Polyhedron 52 (2013) 1118-1125

Contents lists available at SciVerse ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Synthesis and coordination chemistry of a potential precursor to a triarylamminium radical cation ditopic ligand

Kseniya Revunova^a, Serge I. Gorelsky^b, Martin T. Lemaire^{a,*}

^a Department of Chemistry, Brock University, 500 Glenridge Avenue, St. Catharines, Ontario, Canada L2S 3A1 ^b Center for Catalysis Research and Innovation, Department of Chemistry, University of Ottawa, Ottawa, Ontario, Canada K1N 6N5

ARTICLE INFO

Article history: Available online 3 July 2012

We dedicate this manuscript to the centennial anniversary of Alfred Werner's Nobel Prize in Chemistry.

Keywords: Triarylamine ligands Coordination chemistry Bimetallic complexes Magnetic properties Electrochemistry DFT calculations

ABSTRACT

The multi-step synthesis of a new ditopic ligand (7) is reported, which is a potential precursor to a triarylamminium radical cation. The preparation and full characterization of three new bimetallic first row transition metal [M = Mn(8), Ni(9), Cu(10)] coordination complexes containing this ligand are described, including detailed electrochemical and magnetic studies. Of note, a ground triplet state is observed in the bimetallic Cu complex. Chemical oxidation of these precursor complexes generated persistent complexes containing the dication of the ligand, which is confirmed through UV–Vis and EPR spectroscopies. The variable temperature magnetic properties of the dicationic complexes are described and included in the discussion are results from density functional theory calculations of bimetallic radical cation complexes.

© 2012 Published by Elsevier Ltd.

1. Introduction

Spin control in molecular systems has been a topic of enormous interest in the areas of physical organic and coordination chemistry for over 25 years [1–5]. Finding ways to promote ferromagnetic interactions between electrons to align their spin properties to produce structures with a high spin ground state is a very active area of research in modern inorganic chemistry. The applied benefits that arise from isolating high spin molecules are well known and include new single molecule magnets [6–8], magnetic refrigerants [9,10] and paramagnetic contrast agents [11], to name a few.

The metal-radical approach is one synthetic strategy that has been applied toward the preparation of coordination complexes with large *S* values in their ground states [12,13]. This tactic requires the use of stable free radicals as ligands and takes advantage of a strong direct magnetic exchange coupling that is generated by coordination of spin density rich donor atoms to paramagnetic transition metal ions. As another advantage, the sign of the metal-radical magnetic exchange coupling can often be predicted in metal-radical complexes on the basis of the Goodenough–Kanamori orbital symmetry rules [14,15]. Stable radicals that have been used as ligands include nitroxides [16], nitronyl and imino nitroxides [17], verdazyls [18], thiazyls [19], and semiquinone [20] or other N-centered radical anions [21]. In fact, Long and Evans' recent report [22] of single molecule magnet behavior in Dy dimers containing N_2^{3-} radical anion bridging ligands underscores the importance of strong intramolecular exchange coupling in efforts to increase blocking temperatures in molecular nanomagnets.

A large number of metal-radical complexes have been reported, but these tend to contain one maybe two metal ions at best. There are very few reports of metal-radical complexes with more than two metal ions, and many of these have been produced serendipitously (here we refer to discrete molecules; there are a large number of reported one-, two- and three-dimensional metal-radical coordination polymers). We [23] and others [24,25] have been interested in the use triarylamminium radical cations as ligands for transition metal ions. Ultimately, we are interested in the synthesis of large dendritic-type polytriarylamino precursor ligands for the production of polymetallic complexes. Chemical oxidation of these precursor complexes is anticipated to produce metalradical complexes with interesting magnetic properties. Recently we reported the synthesis of 5-(4,4'-dimethoxydiphenylamino)-2,2'-bipyridine (Fig. 1, left) and M(hfac)₂ complexes (M = Mn, Ni, Cu) containing this ligand [23]. Chemical or electrochemical oxidation of these precursor complexes produced metal-triarylamminium radical cation complexes and in the case of M = Mn, we observed ferromagnetic metal-radical exchange coupling. We could rationalize the magnetic properties of these complexes on the basis of a π -spin polarization mechanism for exchange coupling (supported by density functional theory (DFT) calculations).





^{*} Corresponding author. Tel.: +1 905 688 5550x3400; fax: +1 905 682 9020. *E-mail address:* mlemaire@brocku.ca (M.T. Lemaire).



Fig. 1. Ligand reported in [23] (11) and ditopic ligand (7) described in the current work.

In an effort to extend this work to produce bimetallic complexes, herein we describe the synthesis of ditopic ligand **7**. Bimetallic $M(hfac)_2$ complexes ($M = Mn \ 8$, Ni **9**, Cu **10**) containing **7** were prepared and fully characterized, including variable temperature magnetometry experiments, which identified a triplet ground state for **10**. These bimetallic precursors are subject to chemical oxidation and the nature of the oxidation products are analyzed with the aid of DFT calculations.

2. Materials and methods

2.1. General procedures

All reagents were commercially available and used as received unless otherwise stated. Deaerated and anhydrous solvents were obtained from a Puresolve PS MD-4 solvent purification system, and all air and/or moisture sensitive reactions were carried out using standard Schlenk techniques. ¹H/¹³C NMR spectra were recorded on a Bruker Advance 300 (or 600 as indicated) MHz spectrometer with a 7.05 (or 14.1) T Ultrashield magnet using deuterated solvents. FT-IR spectra were recorded on a Shimadzu IRAffinity spectrometer as KBr discs. EI/FAB mass spectra were obtained using a Kratos Concept 1S High Resolution E/B mass spectrometer. UV–Vis spectra were recorded in CH₃CN solution on a Shimadzu 3600 UV–Vis–NIR spectrophotometer using quartz cuvette cells. Elemental analyses were carried out by Guelph Chemical Laboratories LTD, Guelph, ON, Canada.

