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Synthesis and properties of a redox active starburst ligand with three bispicorylamino groups and its trinuclear complexes

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ABSTRACT

A starburst-shaped ligand, 4,4′4″-tris[*N*, *N*-bis(2-pyridylmethyl) aminomethyl] triphenylamine, and its palladium and copper trinuclear complexes were designed and prepared. NMR techniques, COSY and ROESY, were applied to the palladium complex to examine its conformation in solution. The palladium complex was found to prefer a folded conformation even at 75 °C, indicating the occurrence of strong intramolecular stacking interaction. CV measurements of the palladium complex showed reversible TTA/TTA$^{+\cdot}$ redox couples. ETSF measurements showed that the corresponding radical pendant complex is very unstable. Molecular design rules for triarylamine-based spin bearing ligands are discussed.

1. Introduction

One of the promising strategies to achieve molecular magnetic materials is to utilize coordination polymer networks with spin bearing ligands and spin bearing transition metals [1,2]. Until now, nitroxide [1] and nitronyl nitroxide [2] have been widely used as stable spin bearing units. On the other hand, among the diverse topics for molecule-based magnetism, ligands with charged radicals, i.e., cation radicals and anion radicals, have not fully been investigated. Upon electron removal or injection, metal complexes with a redox active organic ligand are expected to exhibit interesting photochemical, electronic, and magnetic properties based on interactions between the metal ion and the organic radical site. Especially, ligands with reversible electron transfer capability enable to control dynamic magnetic properties. One of the difficulties in obtaining this type of compounds is that molecular design rules for redox active organic ligands have not been well established yet. Organic cation radicals formed upon one electron oxidation of neutral molecules generally tend to be very unstable due to lack of thermodynamic or kinetic stabilization, leading to decomposition or dimerization reactions. Therefore, selection of a redox active unit is essential for the molecular design of such ligands. Triarylamines (TAAs) having various substituents at their *para* positions have been widely known to give the corresponding very stable cation radicals upon chemical or electrochemical one electron oxidation [3], serving as stable positive charge and spin bearing units. During the past decade, this salient feature has been utilized for the synthesis of a number of π-extended TAA-based oligomers as models for positively charged purely organic high-spin entities [4] as well as for organic mixed-valence molecular systems [5]. Very recently, Bushby et al. reported a triarylamine-based ligand with a 4-pyridyl unit and its manganese complex [6]. They concluded that Mn(II)-tryarylamine radical cation systems are not promising systems for coordination polymer magnets. The weak spin coupling would be attributed to the monodentate 4-pyridyl group with low coordination ability.

We previously reported the syntheses and properties of redox active ligands with tridentate bispicorylamino groups, 4-(bis-(2-picolyl) aminomethyl)-4′,4″-dimethyltriphenylamine and 4-methoxy-4′,4″-bis [*N*,*N*-bis(2-pyridylmethyl) aminomethyl] triphenylamine and their mono- and dinuclear complexes (**1**–**4**), as shown in Fig. 1 [7]. CV measurements of the complexes showed reversible TTA/TTA$^{+\cdot}$ redox couples. ETSF measurements revealed that the radical pendant mono- and dinuclear complexes do not decompose for over 100 s. The spin–spin interaction of the copper complex with the pendant TAA cation radical, generated upon one electron oxidation of **2** and **4,** was examined by ESR measurements. These results encouraged us to examine more complicated systems with redox active ligands.

In this study, we report synthesis and properties of a novel starburst-shaped ligand (**5**) and its dinuclear palladium (**6**) and copper (**7**) complexes (Fig. 2). The ligand is expected to be a promising

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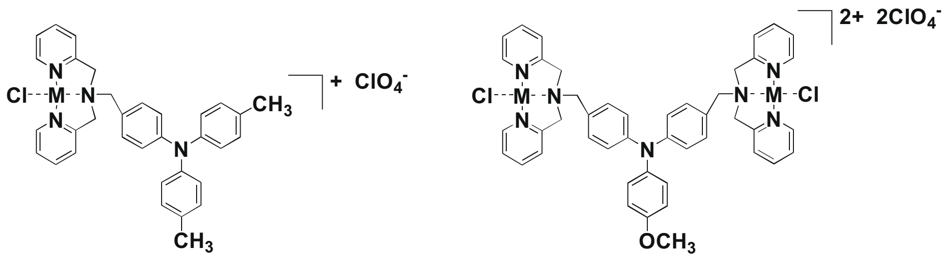
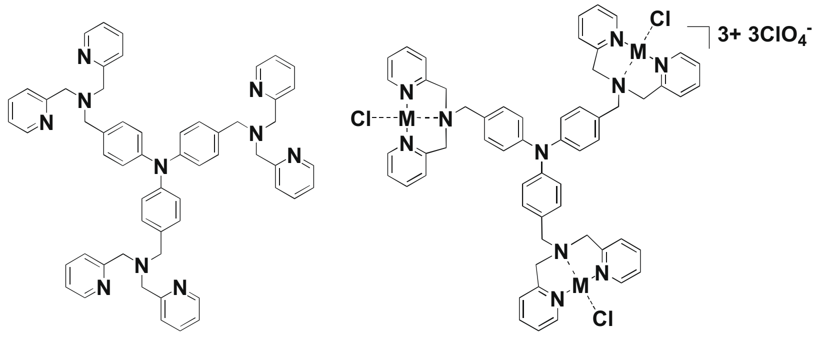


1: M=Pd(II)
2: M=Cu(II)

3: M=Pd(II)
4: M=Cu(II)

Fig. 1. Structures of complexes **1–4**.



