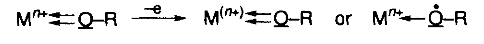
Phenoxyl radical complexes of chromium(III)

Achim Sokolowski, Eberhard Bothe, Eckhard Bill, Thomas Weyhermüller and Karl Wieghardt*

Max-Planck-Institut für Strahlenchemie, Stiftstrasse 34-36, D-45470 Mülheim an der Ruhr, Germany

The hexadentate ligand 1,4,7-tris(3-*tert*-butyl-5-methoxy-2-hydroxybenzyl)-1,4,7-triazacyclononane, H_3L, forms a very stable neutral complex $[Cr^{III}L]\cdot 2MeCN$ 2 with chromium(III) which undergoes electrochemically three one-electron oxidations to yield $[Cr^{III}L]^+$, $[Cr^{III}L]^{2+}$ and $[Cr^{III}L]^{3+}$, respectively; these contain one, two and three coordinated phenoxyl radical ligands; $[Cr^{III}L]\cdot 2MeCN$ and $[Cr^{III}L]ClO_4\cdot 3MeCN$ are characterized by X-ray crystallography.

A coordinated tyrosyl radical has been identified in the active sites of two copper-containing enzymes, galactose oxidase[1] and glyoxal oxidase.[2] The one-electron reduced inactive form of the former has been shown by X-ray crystallography to consist of a mononuclear copper(II) centre in a square-pyramidal ligand environment comprised of two tyrosine, two histidine residues and a buffer-derived acetate ion.[3] From a coordination chemist's point of view one-electron oxidation of a transition-metal ion phenolate moiety may be either metal or ligand centred (Scheme 1).



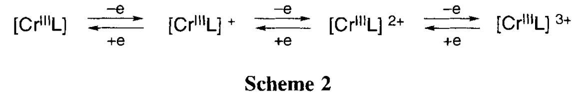
Scheme 1

An interesting question then arises: are the above two product formulations merely resonance structures of a single ground state or do they represent two different ground states with spectroscopically discernible electronic structures? In order to address questions of this kind we have recently synthesized model complexes of iron(III), gallium(III) and scandium(III) which contain coordinated phenoxyl ligands.[4]

Here we report on the corresponding complexes of chromium(III). For the first time we have characterized such a phenoxyl radical complex by X-ray crystallography.

The ligands[4a] 1,4,7-tris(3,5-di-*tert*-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane, H_3L', and 1,4,7-tris(3-*tert*-butyl-5-methoxy-2-hydroxybenzyl)-1,4,7-triazacyclononane, H_3L, react in dry MeCN with $CrCl_2$ (1 : 1). Subsequent air-oxidation yields blue crystals of $[Cr^{III}L']$ **1** and $[Cr^{III}L]\cdot 2MeCN$ **2**.

Cyclic voltammograms of **1** and **2** in MeCN (0.10 mol dm^{-3} $NBu^t_4PF_6$) at a glassy carbon working electrode, (internal reference ferrocenium–ferrocene) exhibit three successive reversible one-electron transfer waves; respectively ($E_{1/2}$ *vs.* Fc^+–Fc for **1**: 0.09, 0.55, 0.77 and for **2**: −0.03, 0.24, 0.45 V) which correspond to ligand centred oxidations (Scheme 2).



Scheme 2

Chemical oxidation of **1** and **2** by 1 equiv. of $[Ni^{III}(tacn)_2][ClO_4]_3$[5] (tacn = 1,4,7-triazacyclononane) in CH_2Cl_2–MeCN (1 : 3) produced red crystals of $[Cr^{III}L']ClO_4$ ($\mathbf{1}ClO_4$) and violet $[Cr^{III}L]ClO_4$ ($\mathbf{2}ClO_4$).

Fig. 1 shows a schematic representation of the neutral complex in crystals of **2** and of the monocation in $\mathbf{2}ClO_4\cdot 3MeCN$. The neutral molecule **2** possesses crystallographic C_3 symmetry; the three phenolate pendent arms are equivalent; the Cr–O and the Cr–N bond distances are 1.920(3) and 2.100(4) Å, respectively. Interestingly, the monocation $\mathbf{2}^+$ does not possess crystallographic symmetry: two coordinated phenolato groups are clearly detected; the average Cr–O bond distance is again 1.920 Å. The third pendent arm is a coordinated phenoxyl radical; the Cr–O distance of the phenoxyl is *longer* at 1.943 Å. The bond distances are in accord with the resonance structures depicted in Fig. 1.

The structures of **2** and $\mathbf{2}ClO_4$ clearly show that a ligand-centred oxidation takes place and that a coordinated phenoxyl radical is generated upon oxidation of **2**.