2.2. Electrochemical measurements

Cyclic voltammetry (CV) experiments were performed with a Bioanalytical Systems Inc. Epsilon electrochemical workstation. Compounds **7–11** were dissolved in anhydrous solvent (CH₃CN), filtered, and then deaerated by sparging with N₂ gas for 20 min. Analyte concentrations were approximately 10^{-3} M containing 0.1 M supporting electrolyte (Bu₄NPF₆). A typical three-electrode set-up (a glassy carbon working electrode, Ag/AgCl reference electrode, and a platinum wire counter electrode) was used. Ferrocene was used in all cases as an internal standard to calibrate the reference electrode and was oxidized at a potential of +0.51 V in our set up. The scan rate for all CV experiments was 100 mV/s or as otherwise stated in the text.

2.3. Variable temperature magnetic susceptibility measurements and EPR spectroscopy

Solid state variable temperature magnetic susceptibility measurements were recorded on a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS) with a 5.5 T magnet (temperature range 1.8–400 K) in an external field of 2000 Oe. Samples of **8–12** were carefully weighed into gelatin capsules, which were loaded into plastic straws, and attached to the sample transport rod. The magnetization of the samples was scanned over a 5–300 K temperature range for **8–10** and for the oxidation products of **8–10**. Diamagnetic corrections to the paramagnetic susceptibilities were accomplished using Pascal's constants. EPR spectra were recorded as acetonitrile solutions at room temperature in quartz tubes on a BrukerElexsys E580 pulsed and CW X-band (9 GHz) spectrometer.

2.4. Computational details

All DFT calculations were performed using the GAUSSIAN 09 package [26] using the B3LYP hybrid functional [27,28] and the TZVP basis set [29] for all atoms. Tight SCF convergence criteria were used for all calculations. For each given spin state, the structures were optimized. The converged wave functions were tested to confirm that they correspond to the ground-state surface. The evaluation of atomic charges and spin densities was performed using the natural population analysis (NPA) [30]. The generation of initial guess wavefunctions for the spin states with the anti-ferromagnetic coupling, the analysis of molecular orbitals in terms of fragment orbital contributions, Mayer bond order calculations [31,32] were carried out using the AOMIX program [33,34].

2.5. Synthesis

2.5.1. 5-Bromo-2-pyridinecarboxaldehyde (1)

Following general procedure of Wang et al. [35], a solution of BuLi (2.5 M in hexanes, 10.0 ml, 25.3 mmol) was slowly added to a solution of 2,5-dibromopyridine (5.0 g, 21 mmol) in dry toluene (250 ml) at -78 °C and the mixture was stirred for 5 h. Next, dry DMF (2.15 ml, 27.6 mmol) was added. After stirring for 1 h at -78 °C, the solution was warmed up to -10 °C and the reaction was quenched with saturated NH₄Cl aqueous solution. The organic phase was separated and the aqueous phase was washed twice with ethyl acetate. All organic fractions were collected, dried over MgSO₄ and the solvent was removed by rotary evaporation. Column chromatography (silica gel, hexane/ethyl acetate 15:1) produced pure **1** (1.8 g, 45%). All characterization is consistent with the literature values.

2.5.2. 5-Bromo-2-(1,3-dioxolan-2-yl)pyridine (2)

Ethylene glycol (2.0 ml, 36 mmol) and *p*-toluenesulfonic acid (400 mg, 2.30 mmol) were added to a solution of 5-bromo-2-pyridinealdehyde (4.0 g, 22 mmol) in toluene (30 ml) and reaction mixture was refluxed with Dean–Stark apparatus for 2 days. After cooling to room temperature, the mixture was quenched with 10% Na₂CO₃ aqueous solution and extracted with ethyl acetate. Organic fractions were washed with water, brine, and then dried over MgSO₄. Solvent was removed by rotary evaporation. The product was purified by column chromatography (silica gel, hexane/ethyl acetate 15:1) to produce 4.2 g (85%) of a pure brown oil. ¹H NMR (300 MHz, CDCl₃) δ 8.64 (d, 1H, J=2.3 Hz), 7.83 (dd, 1H,

J = 8.3 Hz, 2.3 Hz), 7.40 (d, 1H, *J* = 8.3 Hz), 5.78 (s, 1H), 4.07 ppm (m, 4H).

