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A single tripodal ligand stabilizing three different oxidation states (II, III, and IV) of manganese[†]

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A series of mononuclear Mn^{II}, Mn^{III}, and Mn^{IV} complexes was prepared using a single tripodal ligand (H₃L). Addition of a cation (NH₄⁺, K⁺, Na⁺) to [Mn^{III}L] showed a pronounced effect on the redox potentials. Different variants of Jahn–Teller distortion, axial elongation and compression, were observed in the Mn^{III} complexes.

Manganese can have a wide variety of oxidation states. Mixed-valence manganese clusters play an important role in creating single-molecule magnets (SMMs).¹ For example, Langley *et al.* reported a {Mn₃₂} complex involving 18Mn^{II}, 10Mn^{III}, and 4Mn^{IV} displaying probable SMM features.^{1b} In such a polynuclear complex, the Mn ions with different oxidation states are in different coordination environments. It is not easy to isolate Mn complexes in the same ligand system with several different oxidation states. In addition, relatively few mononuclear Mn^{IV} complexes have been isolated and structurally characterized.² Recently, we have shown that the tripodal H₃L ligand (= 1,1,1-tris[(3-methoxysalicylideneamino)methyl]ethane, Fig. 1) containing three imine groups, three phenol groups, and three methoxy groups is a versatile ligand and can accommodate a metal ion with differing nature and size.³

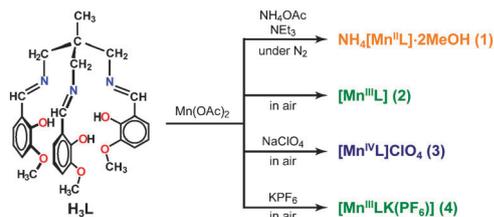


Fig. 1 The H₃L ligand and complexes 1–4.

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[†] Electronic supplementary information (ESI) available: Synthesis and characterisation of the complexes, BVS calculations, X-ray crystal data of all complexes and molecular structures of **3** and **3'**, and preliminary HFEPFR results for **1** and **2**. CCDC 812372–812377. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1cc12418h

We expected that L³⁻ would stabilize all three major oxidation states, II, III, and IV, of manganese. These [Mn^{II}L]⁻, [Mn^{III}L], and [Mn^{IV}L]⁺ complexes would give us a rare opportunity to compare directly the structures and properties between them.

Manganese is involved in a number of redox enzymes, such as superoxide dismutase, the oxygen-evolving center of photosystem II, and catalases.^{4,5} For these processes to take place smoothly, the oxidation state of manganese should change easily. Our complexes will fulfill the requirement. While in most of the manganese metalloproteins and enzymes the active sites involve more than one metal ion, the study of mononuclear model complexes is important because evidence for Mn^{IV} reactive intermediates has been obtained in catalytic reactions of mononuclear Mn^{III} complexes.⁶ Here, we report the preparation, structures, and magnetic and electrochemical properties of mononuclear Mn^{II}, Mn^{III}, and Mn^{IV} complexes of a single H₃L ligand, as well as the effect of a cation on the oxidation state of the complexes.

Mikuriya *et al.*^{2c} reported that the reaction of Mn^{II}(CH₃CO₂)₂·4H₂O with a tridentate ONO Schiff-base ligand such as *o*-(salicylideneaminomethyl)phenol (1:2) in methanol in air gave the Mn^{IV}O₄N₂-type complex. We expected that a similar reaction would afford [Mn^{III}L] and [Mn^{IV}L]⁺, and by adding a suitable counteranion (X⁻), [Mn^{IV}L]X would be isolated. [Mn^{II}L]⁻ should form under anaerobic conditions. The red NH₄[Mn^{III}L]·2CH₃OH complex (**1**) was prepared by the reaction of Mn^{II}(CH₃CO₂)₂·4H₂O, H₃L, NH₄CH₃CO₂, and N(C₂H₅)₃ in a 1:2:2:4 mole ratio in methanol under a N₂ atmosphere. The dark green [Mn^{III}L] complex (**2**) was prepared from Mn^{II}(CH₃CO₂)₂·4H₂O and H₃L (1:1) in dichloromethane–methanol in air. To isolate the Mn^{IV} complex, [Mn^{IV}L]X, the presence of an appropriate counteranion (X⁻) is required, and when we added 1 equiv. of NaClO₄ to the reaction mixture for the preparation of [Mn^{III}L] (**2**), the dark green [Mn^{IV}L]ClO₄ complex (**3**) was obtained. The addition of NaPF₆ instead of NaClO₄ also gave an Mn^{IV} complex, [Mn^{IV}L]PF₆ (**3'**). Thus, the oxidizing agent in these reactions should be O₂. Interestingly, upon addition of KPF₆ instead of NaClO₄ or NaPF₆, dark green [Mn^{III}LK(PF₆)] (**4**) was isolated. Similarly, the addition of KNO₃ gave [Mn^{III}LK(NO₃)] (**5**). The oxidation states of manganese were assigned on the basis of the magnetic susceptibility measurements. The μ_{eff} values at 300 K were 5.98 (**1**),

