

asymmetric and symmetric stretching vibrations of NH_2 group and a band at 1600 due to deformation mode of this group. The bands due to all these three modes are shifted to lower frequencies in the spectra of its adducts indicating the bonding of terminal hydrazide nitrogen to tin(IV)². A band due to $\nu(\text{C}=\text{N})$ observed at 1625 in the spectrum of methyl 3-isopropylidene dithiocarbazate (MIpDTC) is shifted to 1600 in its adduct suggesting the coordination of azomethine nitrogen to tin(IV).

A strong band occurring at 1005 in SMDTC and at 1040 in MIpDTC spectra, due to $\nu(\text{C}=\text{S})$, is shifted to lower frequency in their adducts indicating the bonding of thioketo sulphur to tin(IV). The coordination of thioketo sulphur to tin(IV) in the addition compounds of SMDTC is further confirmed by the positive shift observed in the ligand band at 1150 due to the in-phase ν (NCS) mode having primarily C-N stretching character. A new band appearing around 470 in the spectra of the adducts is tentatively assigned to $\nu(\text{Sn}-\text{S})$ ³. A strong broad band observed between 320 and 270 cm^{-1} in the adducts containing chloride ion is assigned to $\nu(\text{Sn}-\text{Cl})$ and the appearance of this band in this region indicates octahedral geometry for tin(IV).

In the UV spectra (nujol mull) of the ligands, bands observed around 275 and 300 nm are attributed to $\pi-\pi^*$ transitions of the (C=S) and/or (C=N) group. These two bands show slight red shifts in the case of adducts of S-methyl dithiocarbazate giving a broad band in the spectrum of the adduct of BuSnCl_3 with methyl 3-isopropylidene dithiocarbazate. This may be due to the bonding of thioketo group to tin(IV) in the former case and coordination through thioketo sulphur and azomethine nitrogen atoms in the latter. An additional broad band observed at 400 nm in the spectrum of adduct of SnBr_4 with S-methyl dithiocarbazate may be due to a charge-transfer transition involving tin(IV).

The PMR spectrum of S-methyl dithiocarbazate in CDCl_3 gives three signals at 2.68, 5.5 and 8.4 δ assigned to the CH_3 , NH_2 and NH protons respectively. In the spectrum of its adduct with BuSnCl_3 the position of methyl protons (2.80 δ) as expected remains practically unchanged whereas the NH_2 and NH protons give a signal at 8.54 δ , the integration corresponding to three protons. The profound downfield shift of the NH_2 protons in the adduct suggests their deshielding on coordination through amino nitrogen to tin(IV). The butyl protons of the adduct appear as a multiplet between 0.75 and 2.50 δ . Their positions and the integrations are consistent with the proposed stoichiometry and bonding of terminal hydrazido nitrogen as inferred from IR data.

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Complexes of Cu(II) with Some Biologically Active Dihydroxycoumarins

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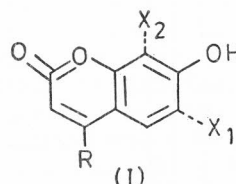
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Complexes of Cu(II) with hydroxycoumarins, viz. esculetin, daphnetin and their 4-methyl and 4-phenyl derivatives have been prepared. The general composition of the complexes is $[\text{Cu}(\text{H}_2\text{O})_2(\text{HL})_2]$. The water molecules are replaced on reaction with pyridine or ammonia to give complexes of the type $[\text{Cu}(\text{L})(\text{X})_4]$ (where $\text{X} = \text{NH}_3$ or $\text{C}_5\text{H}_5\text{N}$). IR studies show that more acidic of the two phenolic hydroxyl groups present at C-7 in the ligand is involved in complexation in the parent complexes. Thermal studies on the parent complexes indicate the formation of two intermediate compounds which correspond to the compositions $[\text{Cu}(\text{HL})_2]$ and $[\text{Cu}(\text{L})]$ but only one intermediate, $[\text{Cu}(\text{L})]$, is formed on heating the pyridine or ammonia adducts.

In continuation of earlier work on the complexes of hydroxycoumarins from our laboratory^{1,2}, we report here Cu(II) complexes of esculetin, daphnetin and their 4-methyl and 4-phenyl derivatives(I). Further, ammonia and pyridine adducts of the parent complexes have also been isolated.

Esculetin and its derivatives and daphnetin and its derivatives were prepared by condensing hydroxyhydroquinone triacetate or pyrogallol respectively with malic acid or appropriate β -keto ester in the presence of sulphuric acid³.