2.5.3. 5-Iodo-2-(1,3-dioxolan-2-yl)pyridine (**3**)

5-Bromo-2-(1,3-dioxolan-2-yl)pyridine (0.90 g, 3.9 mmol) and *N*,*N*-dimethylethylenediamine (34 mg, 0.39 mmol) were added to a solution of copper (I) iodide (37 mg, 0.19 mmol) and sodium iodide (1.17 g, 7.8 mmol) in 10 ml 1,4-dioxane (prior to the reaction inorganic salts were recrystallized and dried in vacuo). The reaction mixture was refluxed for 3 days. After cooling to room temperature the reaction was diluted with 25% NH₄OH aqueous solution and extracted with CHCl₃. The organic fractions were washed with brine and dried over MgSO₄. Column chromatography (silica gel, hexane/ethyl acetate 15:1), which gave yellow-white shiny crystals (865 mg, 80%). ¹H NMR (300 MHz, CDCl₃): δ 8.81 (d, 1H, *I* = 1.9 Hz), 8.04 (dd, 1H, *I* = 7.9, 1.9 Hz), 7.32 (d, 1H, *I* = 8.3 Hz), 5.79 (s, 1H), 4.10 ppm (m, 4H). 13 C NMR (75.5 MHz, CDCl₃): δ 155.4, 145.1, 122.4, 103.1, 65.6 ppm. HRMS, Calc. for C₈H₈NO₂I: 276.9599. Found: 276.95949. FT-IR (KBr): 3449 (w), 2965 (w), 2896 (m), 2875 (m), 2750 (w), 1840 (w), 1635 (w), 1572 (m), 1552 (w), 1468 (w), 1381 (s), 1364 (s), 1206 (m), 1129 (m), 1024 (m), 1004 (s), 975 (s), 943 (s), 862 (m), 825 (m), 753 (w), 717 (w), 668 (m), 624 cm⁻¹ (m).

2.5.4. 6-(1,3-Dioxolan-2-yl)-N-(4-methoxyphenyl)pyridin-3-amine (4)

A Schlenk flask charged with 5-iodo-2-(1,3-dioxolan-2-yl)pyridine (72 mg, 0.26 mmol), p-anisidine (16 mg, 0.13 mmol), palladium (II) acetate (3 mg, 0.013 mmol), BINAP (16 mg, 0.026 mmol) and Cs₂CO₃ (170 mg, 0.52 mmol) was evacuated and back-filled with dinitrogen $(3 \times)$ Next, dry toluene (2 ml) was syringed into the flask and the reaction was stirred at 50 °C for 2 days. Conversion of starting material was monitored by TLC (product $R_f = 0.36$ eluent, EtOAc). After complete consumption of starting material was noted the reaction mixture was cooled to room temperature, filtered and the solvent was removed by rotary evaporation. The product was purified by column chromatography (hexane/EtOAc. 5:1) to produce a dark oil, 28 mg (40%). ¹H NMR (300 MHz, CDCl₃): δ 8.21 (d, 1H, *J* = 2.3 Hz), 7.33 (d, 1H, *J* = 8.7 Hz), 7.19 (dd, 1H, *J* = 8.3, 2.6 Hz), 7.06 (m, 2H), 6.86 (m, 2H), 5.77 (s, 1H), 5.65 (s, 1H), 4.10 (m, 4H), 3.79 ppm (s, 3H). ¹³C NMR (150 MHz, CDCl₃): δ 156.1, 147.1, 142.1, 137.6, 134, 123, 121.2, 121.2, 114.8, 103.8, 65.4, 55.5 ppm. HRMS, Calc. for C₁₅H₁₆O₃N₂: 272.11609. Found: 272.11595. FT-IR (KBr): 3397 (w), 3267 (w), 2955 (w), 2890 (w), 2834 (w), 1593 (m), 1577 (m), 1511 (s), 1465 (w), 1440 (w), 1388 (w), 1330 (w), 1287 (w), 1244 (m), 1180 (w), 1132 (w), 1090 (m), 1032 (m), 987 (w), 943 (w), 829 (s), 751 (s), 518 cm⁻¹ (s).

2.5.5. N-(6-(1,3-Dioxolan-2-yl)pyridin-3-yl)-6-(1,3-dioxolan-2-yl)-N-(4-methoxyphenyl)pyridin-3-amine (**5**)

A Schlenk flask charged with 6-(1,3-dioxolan-2-yl)-N-(4-methoxyphenyl)pyridin-3-amine (0.15 g, 0.55 mmol), 5-iodo-2-(1,3-dioxolan-2-yl)pyridine (0.15 g, 0.55 mmol), palladium (II) acetate (6.0 mg, 0.027 mmol), BINAP (34.3 mg, 0.055 mmol) and Cs₂CO₃ (0.36 g, 1.1 mmol) was evacuated and back-filled with dinitrogen $(3 \times)$. Dry toluene (2 ml) was syringed into the flask and the reaction was stirred at 95 °C for 3 days. The reaction mixture was cooled to room temperature, filtered and the solvent was removed by rotary evaporation. Column chromatography (hexane/EtOAc. 5:1) produced **5** as a pure brown oil 123 mg (53%). ¹H NMR (300 MHz, CDCl₃): δ 8.31 (d, 2H, J = 0 Hz), 7.36 (m, 4H), 7.04 (d, 2H, / = 8.7 Hz), 6.86 (d, 2H, / = 8.7 Hz), 5.79 (s, 2H), 4.11 (m, 8H), 3.79 ppm (s, 3H). ¹³C NMR (150 MHz, CDCl₃): δ 157.5, 143.8, 138, 135.3, 129.4, 127.6, 121.2, 120.9, 115.4, 103.3, 65.6, 55.5 ppm. HRMS, Calc. for C₂₃H₂₃O₅N₃: 421.16377. Found: 421.16402. FT-IR (KBr): 3423 (s), 3061 (w), 2965 (m), 2890 (m), 2362 (w), 2328

(w), 1762 (w), 1636 (m), 1585 (w), 1569 (w), 1531 (w), 1508 (s), 1437 (w), 1388 (m), 1315 (m), 1294 (m), 1246 (s), 1166 (w), 1135 (m), 1091 (s), 1026 (s), 943 (m), 898 (w), 875 (w), 829 (m), 750 (m), 722 (m), 700 (m), 642 (w), 524 cm⁻¹ (m).

