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Metal complexes with varying intramolecular hydrogen bonding networks

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This work is dedicated to Alfred Werner on the 100th Anniversary of his Nobel Prize in Chemistry in 1913.

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ABSTRACT

Alfred Werner described the attributes of the primary and secondary coordination spheres in his development of coordination chemistry. To examine the effects of the secondary coordination sphere on coordination chemistry, a series of tripodal ligands containing differing numbers of hydrogen bond (H-bond) donors were used to examine the effects of H-bonds on Fe(II), Mn(II)–acetato, and Mn(III)–OH complexes. The ligands containing varying numbers of urea and amidate donors allowed for systematic changes in the secondary coordination spheres of the complexes. Two of the Fe(II) complexes that were isolated as their Bu_4N^+ salts formed dimers in the solid-state as determined by X-ray diffraction methods, which correlates with the number of H-bonds present in the complexes (i.e., dimerization is favored as the number of H-bond donors increases). Electron paramagnetic resonance (EPR) studies suggested that the dimeric structures persist in acetonitrile. The Mn(II) complexes were all isolated as their acetato adducts. Furthermore, the synthesis of a rare Mn(III)–OH complex via dioxygen activation was achieved that contains a single intramolecular H-bond; its physical properties are discussed within the context of other Mn(III)–OH complexes.

1. Introduction

Alfred Werner described the primary and secondary coordination spheres in his development of modern inorganic chemistry for which he was awarded the 1913 Nobel prize in chemistry [1]. The primary coordination sphere is concerned with metal–ligand interactions which often govern molecular/electronic structure and reactivity. In the context of coordination chemistry, the secondary coordination sphere includes the microenvironment around a metal center and does not interact with metal centers through covalent bonds. Rather, the secondary coordination sphere is defined as interactions with ligands or other species within close proximity to the metal ion. The integration of these types of interactions within one molecular species is necessary to fully garner the capabilities of transition metal ions and provides many design challenges to modern inorganic chemists. In particular, the ability to control the secondary coordination sphere with non-covalent interactions has hindered progress in transition metal chemistry.

Several groups have been developing approaches whose aim it is to regulate both the primary and the secondary coordination sphere in synthetic transition metal complexes and proteins [2]. Our strategy involves the synthesis of complexes with intramolecular hydrogen bonds (H-bonds) [3]. The design of our ligands has been influenced by the structures found within the active sites of metalloproteins that use H-bonds proximal to metal ions to control many aspects of biological coordination chemistry [4]. These aspects range from physical properties such as redox potentials to substrate specificity and activation of small molecules. We have developed a series of tripodal ligands that allows for the systematic variation in of the number of intramolecular H-bond donors while keeping the primary coordination sphere constant (Fig. 1) [5]. These trianionic ligands utilize amidate/ureate groups that promote trigonal bipyramidal coordination geometry and provide H-bonding networks that can contain up to three intramolecular H-bonds. Previous studies have demonstrated how H-bonds affect the activation of dioxygen in cobalt(II) complexes and the physical properties in a series of Fe(III)-OH complexes [5]. In this report we examine the chemistry associated with a series of M(II) (M = Mn, Fe) complexes and present evidence that H-bonds can affect solution speciation. We further present the preparation and molecular structure of a new Mn(III)–OH complex and compare its structural properties to related complexes using this series of ligands.

2. Experimental details

2.1. General methods

All chemicals were purchased from commercial sources and used as received unless otherwise noted. Potassium hydride, dispersed in mineral oil, was filtered and washed at least five times with pentane and Et_2O, dried on a vacuum line, and stored under

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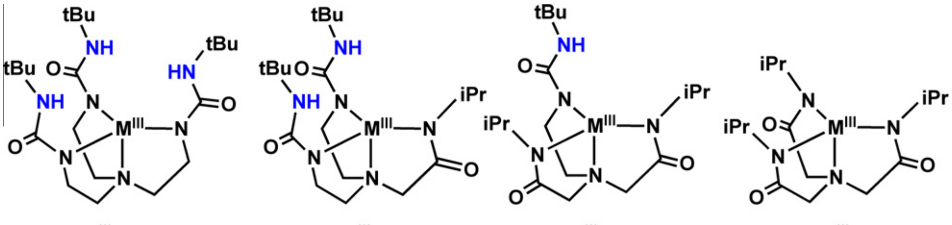

Fig. 1. The series of metal complexes with varying number of intramolecular H-bond donors used in this study.

an argon atmosphere. Ferrocenium tetrafluoroborate was synthesized as described by Geiger [6]. Solvents were purified using a JC Meyer Co. solvent purification system. All metal complexes were prepared in a Vacuum Atmospheres Co. dry box with an argon atmosphere. The ligands were prepared according to literature methods [5]. The $K_2[Mn^{II}H_3buea(\kappa^1\text{-}OAc)]$ salt was prepared as described by literature methods [7].

