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Low temperature X-ray structure analyses combined with NBO studies of a new heteroleptic octa-coordinated Holmium(III) complex with *N,N,N*-tridentate hydrazono-phthalazine-type ligand

Saied M. Soliman [a, b, *], Ayman El-Faham [a, c, *]

[a] Department of Chemistry, Rabigh College of Science and Art, King Abdulaziz University, Saudi Arabia
[b] Department of Chemistry, College of Science, King Saud University, P. O. Box 2455, Riyadh 11451, Saudi Arabia
[c] Department of Chemistry, Faculty of Science, Alexandria University, P.O. Box 426 Ibrahimia, 21321 Alexandria, Egypt

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The new heteroleptic **[HoL(H$_2$O)$_5$]Br$_3$** complex, **L** is hydrazono-phthalazine ligand, is synthesized and its molecular structure aspects were analyzed using single crystal X-ray structure (SCXRD), Hirshfeld (HF) analysis, quantum theory of atoms in molecules (QTAIM) and natural bond orbital (NBO) method. The SCXRD showed that the Ho is octa-coordinated with one *N,N,N*-tridentate ligand **L** and five water molecules. The HF analysis is used to analyze the molecular packing in the **[HoL(H$_2$O)$_5$]Br$_3$**crystal structure. The complex cations are connected via strong O—H···Br and N—H···Br H-bonding interactions which have greater importance than the C—H···Br contacts. Also, all the Ho—N and Ho—O bonds have the characteristics of closed shell interactions using QTAIM. The natural orbitals included in these interactions were analyzed using NBO method. The alpha LP*(8)Ho and beta LP*(4)Ho which have mainly s-orbital characters are the most important anti-bonding natural orbitals included in all Ho-N and Ho—O bonds. The rest of the Ho anti-bonding orbitals which have either p or d-orbital characters shared partially in the Ho-ligands interactions. Natural charges analysis revealed the presence of significant amount of electron density (0.9225–0.9300 e) transferred from the ligands to Ho (2.0700–2.0775 e). Spherical spin density with ~4.0 e is predicted over the Ho atom.

1. Introduction

In recent years, there is increasing interest has been paid to the design and synthesis of lanthanide (Ln) complexes due to their versatile and important applications as optical fiber lasers, electroluminescent displays, and organic light emitting diodes [1–4] as well as for their antibacterial properties [5-8]. Lanthanide ions are considered as hard acids. As a result, these 4f-metal ions have high coordination ability towards O and N-donor ligands making them good candidates for constructing multifunctional complexes with interesting structures and properties [1-4]. Also, the presence of the 4f orbitals in their electronic structure leads to the formation of complexes having high coordination numbers and flexible coordination environments but stricter conditions are needed for the syntheses of their complexes [9,10].

Magnetism is another flourishing application of these complexes as these molecular magnetic materials characterized by the presence of paramagnetic center (Ln-ion). In particular, single molecule magnet (SMM) has been one of the hot topics in this kind of research. Those are called single-ion magnet (SIM) which contain only one single magnetic ion [11–16]. Hence, the SIM is considered the smallest magnet-like molecule. The simpler structure of the SMM complexes compared to the polynuclear ones is another advantage. This structure simplicity allowed us to understand further the relations between the structures and magnetic properties and further to justify their SMM characteristics [13].

In this work, the Schiff base of hydralazine (Scheme 1) as a strong *N,N,N*-tridentate electron donor chelator is used for the synthesis of a new holmium(III) complex. Its low temperature X-ray single crystal structure is determined and discussed with the aid of Hirshfeld (HF) topology analysis of molecular packing. The nature and strength of the Ho-ligands interactions are investigated using quantum theory of atoms in molecules (QTAIM) combined with

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* Corresponding authors. Department of Chemistry, Faculty of Science, Alexandria University, P.O. Box 426 Ibrahimia, 21321 Alexandria, Egypt.

E-mail addresses: Saied1soliman@yahoo.com (S.M. Soliman), aymanel_faham@hotmail.com (A. El-Faham).

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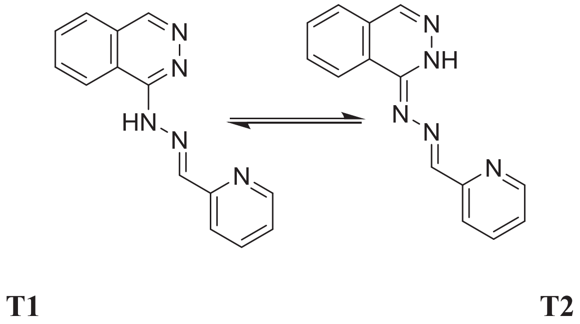

Scheme 1. The possible tautomers of the ligand (**L**).

natural bond orbital (NBO) analysis. Analysis of the spin densities at the metal ion centre and the donor atoms are also discussed.

2. Experimental

2.1. Materials and physical measurements

All chemicals were purchased from Sigma-Aldrich (Sigma-Aldrich Chemie GmbH, 82024 Taufkirchen, Germany) and were used without further purification. Elemental analyses (carbon, hydrogen and nitrogen) were performed on a Perkin-Elmer 2400 elemental analyzer (Perkin Elmer Inc., Waltham, MA USA).