2.5.6. 5,5'-(4-Methoxyphenylazanediyl)dipicolinaldehyde (6)

N-(6-(1,3-Dioxolan-2-yl)pyridin-3-yl)-6-(1,3-dioxolan-2-yl)-N-(4-methoxyphenyl)pyridin-3-amine (0.10 g, 0.24 mmol) was stirred with 5% HCl (3 ml) in THF (5 ml) for 2 days. The reaction mixture was made basic with NaOH pellets and extracted into ethyl acetate. The organic layer was dried over MgSO₄ and the solvent was removed by rotary evaporation. A pure, yellow product was obtained by column chromatography (silica gel, hexane/ EtOAc, 4:1), 68 mg (85%). ¹H NMR (300 MHz, CDCl₃): δ 9.96 (s, 2H), 8.49 (d, 2H, J = 2.3 Hz), 7.86 (d, 2H, J = 8.7 Hz), 7.47 (dd, 2H, *I* = 8.7, 2.3 Hz), 7.12 (m, 2H), 6.96 (m, 2H), 3.84 ppm (s, 3H). ¹³C NMR (75.5 MHz, CDCl₃): δ 191.7, 147.4, 146, 143.4, 136.2, 128.6. 128.2, 122.7, 116, 55.6 ppm. HRMS, Calc. for C₁₉H₁₅N₃O₃: 333.11134. Found: 333.11055. FT-IR (KBr): 3429 (w), 3045 (w), 3008 (w), 2929 (w), 2812 (w), 2709 (w), 2507 (w), 2359 (w), 2034 (w), 1702 (s), 1555 (s), 1480 (s), 1387 (w), 1319 (s), 1287 (s), 1247 (s), 1211 (s), 1030 (s), 819 (s), 736 (w), 669 (w), 617 (w), 547 cm⁻¹ (w).

2.5.7. 5,5'-(4-Methoxyphenylazanediyl)dipicolinaldehyde (7)

Compound 6 (0.20 g, 0.60 mmol) was stirred with 2 equivalents of *p*-anisidine (0.15 mg, 1.2 mmol) and dry MgSO₄ (0.15 g) in DCM (5 ml) for 2 days. The reaction mixture was then filtered and the solvent was removed by rotary evaporation. Crude purification was first carried out by column chromatography (silica gel, hexane/EtOAc, 5:1). Further purification of 7 was accomplished by dissolving the chromatographed product into isopropanol (2 ml) and precipitating it out with weak HCl solution. The product was filtered off, shaken with 10% NaOH solution and then extracted into ethyl acetate. The solvent was removed by rotary evaporation to produce a yellow powder, 280 mg (85%). This product is mildly susceptible to hydrolysis and was stored under an inert atmosphere in the refrigerator. ¹H NMR (300 MHz, CDCl₃): δ 8.56 (s. 2H), 8.42 (d, 2H, / = 2.6 Hz), 8.06 (d, 2H, / = 9.1 Hz), 7.45 (dd, 2H, *J* = 8.3, 2.6 Hz), 7.30 (m, 4H), 7.13 (d, 2H, *J* = 9.1 Hz), 8.93 (m, 6H), 3.84 (s, 3H), 3.83 ppm (s, 6H). ¹³C NMR (150 MHz, CDCl₃): δ 158.7, 158, 157.4, 149, 144.1, 144, 143.4, 137.5, 128.8, 128, 122.6, 122.2, 115.6, 114.4, 55.5, 30.9 ppm. Anal. Calc. for C₃₃H₂₉O₃N₅: C, 72.93; H, 5.34; N, 12.89. Found: C, 73.17; H, 5.58; N, 12.73%. HRMS, Calc. for C₃₃H₂₉O₃N₅: 543.22704. Found: 543.22773. FT-IR (KBr): 3448 (w), 1618 (w), 1560 (w), 1506 (s), 1477 (m), 1319 (w), 1246 (m), 1260 (w), 1031 (w), 829 cm⁻¹ (w).

2.5.8. [Mn(hfac)₂]₂(7) (8)

Mn(hfac)₂·3H₂O (96.3 mg, 0.184 mmol) was dissolved in a mixture of DCM (2 ml) and MeOH (~0.5 ml) and combined with a solution of **7** (50 mg, 0.092 mmol) in DCM (5 ml). The mixture was stirred for 2 days at room temperature. The solvent volume was reduced to 2 ml and after several hours, precipitation of bright brown-orange solid was observed. The product was collected by vacuum filtration, and dried. Yield 68 mg (50%). *Anal.* Calc. for C₅₃₋H₃₃N₅O₁₁F₂₄Mn₂: C, 42.94; H, 2.25; N, 4.73. Found: C, 43.14; H, 2.09; N, 4.79%. MS (FAB –): m/z 1481 (M⁻, 0.3%), 262 [Mn(hfac), 2.5%], 207 (hfac, 100%). FT-IR (KBr): 3448 (s), 2364 (w), 1647 (m), 1617 (w), 1559 (w), 1500 (m), 1316 (w), 1256 (s), 1201 (m), 1146 (s), 1096 (m), 1032 (m), 797 (w), 664 (w), 583 cm⁻¹ (w).