5

6: M=Pd(II)
7: M=Cu(II)

Fig. 2. Structures of a ligand **5** and its trinuclear complexes **6** and **7**.

redox active building unit to construct two-dimensional coordination polymer networks.

2. Experimental

*2.1. Synthesis of 4,4′4″-[**N**-(2-picoryl) aminomethyl] triphenylamine*

To the solution of 4,4′,4″-triformyltriphenylamine (1.151 g) [8] in methanol (150 ml) 2-picorylamine (2.268 g) was added. Then the color of the solution changed to yellow. Acetic acid was slowly added until the color of the solution changed to orange. Sodium tetrahydroborate (6 g) was carefully added at 0 °C and stirred at ambient temperature for 3 days. The solution was neutralized with conc.-hydrochloric acid and evaporated under reduced pressure. The residue was dissolved into chloroform and dried over sodium sulfate. The obtained crude oil was purified by silica gel column chromatography (chloroform: methanol = 10:1) to give pale yellow oil (yield 1.02 g, 48.3%).

^{1}H NMR(CDCl$_3$): δ 3.79 (s, 6H), 3.95 (s, 6H), 7.02 (d, 6H, J = 8.6 Hz), 7.16 (m, 3H), 7.21 (d, 6H, J = 8.6 Hz), 7.34 (d, 3H, J = 7.8 Hz), 7.64 (dt, 3H, J = 7.8 Hz, 1.7 Hz), 8.56 (d, 3H, J = 4.9 Hz).

*2.2. Synthesis of 4,4′,4″-tris[N,N-bis(2-pyridylmethyl)aminomethyl]triphenylamine (**5**)*

To the solution of 4,4′-dimethoxy-4-(2-picorylaminomethyl) triphenylamine (1.02 g) in dry THF (50 ml) was added 2-(bromomethyl) pyridimium hydrobromide (2.54 g) in dry THF (50 ml), triethylamine (1.48 g) and stirred at ambient temperature for 5 days. The solution was filtered and evaporated under reduced pressure. The residue was dissolved into chloroform and dried over sodium sulfate and evaporated under reduced pressure to give crude oil, which was purified by silica gel column chromatography (chloroform: methanol = 10:1) to give orange oil (yield 0.74 g, 50%).

^{1}H NMR(CDCl$_3$): δ 3.63 (s, 6H), 3.82 (s, 12H), 6.97 (d, 6H, J = 8.6 Hz), 7.14 (t, 6H, J = 6.3 Hz), 7.23 (d, 6H, J = 8.6 Hz), 7.64 (d, 12H, J = 8.6 Hz), 8.52 (d, 6H, J = 4.62 Hz).

HRMS: Calc.: 878.4533 for $C_{57}H_{54}N_{10}$, Obsd: 878.4506.

*2.3. Synthesis of palladium(II) dichloro(4,4′,4″-tris[N,N-bis-(2-pyridylmethyl)aminomethyl]- triphenylamine) triperchrorate (**6**)*

4,4′4″-Tris[*N*,*N*-bis(2-pyridylmethyl)aminomethyl]triphenylamine (0.2 g), palladium(II) dichloride (0.13 g) and sodium perchlorate (0.48 g) were dissolved into a small amount of acetonitrile and refluxed for 3 h, which was concentrated to 5 ml and allowed to stand overnight at 5 °C to give pale yellow powders (yield 0.34 g, 93%).

^{1}H NMR(DMSO-d_6): δ 4.15 (s, 6H), 4.68 (d, 6H, J = 16.0 Hz), 5.58 (d, 6H, J = 16.0 Hz), 7.64 (m, 12H, 7.84(d, 6H, J = 8.0 Hz), 8.20 (t, 6H, J = 8.0 Hz), 8.51 (d, 6H, J = 5.6 Hz).

ESI-MS: *m/z* 434.2 $[\mathrm{M{-}3ClO_4^-}]^{3+}$; 701.4 $[\mathrm{M{-}2ClO_4^-}]^{2+}$.

*2.4. Synthesis of copper(II) dichloro(4,4′,4″-tris[N,N-bis-(2-pyridylmethyl)aminomethyl]- triphenylamine) triperchrorate (**7**)*

The copper complex (**7**) was prepared by the similar method for **6** (yield 0.33 g, 99%).

ESI-MS: *m/z* 391.9 $[\mathrm{M{-}3ClO_4^-}]^{3+}$.

CAUTION: Although no problem was encountered in the preparation of the perchlorate salts, suitable care should be taken when handling such potentially hazardous compounds.