The parent complexes of the type $[\text{Cu}(\text{H}_2\text{O})_2(\text{HL})_2]$ were prepared by adding an aqueous solution of copper(II) chloride (0.05 mol) to an ethanolic solution of the corresponding ligand in the stoichiometric ratio of 1:2 and subsequently raising the pH of the mixture gradually to ~ 5.0 by adding dilute solution



- $\text{X}_1 = \text{OH}, \text{X}_2 = \text{H}$, ESCULETIN H_2
 $\text{X}_1 = \text{H}, \text{X}_2 = \text{OH}$, DAPHNETIN H_2
 $\text{R} = -\text{CH}_3$ OR C_6H_5

NOTES

of sodium hydroxide. A green coloured solid separated out. The resultant mixture was refluxed for an hour, cooled, filtered and washed several times with water followed by ethanol to remove unreacted reactants and finally dried *in vacuo* at room temperature ($\sim 25^\circ\text{C}$) over P_4O_{10} . Addition of ethanolic solution of the ligand to an aqueous solution of copper(II) chloride in 1:1 stoichiometric ratio followed by a ten-fold excess of secondary ligand, aqueous ammonia or pyridine and keeping the resulting mixture at 0°C for 24 hr resulted in the formation of mixed ligand complexes of the type $[\text{Cu}(\text{L})(\text{X})_4]$, where $\text{X} = \text{pyridine}$ or ammonia. The complexes were filtered, washed with ethanol and dried *in vacuo* at room temperature ($\sim 25^\circ\text{C}$) over P_4O_{10} .

As the compositions of mixed ligand complexes are independent of the relative proportions of the metal ion, primary ligand and secondary ligand, it may be inferred that only one type of water insoluble complexes are formed in the present case.

The magnetic susceptibilities of the complexes were determined at room temperature by Gouy's method using $[\text{HgCo}(\text{CNS})_4]$ as the calibrant. Infrared spectra ($4000\text{-}200\text{ cm}^{-1}$ region) were recorded in cesium iodide pellets on a Perkin-Elmer double grating recording spectrophotometer model 621. Thermograms of the complexes were recorded on a Setaram Thermoanalyser model G-70 in the O_2 atmosphere and at a heating rate of $6^\circ/\text{min}$.

The elemental analyses and magnetic moment data are presented in Table 1. All the complexes isolated are green in colour. The electronic spectra of all the parent complexes (recorded in nujol mull) exhibit one composite band in the region 14-13 kK while the spectra of adducts shows a band in the region 16-14 kK. The λ_{max} values of complexes have been found to be in the following order : ammonia > pyridine > water, which is in accordance with spectrochemical series.

$[\text{Cu}(\text{H}_2\text{O})_2(\text{LH})_2]$ complexes — Since all the complexes contain an α -benzopyrone skeleton, the IR spectra of the complexes are almost identical with the spectra of ligands⁴ except that additional bands due to $\nu\text{M-O}$ are observed. The bands due to νOH in the region $3420\text{-}3300\text{ cm}^{-1}$ appearing as sharp absorption bands in the present ligands could not be detected because of the broad absorption in this region due to the coordinated water molecules⁷.

However, the C-OH deformation modes present in the spectra of coumarins at $1200\text{-}1100\text{ cm}^{-1}$ shift by $\pm 30\text{ cm}^{-1}$. On the basis of altered position and decrease in intensity of the $\delta\text{-OH}$ band, it may be inferred that proton from the more acidic of the two —OH groups is lost during complexation. Considering the proton dissociation constants of the two —OH groups and the electromeric effect due to C=O group, the —OH at C-7 is evidently more acidic and hence it should be deprotonated on complexation. The spectra show bands in the region $900\text{-}830$, $550\text{-}530$ and $400\text{-}420\text{ cm}^{-1}$, which have been assigned to the rocking, wagging and Cu-O stretching vibrations respectively of the coordinated water molecules.

