

Influence of second sphere hydrogen bonding interaction on a manganese(II)-aquo complex

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Supplementary Information

I. Experimental Section

Syntheses

Ligand synthesis:

2-(4-tertbutyl-2-hydroxyphenyl)-benzimidazole (a): A mixture of 5-tert-Butyl-2-hydroxybenzaldehyde (1 g, 5.6 mmol) in methanol (30 mL) was added 1,2-phenylenediamine (0.607 g, 5.6 mmol, 1 eq) at 0°C. the mixture was stirred for one hour at 0°C. one equivalent of benzofuroxane (0.763g, 5.6 mmol) was dissolved in 5 mL of acetonitrile and added to mixture at room temperature. The brown solution was stirred at 60 °C for four hours, then cooled to 0°C and 10 mL of NaOH(10%) was added. The red solution was poured into 250 mL of water, and concentrated HCl was added to neutralize the solution. To complete the precipitation the mixture was stored in freezer over night. The crude product was collected by filtration, washed with cold water. The resulting solid was extracted by CH₂Cl₂ and dried over MgSO₄. The solution was filtered and the solvent was evaporated from the filtrate, to produce a beige powder that was dried under vacuum. (89% yield). NMR (¹H, 300 MHz, CDCl₃): δ 7.58 (d, 2H), 7.45 (d, 1H), 7.42 (d, 1H), 7.32 (dd, 2H) 7.11 (d, 1H), 1.39 (s, 9H). Positive EI-MS: m/z 266 [M+H⁺].

2-hydroxy-3-(benzimidazole)-4-tertbutylbenzaldehyde (b): was obtained according to literature procedures^[1]. A stirred mixture containing 2-(4-tertbutyl-2-hydroxyphenyl)-benzimidazole (1.173 g, 4.4 mmol), Hexamethylenetetramine (0.618g, 4.4 mmol, 1 eq) and trifluoroacetic acid (TFA, 10 mL) was refluxed for two days. 30 mL of cold water was added to the reaction mixture at room temperature, the brown precipitate was filtered, washed with cold water and dried by suction. The resulting solid was extracted by CH₂Cl₂ and dried over MgSO₄. The solution was filtered and the solvent was evaporated from the filtrate, to produce a yellow-brown powder that was dried under vacuum. (80% yield). NMR (¹H, 300 MHz, CDCl₃): δ 10.14 (s, 1H), 8.79 (s, 1H), 7.77 (d, 2H), 7.34 (dd, 3H), 1.42 (s, 9H). Positive EI-MS: m/z 295 [M+H⁺].

LH₂: To a solution of 451 mg (1.86 mmol) of N,N-bis(2-pyridylmethyl)ethane-1,2-diamine (c)^[2] in 50 mL of dry ethanol was added to one equivalent of 2-hydroxy-3-(benzimidazole)-4-tertbutylbenzaldehyde (b) The solution was stirred at room temperature for 3 hours under argon. The solvents were evaporated and the resulting brown oil was dried under vacuum. The crude product was purified by flash chromatography (CH₂Cl₂/MeOH) to yield the ligand LH₂ as a brown oil (70% yield): ¹H NMR (300 MHz, CDCl₃): δ 11.66 (s, 1H, OH), 8.52 (d, 2H), 8.29 (s, 1H), 7.61-7.04 (m, 8H, H-Ar), 3.94 (s, 4H), 3.75 (t, 2H), 2.95 (t, 2H), 1.49 (s, 9H). Positive EI-MS: m/z 519 [M+H⁺].

Complex synthesis:

Caution: Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small quantities of these compounds should be prepared and they should be handled behind suitable protective shields.

[(LH)Mn(II)(OH₂)](ClO₄)₂. [3](ClO₄)₂: 152 mg (0.420 mmol) of Mn(ClO₄)₂·6(H₂O) dissolved in 2 mL of acetonitrile was added to one equivalent of LH₂ dissolved in 8 mL of ethanol. The brown solution was stirred for 2 h and concentrated by evaporation. A yellow powder was precipitated by addition of diethyl ether collected by filtration, and dried in vacuum (Yield 75 %). The powder was further dissolved in methanol/water, and after slow diffusion of diethyl ether, yellow monocrystals of [3](ClO₄)₂ suitable for X-ray analysis were produced. Elemental analysis for [3](ClO₄)₂·0.5 CH₃OH·0.5H₂O: MnC_{32.5}H₃₉Cl₂N₆O₁₁ calcd (%): C 47.86, H 4.82, N 10.30; found (%): C 47.90, H 4.50, N 10.54. ESI-MS : m/z = 572.26 [(L)Mn]⁺

