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Research paper

Photoluminescent properties of three lanthanide compounds of formulae $LnCl_3$(diphenyl((5-phenyl-4*H*-1λ^4-pyrazol-3-yl)methyl) phosphine oxide)$_2$, Ln = Sm, Eu and Tb: X-ray structural, emission and vibrational spectroscopies, DFT and thermogravimetric studies

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ABSTRACT

The synthesis and properties of a new sensitizing bidentate ligand, diphenyl((5-phenyl-4*H*-1λ^4-pyrazol-3-yl)methyl)phosphine oxide, **2**, capable of demonstrating the emissive properties of lanthanide elements, is described. Two ligands are attached to $LnCl_3$ moieties, Ln = Sm, Eu and Tb, resulting in complexes of formulae $LnCl_3$(**2**)$_2$. These complexes were structurally characterized by single-crystal X-ray crystallography and have geometries that are pentagonal bipyramidal with the two bidentate ligands in a cisoid conformation on the equatorial plane and the three chloride ligands in a *mer*-configuration. The coordination bond distances decrease from Sm to Tb paralleling the decrease in lanthanide ionic radii. The photoluminescent properties of these complexes were examined and, one of them, $TbCl_3$(**2**)$_2$, was assessed a Φ_F of ca. 1.00. DFT calculations were conducted to understand the mechanism of proton transfer in ligand **2** for a hydrogen atom hopping between nitrogen atoms on the pyrazolyl moiety and, to assess aspects of the coordination sphere of the lanthanide complexes.

1. Introduction

We had reported on the utilization of tertiary phosphine oxide ligands in the preparation of catalysts capable of the oxidation of olefins with some of these employing hydrogen peroxide as the oxygen source [1–4]. We also demonstrated the utilization of phosphinate ligands in the synthesis of dimeric [5], trimeric [6–8] and tetrameric [9,10] metal clusters. Phosphine oxide ligands have also been bonded to lanthanide elements for the production of photoluminescent materials. In some of these examples, the phosphine oxide ligand completes the coordination sphere of the lanthanide element and does not absorb radiation; some other separate N-atom based ligand provides this function [11–14]. In others, organic ligands that can absorb light are bonded directly to the phosphine oxide ligand [15]. The absorbance of light leading to an excited state, ^1S, then intersystem crossing (ISC) leading to a triplet excited state, ^3T, followed by energy transfer into one of several excited states of the lanthanide ion followed by the emission of light has been previously described [15]. Difficulties in the syntheses of phosphorus containing ligands pertaining mainly to the air-sensitive nature of the P-atom, may be behind the few studies on visible/emitting phosphine ligands on transition metal complexes [16]. However, as lanthanides are hard Lewis acids [17], perhaps better stability is afforded from binding to an O-atom attached to the P-atom in the desired ligand, i.e., a phosphine oxide ligand.

Nitrogen atom, ring-based molecules such as pyridine [18], phenanthroline [19], phenylpyrazole [20], bipyridine [21], dipicolinates [22], and azaxanthone [23] have been reported to form complexes with lanthanides with interesting photoluminescent properties. Of these *N*-atom based ligands, pyrazoles bonded to palladium [24] and zinc [25] have also displayed luminescent properties. The importance of lanthanide complexes have been reviewed recently as they pertain to the fields of luminescent hybrid materials [26], biolabelling [27], nanoprobes with optical spectroscopy and bioapplications [28], and imaging and sensing [29].

We decided to synthesize a bidentate ligand that would take advantage of the coordinating capabilities of N- and O-donor atom ligands (by combining methyldiphenylphosphine oxide and phenylpyrazole) and the light capturing and transferring capabilities

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of the phenylpyrazole moiety. In this report, we outline the synthesis of this new ligand, 5-phenyl-4*H*-1λ^4-pyrazol-3-yl)methyl)phosphine oxide, illustrate how isomers of this ligand are produced based on the synthetic strategy, and analyze the interconversion of these isomers by theoretical and variable temperature NMR methods. The ligating ability of the ligand is also reported in the form of complexation of the ligand to three lanthanide elements (i.e., Sm, Eu and Tb) and the luminescent properties of these complexes are described.