2.2. Synthesis of the phthalazine ligand (L)

The ligand was prepared by following the method described by our research group [17].

2.3. Synthesis of [HoL(H_2O)$_5$]Br_3

At room temperature, a methanolic solution (10 mL) of **L** (0.25 g, 1 mmol) was added to holmium(III) bromide (0.1 mmol, 0.405 g), in 10 mL aqueous solution. The resulting clear solution was left at room temperature for slow evaporation. After four weeks, the mononuclear **[HoL(H_2O)$_5$]Br_3**was formed as yellow crystals. The obtained crystals were found suitable for single crystal X-ray diffraction (SCXRD) measurement.

Yield; **$C_{14}H_{21}Br_3HoN_5O_5$**;67%. Anal. Calc. C, 22.60; H, 2.85; N, 9.41%. Found: C, 22.61; H, 2.86; N, 9.41%.

2.4. SCXRD analysis and structure determination

The crystallographic measurement of the **[HoL(H_2O)$_5$]Br_3** complex is made using a Bruker D8 Quest diffractometer using graphite monochromated Mo-Kα radiation at 115(2) K and a photon detector. SAINT [18] is used for cell refinement and data reduction. SADABS [19] is used for multi-scan absorption correction. All non-hydrogen atoms were localized on difference Fourier maps and refined in subsequent full-matrix least-squares calculations including anisotropic atomic displacement parameters. All calculations were performed using the Bruker APEX III program system. The structure was first solved using SHELXT [20a] and then refined by full-matrix least-squares techniques on F^2 using SHELXL [20b]. The crystallographic data, criteria for the intensity data collection, and some features of the single crystal structure refinements are listed in Table 1. The CIF CCDC **1580323** of the **[HoL(H_2O)$_5$]Br_3** complex can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif by quoting the CCDC number.

Table 1
Crystal data and structure refinement for the studied complex.

Compound	[HoL(H_2O)$_5$]Br_3
Empirical formula	$C_{14}H_{21}Br_3HoN_5O_5$
Formula weight	744.02 g/mol
Temperature	115(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 1 21/c 1
Unit cell dimensions	a = 9.840(4) Å α = 90(4) ° b = 15.815(7) Å β = 100.03(15)° c = 14.399(7) Å γ = 90(3)°
Volume	2206.5(16) Å^3
Z	4
Density (calculated)	2.240 Mg/m^3
Absorption coefficient	9.052 mm^{-1}
F(000)	1408
Crystal size	0.15 × 0.06 × 0.06 mm^3
Theta range for data collection	2.58 to 25.42°
Index ranges	−11 ≤ h<=11, −19 ≤ k<=19, −17 ≤ l<=17
Reflections collected	16190
Independent reflections	4041 [R(int) = 0.0456]
Completeness to theta = 25.42°	99.40%
Refinement method	Full-matrix least-squares onF^2
Data/restraints/parameters	4041/96/282
Goodness-of-fit on F2	1.051
Final R indices [I > 2sigma(I)]	R1 = 0.0384, wR2 = 0.0940
R indices (all data)	R1 = 0.0487, wR2 = 0.0994
Extinction coefficient	0.00112(13)
Largest diff. peak and hole	1.531 and −1.542 e.Å^{-3}

3. Computational details

Single point calculations using different DFT methods were performed using Gaussian 09 (G09) software [21]. CAM-B3LYP [22] and LC-WPBE [23] DFT methods at the unrestricted level were used for this task. The X-ray structure coordinates of the studied Ho(III) complex were taken from the CIF. The calculations were made using 6-31G(d,p) [24] basis sets for all atoms except Ho. For the latter, Stuttgart RSC 1997 ECP [25] is used. The wavefunction files were created using the same level of theory. The topology analysis [26] is performed using QTAIM with the aid of Multwfn program [27]. Moreover, the G09 built in NBO 3.1 [28] program is used for NBO calculations.

4. Hirshfeld surface analysis

Hirshfeld surfaces (HSs) and 2D fingerprint plots (FPs) were

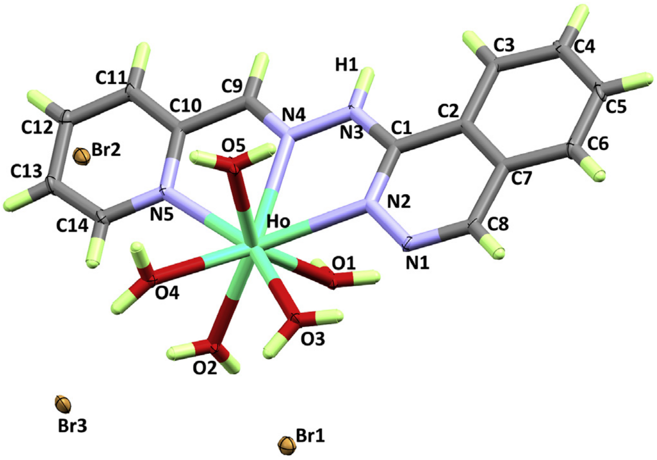

Fig. 1. Thermal ellipsoids at 30% probability of the asymmetric unit and atom numbering scheme of **[HoL(H_2O)$_5$]Br_3**.