2.5.9. [Ni(hfac)₂]₂(7) (9)

 $Ni(hfac)_2 H_2O$ (87 mg, 0.184 mmol) was dissolved in a mixture of hexanes (3 ml) and DCM (3 ml) and combined with a DCM solution of **7** (50 mg, 0.092 mmol). After stirring at room temperature

for approximately 12 h the solvent volume was reduced to 2 ml and the reaction mixture was cooled on ice. An orange-brown precipitate was collected by vacuum filtration and dried. Yield 75 mg (55%). *Anal.* Calc. for $C_{53}H_{33}N_5O_{11}F_{24}Ni_2$: C, 42.73; H, 2.23; N, 4.70. Found: C, 42.73; H, 1.98; N, 4.72%. MS (FAB –): m/z 1489 (M⁻, 0.3%), 472 [Ni(hfac)₂, 26.3%], 207 (hfac, 100%). FT-IR (KBr): 3431 (s), 2921 (w), 2363 (w), 2339 (w), 1644 (m), 1617 (w), 1559 (w), 1507 (m), 1490 (w), 1424 (w), 1317 (w), 1256 (s), 1202 (m), 1149 (s), 1089 (m), 1059 (m), 1033 (m), 870 (w), 837 (w), 794 (w), 668 (w), 558 (w), 467 cm⁻¹ (w).

2.5.10. $[Cu(hfac)_2]_2(7)$ (10)

Cu(hfac)₂·H₂O (91.3 mg, 0.184 mmol) was dissolved in DCM (3 ml) and added to DCM solution of **7** (50 mg, 0.092 mmol). After stirring at room temperature for 12 h precipitation of a red-brown microcrystalline solid was noted, which was isolated by vacuum filtration and dried. Yield 80 mg (58%). *Anal.* Calc. for C₅₃H₃₃N₅O₁₁-F₂₄Cu₂: C, 42.45; H, 2.22; N, 4.67. Found: C, 43.14; H, 2.09; N, 4.79%. MS (FAB –): *m/z* 477 [Cu(hfac)₂, 62%], 207 (hfac, 100%). FT-IR (KBr): 3432 (m), 2364 (w), 1648 (m), 1617 (w), 1582 (w), 1546 (m), 1508 (s), 1425 (w), 1368 (w), 1305 (w), 1256 (s), 1202 (s), 1147 (s), 1084 (w), 1032 (w), 943 (w), 896 (w), 836 (w), 794 (w), 741 (w), 667 (w), 586 (w), 527 (w), 419 cm⁻¹ (w).

2.5.11. Chemical oxidation of 7-10

About 15 mg each of **7–10** were dissolved in 2 or 3 ml of dry, deoxygenated CH₃CN in a 25 ml round bottom flask. One equivalent of NOPF₆ solution (CH₃CN) was added by syringe to produce in all cases but complex **10**, a clear red solution. The solutions were stirred under a dinitrogen atmosphere for 10 min and then the solvent was removed *in vacuo* to produce solids that were immediately loaded into gel caps for squid magnetometry experiments.

3. Results and discussion

3.1. Ligand synthesis and coordination chemistry

The multi-step synthesis of ligand **7**, starting from commercially available 2,5-dibromopyridine, is outlined in Scheme 1. The first three steps culminating in iodo-substituted **3** are literature reactions where only slight modifications of the established methods were required [35–37]. The non-facile preparation of 4 and 5 required the use of palladium catalyzed C-N bond formation methodology; so-called Buchwald-Hartwig conditions [38,39]. Tertiary amine 5 could not be prepared cleanly in one step from anisidine using two or more equivalents of 3 at low or elevated temperatures. In all attempted reactions, significant amounts of both secondary and tertiary amine were produced, including also a large proportion of dehalogenated **3**. Unfortunately, we were unable to separate the mixture of amines by column chromatography and so attempted the preparation of 5 in two steps. Starting with a single equivalent of **3**, we could readily prepare pure secondary amine **4** with a reasonable yield. Reaction between **4** and a second equivalent of **3** at elevated temperatures produced pure tertiary amine **5**, which was deprotected and reacted with two equivalents of anisidine to produce the condensation product 7 as a hydrolytically unstable vellow powder. Storage of **7** in an inert environment is necessary to prevent decomposition.

Bimetallic complexes containing ligand **7** were readily produced by combining two equivalents of hydrated $M(hfac)_2$ salts (M = Mn, Ni, Cu) with **7** in CH₂Cl₂ solution (Fig. 2), which produced analytically pure, microcrystalline precipitates of complexes **8** (Mn), **9** (Ni), or **10** (Cu). Complex **10** produced what appeared to be X-ray diffraction quality crystals via slow evaporation from concentrated methanol solutions but in all our attempts to acquire an X-ray structure, data collection was extremely weak due to poor crystal diffraction. We are confident in the structural interpretation noted in Fig. 2 based on all of our spectroscopic data acquired from these complexes.

3.2. Electronic spectra, electrochemistry and magnetic properties of 7–10

The electronic spectra of ligand **7** and complexes **8–10** were investigated via UV–Vis absorbance spectroscopy and cyclic voltammetry. The absorption spectra of **7–10** in CH₃CN solution are shown in Fig. 3. Ligand **7** features a dominant visible absorption band centered at 410 nm, which is $n-\pi^*$ in origin. Complexes **8–10** each exhibit this same ligand centered transition but at longer wavelengths in all cases relative to **7**. No additional bands that



Scheme 1. Synthesis of 7.



