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Synthesis, crystal structures, and characterization of 4,5-diaza-9-[4,5-bis(methylthio)-1,3-dithiol-2-ylidene]-fluorene (L) metal complexes $[(TPyA)M^{II}(L)](SbF_6)_2$ (M^{II} = Mn, Fe, Co; TPyA = tris(2-pyridylmethyl)amine)

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ABSTRACT

Transition metal complexes incorporating 9′-(4,5-dimethyl-1,3-dithiol-2-ylidene)-4′,5′-diazafluorene (**L**) have been synthesized and single crystal structures of $[(TPyA)Mn^{II}(\mathbf{L})](SbF_6)_2$ (**1**), $[(TPyA)Fe^{II}(\mathbf{L})](SbF_6)_2$ (**2**), and $[(TPyA)Co^{II}(\mathbf{L})](SbF_6)_2$ (**3**) (where TPyA = tris(2-pyridylmethyl)amine) have been characterized. In addition, spectroscopic analysis (IR and UV–Vis) and temperature dependent magnetic susceptibility measurements are reported for all new complexes. Compounds **1**–**3** are isostructural. Solid-state IR and solution UV–Vis spectra in dichloromethane (CH_2Cl_2) are consistent with other metal complexes with the ligand **L** bound to the metal. However, when complexes **1**–**3** are dissolved in acetone and acetonitrile the ligand **L** is labile enough to result in a complex with C_3H_6O or MeCN in the coordination sphere, respectively. This suggests **L** is more substitutionally labile than C_3H_6O and MeCN. Magnetic analyses of **1**–**3** revealed weak ferromagnetic interactions for **1** and **3** and weak antiferromagnetic interactions for **2**. These new molecular synthons may have further applications in the synthesis of new heterobimetallic dinuclear complexes by removal of the methyl group from the dithiolate-end of the ligand **L** that is unbound to a metal ion at this point.

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1. Introduction

The quest for multifunctional molecule-based materials, materials constructed from molecular precursors that exhibit multiple chemical/physical properties, has been at the forefront of various studies over the past decade [1]. Specifically, materials that display unique and/or novel combinations of optical, electronic, and/or magnetic properties have been sought. Transition metal complexes containing pyridine-type ligands (bipyridine and phenanthroline) are of interest due to the σ-donating and π-accepting nature of these ligand types [2]. Additionally, the use of thiolate-based transition metal complexes has been extensively studied over the past half century due their functionality as conducting and magnetic materials [3]. More recently, interest in the use of 9′-(4,5-disubstituted-1,3-dithiol-2-ylidene)-4′,5′-diazafluorene as a ditopic bridging ligand to bind one or more transition metal ions has increased. This is due to these ligands containing both a N-donating bipyridine-type end and S-donating dithiolate-type end binding motifs [4]. The ditopic nature of these ligands (see Scheme 1) allows potential selective binding of two different metal ions, each with their own set of chemical/physical properties (i.e. optical, magnetic). In addition to the selective binding, these ditopic bridging ligands themselves bring along potential properties like luminescence and/or conductivity that may have potential applications in molecule-based electronics. Towards this end, we now report the synthesis, crystal structures, spectroscopic characterization and magnetic analyses of three new 9′-(4,5-dimethyl-1,3-dithiol-2-ylidene)-4′,5′-diazafluorene (**L**) 1st row transition metal complexes: $[(TPyA)Mn^{II}(\mathbf{L})](SbF_6)_2$ (**1**), $[(TPyA)Fe^{II}(\mathbf{L})](SbF_6)_2$ (**2**), and $[(TPyA)Co^{II}(\mathbf{L})](SbF_6)_2$ (**3**). These new complexes may prove to be potential molecular building blocks towards the design and synthesis of new multifunctional molecule-based materials that incorporate the optical/magnetic properties of the metal ions with the potential

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luminescence and/or conductivity properties of the ditopic bridging ligand **L**.