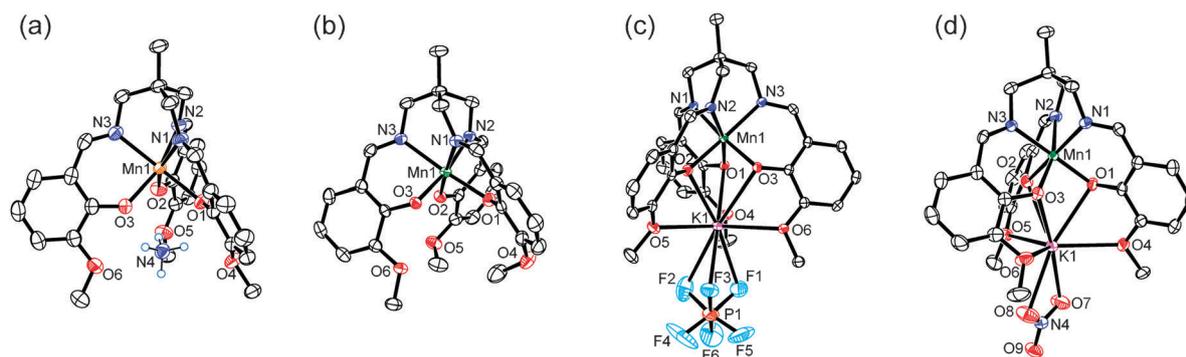


Fig. 2 Molecular structures of (a) $\text{NH}_4[\text{Mn}^{\text{II}}\text{L}]\cdot 2\text{CH}_3\text{OH}$ (**1**), (b) $[\text{Mn}^{\text{III}}\text{L}]$ (**2**), (c) $[\text{Mn}^{\text{III}}\text{LK}(\text{PF}_6)]$ (**4**), and (d) $[\text{Mn}^{\text{III}}\text{LK}(\text{NO}_3)]$ (**5**) with atom numbering schemes showing the 50% probability ellipsoids. Methanol molecules of **1** and the hydrogen atoms except for NH_4^+ (greenish blue) have been omitted for clarity. Color code: orange, Mn^{II} ; green, Mn^{III} ; black, C; blue, N; red, O; light blue, F; pink, K; and reddish orange, P.

5.00 (**2**), 3.90 (**3**), 3.92 (**3'**), 4.95 (**4**), and 4.91 μ_{B} (**5**). These values are in good agreement with the spin-only μ_{eff} values for HS Mn^{II} ($3d^5$: 5.92 μ_{B} , **1**), HS Mn^{III} ($3d^4$: 4.89 μ_{B} , **2**, **4**, and **5**), and Mn^{IV} ($3d^3$: 3.87 μ_{B} , **3** and **3'**).

The structures of the complexes were determined by X-ray diffraction (crystal data, ESI[†]). In each complex unit the point group is C_1 , although the highest point group could be C_3 . If only the chromophore is considered, then the site symmetry around a central Mn cation would be C_{3v} . The coordination polyhedron in every compound is a trigonally distorted octahedron. In the case of the Mn^{III} , the Jahn–Teller effect is operational. There are two deformational E modes resulting in either elongation or compression in one of the O–Mn–N directions. Which one of the two deformations will be stabilized in the solid state, depends on a suitable inter- or intramolecular interaction. Each Mn ion is coordinated by a fully deprotonated L^{3-} ligand *via* three phenolate oxygen atoms and three imine nitrogen atoms (Fig. 2). In **1**, the four H atoms of NH_4^+ are hydrogen bonded to the six O atoms of the L^{3-} ligand. In accordance with the Jahn–Teller theorem, the pseudo-octahedron about $[\text{Mn}^{\text{III}}\text{L}]$ (**2**) is distorted and elongation is observed along the O1–Mn1–N3 direction. In the crystal of **4**, the K atom is nine-coordinated by three methoxy and three phenolate O atoms, and three F atoms of PF_6^- (Fig. 2(c)), and **4** is best formulated as $[\text{Mn}^{\text{III}}\text{LK}(\text{PF}_6)]$. Jahn–Teller distortion is also observed in **4** and the distortion is seen along the O3–Mn1–N1 direction. However, compression is observed in this complex. There are many examples of HS Mn^{III} complexes exhibiting a tetragonal elongation or a rhombic distortion; however, those that display axially compressed octahedral environments are uncommon.⁷ It is to be noted that a closely related Mn^{III} complex, $[\text{Mn}^{\text{III}}\text{LK}(\text{NO}_3)]$ (**5**), shows an elongation along the O3–Mn1–N2 direction (Fig. 2(d)). In $[\text{Mn}^{\text{IV}}\text{L}]\text{ClO}_4$ (**3**), a ClO_4^- ion exists as a counteranion (Fig. S1, ESI[†]), and the coordinate bonds are shorter than those of the Mn^{III} complexes. The Mn^{II} complex (**1**) has the longest coordinate bonds among the five complexes. The differences in coordinate bond lengths (Tables S1–S3, ESI[†]) correspond well with the differences in the effective ionic radii of six-coordinate Mn (HS Mn^{2+} , 0.83 Å; HS Mn^{3+} , 0.645 Å; Mn^{4+} , 0.53 Å),⁸ confirming that the oxidation states of **1**, **2**, **3**, **4**, and **5** are II, III, IV, III, and III, respectively. The bond valence sum (BVS) calculations supported these assignments (Table S4, ESI[†]).

