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Synthesis and characterization of heterobimetallic molybdenum and nickel complexes derived from polyfunctional disalicylaldehyde oxaloyldihydrazone

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ABSTRACT

Heterobimetallic nickel and molybdenum complexes of the composition $[Ni(L)MoO_2(A)_4]\cdot nH_2O$ (A = H_2O (1), py (2), 2-pic (3), 3-pic (4), and 4-pic (5); n = 0, 2) and $[Ni(L)(MoO_2)(BB)_2]$(BB = bpy (6) and (phen (7)) have been synthesized from the multidentate ligand disalicylaldehyde oxaloyldihydrazone (H_4L) in methanol. The composition of the complexes has been established based on data obtained from elemental analyses, thermoanalytical, mass spectral and molecular weight studies. The probable structures of the complexes have been discussed in the light of molar conductance, magnetic moment data and electronic, EPR and infrared spectral studies. In all of the complexes, the dihydrazone is present in enol form and coordinates to the metal centre as a tetrabasic hexadentate ligand. All of the complexes are normal paramagnetic to the extent of two unpaired electrons per nickel atom. The μ_{eff} values for the complexes lying in the region 2.87–3.07 B.M. are consistent with the octahedral stereochemistry of nickel(II) in the heterobimetallic complexes. The EPR and electronic spectral data also support the distorted octahedral stereochemistry of the nickel(II) centre. Both nickel and molybdenum have octahedral geometry in the complexes.

1. Introduction

The chemistry of the polyfunctional metal complexes has become a fascinating area of research in contemporary coordination chemistry in view of the importance of monometallic and multimetallic metal sites in several enzymes [1–8] and development of novel functional materials showing molecular ferromagnetism [9–13] and specific catalytic properties [14–16]. These properties may be modified by the character of the bridging species [17]. Polyfunctional ligands containing o-hydroxy-aromatic aldehydes and ketones, azomethine and amide functions are of interest because such ligands form complexes with appropriate transition metals displaying intramolecular magnetic exchange in the compounds [18]. Magnetic exchange involving M—O—M bridge has been postulated to result from a σ- and π-overlap super-exchange pathway involving a σ-/π-electrons of o-hydroxy aromatic aldehydes and ketones [19]. Further, there have been numerous reports of transition metal complexes containing polyfunctional ligands derived from aromatic aldehydes and ketones [17,18] with two nitrogen and two oxygen donor atoms as well as other similar ligands [20] in which one or both aryl rings are electron withdrawing. Dihydrazones derived from condensation of acyl-, aroyl- and pyridoyl-dihydrazones with o-hydroxy aromatic aldehydes and ketones are related ligands possessing four oxygen and four nitrogen donor atoms [21]. As the growth of the interest in the use of polyfunctional ligands containing electron-withdrawing bulky fragments in their molecular skeleton becomes more significant [17,18,22], we are interested in the synthesis and characterization of the heterobimetallic metal complexes derived from polyfunctional ligands containing electron withdrawing aromatic fragments in their molecular skeleton and to see if they could readily be prepared and how the chemical reactivity of these complexes varies relative to their corresponding non-aromatic and mixed aromatic and non-aromatic dihydrazone complexes [23]. The ligand disalicylaldehye oxaloyldihydrazone (H_4L), an example of polyfunctional dihydrazones, has been selected in the present study. The ligand has been derived from condensation of salicylaldehyde with oxaloyldihydrazine and possesses as many as eight oxygen and nitrogen donor atoms. In this dihydrazone, the two hydrazone fragments are directly bonded to one another giving better multidentate character than monoacylhydrazones. Depending upon the preferred stereochemical disposition of the metal valences, it offers several alternate modes of bonding, capable of giving rise to monometallic, homobimetallic and heterobimetallic complexes.

A survey of literature reveals that although metal complexes of monoacylhydrazones, aroylhydrazones and pyridoylhydrazones

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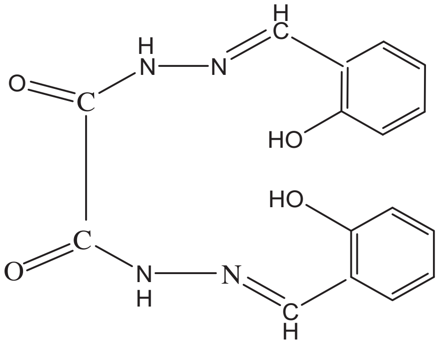

Fig. 1. Disalicylaldehyde oxaloyldihydrazone.

have been studied in some greater details [24–26], those of acyl-, aroyl- and pyridoyldihydrazones have received attention in recent years only [21–23,27,28]. Further, the reported existence of heterobimetallic complexes of dihydrazones is quite meager [27]. Moreover, the work on synthesis and characterization of heterobimetallic complexes of nickel and molybdenum, i.e. a combination of an electron rich and an electron deficient metal atom which are widely divergent from one another also, is virtually absent to the best of our knowledge.

In view of the above importance of the bi- or polynuclear and heteropolymetallic complexes, much less work on heterobimetallic complexes of nickel and molybdenum derived from polyfunctional ligands, the present paper aims at synthesis and characterization of the heterobimetallic complexes derived from polyfunctional dihydrazone disalicylaldehyde oxaloyldihydrazone (H_4L) (Fig. 1).