Temperature-dependent magnetic susceptibility data (2–300 K) reveal that both **1** and **2** have temperature-independent magnetic moments of 3.87 μ_B indicating an $S = 3/2$ ground state for an octahedral chromium(III) species. By contrast, for $\mathbf{1}ClO_4$ and $\mathbf{2}ClO_4$ temperature-independent magnetic moments of 2.83 μ_B indicate an $S = 1$ ground state. Thus strong intramolecular antiferromagnetic exchange coupling between a

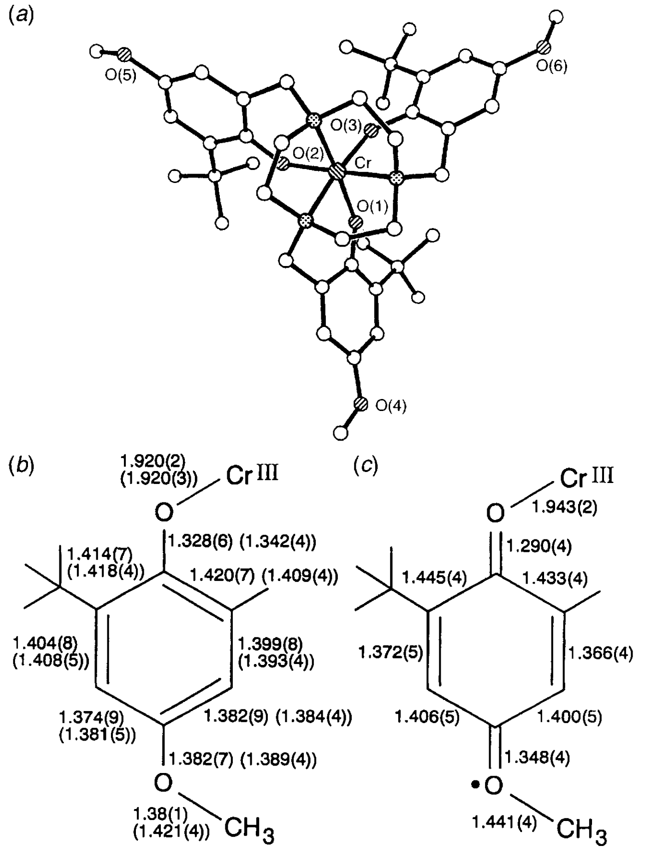


Fig. 1 (*a*) Ball-and-stick representation of a neutral molecule $[Cr^{III}L]$ in crystals of **2** and the monocation $[Cr^{III}L]^+$ in crystals of $\mathbf{2}ClO_4$. In **2** the three pendent phenolate arms are equivalent (C_3 symmetry); the respective bond lengths are given in (*b*). In $\mathbf{2}ClO_4$ two inequivalent phenolate and one phenoxyl radical ligand are present; bond lengths for the former are given in parentheses (averaged values) in (*b*) and for the latter in (*c*).

Cr^{III} ion (S = 3/2) and the coordinated phenoxyl radical (S = 1/2) is observed. X-Band EPR spectra are in accord with these ground states. For **2** in MeCN an axial signal with broad lines at *ca.* $g_\perp$ = 4 and $g_\parallel$ = 2 is observed at 10 K whereas similar solutions of **1**$^+$ and **2**$^+$ are EPR silent. Interestingly, the electrochemically generated **2**$^{2+}$ species in MeCN shows an S = 1/2 signal at g = 1.97 (10 K) whereas **2**$^{3+}$ is EPR silent (S = 0). This is in excellent agreement with the notion that one coordinated and antiferromagnetically coupled phenoxyl radical in the monocations yields an S = 1 ground state, two in the dications yield an S = 1/2 ground state and three give rise to diamagnetism (S = 0). This resembles the behaviour of mono-, bis- and tris-(semiquinonate)chromium(III) complexes.[6]

Fig. 2 shows the electronic spectra of MeCN solutions of blue **2** and of its electrochemically generated violet (mono-), purple (di-) and red (tri-cation). In the spectrum of **2** two rather weak spin-allowed d–d transitions are observed in the visible region at 445 nm (ε = 460 dm^3 mol^{-1} cm^{-1}) and 586 (680). The spectra of **2**$^+$ and **2**$^{2+}$ show new intense absorption maxima at 405 nm (ε = 5.6 × 10^3 dm^3 mol^{-1} cm^{-1}) and 403 (6 × 0·10^3), respectively, typical for phenoxyl radicals. In **2**$^{3+}$ this absorption is only seen as shoulder. The spectrum of **2**$^{3+}$ is rather unusual and resembles those reported from tris(semiquinonate)chromium(III) complexes.[6,7] In agreement with Dei and coworkers[7] we assign the sharp and intense peak at 622 nm (ε = 6.4 × 10^3 dm^3 mol^{-1} cm^{-1}) to a spin-forbidden transition $^4A_{2g} \rightarrow {}^2E_g$ corresponding to a spin flip in the ground state. This transition gains intensity by three orders of magnitude by strong exchange coupling between the Cr^{III} ion and the three phenoxyl radicals. The spectra of **1**, **1**$^+$ and **1**$^{2+}$ are similar; **1**$^{3+}$ is not stable in solution.