[(LH)Mn(II)(Cl)](PF₆). [2](PF₆): 83.1 mg (0.420 mmol.) of Mn(Cl)₂·4(H₂O) dissolved in 2 mL of acetonitrile was added to One equivalent of LH₂ dissolved in 8 mL of ethanol. The brown solution was stirred for 2 h. Two equivalents of NaPF₆ (102.7 mg, 0.840 mmol) were then added and the brown solution which was stirred for an additional 3h, and concentrated by evaporation. A yellow powder was precipitated by addition of diethyl ether collected by filtration, and dried in vacuum (Yield 65 %). Elemental analysis for [2](PF₆): MnC₃₂H₃₃ClN₆OPF₆ calcd (%): C 51.04, H 4.42, N 11.16; found (%): C 50.90, H 4.50, N 11.44. ESI-MS : m/z = 572.32 [(L)Mn]⁺.

Elemental analyses: were carried out at the Services de Microanalyse, ICSN-CNRS, Gif-sur-Yvette, France.

Electrospray Ionization Mass Spectrometry: Mass spectra were recorded with a Finnigan MAT95S in a BE configuration at low resolution on micromolar acetonitrile solution.

NMR spectroscopy: ¹H-NMR spectra were recorded on a Bruker DPX 300 MHz with a ONP probe at room temperature in *d*₁-CDCl₃ (δ = 7.24 ppm).

EPR spectroscopy: 9.4 GHz EPR (X-band) spectra were recorded on a Bruker ELEXSYS 500 spectrometer equipped with an Oxford Instrument continuous flow liquid helium cryostat and a temperature control system. A dual mode cavity (Bruker ER 4116DM) was used for perpendicular and parallel mode detection, respectively. Solutions spectra were recorded in MeCN containing 0.2 M Bu₄NPF₆.

EPR recording conditions: microwave frequency 9.42 GHz; modulation frequency 100 kHz; microwave power 0.25 mW (perpendicular mode) and 1 mW (parallel mode); modulation

amplitude 1 mT and 0.7 mT (parallel mode); T 10 K (perpendicular mode) and 5 K (parallel mode).

Cyclic voltammetry and bulk electrolysis: All electrochemical experiments were run under Argon atmosphere. Cyclic voltammetry and coulometry measurements were recorded either an Metrohm potentiostat (AUTOLAB model). For cyclic voltammetry, the counter electrode used was a Pt wire and the working electrode a glassy carbon disk carefully polished before each voltammogram with a 1 μm diamond paste, sonicated in ethanol bath and then washed with ethanol. The reference electrode used was an Ag/AgClO₄ electrode with acetonitrile as solvent (0.3 V vs. SCE electrode), isolated from the rest of the solution by a fritted bridge. For bulk electrolysis, the counter electrode used was a piece of Pt, separated from the rest of the solution with a fritted bridge. The working electrode was a cylinder of glassy carbon. Supporting electrolyte NBu₄PF₆ (Aldrich, puriss) was 0.1 M (20°C) or a 0.2 M (low temperature) in acetonitrile (Aldrich, puriss). Low temperature regulation was ensured by a Julabo circulation cryostat.

X-ray diffraction: data were collected on a Kappa X8 APPEX II Bruker diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). The temperature of the crystal was maintained at the selected value (100K) by means of a 700 series Cryostream cooling device within an accuracy of ± 1 K. The data were corrected for Lorentz polarization, and absorption effects. The structures were solved by direct methods using SHELXS-97^[3] and refined against F^2 by full-matrix least-squares techniques using SHELXL-97^[4] with anisotropic displacement parameters for all non-hydrogen atoms. Treatment on H: H atoms of the ligand were added geometrically and refined by the riding model. H atoms of water moieties were added from the difference Fourier map, and refined by DFIX instructions in which O-H distances were set 0.96(3) \AA and H-H distances 1.52(3) \AA according to the ideal molecular geometry of water, and with one common isotropic thermal parameter. All calculations were performed by using the Crystal Structure crystallographic software package WINGX.^[5]

CCDC 817802/CCDC 828978 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

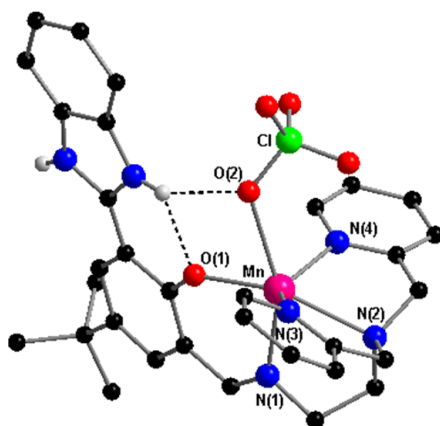


Fig 1. Crystal structure of $[3\text{ClO}_4]^+$. Hydrogen atoms counter anions and solvent molecules were omitted for clarity.

