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Binuclear Metal Chelates of 1,2,5,6 Tetra Phenyl-1,6-Dioxo-3,4-Diazahexa-2,4-Diene-1,6-Dihydrazone with Ni(II), Co(II), Fe(II) and Cu(II)

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A series of metal chelates of Ni(II), Cu(II), Co(II) and Fe(II) with the ligand 1,2,5,6-tetraphenyl-1,6-dioxo-3,4-diazahexa-2,4-diene-1,6-dihydrazone of the type $Ni_2L_3X_4$, $Ni_2L_2X_4$, $Co_2L_2X_4$, $Cu_2L_2X_4$ and FeL_3X_2 where $X=Cl^-, Br^-, I^-, SCN^-, NO_3$ have been isolated, IR spectra indicate co-ordination of the ligand with the metal ions through azomethine nitrogen atoms and in binuclear complexes it spans two metal ions in a bi-bidentate manner. Electronic spectra and magnetic moment show approximately octahadral arrangement of ligands around metal ion with a distortion along the trigonal axis for the tris-complexes and along the tetragonal axis for bis-complexes.

INTRODUCTION

A series of polydentate ligands which can co-ordinate to two or more metal ions have been extensively studied.[1–3] The present paper deals with the isolation and structural elucidation of Ni(II), Co(II), Cu(II) and Fe(II) complexes with the ligand(I).

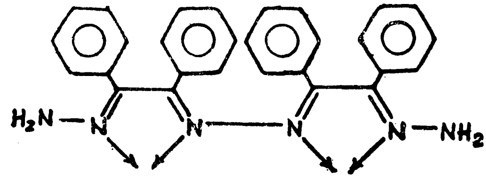

Fig. 1. Ligand(1).

Both azine nitrogens and those present in azomethine groups can undergo co-ordination with two different metal centres due to steric factors of the bulky group.

EXPERIMENTAL

The new ligand was synthesised by the reported method.[3]

Tris-(1,2,5,6-tetra phenyl-1,6-dioxo-3,4-diazahexa-2,4-diene-1,6-dihydrazone) dinickel(II) tetrachloride $[Ni_2L_3]Cl_4$

The ligand (0.009 mol.) was dissolved in nearly 45 ml. of absolute

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alcohol. To this warm solution, an ethanolic solution of nickel(II) chroride hexahydrate (0.006 mol.) was added dropwise with stirring. The solution was refluxed on hot water bath for an hour. Grey crystals appeared within a day. Crystals were filtered, washed with alcohol, ether and dried in vacuo. The bromide, iodide and nitrate complexes were prepared by a similar procedure.

(Tetra thiocyanato)-bis-(1,2,5,6-tetra phenyl-1,6-dioxo-3,4-diazahexa-2,4-diene-1,6-dihydrazone) dinickel(II) $[Ni_2L_2(SCN)_4]$

The ligand (0.008 mol) was dissolved in 40 ml. of absolute alcohol by gently warming. To this warm solution, an alcoholic solution of nickel(II) nitrate hexahydrate (0.008 mol in 6 ml.) was added dropwise with constant stirring. Undissolved material was filtered and to the deep red filtrate, a solution of KSCN in more than the stoichiometric requirement was added. The whole solution was refluxed on hot water bath for 1½ hrs. After cooling the solution in ice overnight, yellowish brown crystals separated out. Crystals were filtered, washed with ethanol and ether and dried in vacuo.

(Tetrachloro)-bis-(1,2,5,6-tetraphenyl-1,6-dioxo-3,4-diazahexa-2,4-diene-1,6-dihydrazone) dicobalt(II) $[Co_2L_2Cl_4]$

The ligand (0.008 mol) was dissolved in 40 ml. of absolute alcohol by slowly warming. To this warm solution, an ethanolic solution of cobalt(II) chloride hexahydrate (0.008 mol in 5 ml) was added dropwise with constant stirring. It was refluxed on hot water bath for 1½ hrs. Grey crystals were obtained within a day. It was filtered, washed with alcohol and ether and dried in vacuo. Bromo, iodo and nitrato complexes were prepared by similar methods. The thiocyanato cobalt(II) complex was prepared as the thiocyanato nickel(II) complex.

Copper(II) complexes were prepared by similar procedures as the cobalt(II) complexes.

Tris-(1,2,5,6-tetraphenyl-1,6-dioxo-3,4-diazahexa-2,4-diene-1,6-dihydrazone Iron(II) diiodide $[FeL_3]\ I_2$

The Ligand (0.009 mol) was dissolved in nearly 45 ml. o absolute alcohol. To this warm solution, a solution of $FeSO_4.7H_2O$ (0.003 mol in minimum quantity of dil. H_2SO_4) was added dropwise with constant stirring. After 30 minutes of stirring a deep red solution was obtained. The solution was filtered and aqueous solution of KI (3–4 times more than the stoichiometric amount) was added to the above filtrate. The whole solution was refluxed on hot water bath for an hour. Yellow crystals separated out within a day. The crystals were washed with alcohol, ether and dried in vacuo. Bromo complex was prepared in a similar way using KBr.