2. Experimental

2.1. Materials

Chemicals were purchased from Sigma-Aldrich Chemicals and solvents were purified as needed. Elemental analyses were conducted by Galbraith Laboratories, Knoxville, TN. IR spectra were recorded on a PerkinElmer Spectrum One (neat) spectrometer. ^{1}H and ^{31}P NMR data were recorded on a Varian XL-400 spectrometer referenced to $CDCl_3$ or acetone d_6 and 85% H_3PO_4 respectively. The TGA analyses were conducted on a Shimadzu TGA-50 analyzer. Absorbance spectra were obtained using quartz cells in a Perkin Elmer Lambda 35 UV/Vis Spectrometer. Fluorescence spectra were obtained using quartz cells (solution) and glass capillaries (solid) on a Horiba (Jobin Yvon) Fluoromax-4 Spectrofluorometer. A comparative method, involving the use of well characterized samples with known Φ_F values was utilized to assess the Φ_F [30].

3. Synthesis of ligand

3.1. Preparation of $(C_6H_5)_2PO(CH_2COCH_3)$, 1

Methyldiphenylphosphine oxide, 2.824 g. (0.013 mol), was dissolved in 90 ml dried THF and cooled to 0 °C with an ice bath under nitrogen. ^{n}Butyl lithium in hexane, 1.5 M, 9.1 ml (0.014 mol) was added and the solution was cooled to −77 °C with an ethanol/liquid nitrogen bath. 1.5 ml (0.015 mol) of dried ethyl acetate was added dropwise and the solution allowed to warm to room temperature and then stirred for 3 h. The mixture was quenched with saturated ammonium chloride solution, the solvent evaporated and the crude product recrystallized from ethyl acetate. 0.780 g (0.003 mol) of $(C_6H_5)_2PO(CH_2COCH_3)$, **1**, was produced in a 23.2% yield. ^{31}P NMR (CH_2Cl_2): $\delta = 25.70$ ppm. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.30$ (s, 3H, CH_3), $\delta = 3.58$ (d, $J_{HP} = 16$ Hz, 2H, CH_2), $\delta = 7.40–7.80$ (m, 10H, $(C_6H_5)_2$). IR (cm^{-1}): 3316br, 3057w, 2947br, 1707vs (νC=O), 1438m, 1359m, 1223s, 1179vs (νP=O), 1120s, 1102sh, 733s, 692s.

3.2. Preparation of $(C_6H_5)_2PO(C_3H_2N_2\text{-}C_6H_5)$, 2

Compound **1**, 1.292 g (0.005 mol) was dissolved in 50 ml of dried THF under nitrogen and cooled to 0 °C with an ice bath. In a separate flask, 10 ml of 1.5 M ^{n}BuLi in hexane was added to 1.5 ml of diisopropylamine in 25 ml of dry THF under nitrogen and stirred for 20 min. The ^{n}BuLi mixture was then added to the flask containing **1** slowly via a canula and allowed to stir for 30 min. The color of the solution changed from clear to dark red. The solution was cooled to −77 °C with an ethanol/liquid nitrogen bath and 0.625 ml of methyl benzoate added dropwise. The color of the solution turned yellow-red. This solution was allowed to warm to RT and left to stir for 1.75 h. The reaction mixture was then quenched with 5 ml of a saturated ammonium chloride solution. The solution was removed to give a yellowish oil which was then dissolved in 30 ml of ethanol. 1.28 g of (50%–60% in H_2O) hydrazine was added and the solution was allowed to stir overnight. Ligand **2** in the form of a white precipitate, 0.639 g, was obtained by filtration in a 37.5% yield. An ^{1}H NMR spectrum of pure sample at this stage suggested that two isomers with a H atom attached to either of the two N atoms in the pyrazole moiety were produced. ^{1}H NMR of the isomers (400 MHz, CD_3SOCD_3): $\delta = 3.85$ (d, $J_{HP} = 12$ Hz, CH_2), $\delta = 3.95$ (d, $J_{HP} = 12$ Hz, 2H, CH_2), $\delta = 6.10$ (s, 1H, CH_1), $\delta = 6.32$ (s, 1H, CH_1), $\delta = 7.20–7.90$ (m, 15H, $(C_6H_5)_3$ Fig. S1. One isomer could be isolated as it is soluble in acetone. Anal. Calc. for $C_{22}H_{19}N_2OP$: C, 73.73; H, 5.34. Found: C, 73.82; H, 5.44%. ^{31}P NMR (CH_2Cl_2): $\delta = 30.25$ ppm; ($CDCl_3$): $\delta = 30.70$ ppm; (THF): $\delta = 28.65$ ppm. ^{1}H NMR of a pure sample (400 MHz, $CDCl_3$): $\delta = 3.74$ (d, $J_{HP} = 12$ Hz, 2H, CH_2), $\delta = 6.36$ (s, 1H, CH_1), $\delta = 7.20–7.90$ (m, 15H, $(C_6H_5)_3$), Fig. S2. IR (cm^{-1}): 3184–2892 multiple small ridges, 1573sh, 1564m, 1463s, 1436s, 1234m, 1170vs (νP=O), 1118s, 1103s, 1069m, 1027m, 998m, 955s, 917m, 837s, 806m, 791m, 766s, 747m, 731m, 695s, 684vs.