TABLE 1 — ELEMENTAL ANALYSES, MAGNETIC MOMENT AND DECOMPOSITION TEMP. DATA OF $\text{Cu}(\text{II})$ COMPLEXES

Complex*	Found (Calc.) %			Dec. temp. ($^\circ\text{C}$)	μ_{eff} B.M	
	C	H	Cu			
Cu-ES. H	47.2 (47.6)	3.0 (3.1)	13.08 (14.0)	110	1.88	
Cu-4ME. H	49.6 (49.8)	3.5 (3.7)	13.0 (13.2)	112	1.97	
Cu-4PE. H	59.2 (59.5)	3.4 (3.6)	10.2 (10.6)	115	1.98	
Cu-Da. H	47.3 (47.6)	2.9 (3.1)	13.7 (14.0)	120	1.98	
Cu-4MD. H	49.6 (49.8)	3.6 (3.7)	13.0 (13.2)	125	2.10	
Cu-4PD. H	59.3 (59.5)	3.4 (3.6)	10.3 (10.6)	120	2.18	
	C	H	N	Cu		
Cu-ES(NH_3) ₄	35.0 (35.1)	5.0 (5.2)	18.0 (18.2)	20.5 (20.7)	53	1.89
Cu-4ME(NH_3) ₄	37.0 (37.3)	5.3 (5.6)	17.2 (17.4)	19.4 (19.8)	55	2.20
Cu-4PE(NH_3) ₄	46.5 (46.9)	5.0 (5.2)	14.2 (14.6)	16.3 (16.6)	54	2.20
Cu-Da(NH_3) ₄	34.9 (33.1)	4.9 (5.2)	18.0 (18.2)	20.4 (20.7)	57	2.05
Cu-4MD(NH_3) ₄	37.1 (37.3)	5.2 (5.6)	17.1 (17.4)	19.5 (19.8)	60	2.10
Cu-4PD(NH_3) ₄	46.7 (46.9)	5.0 (5.2)	14.3 (14.6)	16.4 (16.6)	66	2.20
Cu-ES(Py) ₄	62.2 (62.4)	4.8 (5.0)	9.8 (10.0)	11.1 (11.4)	130	1.90
Cu-4ME(Py) ₄	62.1 (62.3)	4.5 (4.9)	9.6 (9.8)	11.0 (11.1)	134	1.98
Cu-4PE(Py) ₄	64.0 (64.3)	4.4 (4.6)	8.4 (8.6)	9.2 (9.7)	137	2.10
Cu-Da(Py) ₄	62.2 (62.4)	4.8 (5.0)	9.8 (10.0)	11.0 (11.4)	144	1.92
Cu-4MD(Py) ₄	62.1 (62.3)	4.7 (4.9)	9.6 (9.8)	11.04 (11.1)	146	2.10
Cu-4PD(Py) ₄	64.1 (64.3)	4.2 (4.6)	8.4 (8.6)	9.2 (9.7)	149	2.20

*ES.H₂ = Esculetin, ME.H₂ = Methylsculetin, PE.H₂ = Phenylsculetin, Da.H₂ = Daphnetin, MD.H₂ = Methyl-daphnetin, PD. H₂ = Phenyl-daphnetin.

A steady weight loss is recorded on heating upto $\sim 150^\circ\text{C}$ corresponding to the elimination of two molecules of water per molecule of the complex. The first decomposition step lasts till 260°C . At this stage weight of the residue corresponds to the formation of a 1:1 complex. A further weight loss recorded upto 560°C indicates the formation of thermally stable oxide (Table 1)⁵.

The general course of reaction is as follows : $[\text{Cu}(\text{H}_2\text{O})_2(\text{HL})_2] \rightarrow [\text{Cu}(\text{HL})_2] \rightarrow [\text{Cu}(\text{L})] \rightarrow \text{CuO}$.

$[\text{Cu}(\text{L})(\text{X})_4]$ complexes — Ammonia complexes show a strong absorption band in the region $3400\text{-}3000\text{ cm}^{-1}$ characteristic of ν_{as} and ν_{s} modes of NH_3 and $\nu\text{-OH}$ mode⁶. The C-OH deformation mode present in the spectra of coumarins and the parent complexes is not observed in the spectra of adducts. This suggests the deprotonation of both the OH groups during adduct formation with NH_3 or pyridine. The presence of NH_3 is also supported by the appearance of new bands at $1550\text{-}1530$, $1000\text{-}900$ and $650\text{-}580\text{ cm}^{-1}$ due to degenerate deformation,

symmetric deformation and rocking modes of NH_3 . Pyridine complexes exhibit new bands in the regions 660-640 and 450-440 cm^{-1} on account of the in-plane and out-of-plane deformation modes of pyridine. A band appearing at 270-250 cm^{-1} in the far IR region is identified as due to Cu-pyridine stretching modes. A broad band in the region 430-400 cm^{-1} is due to $\nu_{\text{Cu-N}}$ mode whereas the one at 290-270 cm^{-1} indicates the presence of Cu-O group.