In summary, we have synthesized and structurally characterized the first genuine phenoxyl radical chromium(III) complexes. The three successive one-electron oxidations of the pendent phenolate arms in **1** and **2** are ligand centred and the +III oxidation state of the central metal ion is retained. From the crystal structure of **2**ClO$_4$ it follows that the unpaired electron of the coordinated radical is delocalised over one organic ring.

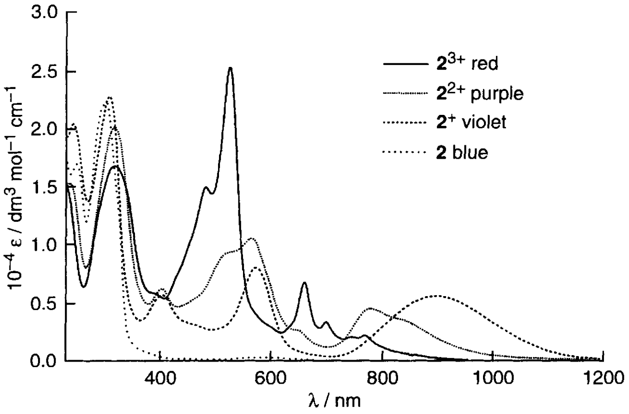


Fig. 2 UV–VIS spectra of **2** and of **2**ClO$_4$ in MeCN and of electrochemically generated **2**$^{2+}$ and **2**$^{3+}$ in MeCN (0.10 mol dm^{-3} [NBu$^t_4$]PF$_6$) at 298 K

Footnotes

† *Preparation of complexes*: to a solution of the ligands H$_3$L′ or H$_3$L (0.71/0.78 g, 1.0 mmol) in dry MeCN (100 ml) under an Ar atmosphere was added Cr^{II}Cl$_2$ (0.14 g, 1.0 mmol), respectively. After heating to reflux for 30 min the clear green solutions were exposed to air which initiated a colour change to blue. After 10 h at 20 °C blue microcrystals of **1** or **2** precipitated (yields *ca.* 52%). Blue crystals of **2**·2MeCN suitable for X-ray crystallography were obtained by slow recrystallization from a MeCN solution. The oxidized forms **1**ClO$_4$ and **2**ClO$_4$ were obtained from CH$_2$Cl$_2$–MeCN (1 : 3) (100 ml) of **1** or **2** (0.41/0.37 g, 0.50 mmol respectively) to which [Ni^{III}(tacn)$_2$][ClO$_4$]$_3$ (0.30 g, 0.50 mmol) was added at ambient temperature. Within 12 h at 20 °C crystals of red **1**ClO$_4$ and violet **2**ClO$_4$ precipitated in *ca.* 40% yield. Single crystals of **2**ClO$_4$ were obtained by slow recrystallization from CH$_2$Cl$_2$–MeCN (1 : 4) at ambient temperature. Satisfactory analyses and ESI mass spectra were obtained for all complexes.

‡ *Crystal data*: C$_{46}$H$_{66}$CrN$_5$O$_6$ (**2**·2MeCN), M = 837.04, trigonal, space group $P\bar{3}c1$, a = 14.175(1), c = 29.486(2) Å, U = 5130.9(6) Å^3, Z = 4, D_c = 1.084 g cm^{-3}, λ(Mo-Kα) = 0.71073 Å, F(000) = 1796, μ = 0.268 mm^{-1}, T = 173(2) K, 1851 observed reflections with $F > 4.0\,\sigma(F)$ were used in the refinement; R = 0.082.

C$_{48}$H$_{69}$ClCrN$_6$O$_{10}$ (**2**ClO$_4$·3MeCN), M = 977.54, monoclinic, space group $P2_1/c$, a = 17.473(1), b = 17.189(1), c = 16.885(1) Å, β = 97.152(3)°, U = 5031.8(5) Å^3, Z = 4, D_c = 1.29 g cm^{-3}, λ(Mo-Kα) = 0.71073 Å, F(000) = 2080, μ = 0.341 mm^{-1}, T = 173(2) K, 6100 observed reflections with $F > 4.0\sigma(F)$ were used in the refinement; R = 0.051. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/122.

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