

Synthesis, spectral, optical and anti-inflammatory activity of complexes derived from 2-aminobenzohydrazide with some rare earths

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Abstract: Three new metal complexes derived from Er(III), Dy(III) and Zr(IV) with 2-aminobenzohydrazide (ABH) were synthesized and characterized by elemental analyses, IR, ¹H-NMR, ES-MS and transmission electron microscopy (TEM). The morphology and the particle size were determined by TEM. The results showed that the ligand acted as neutral bi-dentate coordinating to the metal ions through the carbonyl oxygen and amidic amino nitrogen. The aromatic amine group remained inert towards coordination. The optical band gap was measured and found to be 3.3, 3.5 and 4.3 eV for Er(III), Dy(III) and Zr(IV), respectively. The optical band gap values indicated a semi-conducting nature of the investigated complexes. The anti-inflammatory and analgesic activities of the tested compounds were determined and compared with standard meloxicam.

Keywords: Er(III); Dy(III); Zr(IV); metal complexes; optical band gap; rare earths

Metal complexes of rare earth metals have attracted much more attention because of their wide applications as anti-tumor, anti-bacterial and anti-fungal agents^[1-3]. Also, they are used as catalyst in organic synthesis^[4] and as optical materials^[5].

Hydrazides have increasing applications in medicine, analytical chemistry, syntheses of novel heterogeneous catalysts of oxido-reduction processes, molecular semi-conductors, as well as in numerous fields of science and technology^[6]. Derivatives of anthranilic acid are used as non-steroidal anti-inflammatory drugs (NSAIDs), prescribed for different types of arthritis^[7-9]. The hydrazide moiety not only has anti-inflammatory activity^[10], but also has anti-tuberculosis, anti-tumor, anti-hypertensive and peripheral vasodilator action^[11-14]. The remarkable biological activity of acid hydrazides comes from their ability to bind with the transition metal ions present in the living system^[15,16].

No work has been carried out on the metal complexes of 2-aminobenzohydrazide with lanthanides or zirconium. In this work, we synthesized three new metal complexes of Er(III), Dy(III) and Zr(IV) with 2-aminobenzohydrazide (ABH). The isolated complexes were characterized by different physicochemical techniques. The optical band gaps of the isolated complexes were determined and indicated semi-conducting properties of the isolated complexes. The analgesic and anti-inflammatory activities of the organic ligand and its metal complexes were studied and compared with meloxicam.

1 Experimental

All chemicals were of analytical grade and were used without further purification. Molar conductance measurements of the complexes (10^{-3} mol/L) in DMSO were carried out with a conductivity bridge YSI model 32. Infrared spectra were measured using KBr discs on a Mattson 5000 FTIR spectrometer. Electronic spectra were recorded on a UV2 Unicam UV/vis spectrometer using silica cells. Thermal analysis measurements (TGA) were carried out on a Shimadzu model 50 H instrument. The nitrogen flow rate and heating rate were 20 cm³/min and 10 °C/min, respectively. ¹H-NMR spectra were obtained on a JEOL spectrophotometer at 500 MHz, using TMS as an internal reference and DMSO-d₆ as solvent. TEM images of the products were obtained by a CM20PHILIPS electron microscope.

1.1 Synthesis of metal complexes

The following general procedures were followed in the preparation of the metal complexes: 0.01 mol of DyCl₃·6H₂O, Er(NO₃)₃·5H₂O or ZrCl₄ was added to 0.01 mol of 2-aminobenzohydrazide in 25 mL ethanol. The reaction was refluxed for 4 h in case of Dy(III) and Er(III), while ZrCl₄ was injected and the reaction mixture was refluxed under nitrogen for 6 h. A brown precipitate was isolated in case of Er(III) and Dy(III), while yellow precipitate was formed in case of Zr(IV). The precipitate was filtered under vacuum then, washed with ethanol and

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kept under vacuum. Anal. Calc. for $[\text{Zr}(\text{ABH})_2(\text{OC}_2\text{H}_5)_2]\text{Cl}_2 \cdot 5/2\text{C}_2\text{H}_5\text{OH}$: C, 41.3; H, 6.4; N, 12.5; Zr, 13.6. Found: C, 41.8; H, 5.6; N, 13.0; Zr, 14.50%. Anal. Calc. for $[\text{Er}(\text{ABH})(\text{NO}_3)_3\text{H}_2\text{O}]\text{H}_2\text{O}$: C, 15.5; H, 2.4; N, 15.5. Found: C, 15.7; H, 3.0; N, 16.0% and Anal. Calc. for $[\text{Dy}(\text{ABH})\text{OHCl}_2\text{H}_2\text{O}]\text{H}_2\text{O} \cdot 1/2\text{EtOH}$: C, 21.2; H, 3.3; N, 9.2; Cl, 15.7. Found: C, 21.60; H, 3.3; N, 8.5; Cl, 16.2%.

1.2 Pharmacological studies

More details about the pharmacological and quantitative structure activity relationship (QSAR) studies are presented in literature^[17].