RESULTS AND DISCUSSION

The analytical and physical data of the compounds are presented in Table 1. From the IR spectra of free ligand it appears that the two

TABLE 1

ANALYTICAL DATA OF THE COMPOUNDS

Sr. No.	Compounds	Colour	Found (Calc.)%			Magnetic moment B.M.
			Metal	Nitrogen	Anion	
1.	Benzil azine dihydrazone	Yellow	—	18.80 (18.97)	—	—
2.	$[Ni_2L_3]Cl_4$	Grey	7.12 (7.35)	15.78 (15.84)	8.87 (8.93)	2.96
3.	$[Ni_2L_3](NO_3)_4$	Brownish green	6.84 (6.89)	18.00 (18.15)	—	2.93
4.	$[Ni_2L_3(SCN)_4]$	Yellowish brown	9.42 (9.46)	13.42 (13.58)	18.61 (18.75)	3.15
5.	$[Ni_2L_2Cl_4]$	Greenish yellow	9.02 (9.35)	13.02 (13.25)	18.51 (18.62)	2.92
6.	$[Co_2L_2Cl_4]$	Grey	10.22 (10.28)	14.45 (14.63)	12.18 (12.37)	4.66
7.	$[Co_2L_2(SCN)_4]$	Dark-grey	9.43 (9.53)	13.41 (13.57)	18.60 (18.74)	4.90
8.	$[Cu_2L_2]NO_3)_4$	Green	9.95 (10.06)	17.65 (17.73)	—	1.92
9.	$[FeL_3]Br_2$	Yellow	3.60 (3.62)	16.12 (16.28)	10.32 (10.34)	3.36
10.	$[FeL_3]I_2$	Deep yellow	3.40 (3.41)	15.30 (15.35)	15.39 (15.47)	1.12

L—Benzil azine dihydrazone.

bands in the region 3290–3200 cm^{-1} of medium intensity are due to asymmetric and symmetric vibrations of free —NH_2 groups.[2] These bands remain more or less unshifted in metal complexes showing presence of free-NH_2 groups of the hydrazone link. The other two broad bands of structural significance centred at 2900 cm^{-1} of medium to weak intensity can be assigned to νC–H stretching vibrations[4]. The bands are broadened due to different types of interaction among the various groups. A band near 1625 cm^{-1} is assigned to the δNH_2 vibration. The band position is slightly perturbed in metal complexes showing 25 to 50 cm^{-1} change in band position on high energy side. The sharp band in the lower frequency region *ca.* 1535 cm^{-1} in the ligand is ascribed to $\nu C{=\!=}N$ azine link and another band at 1575 cm^{-1} of medium intensity to $\nu C{=\!=}N$ hydrazone groups[5,6]. The C=N stretching vibration is absent or very weak in all the Fe(II) complexes and has been attributed to delocalisation of d-electron density to the π^*-orbitals of α-diimine. Three bands are located at 1485, 1445 and 1395 cm^{-1} which may be assigned to phenyl ring vibrations[7]. In thiocyanato complex of Ni(II) a broad band is observed at 2070 cm^{-1} giving support in favour of bonding through N atom[8] of SCN^- group but not as bridging group as the C=N frequency of bridging thiocyanate group gives a band at 2200 cm^{-1}.

Electronic Spectra

The tris-complexes of Ni(II) are of spin free type with the values of magnetic moments lying in the range 2.93–3.15 B.M. The data indicate characteristic features of octahedral arrangement of ligands around metal ion with slight distortion. Three bands appear in the energy range 8,600, 20,500 and 28,500 cm^{-1} which can be assigned under octahedral microsymmetry[9] to $^3A_{2g} \rightarrow {}^3T_{2g}$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$, $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ respectively. The width of the first band manifests distortion of the complex most probably along the trigonal axis. The thiocynato complex on the other hand shows a quarter of ligand field bands at 8,300; 10,500; 19,000 and 30,000 cm^{-1} implying tetragonal distortion[8]. The bands are represented by $^3B_{1g} \rightarrow {}^3B_{2g}$, $^3B_{1g} \rightarrow {}^3E_g$, $^3B_{1g} \rightarrow {}^3T_{1g}(F)$ and $^3B_{1g} \rightarrow T_{1g}(P)$ transitions respectively[2]. Since Ni(II) complex neither oxidises nor reduces, hence there is not given charge transfer transition[2].

Co(II) complexes possess magnetic moment values within the range 4.66–4.90 B.M. These complexes show ligand field bands in the region 16,000 to 20,000 possessing multiple band and are assignable to $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transition in admixture with spin forbidden transition arising from free ion ^2G and ^2H terms, characterising octahedral or tetragonal ligand field[10–12] about the metal ion. The thiocyanato complex shows an additional band near 10,500 cm^{-1} which may be assigned as $^4T_{1g}(F) \rightarrow {}^4T_{2g}$ transition under octahedral symmetry. Co(II) complexes show a charge transfer band near 29,500 cm^{-1}.

The Fe(II) complexes show subnormal magnetic moment[13,14]. The mononuclear iodide and bromide complexes do not show evidence of any ligand field band near 10,000 cm^{-1} which may be expected for spin free octahedral Fe(II) ion. These complexes show a strong charge transfer band near 24,000 cm^{-1}. The absence of any ligand field band for

${}^5T_{2g} \rightarrow {}^5E_g$ transition might be due to low extinction co-efficients as well as trailing of strong charge transfer transitions.

The magnetic moment of nitrato complex of copper(II) was found to be 1.92 B.M. The complex exhibition unsymmetric and broad ligand field band near 14,800 cm^{-1}. The width and asymmetry show two or three superimposed bands associated with Jahn-Teller distortion[15].

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