Fig. 2. Structures of complexes 8-10 (hfac is 1,1,1,5,5,5-hexafluoroacetylacetonato).



Fig. 3. Electronic absorption spectra of 7-10 (CH₃CN solution).

could be attributed to metal-centered transitions (d-d) or metalligand charge transfer transitions are observed in the visible region of the spectra of these complexes.

Cyclic voltammograms were acquired for each of 7-10 in acetonitrile solution and the CVs of 7 and 10, as examples, are displayed in Fig. 4. In the oxidation scan, ligand 7 exhibits three closely spaced and irreversible waves centered at +0.6, 0.9 and 1.2 V (versus ferrocene). The first and second waves likely represent production of radical-cation and dication, respectively. The third wave is of an unknown origin, but may represent a metal-centered oxidation (for complexes 8–10), or oxidation of a decomposition product formed from one of the first two oxidation processes. In the reduction scan, the CV of 7 is unremarkable, featuring an irreversible imine reduction centered at -2.3 V. In complexes 8-10 the same pattern of three irreversible oxidative processes are noted, but are shifted to higher potentials relative to 7 (Fig. 4, right). The waves are also more closely spaced than in 7, with the first two waves separated by only approximately 100 mV. This is in stark contrast to **11**, in which M(hfac)₂ coordination stabilized the radical-cation and produces reversible electrochemistry at potentials lower than in the free ligand. Complexes 8-10 also exhibit irreversible cathodic waves at potentials centered at -1.6 and -2.4 V, which represent hfac and imine reductions, respectively.

The variable temperature magnetic properties of **8–10** were investigated by SQUID magnetometry in a 5–300 K temperature range, in an external field of 2000 Oe (Fig. 5A–C). For each complex, the data were fitted [40] to numerical expressions derived from the van Vleck equation for simple bimetallic complexes containing Mn, Ni or Cu, based upon the following isotropic spin Hamiltonian:

$$\hat{H} = J\hat{S}_M\hat{S}_M \tag{1}$$

The best fit parameters for **8** (g = 2.0, $J_{MnMn} = -0.025 \text{ cm}^{-1}$, $\rho = 0.025, \theta = -0.4 \text{ K}, R = 0.0086$) and **9** (g = 2.26, $J_{\text{NiNi}} = -0.20 \text{ cm}^{-1}$, TIP = 900×10^{-6} cm³ mol⁻¹ K⁻¹, θ = -0.9 K, R = 0.028) each include very weak intra- and intermolecular anti-ferromagnetic coupling terms. However, only very slightly poorer fits can also be obtained with very small ferromagnetic coupling terms, so the actual sign of the coupling is not unambiguous. It is best to describe complexes 8 and **9** as very weakly coupled systems. On the other hand, the best fit parameters for complex **10** suggest a weak, but measureable ferromagnetic coupling may be operative been the copper ions (g = 2.30, J_{CuCu} = +2.0 cm⁻¹, ρ = 0.020, TIP = 500 × 10⁻⁶ cm³ mol⁻¹ K^{-1} , $\theta = -0.6$ K, R = 0.0031). In an effort to confirm a ground triplet state for 10, a low temperature (4 K) magnetization versus field experiment was performed (Fig. 5D). While the magnetization does not saturate up to 5 T, the experimental data points are similar to the theoretical curve calculated for a triplet state at 4 K (assuming a g parameter equal to that obtained from the fit of the magnetic susceptibility data). The observed ferromagnetic coupling in 10 can be rationalized through a π -spin polarization mechanism (Fig. 6) [41,42]. The positive spin density on Cu (indicated as an up arrow) is likely concentrated in a $d_{x^2-y^2}$ based molecular orbital; as this orbital is orthogonal to the bridging ligand π -system, spin delocalization imparts spin density of the same sign on the coordinated N atom from the pyridine ring. Alternation of the spin density to the other Cu ion results in a ferromagnetic interaction.

3.3. Oxidations of 7-10

In an effort to produce the radical cation of ligand 7 and complexes 8-10, chemical oxidations were carried out in acetonitrile solution by careful addition of $NO(PF_6)$ (one equivalent) at room temperature under anhydrous and aerobic conditions. Instantly, a color change to deep cherry-red was noted in all reactions upon oxidant addition. With the exception of complex 9, the visible absorption spectra of the oxidation products are all very similar and feature a longer wavelength band (relative to the neutral precursors) together with a higher energy shoulder (Fig. 7). Addition of a second (or more) equivalent of oxidant results in no further changes to the absorption spectra. Indeed, these absorption spectra are very different from those produced by chemical oxidation of M(hfac)₂ complexes containing **11** and the spectra of other reported triarylamminium radical cations and are in fact more representative of spectra produced from reported diamagnetic dicationic species [43,44]. To probe this further we attempted to obtain the EPR spectra of oxidized 7 and 8 at room temperature



Fig. 4. Cyclic voltammograms of ligand 7 (left) and complex 10 (right) in CH₃CN solution containing 10⁻³ M ⁿBu₄N(PF₆). In all CV experiments that scan rate was 100 mV/s.



Fig. 5. Plots A, B, and C: Effective magnetic moment vs. temperature plots for complexes **8** (\Box), **9** (\triangle), and **10** (\bigcirc) (2000 Oe external field). The lines through the points represent best fits based on appropriate spin Hamiltonians with best fit parameters as described in the text. Plot D: Reduced magnetization vs. field data for complex **10** at 4 K. The solid line represents the theoretical curve for an *S* = 1 state at 4 K (*g* = 2.3).



