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Synthesis and characterization of 1-phenyl-2,3-dimethyl-4-isovalerylpyrazolo-5-one and its lanthanide complexes of praseodymium(III) and dysprosium(III)

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Abstract
The ligand, 1-phenyl-2,3-dimethyl-4-isovalerylpyrazol-5-one, here denoted with (ipy) and its complexes of praseodymium (III) and dysprosium(III) were synthesized and characterized spectroscopically using infra red (IR). Percentage yield was determined for the complexes synthesized. Physical properties including colour, melting points and conductivity measurements were also investigated. Pr(III) and Dy(III) reacted with the ligand in the metal-ligand mole ratios of 1:3 to form neutral complexes of diaquo-trischelate $Pr(ipy)_3.2H_2O$ and, $Dy(ipy)_3.2H_2O$ respectively, giving coordination number of eight for both complexes.

Keywords: Praseodymium(III), dysprosium(III), synthesis, complexes, lanthanides, 1-phenyl-2,3-dimethyl-4-isovalerylpyrazolo-5-one and characterization

Introduction

β-Diketones and related ligands have attracted the interest of researchers since the dawn of coordination chemistry, with the preparation of acetylacetone first described by Claisen more than 100 years ago [1].

Much efforts have been devoted to the preparation and characterization of functionalized β-diketones suitable to finely modulate the physico-chemical features of the corresponding metal complexes, for example volatility and thermal stability sufficient to employ them as molecular precursors in chemical vapour deposition (CVD) techniques, or luminescence in view of potential application in the fabrication of polymer light-emitting diodes for low-cost, full-colour, flat-panel displays, or even magnetic and electronic properties of metal β-diketonates as liquid crystal phases. But transition- and lanthanide-metal derivatives also display interesting catalytic features, where the β-diketonates are important spectator donors for metal-intermediate species involved in a number of organic reactions, and find increasing interest as supramolecular assemblies in material chemistry [1]. Besides classical β-diketones, an interesting functionalization has been the fusion of a pyrazole ring to the chelating arm (R_3-C=O), affording a novel family of enolizable ligands, named 4-acylpyrazolo-5-ones as shown in Figure 1. [2]

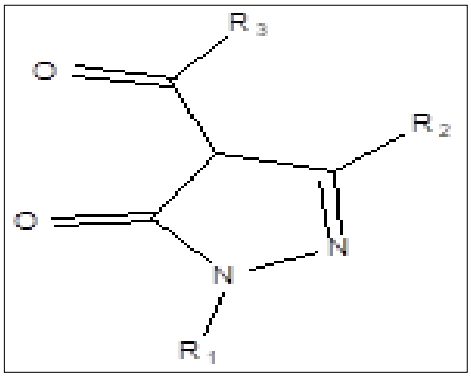

Figure 1: Generic structure for acylpyrazolones

In our earlier works [2, 3], the 4-butanoyl (-C_3H_7C=O) and the 4-stearoyl (-$C_{17}H_{35}C$=O) substituents and their complexes with some transition metals were studied.

In the recent work, the R_3 substituent has been extended to include a more branched group, hence the -2,3-dimethyl-4-isovaleryl and the lanthanides.

The present study was carried out to synthesize and characterize 1-phenyl-2,3-dimethyl-4-isovalerylpyrazolo-5-one, a 4-acylpyrazol-5-one having more methyl substituents and its lanthanide complexes of praseodymium (III) and dysprosium (III), to access the mode of interaction between the lanthanide metals and the ligand in aqueous solution and the possible structures of the complexes are proposed.

Experimental and METHODS

1. Reagents

Analytical grade reagents including: 1-phenyl-2,3-dimethylpyrazolone-5, Pr $(NO_3)_3{\cdot}5H_2O$, Dy $(NO_3)_3{\cdot}5H_2O$, isovaleryl chloride, calcium hydroxide, hydrochloric acid, sodium hydroxide, dioxane, methanol, water

2. Synthetic procedure for the ligand, 1-phenyl-2,3-dimethyl-4-isovalerylpyrazolo-5-one (ipy)

The ligand was prepared as described by Jensen [4, 5] and Ehirim *et al* [3]. The process involved the condensation of 1-phenyl-2,3-dimethylpyrazolone-5 with isovaleryl chloride in dioxane, catalyzed by suspended calcium hydroxide.