$[K(18\text{-}crown\text{-}6)]_2[Mn(II)H\mathbf{1}(OAc)]$. $H_4\mathbf{1}$ (100 mg, 0.28 mmol) was treated with KH (34 mg, 0.85 mmol) in 3 mL of DMA and allowed to stir until gas evolution ceased (~1 h). The foamy reaction mixture was treated with $Mn(OAc)_2$ (48 mg, 0.28 mmol) and allowed to stir for 2 h during which potassium acetate precipitated and was removed by filtration with a medium porosity glass fritted funnel. The filtrate was treated with 18-crown-6 (150 mg, 0.57 mmol) and stirred until completely dissolved. The solvent was removed under reduced pressure and the resulting white residue was treated with Et_2O until a white precipitate persisted, which was then collected on a glass fritted funnel and dried for 1 h under vacuum to yield a free flowing white powder (232 mg, 71%). FTIR (Nujol, cm^{-1}) ν(NH) 3373, 3170; ν(CO) 1641, 1552. *Anal.* Calc. for $[K(18\text{-}crown\text{-}6)]_2[Mn^{II}H\mathbf{1}(OAc)]\cdot DMA$, $C_{47}H_{92}K_2MnN_6O_{18}$: C, 48.31; H, 8.09; N, 7.59. Found: C, 48.56; H, 7.98; N, 7.23%. X-band EPR (DMSO, 77 K) $g = 23.45, 4.39, 3.12, 2.46, 1.96$.

$[K(18\text{-}crown\text{-}6)]_2[Mn^{II}H_2\mathbf{2}(OAc)]$. The same procedure for preparation of $[[K(18\text{-}crown\text{-}6)]_2[Mn^{II}H\mathbf{1}(OAc)]$ was followed using $H_5\mathbf{2}$ (100 mg, 0.25 mmol), KH (30 mg, 0.75 mmol), $Mn(OAc)_2$ (43 mg, 0.25 mmol), and 18-crown-6 (13 mg, 0.50 mmol) to afford 280 mg (44%) of the desired salt. ESIMS (*m*/*z*): 452.2 $[Mn^{II}H_2\mathbf{2}]^-$; 512.3 $[Mn^{II}H_2\mathbf{2}(OAc)]^-$. *Anal.* Calc. for $[K(18\text{-}crown\text{-}6)]_2$ $[Mn^{II}H_2\mathbf{2}(OAc)]\cdot DMA$, $C_{49}H_{97}K_2MnN_7O_{18}$: C, 48.88; H, 8.33; N, 8.10. Found: C, 48.82; H, 8.11; N, 8.13%. X-band EPR (DMA, 77 K) 28.45, 5.90, 3.06, 2.48, 1.96.

$[K(18\text{-}crown\text{-}6)]_2[Mn(II)\mathbf{0}^{cyp}(OAc)]$. The same procedure for preparation of $[K(18\text{-}crown\text{-}6)]_2[Mn^{II}H\mathbf{1}^{iPr}(OAc)]$ was followed using $H_3\mathbf{0}^{cyp}$ (100 mg, 0.26 mmol), KH (31 mg, 0.77 mmol), $Mn(OAc)_2$ (44 mg, 0.26 mmol), and 18-crown-6 (140 mg, 0.53 mmol) to yield 220 mg (73%) of the desired salt. FTIR (Nujol, cm^{-1}) ν(NH) 3165; ν(CO) 1646, 1554. *Anal.* Calc. for $[K(18\text{-}crown\text{-}6)]_2[Mn^{II}\mathbf{0}^{cyp}(OAc)]\cdot DMA$, $C_{51}H_{93}K_2MnN_5O_{18}$: C, 51.47; H, 8.01; N, 5.65. Found: C, 51.15; H, 7.83; N, 5.85%. X-band EPR (DMSO, 77 K) $g = 15.59, 5.61, 3.88, 2.87, 2.33, 1.91$.

$[K(18\text{-}crown\text{-}6)]_2[Mn(II)\mathbf{0}^{ipr}(OAc)]$. The same procedure for preparation $[K(18\text{-}crown\text{-}6)]_2[Mn^{II}H\mathbf{1}(OAc)]$ was followed using $H_3\mathbf{0}^{ipr}$ (100 mg, 0.32 mmol), KH (38 mg, 0.96 mmol), $Mn(OAc)_2$ (55 mg, 0.32 mmol), and 18-crown-6 (170 mg, 0.64 mmol) to produce 220 mg (68%) of the desired salt. FTIR (Nujol, cm^{-1}) ν(NH) 3168; ν(CO) 1647, 1553. *Anal.* Calc. for $[K(18\text{-}crown\text{-}6)]_2[Mn^{II}\mathbf{0}^{ipr}(OAc)]$, $C_{41}H_{78}K_2MnK_2N_4O_{17}$: C, 47.76; H, 7.89; N, 5.62. Found: C, 47.71; H, 7.62; N, 5.43%. X-band EPR (DMA, 77 K) $g = 16.18, 5.98, 3.94, 2.95, 2.44, 2.97$.