Fig. 6. Proposed spin density distribution in 10.





Fig. 8. Proposed structure of dication complexes of 8 and 10.

to have structures as outlined in Fig. 8. Given the irreversible nature and meagre separation (less than 200 mV) between the purported oxidation waves for radical cation and dication observed in the CV it is clear that isolating persistent radical cation complexes is not possible with the given system.



Fig. 7. Left: Visible absorption spectra of 7 (solid line) and 7^{2+} (dashed line). Right: Visible absorption spectra of 8 (solid line) and 8^{2+} . Spectra were recorded at room temperature in CH₃CN.



Fig. 9. Effective magnetic moment vs. temperature plots for the oxidation products of complexes 8 (**u**) and 10 (**o**) (2000 Oe external field).

The variable temperature magnetic properties of dication **8** and **10** were investigated by SQUID magnetometry over a 5-150 K temperature range and indicate essentially no coupling between the metal ion spins (Fig. 9). Given the uncertainty in the mass and purity of these products we did not attempt to fit these data but the magnitude of the magnetic moments and curve profiles with decreasing temperature suggest extremely weak interactions at

best. DFT calculations for the dication of complex **8** suggest a singlet ground state (Fig. S3).

3.4. DFT calculations

3.4.1. $M(hfac)_2$ -radical cation (7⁺) complexes (M = Ni, Mn)

For comparison, the structures, relative energies and spin density distributions were calculated for hypothetical bimetallic $M(hfac)_2$ (M = Ni, Mn) containing the radical cation of ligand 7. Calculations were performed on the S = 11/2 and 9/2 states of the Mn(hfac)₂ complex, which corresponds to Mn^{II}–N radical ferromagnetic and anti-ferromagnetic coupling, respectively. The spin density distributions for the two geometry-optimized structures are shown in Fig. 10. The individual Mn^{II} ions are in the high-spin configuration and NPA-derived atomic spin densities for the Mn atoms are 4.74–4.75 for both S = 11/2 and 9/2 states, respectively (Fig. 10). The Mn^{II}-ligand bonds in these complexes have fairly small covalency [32] as can be seen from the Mn–O and Mn–N bond orders (0.25–0.29 and 0.21–0.23, respectively). The complex with the S = 9/2 spin that corresponds to the anti-ferromagnetically coupled Mn^{II}-N radical description is calculated to have a lower energy than the complex with the ferromagnetic spin interactions by 91 cm⁻¹. This is in contrast to the reported Mn(hfac)₂ complex with the radical cation of 11, which was demonstrated to exhibit a weak ferromagnetic Mn-radical spin interaction, which was ratio-



Fig. 10. Calculated spin density distributions in optimized structures for the *S* = 11/2 and 9/2 states of the radical cation of complex **8**. The NPA-derived atomic spin densities for the metal ions and the triarylamminium nitrogen are shown. Spin densities are shown with the isosurface contour value of 0.004.



Fig. 11. Calculated spin density distributions in optimized structures for the *S* = 5/2 and 3/2 states of the radical cation of complex **9**. The NPA-derived atomic spin densities for the metal ions and the triarylamminium nitrogen are shown. Spin densities are shown with the isosurface contour value of 0.004.

nalized on the basis of a π -spin polarization mechanism (supported by DFT calculations). The spin density distribution in the bimetallic complex is different from Mn(hfac)₂**11**, including essentially zero spin density on the coordinate N atom of the pyridine ring or the C atom bonded to the amminium N atom.

Calculations were also performed on the S = 5/2 or 3/2 states of the bimetallic Ni(hfac)₂ complex (Fig. 11) of same radical cation ligand of **7**. The individual Ni^{II} ions are in the high-spin configuration and NPA-derived atomic spin densities for the Ni atoms are 1.65 for both S = 5/2 and 3/2 states, respectively. Due to lower-energy acceptor metal orbitals of the metal ion [32], the Ni^{II}-ligand bonds have stronger covalency as can be seen from the Ni–O and Ni–N bond orders (0.33–0.35 and 0.33–0.34, respectively) relative to the Mn^{II} analog (see above). The energy of the S = 3/2 state (with Ni^{II}-radical anti-ferromagnetic spin coupling) is lower by 56 cm⁻¹ relative to the S = 5/2 state (with the ferromagnetically coupled ions).

4. Conclusions

We have described the multistep synthesis of a new ditopic triarylamino-type ligand and the full characterization of bimetallic $M^{II}(hfac)_2$ complexes ($M^{II} = Mn$, Ni, Cu) containing this ligand. In the neutral precursor complexes, very weak magnetic interactions persist between the coordinated metal ions; including a weak ferromagnetic interaction mediated by spin polarization when M = Cu. Chemical oxidation of the precursor complexes produces persistent complexes of the dication of 7, which we could identify by UV-Vis and EPR spectroscopies. Unfortunately, we could not isolate complexes containing the radical cation of 7, perhaps owing to the irreversible nature and poor separation of the first and second oxidation waves observed in the ligand. In fact, DFT calculations on a bimetallic Mn(hfac)₂ complex containing the dication of 7 indicate a lower energy than the analogous radical-cation complex. Currently, we are exploring the synthesis of related diand polytopic ligands but with structural features that enable reversible oxidation to radical cation products.