3.3. Preparation of $SmCl_3[(C_6H_5)_2PO(C_3H_2N_2\text{-}C_6H_5)]_2$, 3

0.025 g (0.069 mmol) of $SmCl_3{\cdot}6H_2O$ was dissolved in 2.5 ml of THF and added to 0.047 g (0.131 mmol) of **2** which was dissolved in 10 ml of boiling THF in a 50 ml Erlenmeyer flask exposed to the atmosphere. The solution went from cloudy to clear at which stage heating was turned off and the mixture allowed to stir overnight. A white precipitate formed which was obtained by filtration resulting in 0.037 g (0.033 mmol) of **3**, 48.3% yield. The crude product was dissolved in methylene chloride, precipitated by the addition of hexanes, obtained by filtration and dried. Anal. Calc. for $C_{44}H_{38}N_4O_2P_2Cl_3Sm{\cdot}0.3CH_2Cl_2$: C, 53.26; H, 3.89. Found: C, 53.29; H, 3.89%. IR (cm^{-1}): 3220br, 3058br, 2957br, 1589m, 1565m, 1489s, 1470s, 1431vs, 1397m, 1301m, 1263m, 1154vs, 1121vs, 1092vs, 1068s, 1011vs, 959m, 907br, 849s, 753s, 719s, 686vs.

3.4. Preparation of $EuCl_3[(C_6H_5)_2PO(C_3H_2N_2\text{-}C_6H_5)]_2$, 4

This complex was prepared in a similar manner to that for complex **3** from 0.049 g (0.137 mmol) of **2** with 0.025 g (0.068 mmol) of $EuCl_3{\cdot}6H_2O$) and resulted in 0.057 g (0.051 mmol) of **4**, 74.6% yield. The crude produce was dissolved in methylene chloride, precipitated by the addition of hexanes, obtained by filtration and dried. Anal. Calc. for $C_{44}H_{38}N_4O_2P_2Cl_3Eu{\cdot}0.3CH_2Cl_2$: C, 53.18; H, 3.90. Found: C, 53.34; H, 3.90%. IR (cm^{-1}): 3224br, 3055m, 2951m, 2869m, 1585sh, 1563s, 1497s, 1459s, 1431vs, 1387m, 1299m, 1271m, 1145vs, 1123vs, 1112vs, 1090vs, 1062m, 1013vs, 959m, 905br, 838s, 748m, 715s, 688vs.

3.5. Preparation of $TbCl_3[(C_6H_5)_2PO(C_3H_2N_2\text{-}C_6H_5)]_2$, 5

This complex was prepared in a similar manner to that for complex **3** from 0.048 g (0.134 mmol) of **2** with 0.025 g (0.067 mmol) of $TbCl_3{\cdot}6H_2O$) and resulted in 0.041 g (0.036 mmol) of **4**, 54.36% yield. The crude produce was dissolved in methylene chloride precipitated by the addition of hexanes, obtained by filtration and dried. Anal. Calc. for $C_{44}H_{38}N_4O_2P_2Cl_3Tb{\cdot}0.3CH_2Cl_2$: C, 52.81; H, 3.86. Found: C, 52.66; H, 4.00%. IR (cm^{-1}): 3230br, 3054br, 2963br, 2901bmp, 2867br, 1591s, 1562s, 1490vs, 1461s, 1434vs, 1388br, 1316sh, 1297m, 1268m, 1149vs, 1120vs, 1091s, 1076s, 1014vs, 962m, 915m, 843s, 795sh, 751s, 727s, 689vs.

3.6. X-ray crystallography

X-ray quality crystals for compound **3** were obtained by diffusion of hexanes into a THF solution of **3** and those for **4** and **5** were obtained by the slow diffusion of hexanes into methylene chloride solutions of compounds **3**–**5**. Diffraction data for all compounds were collected using a Bruker AXS SMART APEX CCD diffractometer