

Iodomanganesecorrole – a stable Mn^{IV}–I species

Martin Bröring,* Christian Hell and Carsten D. Brandt

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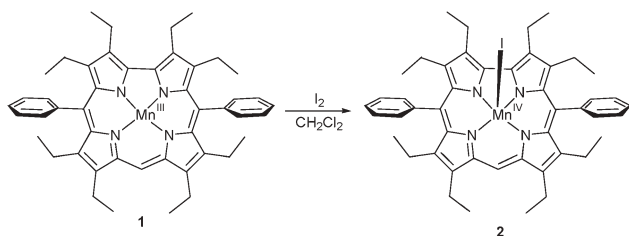
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The first compound with a Mn^{IV}–I bond has successfully been prepared by oxidation of a manganese(III) corrole with molecular iodine and was structurally characterized by X-ray diffraction.

A well-established reaction of the halogenide anions Cl[−], Br[−] and I[−] is their ready oxidation to the corresponding diatomic halogens and beyond upon contact with Mn^{IV} and other high-valent manganese species. The oxidative power of a Mn ion, however, can easily be tuned by binding it to a suitable ligand, and several isolable chloro- and even bromo complexes of manganese in higher oxidation states have been obtained in the past by this approach.^{1,2} In order to prepare iodomanganese(IV) species an even larger degree of stabilization of the high oxidation state at the metal atom would be required. However, suitable ligands are rare, and examples of respective compounds have not yet appeared in the scientific literature.

One such ligand capable of stabilizing high oxidation states is the tetrapyrrolic macrocycle corrole, which deviates from the porphyrin by the formal loss of one methine carbon.³ Corroles have often been employed in recent years in order to stabilize unusually high oxidation states of manganese like +5^{2b,4} and even +6.⁵ As we could show earlier manganese(III) corroles are formed in an oxidative macrocyclization reaction upon treatment of the open-chain tetrapyrrole 2,2'-bidipyrrole with Mn(OAc)₂ and molecular dioxygen in reasonable yields. The manganese ion in these complexes is easily oxidized to the +4 oxidation state by *e.g.* chromatography on silica with dichloromethane in air.⁶ As shown below the stabilizing effect of the corrole macrocycle is in fact sufficiently strong to prepare even the iodo derivative of a manganese(IV) corrole.

As depicted in Scheme 1, the reaction of the Mn^{III} chelate **1** with a slight excess of molecular iodine in dichloromethane results in a clean transformation to the iodomanganese(IV) corrole **2**



Scheme 1 Preparation of iodomanganese(IV) corrole **2** by oxidation of manganese(III) corrole **1** with molecular iodine.

Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Straße, 35043, Marburg, Germany.
E-mail: Martin.Broering@chemie.uni-marburg.de

which is isolated in 93% yield.[†] The composition C₄₇H₅₁N₄MnI of the new compound was proven by elemental analysis while mass spectra only show the signal at *m/z* = 726 for the [M – I]⁺ ion. Thermally, **2** is surprisingly stable and decomposes only above 265 °C.

A suitable crystal for a X-ray crystallographic analysis of **2** was obtained by slow evaporation of a saturated solution of the compound in a dichloromethane-*n*-hexane mixture.[‡] **2** crystallizes in the triclinic system, space group *P* $\bar{1}$, with two formula units in the unit cell. Fig. 1 shows the molecular structure of **2** and summarizes selected data.

The iodo ligand is bound to the manganese(IV) atom in a distance of 2.6626(4) Å. As expected this value is smaller than that found in a related case for a manganese(III) tetraphenylporphyrin (tpp)MnI with 2.767 Å.⁷ In addition, the iodo ligand in **2** is slightly tilted towards the bipyrrolic unit by approximately 5°. The Mn–N bond lengths are found from 1.9200(18) to 1.9447(18) Å with the two bonds to the N atoms of the bipyrrole fragment being shorter than the other two. The average Mn–N bond length of 1.932 Å, however, is very similar to those found for two chloro- (1.932 and 1.934 Å) and the one bromomanganese(IV) corrole (1.925 Å)³ which had been structurally characterized before. The manganese atom of **2** is displaced 0.3798(4) Å from the least-squares plane formed by the pyrrole nitrogen atoms and displays a domed square-pyramidal coordination. This displacement value is much larger than in the Mn^{III} case of (tpp)MnI, but resembles roughly those found in other halogenomanganese(IV) corroles (Table 1), for which only insignificantly smaller value have been reported.