Acknowledgements

M.T.L. acknowledges NSERC (Discovery & RTI) and CFI (Leaders Opportunity Fund) for financial support to carry out this research. Mr. Samuel Mula is acknowledged for help with EPR experiments.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2012.06.059.

References

- [1] D.A. Dougherty, Acc. Chem. Res. 24 (1991) 88.
- [2] O. Kahn, Inorg. Chim. Acta 62 (1982) 3.
 [3] A. Rajca, Chem. Rev. 94 (1994) 871.
- [3] A. Rajca, Chem. Rev. 94 (1994) 871.
 [4] H. Iwamura, J. Phys. Org. Chem. 11 (1998) 299.
- [5] T. Glaser, H. Theil, M. Heidemeier, C. R. Chim. 11 (2008) 1121.
- [6] R. Sessoli, A.K. Powell, Coord. Chem. Rev. 253 (2009) 2328.
- [7] M. Murrie, Chem. Soc. Rev. 39 (2010) 2986.
- [8] T. Glaser, Chem. Commun. 47 (2011) 116.
- [9] M. Evangelisti, E.K. Brechin, Dalton Trans. 39 (2010) 4672.
- [10] Y.-Z. Zheng, M. Evangelisti, R.E.P. Winpenny, Chem. Sci. 2 (2011) 99.
- [11] Y. Wang, W. Li, S. Zhou, D. Kong, H. Yang, L. Wu, Chem. Commun. 47 (2011) 3541
- [12] A. Caneschi, D. Gatteschi, R. Sessoli, P. Rey, Acc. Chem. Res. 22 (1989) 392.
- [13] M.T. Lemaire, Pure Appl. Chem. 76 (2004) 277.
- [14] J.J. Kanamori, J. Phys. Chem. Solids 10 (1959) 87.
- [15] J.B. Goodenough, J. Phys. Chem. Solids 6 (1958) 287.
- [16] A. Caneschi, D. Gatteschi, P. Rey, Prog. Inorg. Chem. 39 (1991) 331.
- [17] D. Luneau, P. Rey, Coord. Chem. Rev. 249 (2005) 2591.
- [18] B.D. Koivisto, R.G. Hicks, Coord. Chem. Rev. 249 (2005) 2612.
- [19] K.E. Preuss, Dalton Trans. 23 (2007) 2357.
- [20] D.A. Shultz, Comment Inorg. Chem. 23 (2002) 1.
- [21] J.S. Miller, Chem. Soc. Rev. 40 (2011) 3266.
- [22] J.D. Rinehart, M. Fang, W.J. Evans, J.R. Long, Nat. Chem. 3 (2011) 538.
 [23] S. Adugna, K. Revunova, B. Djukic, S.I. Gorelsky, H.A. Jenkins, M.T. Lemaire, Inorg. Chem. 49 (2010) 10183.
- [24] R.J. Bushby, C. Kilner, N. Taylor, R.A. Williams, Polyhedron 27 (2008) 383.
- [25] M. Yano, K. Inoue, T. Motoyama, Y. Azuma, M. Tatsumi, O. Yamauchi, M. Oyama, K. Sato, T. Takui, Polyhedron 24 (2005) 2112.
- [26] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, Ö. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian 09, Revision A.02, Gaussian, Inc., Wallingford, CT, 2009.
- [27] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
- [28] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B37 (1988) 785.
- [29] A. Schafer, C. Huber, R. Ahlrichs, J. Chem. Phys. 100 (1994) 5829.
- [30] A.E. Reed, L.A. Curtiss, F. Weinhold, Chem. Rev. 88 (1988) 899.
- [31] I. Mayer, Int. J. Quantum Chem. 29 (1986) 73.
- [32] S.I. Gorelsky, L. Basumallick, J. Vura-Weis, R. Sarangi, B. Hedman, K.O. Hodgson, K. Fujisawa, E.I. Solomon, Inorg. Chem. 44 (2005) 4947.
- [33] S.I. Gorelsky, AOMix Version 6.6, University of Ottawa, Ottawa, Canada, 2012.
- [34] S.I. Gorelsky, A.B.P. Lever, J. Organomet. Chem. 635 (2001) 187.
- [35] X. Wang, P. Rabbat, P. O'Shea, R. Tillyer, E.J.J. Grabowski, P.J. Reider, Tetrahedron Lett. 41 (2000) 4335.
- [36] A. Landa, A. Minkkilä, G. Blay, K.A. Jørgensen, Chem. Eur. J. 12 (2006) 3472.
- [37] T. Furuyama, M. Yonehara, S. Arimoto, M. Kobayashi, Y. Matsumoto, M. Uchiyama, Chem. Eur. J. 14 (2008) 10348.
- [38] A.S. Guram, R.A. Rennels, S.L. Buchwald, Angew. Chem., Int. Ed. 34 (1995) 1348.
- [39] J. Louie, J.F. Hartwig, Tetrahedron Lett. 36 (1995) 3609.
- [40] L.K. Thompson, Z. Xu, Magmun Version 4.1 ed., Memorial University of Newfoundland, St. John's, Canada, 20XX.
- [41] H.C. Longuet-Higgins, J. Chem. Phys. 18 (1950) 265.
- [42] T. Glaser, M. Heidemeier, S. Grimme, E. Bill, Inorg. Chem. 43 (2004) 5192.
- [43] S. Amthor, B. Noller, C. Lambert, Chem. Phys. 316 (2005) 141.
- [44] R.J. Bushby, N. Taylor, R.A. Williams, J. Mater. Chem. 17 (2007) 955.