$[Bu_4N]_2[Fe(II)H_3buea]_2$. A solution of H_6buea (200 mg, 0.45 mmol) dissolved in 4 mL of anhydrous DMA was treated with solid KH (55 mg, 1.36 mmol) and stirred until gas evolution ceased. $Fe(OAc)_2$ (79 mg, 0.45 mmol) was added to the pale yellow solution, and stirring was continued for 30 min. The resulting amber filtrate was treated with $[Bu_4N][OAc]$ (140 mg, 0.45 mmol) and stirred for 2 h, resulting in the precipitation of a white solid (305 mg) that was filtered, washed twice with Et_2O, and dried under vacuum. The white solid was stirred in CH_3CN for 1 h and filtered to remove KOAc (105 mg, 96%). The light yellow filtrate was concentrated to half its original volume and the slow addition of Et_2O resulted in the formation of a white solid, which was then filtered, washed with Et_2O, and dried under vacuum to afford 150 mg (47%) of the desired salt. *Anal.* Calc. for $[Bu_4N]_2[Fe^{II}H_3buea]_2$, $C_{74}H_{156}Fe_2N_{16}O_6$: C, 60.14; H, 10.64; N, 15.16. Found: C, 61.19; H, 10.89; N, 15.68%. FTIR (Nujol, cm^{-1}) ν(NH) 3335, ν(CO) 1663, 1592, 1571, 1556. Single crystals were grown by diffusion of Et_2O into a CH_3CN solution of the crude complex.

$[Bu_4N]_2[Fe(II)H_2\mathbf{2}^{iPr}]_2$ was prepared following a similar procedure to that of $[Bu_4N]_2[Fe(II)H_3buea]_2$ with $H_5\mathbf{2}^{iPr}$ (150 mg, 0.37 mmol), KH (45 mg, 1.12 mmol), $Fe(OAc)_2$ (66 mg, 0.37 mmol), and $[Bu_4N][OAc]$ (113 mg, 0.37 mmol). The amount of KOAc obtained was 105 mg (96% for 3 equiv) and 100 mg (42%) of $[Bu_4N]_2$ $[Fe^{II}H_2\mathbf{2}^{iPr}]$ was isolated. Single crystals were grown by diffusion of Et_2O into a CH_3CN solution of the complex. FTIR (Nujol, cm^{-1}) ν(NH) 3332, ν(CO) 1661, 1590, 1561, 1520. Repeated attempts to obtain a satisfactory elemental analysis were unsuccessful.

$K_2[Mn(II)H\mathbf{1}(OH)]$. $H_4\mathbf{1}$ (0.050 mg, 0.14 mmol) was deprotonated with 4 equiv KH (23 mg, 0.57 mmol) in 3 mL of DMA and allowed to stir for 4 h. To the thick foamy suspension was added $Mn(OAc)_2$ (26 mg, 0.15 mmol) after which the reaction mixture was stirred for 30 min. H_2O (2.5 μL, 0.14 mmol) was added and allowed to stir for 30 min. The mixture was filtered and the resulting DMA solution was allowed for slow vapor diffusion of Et_2O yielding a white microcrystalline solid, which after several days was isolated on a fritted glass funnel and washed 3 × 3 mL MeCN, 3 × 5 mL Et_2O (32 mg, 46%). FTIR (Nujol, cm^{-1}) ν(OH) 3503; ν(NH) 3244, 3142; ν(CO) 1655, 1567, 1507. *Anal.* Calc. for $K_2[Mn^{II}H\mathbf{1}(OH)]\cdot 0.5DMA$, $C_{19}H_{37.5}K_2MnN_{5.5}O_{4.5}$: C, 41.93; H, 7.37; N, 13.65. Found: C, 41.63; H, 6.89; N, 14.05%. X-band EPR (DMF, 77 K) $g = 14.32, 5.81, 1.99, 1.55, 1.28$.

$K[Mn(III)H\mathbf{1}(OH)]$. Method A. $H_4\mathbf{1}$ (110 mg, 0.30 mmol) was dissolved in 3 mL of DMA and treated with KH (36 mg, 0.90 mmol) and the reaction mixture was allowed to stir. After ~19 h the reaction mixture was treated with $Mn(OAc)_2$ (51 mg, 0.29 mmol) and stirred for an addition 1 h, after which the reaction was filtered to remove 1 equiv of KOAc (26 mg, 91%). The pale yellow filtrate was treated with O_2 (7.2 mL, 0.29 mmol, 298 K, 1 atm) causing an immediate color change to dark forest green, which slowly turned brownish green. After stirring for an additional 1 h the system was evacuated to remove excess O_2 and brought back into an anaerobic drybox. The solvent was removed under reduced pressure and the resulting residue was extracted with MeCN (1 mL) and DMA (1 mL) and passed through a fritted glass funnel to remove a second equiv of KOAc. The green filtrate was concentrated to less than 1 mL and Et_2O was added to precipitate the salt, which was collected on a fritted glass funnel. A brown species was removed from the crude green solid by washing up to 3 × 0.5 mL DMA (or until washings