2. Experimental

All reagents were commercial grade materials used without further purification. $MoO_2(acac)_2$, the precursor complex $[Ni(H_2L)(H_2O)_3]$ and the ligand disalicyldehyde oxaloyldihydrazone were prepared by literature methods [28,29]. In order to purify dimethylsulfoxide (m.p. 18.4 °C), it was shaken for 2–3 h with approximately 1 cm depth of basic aluminium oxide, having activity grade 1 added to the pint bottle of the solvent. It was then filtered by decanting into a fine sintered glass funnel containing 1 cm layer of neutral aluminium oxide reagent having activity grade 1. This operation was carried out under dinitrogen atmosphere.

Carbon, hydrogen and nitrogen analyses were performed using a Perkin Elmer 240C microanalyzer. The mass losses were determined by heating the complexes at 110, 180 and 220 °C in an electronic oven. Thermogravimetric studies of the complexes were carried out on Perkin–Elmer STA 6000 model in a ceramic crucible after purging with dinitrogen. The heating rate of the samples was maintained at 20 °C min^{-1}. The DTA standard used in the experiment is Pt10%Rh. The APCI mass spectra of the complexes were recorded on a Water ZQ4000 Micromass spectrometer. The nickel and molybdenum contents of the complexes were determined by following standard literature methods [30] using chemical analysis method. Nickel was determined as nickel dimethylglyoximate while molybdenum was determined as molybdenyl oxinate. IR spectra were recorded on either Perkin–Elmer model 983 spectrophotometer or Nicolet-Impact 410 FT-IR spectrophotometer in KBr pellets in the 4000–400 cm^{-1} range. EPR spectra of the complexes were recorded at X-band frequency on Varian E-112 E-Line Century Series EPR spectrometer using TCNE ($g = 2.0027$) as an internal field marker. UV–Vis spectra for the dihydrazone ligand and the complexes were recorded on a Perkin–Elmer Lambda 25 spectrophotometer. Magnetic susceptibility measurements were carried out on a Sherwood Magnetic Susceptibility Balance. Molar conductance of the complexes in DMSO solution at 10^{-3} M dilution was measured on Direct Reading Conductivity meter-304 with a dip-type conductivity cell at room temperature.

2.1. Molecular weight determination

In order to determine the molecular weight of the complexes in DMSO ($K_f = 4.07$) [31] as a solvent, lowering of the freezing points of DMSO (18.5 °C) containing different amounts of complexes were made with a Beckman's freezing point depression instruments. It consisted of a Beckman thermometer and a stirrer with a non-conducting handle of wood fitted into a tube through a rubber stopper fixed at its upper end. This tube was supported through a rubber stopper in a bigger glass tube thoroughly purged with dry dinitrogen which acts as a dry nitrogen jacket and ensures slow and uniform cooling of the inner tube. The outer tube is immersed in a 1,2-dimethyl-3-nitrobenzene (F.P. 15 °C) freezing bath contained in a glass jar. The jar was covered with a lid of plastic which carries three holes, one for inserting the inner tube, other for large metal stirrer and third for inserting the ordinary thermometer. The molecular weight apparatus was enclosed in a dry box that was constantly purged with dry nitrogen to minimize the error due to highly hygroscopic nature of DMSO. All of the samples were placed in an entry port and purged overnight with dry nitrogen before bringing them into the dry box.

Twenty grams of DMSO was transferred into the thoroughly cleaned and dried freezing point tube purged with dry nitrogen. About 0.6 g of the complex was accurately weighed and inserted into the DMSO solution. The tube was heated to dissolve the compound and then brought to room temperature. Finally the upper surface of the liquid in the tube was purged with dry nitrogen and then adjusted into the outer tube. The freezing point temperatures of the solvent and the solutions were directly measured with this apparatus through a magnifying glass fitted into the dry box.

2.2. Preparation of $[Ni(L)MoO_2(A)_4]\cdot nH_2O$ (where A = H_2O (1) pyridine (py) (2), 2-picoline (2-pic) (3), 3-picoline (3-pic) (4) and 4-picoline (4-pic) (5), n = 0, 2}and $[Ni(L)MoO_2(BB)_2]$ {where BB = 2,2′-bipyridine (bpy)) and 1,10-phenanthroline (phen) (7)}

The complex $[Ni(H_2L)(H_2O)_3]$ (1.00 g, 2.32 mmol) was suspended in methanol (60 mL) with constant stirring for about 30 min to make the suspension homogeneous. This suspension was then slowly added to a solution of $MoO_2(acac)_2$ (0.86 g, 2.64 mmol) in 30 mL methanol over a period of 30 min accompanied by continuous stirring. The resulting mixture was put to reflux for about 5 h. This precipitated a dull yellow coloured complex which was suction filtered in hot condition, washed three to four times with 20 mL hot methanol each time followed by ether and then finally dried over anhydrous $CaCl_2$.

In order to prepare the complex $[Ni(L)MoO_2(py)_4]\cdot 2H_2O$ (2), $[Ni(L)MoO_2(H_2O)_4]$ (1) (1.00 g, 1.71 mmol) was suspended in methanol (50 mL) accompanied by continuous stirring over a period of 10–15 min. The stirring was further continued for another 30 min to make the suspension homogeneous. To this homogeneous suspension was added 1.36 mL of pyridine drop by drop over a period of 30 min and the resulting mixture was refluxed for about 1 h. This precipitated a dull yellow coloured complex which was suction filtered in hot condition, washed three to four times with 30 mL hot methanol followed by ether and finally dried over anhydrous $CaCl_2$.

The complexes $[Ni(L)MoO_2(A)_4]$ {where A = 2-pic (3), 3-pic (4) and 4-pic (5)}, were also prepared essentially by following the