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Transition metal complexes containing a ditopic redox active ligand featuring very intense visible absorption bands

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ABSTRACT

The preparation and structural properties of a new ditopic redox active arylazo ligand 10-[6-(10-hydroxy-9-phenanthrylazo)-4-pyrimidinylazo]-9-phenanthrol is described along with the electronic and magnetic properties of nickel(2+) and manganese(2+) complexes containing this ligand. Spectroscopic and structural data support the formation of tetranuclear grid-type [2 × 2] complexes for the transition metal complexes, which would mark the first examples of such complexes with redox active arylazo ligands; however, one dimensional coordination polymers are another possible structural interpretation. In any case, the electronic spectrum of each complex exhibits extremely intense visible absorption bands, which are particularly strong in the nickel complex. These lower energy absorptions result from transitions between frontier molecular orbitals that are nearly completely ligand in character as suggested by density functional theory calculations. The nickel complex features rich cathodic electrochemical behavior resulting from the reduction of the multiple azo groups present in this material.

1. Introduction

Light harvesting materials have garnered much recent attention with the recent wide ranging interest in dye-sensitized solar cells for energy conversion and other opto-electronic materials [1]. The development of new dye materials is at the forefront of research efforts in this regard as well as for the production of novel materials with interesting optical properties [2]. We are interested in the synthesis of polynuclear transition metal or lanthanide ion complexes featuring ligands that impart interesting electronic, magnetic or optical properties. Recently we have been investigating the electronic properties of transition metal complexes bound to redox active azo aromatic ligands, including the anion of 1-(2-pyridylazo)-2-phenanthrol (PAPL **1**, Fig. 1) [3]. Complexes containing PAPL can be reversibly reduced by two or more electrons and feature very intense visible absorption bands resulting from ligand centered electronic transitions. One outstanding synthetic challenge is to prepare polynuclear redox-active ligand complexes. Grid-type [2 × 2] complexes are an attractive structural motif in this regard and have been reported with a wide variety of non-redox active ligands [4]. We envisioned expansion of the PAPL ligand framework using a 1,3-pyrimidine spacer substituted in the 4 and 6 ring positions should produce a ditopic ligand with the ability to coordinate multiple metal ions to generate [2 × 2] grid-type complexes, which we anticipated would offer very interesting electro-optical properties. Another feature offered by grid complexes containing redox active ligands is the potential ability to produce ligand centered free radicals by oxidation or reduction of the coordinated ligands in the complexes. This injection of unpaired spin density into the ligand can, under appropriate conditions of magnetic orbital symmetry, lead to the production of polynuclear metal-radical complexes with strong metal-radical magnetic exchange interactions and well isolated high-spin ground states [6,7]. In this regard, new variants of single molecule magnet materials are promising targets provided the metal ions feature the required axial magnetoanisotropy [8]. Other possibilities may exist for the observation of thermally reversible intramolecular electron transfer between electron rich transition metals and coordinated redox active ligands with low lying empty orbitals susceptible to reduction. Herein we describe the synthesis and structural properties of a new ditopic redox active ligand (**2**) as well as the preparation, electrochemical, optical and magnetic properties of Ni (**3**) or Mn (**4**) complexes containing **2**. Based on spectroscopic data, complexes **3**

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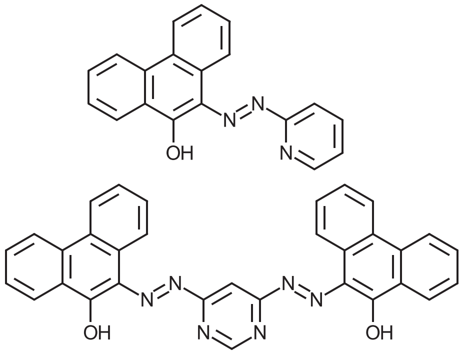

Fig. 1. Structures of PAPL (**1**, top) and ditopic (**2**) reported in this work.

and **4** may be interpreted as [2 × 2] grid complexes, or one-dimensional coordination polymers.

2. Materials and methods

2.1. General procedures

All reagents were commercially available and used as received unless otherwise stated. Anhydrous solvents were obtained from a Puresolve PS MD-4 solvent purification system. FT-IR spectra were recorded on a Shimadzu IRAffinity spectrometer as KBr discs. UV–Vis measurements were recorded on a Shimadzu 3600 UV–Vis–NIR spectrophotometer in DMF solution using infrasil cuvette cells. Elemental analyses were carried out by Canadian Microanalytical Services, LTD., Delta, BC, Canada. MALDI-TOF mass spectra were run on a Bruker Autoflex II TOF/TOF in DMF solution using an HCCA matrix. LC-MS experiments were recorded on an Agilent 1260 Infinity liquid chromatograph/6530 accurate mass Q-TOF in high resolution mode in 70:30 acetonitrile/water using positive mode electrospray ionization (HPLC grade solvents). Cyclic voltammetry (CV) experiments were performed with a Bio-analytical Systems Inc. (BASI) Epsilon electrochemical workstation. Compound **2** and **3** were dissolved in anhydrous solvent (DMF), and then deaerated by sparging with N_2 gas for 10 min. Solution concentrations were approximately 10^{-3} M in analyte containing 0.1 M supporting electrolyte (Bu_4NPF_6). A typical three-electrode set-up was used including a platinum working electrode, Ag/AgCl reference electrode, and a platinum wire auxiliary electrode. The scan rate for all CV experiments was 100 mV/s, unless noted otherwise. Variable temperature magnetic susceptibility measurements for **3** and **4** were recorded on an MPMS SQUID magnetometer at an external magnetic field of 2000 Oe over a temperature range of 2–300 K. Samples were weighed into gel caps and diamagnetic contributions were calculated using Pascal's constants.