2. Experimental

2.1. General procedures and materials

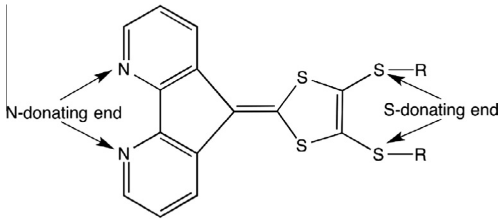
All manipulations were carried out under dry N_2 atmosphere (<1 ppm O_2) using Schlenk techniques or in an inert atmosphere dry-box. The ligand 4,5-diaza-9-[4,5-bis(methylthio)-1,3-dithiol-2-ylidene]-fluorene (**L**) [5], $[\mathrm{Mn^{II}(NCMe)_6}](\mathrm{SbF_6})_2$ [6], $[\mathrm{Fe^{II}(NCMe)_6}](\mathrm{SbF_6})_2$ [6b,c], and $[\mathrm{Co^{II}(NCMe)_6}](\mathrm{SbF_6})_2$ [6b,c] were prepared via published routes. Tris(2-pyridylmethyl)amine (**TPyA**) was purchased from Aldrich and used as received. Acetone was purchased from Fisher Scientific and deoxygenated via sparging with dry N_2 for a minimum of 2 h. Anhydrous diethyl ether (Et_2O), acetonitrile (MeCN), and dichloromethane (CH_2Cl_2) (packed under N_2 gas) were purchased from Aldrich and used as received.

2.2. Physical methods

Infrared spectra were recorded from 400 to 4000 cm^{-1} on a Bruker EQUINOX 55 infrared spectrophotometer (±2 cm^{-1}) as KBr pellets. Electronic absorption spectra were measured from 200 to 800 nm and reported from 250 to 600 nm on an Ocean Optics USB4000 spectrophotometer. Both dichloromethane (CH_2Cl_2) and acetone solutions of the complexes **1**–**3** were loaded in an inert atmosphere glove-box in 1.00 cm quartz cuvettes equipped with a Teflon stopper to protect the solutions from exposure to ambient atmospheric conditions during analysis. Magnetic susceptibility measurements were measured as previously described [7] in a 1000 Oe applied field (H) between 5 and 300 K on a Quantum Design (QD) 5T MPMS superconducting quantum interference device (SQUID) equipped with a reciprocating sample measurement system, low field option, and continuous low temperature control with enhanced thermometry features. Measurements were made on crystalline materials loaded in gelatin capsules and the data were corrected for core diamagnetic corrections of -520, -519, and -518×10^{-6} emu/mol that were calculated from Pascal's constants for complexes **1**, **2**, and **3**, respectively [8].

2.3. Synthesis of $[(\mathrm{TPyA})\mathrm{M^{II}}(\mathbf{L})](\mathrm{SbF_6})_2$ complexes **1**–**3**

For each reaction, 0.096 g (1.2×10^{-4} mol) of $[\mathrm{M^{II}(NCMe)_6}](\mathrm{SbF_6})_2$ (M = Mn, Fe, or Co) were dissolved in approximately 5 mL of acetone resulting in colorless solutions for both Mn and Fe, but a pink solution for Co. Next, 0.036 g (1.2×10^{-4} mol) of **TPyA** dissolved in minimal amounts of acetone were quantitatively transferred to each stirring solution of $[\mathrm{M^{II}(NCMe)_6}](\mathrm{SbF_6})_2$ resulting in homogenous solutions of $[\mathrm{M^{II}(NCMe)_6}](\mathrm{SbF_6})_2$ and **TPyA** (colorless for Mn, light yellow for Fe, and violet for Co). Finally, 0.044 g (1.2×10^{-4} mol) of **L** partially dissolved in 20 mL of acetone (yellow suspension) were transferred to stirring solutions of $[\mathrm{M^{II}(NCMe)_6}](\mathrm{SbF_6})_2$ and **TPyA** resulting in homogeneous yellow and orange solutions for Mn and Fe, respectively; where as a heterogeneous orange solution (fine suspension) was obtained for Co. Enough acetone was added to each reaction to bring the total volumes of these solutions to approximately 50 mL. The Mn reaction solution was stirred for 1 h at room temperature, filtered, and taken to dryness under vacuum yielding an orange film. The Fe and Co reaction solutions were taken out of the glove box, attached to the Schlenk line, and allowed to reflux for approximately 3 h with a water-cooled condenser. After refluxing, these solutions were allowed to cool, taken inside the glove box, filtered, and concentrated to dryness under vacuum both resulting in uniform orange films. All three films of the products were re-dissolved in minimal amounts of acetone (~3–4 mL) and gravity filtered into 20 mL scintillation vials. These vials were then placed inside vapor jars containing Et_2O in the dry-box. After 2 days, yellow crystals of **1**, orange crystals of **2**, and dark orange crystals of **3** suitable for single crystal X-ray analyses were formed. Yield and IR spectral data of **1**–**3** are summarized below.