Magnetic properties of complexes **1–5** were investigated by bulk magnetometry, and by high-frequency and -field electron paramagnetic resonance (HF-EPR). In this Communication we will present magnetic properties of the structurally most interesting complex **4**. Preliminary HF-EPR results for complexes **1** and **2** are given in Fig. S3 and S4 (ESI[†]), respectively.

The room-temperature magnetic moment of **4** (4.95 μ_{B}) agrees with the $S = 2$ ground state of the complex. The steep drop at low temperatures is a signature of zero-field splitting (zfs) effects. The full temperature dependence has been fitted to the spin Hamiltonian of the form

$$\mathcal{H} = \beta B g S + D(S_z^2 - S(S + 1)/3). \quad (1)$$

where D stands for the axial zfs parameter and the remaining symbols adopt their usual meaning. The resulting values are $|D| = 3.5 \pm 0.5 \text{ cm}^{-1}$, and $g_{\text{iso}} = 2.02 \pm 0.01$. The sign of D could not be determined. The experimental and simulated plots of magnetic moment vs. temperature are shown in the inset to Fig. 3.

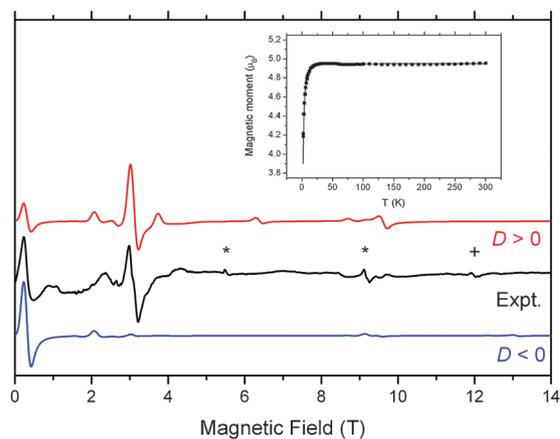


Fig. 3 Inset: Experimental plot of effective magnetic moment vs. temperature for **4** (squares) together with a simulated dependence (represented by the curve) using spin Hamiltonian parameters $S = 2$, $|D| = 3.5 \text{ cm}^{-1}$, $g_{\text{iso}} = 2.02$. Main part: experimental (black trace) and simulated (color traces) HF-EPR spectra of **4** at 10 K and 331.2 GHz. Simulation parameters: $S = 2$, $|D| = 4.15$, $|E| = 0.75 \text{ cm}^{-1}$, $g_{\text{iso}} = 2.00$, isotropic single-crystal linewidth 80 mT. Resonances marked with an asterisk originate from molecular dioxygen, the resonance with a plus sign from a $g = 2$ impurity (presumably $\text{Mn}(\text{II})$).

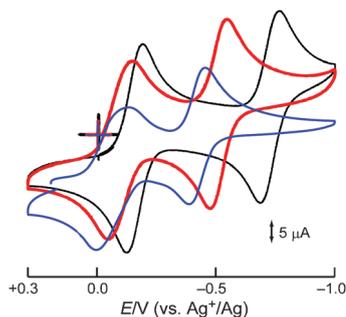


Fig. 4 CVs of $[\text{Mn}^{\text{III}}\text{L}]$ (**2**, black), $[\text{Mn}^{\text{III}}\text{LK}(\text{PF}_6)]$ (**4**, red), and $\text{NH}_4[\text{Mn}^{\text{II}}\text{L}]$ (**1**, blue) in acetonitrile containing 0.1 M $(n\text{-Bu})_4\text{NBF}_4$ at a glassy carbon electrode at a sweep rate of 100 mV s^{-1} .