A weighed mass of 18.82 g (0.10 M) of 1-phenyl-2,3-dimethylpyrazolone-5 was dissolved in 60 ml dioxane with gentle heating in a 500 ml three-necked round bottom "quick fit" flask equipped with a magnetic stirrer, separatory funnel and reflux condenser. Calcium hydroxide (14.8 g, 0.20 M) was added to form paste followed by drop-wise addition of isovaleryl chloride (12.2 ml, 0.10 M) within 1 minute. The temperature of the mixture increased during the first few minutes. The mixture was heated to reflux for 90 minutes. The calcium complex in the flask was decomposed by pouring the mixture into 200 ml of 2 M HCl, which caused cream coloured 1-phenyl-2,3-dimethyl-4-

isovalerylpyrazolone-5 to precipitate. The crude product obtained was suction filtered and recrystallized from methanol-water slightly acidified with hydrochloric acid (80:19:1) to destroy any undecomposed calcium complex, then dried in a desiccator.

3. Synthetic procedure for 1-phenyl-2,3-dimethyl-4-isovalerylpyrazolo-5-one lanthanide complexes of Pr (III) and Dy (III)

The complexes of Pr (III) and Dy (III) with 1-phenyl-2,3-dimethyl-4-isovalerylpyrazolone-5 (HIPz) were prepared by dissolving 1.25 g (3 mmol) of Pr $(NO_3)_3 \cdot 5H_2O$ and 1.32 g (3 mmol) of Dy $(NO_3)_3 \cdot 5H_2O$, respectively, in 10 ml methanol. Each of the Pr (III) and Dy (III) solutions was added drop-wise with stirring to a 30 ml hot ethanol solution of 2.45 g (9 mmol) HiPz, giving a metal-ligand ratio of 1:3. Sodium hydroxide (3 mmol) was added to maintain the pH at 5 ~ 6. In all cases, the mixed solutions were refluxed for 30 minutes and allowed to cool to room temperature. The precipitates formed in each case were suction filtered, recrystallized from 2:1 ethanol–water solution, air-dried, and stored in a desiccator [3, 4, 6].

4. Physicochemical measurements

The melting points of the ligand and the complexes were determined using the simple capillary tube method. The colours were recorded as observed [3, 7].

Conductance measurements were made with a Philips PW 9506 conductivity meter, which was standardized using 0.01 M KCl and the cell with platinum electrodes.

The solubilities of the ligand and the complexes were carried out in various solvents including water, ethanol, acetone, petroleum ether, n-hexane, *etc*.

IR characterization

The infrared (IR) spectral measurements of the ligand and the complexes were obtained in the 4000-400 cm^{-1} on a Shimadzu FTIR-8400S Fourier Transform Infrared Spectrophotometer

Results and discussion

The results of the analyses are presented on Table 1 and Figures 2 – 4.

Table 1: Results of the analyses

Compound	Colour	% Yield	Melting point (°C)	Conductance µS $mol^{-1}cm^{-1}$
iPy	white	85	310	-----
$Pr(iPy)_3.2H_2O$	Gray	80	328	15.5
$Dy(iPy)_3.2H_2O$	Gray	75	320	14.8

Discussion

The conductivity measurements on both the ligands and the metal complexes in acetone (10^{-3} M) gave values lower than 30 Siemens $mol^{-1}cm^{-1}$, showing that they are non-ionic compounds [7]. The lower the conductivity value, the more covalent a compound is. No values were observed for the ligand, indicating its pure covalent nature. The complexes had conductance values of 15.5 µS$mol^{-1}cm^{-1}$ and 14.8 µS$mol^{-1}cm^{-1}$, for the Pr(iPy); and Dr(iPy) respectively.

The melting point determination of the ligand and the complexes show that both complexes have higher values than the ligand. This further confirms the more covalent nature of the ligand as was reported in their conductivity.

