligands in the spectrochemical series.

A comparison of the nujol spectra of complexes with the spectra of the parent ligands in acetonitrile solution shows a negative shift in amide I ($10\text{--}45\text{ cm}^{-1}$), amide II ($5\text{--}22\text{ cm}^{-1}$), $\beta(\text{NH}_2)$ ($12\text{--}46\text{ cm}^{-1}$) a positive shift in $\nu(\text{N--N})$ ($24\text{--}65\text{ cm}^{-1}$) and new bands in $450\text{--}345$, $310\text{--}230\text{ cm}^{-1}$ regions attributed to $\nu(\text{M--O})$ ¹⁶ and $\nu(\text{M--N})$ ¹⁶ in all 1:1 complexes except 1:1 cobalt(II) complexes. The remaining complexes show a negative shift in amide I ($10\text{--}60\text{ cm}^{-1}$), amide II ($5\text{--}15\text{ cm}^{-1}$), practically no shift in $\beta(\text{NH}_2)$ and $\nu(\text{N--N})$ and a new band in $460\text{--}325\text{ cm}^{-1}$ region due to $\nu(\text{M--O})$ ¹⁶. MDH and SDH thus behave as tetradentate ligands in the former complexes co-ordinating through both carbonyl oxygens and terminal nitrogens and as bidentate ligands in the latter complexes bonding sites being both the carbonyl oxygens. The presence of a strong intensity band centered at $\sim 1380\text{ cm}^{-1}$ and a medium intensity band at 825 cm^{-1} indicate that NO_3^- is ionically¹⁷ bonded in the nitrate complexes. The appearance of a band in $760\text{--}740\text{ cm}^{-1}$ region in hydrated nickel

(II) nitrate complexes and its absence in hydrated nickel(II) chloride complexes indicate that the water molecules are coordinated¹⁸ in the former complexes and lattice held in the latter.

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