Scheme 1. Structure of L (R = Me) depicting the ditopic nature the ligand.

$[(\mathrm{TPyA})\mathrm{Mn^{II}}(\mathbf{L})](\mathrm{SbF_6})_2$, **1**. Yield: 72%. IR (KBr); ν, cm^{-1}: 3095 (vw), 3080 (vw), 2928 (w), 2907 (vw), 1609 (s), 1583 (w), 1576 (m), 1534 (s), 1474 (s), 1445 (m), 1421 (m), 1407 (m), 1400 (vw), 1376 (vw), 1355 (w), 1329 (vw), 1314 (w), 1299 (w), 1268 (vw), 1235 (m), 1180 (m), 1160 (m), 1116 (w), 1101 (w), 1056 (w), 1032 (vw), 1020 (m), 999 (w), 978 (w), 969 (w), 909 (w), 887 (vw), 870 (m), 835 (vw), 813 (m), 794 (vw), 765 (s), 744 (m), 673 (vw), 660 (vs), 582 (vw), 572 (vw), 543 (vw), 528 (vw), 516 (vw), 499 (w), 483 (m), 474 (vw), 459 (vw), 444 (m), 420 (w), 410 (w).

$[(\mathrm{TPyA})\mathrm{Fe^{II}}(\mathbf{L})](\mathrm{SbF_6})_2$, **2**. Yield: 80%. IR (KBr); ν, cm^{-1}: 3095 (vw), 3078 (vw), 2927 (w), 2904 (vw), 1609 (s), 1576 (s), 1533 (vs), 1472 (vs), 1445 (m), 1421 (m), 1405 (w), 1399 (m), 1375 (w), 1354 (m), 1325 (vw), 1306 (vw), 1296 (w), 1270 (vw), 1234 (m), 1179 (m), 1159 (m), 1123 (vw), 1116 (vw), 1102 (m), 1090 (vw), 1056 (w), 1022 (m), 996 (w), 977 (vw), 968 (w), 957 (vw), 909 (w), 890 (vw), 869 (s), 834 (vw), 811 (s), 793 (vw), 764 (s), 754 (vw), 742 (s), 727 (vw), 660 (vs), 576 (vw), 518 (vw), 497 (vw), 482 (w), 473 (vw), 458 (vw), 449 (w), 443 (vw), 423 (vw), 419 (w), 411 (w).

$[(\mathrm{TPyA})\mathrm{Co^{II}}(\mathbf{L})](\mathrm{SbF_6})_2$, **3**. Yield: 85%. IR (KBr); ν, cm^{-1}: 3095 (vw), 3080 (vw), 2927 (w), 2909 (vw), 1610 (s), 1577 (m), 1532 (s), 1488 (vw), 1471 (s), 1445 (m), 1423 (m), 1399, (m), 1375 (w), 1356 (m), 1325 (vw), 1307 (w), 1295 (vw), 1267 (vw), 1234 (m), 1178 (m), 1159 (m), 1117 (vw), 1102 (m), 1091 (vw), 1055 (m), 1023 (m), 995 (w), 977 (vw), 968 (w), 958 (vw), 906 (w), 890 (vw), 870 (m), 837 (vw), 810 (m), 793 (vw), 766 (s), 755 (vw), 743 (m), 672 (m), 660 (vs), 519 (vw), 500 (vw), 483 (w), 449 (vw), 443 (w), 427 (vw), 415 (w).

2.4. X-ray structure determination

Single crystals of **1**–**3** were covered by paratone-n® oil in ambient conditions and attached to the tip of a MiTeGen MicroMount© and mounted in a stream of cold nitrogen at 100(2) K and centered in the X-ray beam using a video camera. All crystals were protected under the mother liquor until selected. Crystal evaluation and data collection were performed on a Bruker Quazar SMART APEXII diffractometer with Mo Kα radiation (λ = 0.71073 Å) and a crystal to diffractometer distance of 4.96 cm. Initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 12 frames collected at intervals of 0.5° in a 6° range about ω with exposure times of 3 s/frame for **1** and **3** and 10 s/frame for **2**. Reflections were successfully indexed by an automated indexing routine built in the APEXII program suite. Final cell constants were calculated from a set of 9487 (**1**), 9375 (**2**), and 9922 (**3**) strong reflections from the actual data collection, respectively. Data were collected using the full sphere data collection routine to survey the reciprocal space to the extent of