II. Crystallographic Data

Table 1. Selected bond lengths [\AA] and angles [$^\circ$] for $[3]^{2+}$ and $[3\text{ClO}_4]^+$

$[3]^{2+}$			
Mn – O(1)	2.056(4)	Mn – N(3)	2.164(4)
Mn – N(1)	2.233(5)	Mn – N(4)	2.190(4)
Mn – N(2)	2.363(5)	Mn – O(2)	2.292(4)
O(1) – Mn – O(2)	77.69(14)	N(1) – Mn – N(4)	103.35(17)
O(1) – Mn – N(1)	81.04(15)	N(2) – Mn – N(3)	75.84(17)
O(1) – Mn – N(2)	155.22(16)	N(2) – Mn – N(4)	74.35(16)
O(1) – Mn – N(3)	114.99(17)	N(2) – Mn – O(2)	125.90(16)
O(1) – Mn – N(4)	101.19(15)	N(3) – Mn – N(4)	142.94(17)
N(1) – Mn – N(2)	76.50(17)	N(3) – Mn – O(2)	90.69(17)
N(1) – Mn – O(2)	157.03(16)	N(4) – Mn – O(2)	89.27(16)
N(1) – Mn – N(3)	90.49(17)		
$[3\text{ClO}_4]^+$			
Mn – O(1)	2.043(2)	Mn – N(3)	2.157(3)
Mn – N(1)	2.215(3)	Mn – N(4)	2.176(3)
Mn – N(2)	2.367(3)	Mn – O(2)	2.429(3)
O(1) – Mn – O(2)	74.30(9)	N(1) – Mn – N(4)	107.70(11)
O(1) – Mn – N(1)	81.32(11)	N(2) – Mn – N(3)	75.27(10)
O(1) – Mn – N(2)	156.61(11)	N(2) – Mn – N(4)	74.98(12)
O(1) – Mn – N(3)	117.91(11)	N(2) – Mn – O(2)	128.32(11)
O(1) – Mn – N(4)	103.45(12)	N(3) – Mn – N(4)	132.91(11)
N(1) – Mn – N(2)	76.04(12)	N(3) – Mn – O(2)	83.31(10)
N(1) – Mn – O(2)	155.59(10)	N(4) – Mn – O(2)	87.42(11)
N(1) – Mn – N(3)	99.48(12)		

Table 2. Crystallographic Data for [3](ClO₄)₂. 0.5 CH₃OH and [3ClO₄](ClO₄).CH₃CN.

Empirical formula	C _{32.5} H ₃₈ Cl ₂ MnN ₆ O _{10.5}	C ₃₄ H ₃₇ Cl ₂ MnN ₇ O ₉
Formula weight	806.53	813.55
Temperature (K)	100(1)	100(1)
Wavelength (Å)	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ /n	<i>P</i> 2 ₁ /n
Unit cell dimensions		
<i>a</i> (Å)	9.0226(7)	9.4655(5)
<i>b</i> (Å)	16.6220(17)	13.8053(7)
<i>c</i> (Å)	25.429(3)	27.3775(15)
α (°)	90.00	90.00
β (°)	100.063(2)	94.840(2)
γ (°)	90.00	90.00
<i>V</i> (Å ³)	3755.0(6)	3564.8(3)
<i>Z</i>	4	4
D _{calc.} (Mg.m ⁻³)	1.427	1.516
Absorption coefficient (mm ⁻¹)	0.557	0.586
F (0 0 0)	1672	1680
Reflection collected	52480	73536
Independent reflections (Rint)	9098 (0.0998)	10833 (0.0506)
Observed reflections (<i>I</i> > 2σ(<i>I</i>))	5284	8332
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	0.0747	0.0793
<i>S</i>	1.027	1.059
(Δ ρ) _{max, min} [e Å ⁻³]	1.035, -0.915	1.047, -0.963

References

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