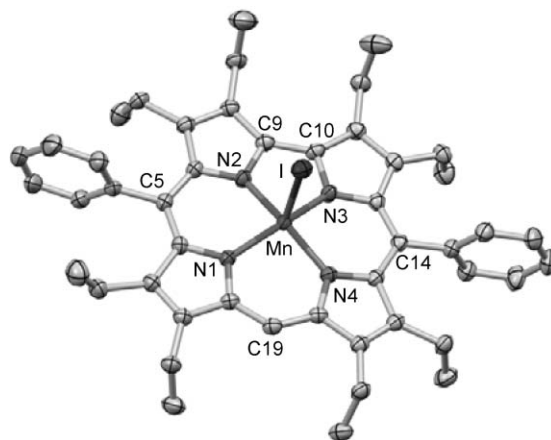


Fig. 1 Molecular structure of **2**. Selected bond lengths (Å) and angles (°): Mn–I 2.6626(4), Mn–N1 1.9447(18), Mn–N2 1.9200(18), Mn–N3 1.9242(18), Mn–N4 1.9441(18); N1–Mn–I 103.71(6), N2–Mn–I 98.71(6), N3–Mn–I 99.51(6), N4–Mn–I 102.74(6), N1–Mn–N2 88.00(8), N1–Mn–N3 155.04(8), N1–Mn–N4 95.61(8), N2–Mn–N3 79.50(8), N2–Mn–N4 156.70(8), N3–Mn–N4 88.01(8).

Table 1 Selected metrical parameters of halogenomanganese corroles and porphyrins

Compound	Mn–X/Å	Mn–Ct(N ₄) ^a /Å
(oec)Mn ^{IV} Cl ^{2a}	2.310	0.437
(tpfc)Mn ^{IV} Cl ^{2b}	2.312	0.43
(tpfc)Mn ^{IV} Br ^{2b}	2.428	0.42
(oedpc)Mn ^{IV} I 2	2.6626	0.3798
(tpp)Mn ^{III} I ⁷	2.767/2.730	0.240/0.251

^a Distance between the Mn ion from the mean plane of the four N atoms.

The high degree of substitution – ten out of eleven positions of the corrole ligand of **2** carry alkyl or aryl substituents – does not influence the macrocycle conformation to a measurable amount. An almost planar tetrapyrrole is found with deviations of single atoms of the C₁₉N₄ perimeter from the mean plane of a maximum of 0.190(2) Å. The steric congestion is however visible at the phenyl substituents which are rotated by close to 90° with respect to the tetrapyrrole, so that the three aromatic moieties of **2** are in orthogonal arrangements throughout.

In summary we have described the preparation and structural details for the first iodomanganese(IV) complex and shown, that the concept of “stabilizing high oxidation states” can apply not only for the metal ion in question, but also for the stability of redox sensitive co-ligands.

Notes and references

† Preparation of **2**: Manganese(III) corrole **1** (72.6 mg, 0.1 mmol) and iodine (13 mg, 0.055 mmol) were stirred together in dichloromethane (100 ml) for 2 h. Subsequently the solution is concentrated *in vacuo* to 10 ml and treated with *n*-hexane (50 ml), whereupon **2** crystallized in violet

blocks, mp 265 °C. Yield: 79 mg, 93%. Anal. Calc. for C₄₇H₅₁N₄MnI (853.78): C 66.12, H 6.02, N 6.56. Found: C 65.88, H 5.99, N 6.37%. MS (MALDI): *m/z* 726 ([M – I]⁺).

‡ Crystal data for C₄₇H₅₁N₄MnI **2**: violet blocks, *M* = 853.76, triclinic, space group *P* $\bar{1}$, *a* = 10.8280(9), *b* = 13.8006(11), *c* = 14.7237(11) Å, α = 82.033(1), β = 79.093(1), γ = 67.676(1)°, *V* = 1993.1(3) Å³, *Z* = 2, *D*_c = 1.423 g cm⁻³, μ (Mo–K α) = 11.44 cm⁻¹, 37720 reflections collected (1.60 < θ < 26.37°) at 173(2) K, 8157 independent, that are used in the structure refinement; *R*₁ = 0.0334 [*I* > 2 σ (*I*)], *wR*₂ = 0.0855 (all data), GOF = 1.094 for 486 parameters, largest difference peak, hole = 0.930, –0.315 e Å⁻³. CCDC 633171. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b700411g

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