The results on the IR of the ligand and its complexes of Pr (III) and Dy (III) are shown on Figures 2 –4

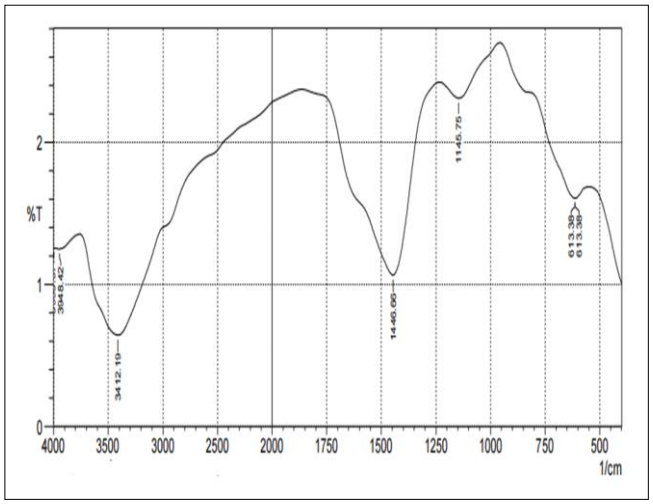

Figure 2: IR spectrum of the ligand, 1-phenyl-2,3-dimethyl-4-isovalerylpyrazolo-5-one

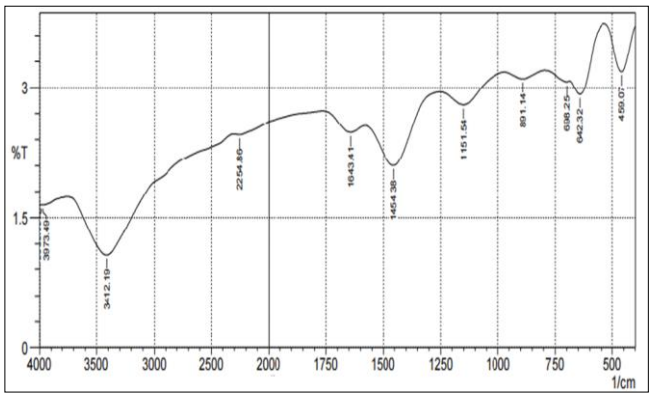

Figure 3: IR spectrum of the Praesodinium 1-phenyl-2,3-dimethyl-4-isovalerylpyrazolo-5-one complex

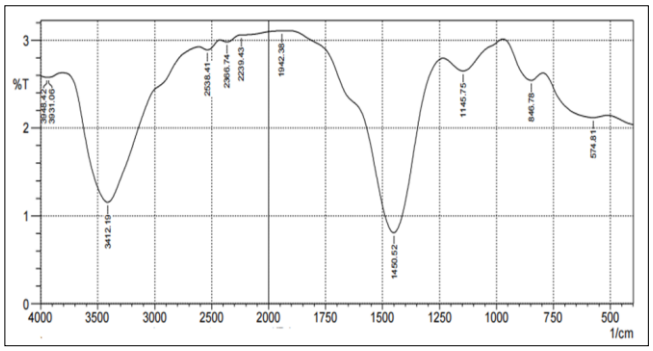

Figure 4: IR spectrum of the dysprosium 1-phenyl-2,3-dimethyl-4-isovalerylpyrazolo-5-one complex

The observed IR frequencies have been assigned by comparison with those of previous reports on 4-acylpyrazolones-5 and their metal complexes. There are more peaks in the metal complexes than in the ligand, as shown by their spectra.

The intense very strong peak at 3412.19 cm^{-1} of the ligand, with intensity of 0.6425 is assigned to the νO-H frequency of the enol form of the ligand [8]. Similar broad bands

centred at 3412.19 cm^{-1} with higher intensities of 1.0705 and 1.1549 for the Pr(III) and Dy(III) complexes respectively, have been assigned to the νOH of the adduct water molecules coordinated to the central metal ion and residing in the crystal lattice of the complexes [9]. The higher intensities could be due to hydrogen bonding between the H atom of the coordinated H_2O molecules and the oxygen atom (O) of the ligand bonded to the Pr and Dy of the complexes.

The broad vibrational frequencies observed at 1446.66, 1450.52 and 1454.38 cm^{-1} for the ligand, Dy and Pr complexes respectively have been assigned to $–CH_3$ bending vibration. These values are present both in the ligands and the complexes.

Both the ligand and the Dy metal complex showed absorption bands at 1145.75 while Pr had 1151.54 cm^{-1} region. This has been assigned to C-H vibrational frequency resulting from bending vibrations in the molecules, and the C-H in-plane deformation of the phenyl ring in the complexes. The comparison of the spectra of the ligands with those of the metal complexes show that there is little or no shift in the above frequencies, indicating that the π-system of the unsubstituted phenyl ring of the free ligand moiety is not involved in the coordination with the metal ions studied [9].