2.2. Computational details

All calculations were carried out using the suite of programs included in the Turbomole 6.5 package [9–11]. The geometry optimization of $[Zn_4(\mathbf{2}^{2-})_4]$ was performed at the def2-SVP [12,13] level of theory using the BP86 functional [14–16] with the Resolution-of-the-Identity (RI) approximation switched on [17–21]. The calculated geometry was checked to ensure that it was a minimum on the potential energy surface (no negative frequencies). Qualitative single point calculations and TD-DFT calculations were carried out using the coordinates of the optimized geometry at the def2-SVP level of theory using the B3LYP functional. Tight self-consistent field convergence criteria was used for the optimization calculation. Single point and TD-DFT calculations were carried out with looser self-consistent field convergence criteria.

2.3. Synthesis

10-[6-(10-hydroxy-9-phenanthrylazo)-4-pyrimidinylazo]-9-phenanthrol 2. 9,10-phenanthrenequinone (0.80 g, 3.8 mmol) was slurried with glacial acetic acid (100 mL) and heated until dissolution was noted. A solution of 4,6-dihydrazinyl-1,3-pyrimidine (0.28 g, 2.0 mmol) in glacial acetic acid (10 mL) was added by pipet resulting in a clear orange solution. Precipitation of a bright orange solid was noted and the mixture was heated to reflux (140 °C) for 24 h. The bright orange precipitate was isolated by vacuum filtration and washed with glacial acetic acid and water. Yield, 0.21 g (21%). Anal., calc'd for (found) $C_{32}H_{20}N_6O_2{\cdot}0.5CH_3CO_2H$, C, 72.17 (72.20); H, 4.01 (3.95); N, 15.35% (15.29). FT-IR (KBr, cm^{-1}): 3066 (w), 1747 (w), 1700 (w), 1593 (m), 1558 (w), 1497 (s), 1473 (m), 1448 (m), 1440 (m), 1363 (w), 1327 (w), 1280 (w), 1192 (w), 1142 (m), 1124 (w), 1061 (w), 1020 (s), 947 (m), 852 (w), 754 (w), 721 (w). UV–vis (DMF): λ_{max} nm (ε M^{-1} cm^{-1}): 397 (4×10^3), 479 (8×10^3), 566 (2×10^3).

3 and 4. 2 (72 mg, 0.14 mmol) was slurried in DMF (10 mL) and 7 drops of triethylamine were added and the mixture was gently heated. $M(ClO_4)_2{\cdot}6H_2O$ (M = Ni or Mn) (56 mg, 0.15 mmol) was added resulting in a deep royal blue color. The solution was stirred warm for about 15 min and then water was added (20 mL) and the microcrystalline precipitates were isolated by vacuum filtration and washed with water. Yield 70–80 mg (80–85%). (**3**) Anal. calc'd for (found) $Ni_4C_{128}H_{72}N_{24}O_8{\cdot}7.2H_2O$: C, 63.04 (62.62); H, 3.57 (3.14); N, 13.78 (13.68); Cl, 0.00% (<0.03%). MALDI-TOF (HCCA matrix): *m/z* 2309 (MH^+). FT-IR (KBr, cm^{-1}): 3064 (w), 1606 (m), 1585 (m), 1541 (w), 1497 (m), 1448 (w), 1435 (w), 1382 (m), 1363 (m), 1294 (m), 1263 (m), 1232 (m), 1196 (s), 1138 (s), 1066 (s), 1033 (s), 970 (w), 908 (w), 756 (w), 723 (w), 624 (w). UV–vis (DMF): λ_{max} nm (ε M^{-1} cm^{-1}): 612 (2.6×10^5), 660 (3.0×10^5). (**4**) Anal. calc'd for (found) $Mn_4C_{128}H_{72}N_{24}O_8{\cdot}2.4H_2O$: C, 65.81 (65.69); H, 3.31 (3.12); N, 14.39 (14.20); Cl, 0.00% (<0.03%). MALDI-TOF (HCCA matrix): *m/z* 2294 (MH^+). FT-IR (KBr, cm^{-1}): 3065 (w), 1603 (m), 1585 (m), 1541 (w), 1497 (m), 1448 (w), 1430 (w), 1375 (m), 1338 (w), 1292 (m), 1265 (m), 1231 (m), 1198 (s), 1132 (s), 1063 (s), 1036 (s), 968 (w), 905(w), 756 (w), 723 (w), 619 (w). UV–vis (DMF): λ_{max} nm (ε M^{-1} cm^{-1}): 636 (1.8×10^5), 660 sh (1.7×10^5).

3. Results and discussion

3.1. Synthesis and structural properties

The ligand PAPL **1** is readily prepared in one step as described earlier (Scheme 1) [4,5]. Ditopic derivative **2** is prepared in two steps, with the final step including reaction of 4,6-dihydrazinyl-1,3-pyrimidine (produced by reaction of 4,6-dichloro-1,3-pyrimidine with excess hydrazine hydrate) with a slight stoichiometric deficit of 9,10-phenanthrenequinone in refluxing glacial acetic acid. We have observed that the outcome of this reaction is very sensitive to concentration and temperature. Only under relatively dilute conditions at 140 °C do we isolate pure **2** as a bright orange precipitate, and only in about 20–25% yield. Under all the other reaction conditions we attempted, rather than isolating **2**, an orange-yellow precipitate is obtained, which results from the condensation of one equivalent each of 9,10-phenanthrenequinone and the solvent, glacial acetic acid, with 4,6-dihydrazinyl-1,3-pyrimidine. The structural assignment of this unwanted reaction side product has been confirmed using high resolution electrospray mass spectrometry [22]. Unfortunately, once obtained we observed that **2** is