On heating the mixed complexes, the first decomposition step in both the cases corresponds to the loss of four molecules of ammonia/pyridine per molecule of a complex (decomposition temperature is given in Table 1). The weight of residue corresponds to the 1:1 binary complex and it then steadily decreases, ultimately forming copper oxide: $[\text{Cu}(\text{L})(\text{X})_4] \rightarrow [\text{Cu}(\text{L})] \rightarrow \text{CuO}$.

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Mixed Ligand Complexes of Trivalent Lanthanides with 2,2,6,6-Tetramethyl-3,5-heptanedione & Piperazine

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Mixed ligand complexes of trivalent lanthanides with 2,2,6,6-tetramethyl-3,5-heptanedione (Hdpm) and piperazine have been synthesised and characterized on the basis of elemental analyses, molar conductance, IR spectral, electronic spectral, thermogravimetric and differential thermal analyses data. The magnetic moments have been measured in the solid state by the Faraday method and in solution by NMR technique. Nephelauxetic parameter, β and covalency parameters ($b^{1/2}$ and δ) have been calculated and discussed.

A NUMBER of lanthanide(III) complexes have been prepared^{1,2} and interesting studies have been reported on the chemistry of these elements specially on their optical spectra for ascertaining the dependence of hypersensitive bands on the environment around the lanthanide ions³, and to find $f-f$ transitions⁴ on complexation. These have also been used as NMR shift reagents⁵.

The present note deals with the synthesis and characterization of the mixed ligand complexes of the trivalent lanthanides with 2,2,6,6-tetramethyl-3,

5-heptanedione (Hdpm) and piperazine. Their spectral features, nephelauxetic ratio (β), bonding parameter ($b^{1/2}$) and covalency parameter (δ) have been calculated for some of the complexes⁶⁻⁸.

Rare earth oxides (Leico Chem., USA) were converted to the corresponding chlorides. Hdpm (Pierce Chem., USA) and piperazine (E. Merck) were used as such in this study.

Synthesis — The $\text{Ln}(\text{dpm})_3$ chelates were prepared by the method of Eisentraut and Sievers⁹. The adducts of all the lanthanides (except Ce and Pm) with piperazine were prepared by mixing $\text{Ln}(\text{dpm})_3$ and piperazine in 1 : 1 molar ratio in carbon tetrachloride and refluxing on a water-bath. On cooling the solutions, solids were deposited. These were washed with *n*-hexane and CCl_4 repeatedly and dried *in vacuo* over P_2O_5 .

Carbon, hydrogen and nitrogen contents in the complexes were estimated by microanalyses while the metals were estimated by complexometric titrations with EDTA using xylenol orange as the indicator. The IR spectra were recorded on a Perkin Elmer model 621 spectrophotometer. A Beckman DU-2 spectrophotometer was used to obtain optical spectra. TGA data were obtained on a manual apparatus with a slow heating rate (6°/min). DTA studies were carried out at RRL Hyderabad. The magnetic susceptibilities were measured on a Faraday balance (in solid state) and by Evans¹⁰ NMR method (in DMSO solution) on a Varian A-60 NMR machine at the probe temperature.

The mixed ligand complexes, on the basis of their elemental analyses (Table 1) and molar conductances (20-30 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ in DMSO), have been assigned the general formula: $[\text{Ln}(\text{dmp})_3 \text{ piperazine}]$. These adducts are well-defined crystalline solids, stable in air. These are soluble only in warm DMSO. The adducts melt with decomposition (which is also supported by DTA studies) and the melting points are higher than those of any mixed ligand complex of trivalent lanthanide and tris(dpm). The high melting points and insolubility in almost all organic solvents, suggest that these complexes are polymeric in nature. The magnetic moments of these adducts (Table 1), when plotted against increasing atomic numbers, show the characteristic unequal double humped curve.

The thermograms of these complexes show a weight loss of about 10.5-11.0% in the temperature range 200-264°C. The total weight loss is consistent with the loss of piperazine (theoretical weight loss for piperazine is 10.70-11.1%). One sharp DTA peak is identified in all the cases in this temperature range. This shows coordinated nature of piperazine. In the second step of decomposition two molecules of (dpm) are eliminated and one DTA peak is seen in the temperature range 300-380°. The third mole of (dpm) is eliminated above 500°C.

The IR spectra of $\text{Ln}(\text{dpm})_3$, piperazine and $[\text{Ln}(\text{dpm})_3 \text{ piperazine}]$ have been compared in order to characterize the compounds. A sharp band appearing in piperazine at 3205 cm^{-1} (N-H stretching) is shifted to higher frequencies (3280-3268 cm^{-1}) in the spectra of the adducts. Another very strong band appearing