The weak bands in the IR spectra of the metal complexes appearing at 459.07 and 574.81 cm^{-1} present in $Pr(ipy)_3$ and $Dy(ipy)_3$ respectively have been assigned to ν(Pr-O) and ν(Dy-O). Such bands are absent in the IR of the ligand, indicating involvement of the hydroxyl (-OH) in bonding, resulting in the formation of a metal-oxygen bond (M-O) in place of the hydrogen—oxygen bond (H-O) in the ligand anion, i.e., deprotonation of the OH group of the ligand and its replacement by the metals during chelation.

From the results of the analyses, the proposed structures of the metal complexes are as shown in Figures 5, where each of the Pr and Dy exhibited a coordination number of 8 (three moles of the ligand each coordinated in bidentate mode and two moles of H_2O molecules, each in unidentate coordination).

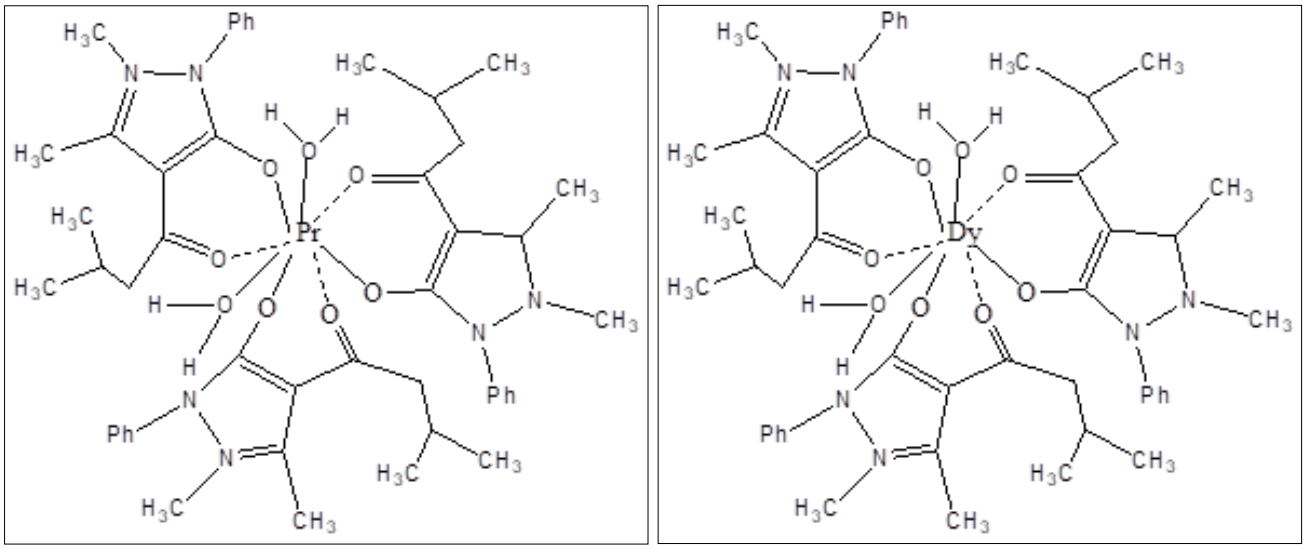

Figure 5: Structures of $[Pr(ipy)_3.2H_2O)]$ and $[Dy(ipy)_3.2H_2O)]$

Conclusion

The analytical data show that the compositions or stoichiometries of the complexes formed between the ligand and the metal ions are in the mole ratios of 1:3 for both Pr(III) and Dy(III), associated with molecules of water of crystallization from aqueous solution. The metal complexes are polar while the ligand is typically covalent.

The coordination or mode of interaction between the metal ions and the ligand is mainly through δ-bond formation between metal ions (M^{n+}) and the oxygen atoms of the carbonyl group (C=O) of the ligand, resulting to chelate formation through C—O—M bond, via deprotonation of the enolic hydrogen (–OH) of the ligand. Such observation has been reported elsewhere

From the foregoings, the ligand, 1-phenyl-2,3-dimethyl-4-isovalerylpyrazol-5-one and its complexes of Praseodymium (III) and Dysprosium(III) have been synthesized and characterized.

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