All complexes investigated as solids showed a strong response in HFEP experiments. The quality of EPR data for **4** was adversely affected by very strong field-induced torquing effects that could be only partly prevented by pressing a pellet. Fig. 3 (main part) shows a low-temperature EPR spectrum of **4** together with two simulations using the same magnitude of $|D| = 4.15 \text{ cm}^{-1}$, but differing in sign.[†] Although the agreement between the simulations and experiment is not as good as in many other Mn^{III} complexes studied so far (or other Mn^{III} complexes in the discussed series), it is clearly much better for the case of positive D than for negative D . Thus, as expected by a simple ligand-field theory, and indeed previously observed by EPR,^{7e} the Jahn–Teller compression results in positive D . We note at this point that certain Mn^{III} complexes have been shown to exhibit polymorphism, with different structures showing either a Jahn–Teller elongation or a compression.^{7f,9} Such a possibility cannot be excluded for **4**.

As described above, **2** ($[\text{Mn}^{\text{III}}\text{L}]$) was obtained by the reaction of $\text{Mn}^{\text{II}}(\text{CH}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$ and H_3L in air, while addition of NaClO_4 and NaPF_6 to this reaction mixture yielded $[\text{Mn}^{\text{IV}}\text{L}]\text{ClO}_4$ (**3**) and $[\text{Mn}^{\text{IV}}\text{L}]\text{PF}_6$ (**3'**), respectively. We were intrigued by the fact that the addition of KPF_6 gave the Mn^{III} complex, $[\text{Mn}^{\text{III}}\text{LK}(\text{PF}_6)]$ (**4**) rather than $[\text{Mn}^{\text{IV}}\text{L}]\text{PF}_6$ (**3'**). The results suggest that K^+ prevents the oxidation of Mn^{II} from proceeding to Mn^{IV} . To study the effect of K^+ on the redox potential, we compared the cyclic voltammograms (CVs) of the two Mn^{III} complexes, $[\text{Mn}^{\text{III}}\text{L}]$ (**2**) and $[\text{Mn}^{\text{III}}\text{LK}(\text{PF}_6)]$ (**4**), in acetonitrile (Fig. 4). Both complexes showed two reversible redox couples, $\text{Mn}^{\text{IV}}/\text{Mn}^{\text{III}}$ (**2**: $E_{1/2}^1 = -0.156 \text{ V}$; **4**: $E_{1/2}^1 = -0.090 \text{ V}$) and $\text{Mn}^{\text{III}}/\text{Mn}^{\text{II}}$ (**2**: $E_{1/2}^2 = -0.727 \text{ V}$; **4**: $E_{1/2}^2 = -0.505 \text{ V}$). The $\text{Mn}^{\text{IV}}/\text{Mn}^{\text{III}}$ redox potential ($E_{1/2}^1$) of **4** is observed at a less negative potential than that of **2** by 0.066 V, and thus **4** is more difficult to oxidize to Mn^{IV} . Addition of Na^+ (1 equiv.) to an acetonitrile solution of **2** also shifted the redox potentials to less negative values; however, the position of $E_{1/2}^1 = -0.13 \text{ V}$ is more negative than the position ($E_{1/2}^1 = -0.09 \text{ V}$) with K^+ (1 equiv.), in accordance with the fact that the Mn^{IV} complexes (**3**, **3'**) were obtained by the addition of NaClO_4 and NaPF_6 . The $E_{1/2}^1$ value (-0.060 V) of **1** was observed at a less negative potential than that of the other complexes, **2–4** (Fig. 4). When NH_4^+ (1 equiv.) was added to a solution of **2**, the same CV as that of **1** was obtained. Thus, counteranions show a pronounced effect on the redox potentials of $[\text{Mn}^{\text{III}}\text{L}]$.

The effect decreases in the order: $\text{NH}_4^+ > \text{K}^+ > \text{Na}^+$. Hydrogen bonding of NH_4^+ or coordination of an alkali metal ion to $[\text{Mn}^{\text{III}}\text{L}]$ via three methoxy and three phenolate oxygen atoms results in a decrease in electron density on Mn, thus the metal becomes difficult to oxidize to Mn^{IV} and easier to reduce to Mn^{II} .

It is known that mononuclear hexacyanomanganate complexes can have a wide variety of oxidation states from Mn^{I} ($[\text{Mn}^{\text{I}}(\text{CN})_6]^{5-}$) to Mn^{IV} ($[\text{Mn}^{\text{IV}}(\text{CN})_6]^{2-}$).¹⁰ However, cyanide is an unusual ligand with both strong σ -donating and π -accepting abilities. To the best of our knowledge, the present work is the first example of the isolation of Mn complexes of a single ligand containing oxygen and nitrogen donor atoms with three different oxidation states whose structures have been characterized by X-ray analysis.

Notes and references

[†] The spin Hamiltonian used in the simulations was the same as in eqn (1) except for an additional zfs rhombic term, E .

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