2 Results and discussion

All the isolated complexes are colored, Zr(IV) complex is yellow and stable in air, while Er(III) and Dy(III) complexes are yellowish brown and hygroscopic. All the complexes are soluble in DMF and DMSO. The molar conductivity values of 1×10^{-3} mol in DMF at 25 °C are $75 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$ for Zr(IV) complex and $4.0\text{--}9.0 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$ for Er(III) complex and Dy(III) complex, respectively. These values suggest 1:2 electrolytic nature of Zr(IV) complex and non-electrolytic nature of both Er(III) and Dy(III) complexes^[18].

2.1 IR spectra of ABH and its metal complexes

The most important IR bands of the ligand and its complexes are collected in Table 1.

The ligand ABH shows several bands at 3346, 3326 and 3028 cm^{-1} assigned to νNH_2 of the amide and the ring. The ligand also shows band at 1680 assigned to $\nu \text{C}=\text{O}$ ^[19]. This band has been shifted to the range of $1660\text{--}1666 \text{ cm}^{-1}$ in the spectra of the complexes (Fig. 1), indicating the participation of this group in bonding. The bands assigned to NH_2 of the ring remain approximately in its position in the spectra of the complexes, indicating the inertness of this group towards coordination. The spectrum of Dy(III) complex shows a new band at 1033 cm^{-1} assigned to δOH (free). The band at 1663 cm^{-1} assigned to νCONH in the spectrum of the free ligand is shifted to the region of $1627\text{--}1650 \text{ cm}^{-1}$ in the spectra of the complexes due to the coordination of the carbonyl oxygen. The presence of this band confirms that the ligand chelates the metal ions in the keto form. Several new bands are observed in the spectra of the three complexes in the range of $439\text{--}451$ and $514\text{--}545 \text{ cm}^{-1}$ as-

signed to $\nu \text{M}\text{--}\text{N}$ and $\nu \text{M}\text{--}\text{O}$, respectively^[20].

From the above findings, it could be concluded that, the ligand (ABH) binds to the metal ions in a neutral bi-dentate manner, through amidic nitrogen and carbonyl oxygen (Figs. 2–4).

In case of Zr(IV) complex the ligand may exist either in N–N cis, O–O cis or N–N trans, O–O trans. Since Zr(IV) complex gives negative test with biacetyl, it is suggested that the ligand coordinates in the trans form^[11].

2.2 ¹H-NMR spectrum

The ¹H-NMR spectrum of Zr(IV) complex in DMSO-*d*₆ shows singlet signal in the downfield region at 8.5 ppm, corresponding to the protons of the amidic --NH_2 . The shift of this signal to downfield regions compared with its position in the free ligands (7.21 ppm) indicates that this group coordinates to the metal ion. Another singlet signal has been observed at 10.5 ppm assigned to --NH of the amidic group ($\text{CO}\text{--}\text{NH}\text{--}$). The presence of this signal in the spectra of the complex confirms the coordination of the ligand in the keto form. The spectrum of Zr complex also shows singlet signal at 6.3 ppm assigned to NH_2 of the ring, it remains in its position as the free ligand, confirming the inertness of NH_2 of the ring towards coordination^[11]. The broadening of this signal was attributed to the presence of hydrogen bond between NH_2 and CO groups. The aromatic protons appear as multiplet in the region of 6.48–7.42 ppm.

2.3 ES-MS of Er(III), Dy(III) and Zr(IV) complexes

Mass spectrum of Er(III) complex shows the exact mass at $m/z=541$. Two possible pathways in fragmenta-

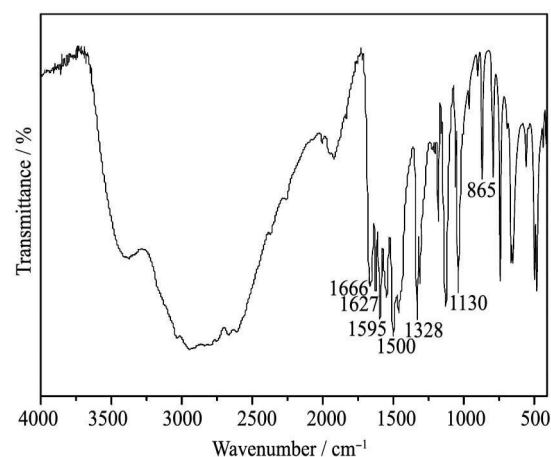


Fig. 1 IR spectrum of Zr(IV) complex

Table 1 IR bands (cm^{-1}) of the ligand (ABH) and its complexes

Compound	$\nu(\text{NH}_2)$	$\nu(\text{C}=\text{O})$	$\nu(\text{CONH})$	$\nu(\text{M}\text{--}\text{O})$	$\nu(\text{M}\text{--}\text{N})$
(ABH)	3444, 3346, 3326, 3028	1680	1663	–	–
$[\text{Er}(\text{ABH})(\text{NO}_3)_3\text{H}_2\text{O}]\text{H}_2\text{O}$	3443, 3345, 3317, 3272	1660	1650	514	477
$[\text{DyC}_7\text{H}_{11}\text{N}_3\text{Cl}_2\text{OH}]\text{H}_2\text{O} \cdot 1/2\text{EtOH}$	3440, 3350, 3305, 3282	1663	1651	527	451
$[\text{Zr}(\text{ABH})_2(\text{OC}_2\text{H}_5)_2]\text{Cl}_2 \cdot 5/2\text{C}_2\text{H}_5\text{OH}$	3379, 3203	1666	1627	558	439

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