Synthesis and first structural characterisation of a homoleptic tetraorganochromate(III) salt

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The homoleptic, pseudo-octahedral, d³ species [Li(thf)₄]-[Cr^{III}(C₆Cl₅)₄] 1 has been obtained and characterised by analytical, spectroscopic and X-ray diffraction methods.

The synthesis of aryl derivatives of chromium(III) and the study of their properties have drawn the attention of numerous research groups since the very beginning of this century, shortly after the synthesis of the first organomagnesium reagents. Early reports, however, were discouraging[1] or puzzling[2] and it was not until the late fifties that σ-aryl complexes of chromium(III) were isolated and recognised as species of limited stability, which are prone to rearrange, eventually yielding π-arene compounds of low-valent chromium.[3] This tendency to decompose is more pronounced in compounds with some degree of coordinative unsaturation,† which may be a principal reason for the lack of homoleptic (*i.e.*, not bearing additional stabilising ligands) organometallic compounds of formula [Cr^{III}R₄]⁻. As far as we know, the only organometallic precedents for this stoichiometry are probably the salts Li[Cr(C₆H₄OMe-2)₄]·Et₂O[5] and Li[Cr(C₆H₂Me₃-2,4,6)₄]·4thf;[6] however, no structural information is available for them.‡ Interestingly, some related tetraalkylchromate(III) salts had also been detected as solution species but could not even be isolated because they readily suffered oxidation giving the more stable neutral tetraalkychromium(IV) derivatives.[8]

We have prepared the tetraorganochromate(III) salt [Li-(thf)₄][Cr^{III}(C₆Cl₅)₄] **1** by arylation of [CrCl₃(thf)₃][9] with LiC₆Cl₅[10] in 1 : 5 molar ratio.§ Complex **1** is a violet solid of limited thermal stability; since it is also air- and moisture-sensitive, it must be synthesised, stored and handled under an inert atmosphere and at low temperatue (below 0 °C).

The solid-state structure of **1** has been established by single-crystal X-ray diffraction analysis.¶ The lattice contains the separate ions [Li(thf)₄]⁺ and [Cr(C₆Cl₅)₄]⁻ together with interstitial solvent molecules. The cation has a tetrahedral geometry (local at the Li⁺ ion) as usually found in other salts.[13] The core of the anion contains four σ Cr–C bonds and two additional Cr–Cl interactions, thus resulting in a pseudo-octahedral environment for the Cr atom (Fig. 1). Two of the C₆Cl₅ groups act as monodentate σ-bonded ligands, while the other two act as chelating ligands through their *ipso*-C and one of the *o*-Cl atoms. The small bite-angle of the chelating C₆Cl₅ group yields two strained four-membered metallacycles with C–Cr–Cl angles of *ca.* 60°. These acute angles are responsible for the severe deviations of the metal coordination environment from the ideal octahedral geometry. The two Cr–C distances involving C-*trans*-to-Cl atoms are virtually identical and in good agreement with those described in other σ-aryl derivatives of Cr^{III} (mean value 207 pm).[14] The two Cr–C distances involving C-*trans*-to-C atoms are slightly longer, probably due to the higher *trans* influence exerted by the anionic C atom of the aryl group. The Cr–Cl distances are clearly dissimilar and much longer than found in standard terminal chloro-complexes of chromium (mean value 232 pm).[14] The long Cr–Cl distances can be ascribed to both the poor donating ability of halocarbons

and the strain of the metallacycle formed. The overall geometry of the [Cr(C₆Cl₅)₄]⁻ anion is similar to that found in the related heavy-metal complexes [Pt(C₆Cl₅)₄][15] and [Rh(C₆Cl₅)₄]⁻.[16]

The EPR spectrum of **1** was registered (Fig. 2)‖ and analysed as a particular case** of an ($S = 3/2$) spin system that behaves as an ($S = 1/2$) system with the following spin Hamiltonian:

$$H = \mu_B B(g_x' l_x S_x + g_y' l_y S_y + g_z' l_z S_z) \qquad (1)$$

In the preceding equation l_i ($i = x, y, z$) are the direction cosines of the magnetic field of magnitude B referred to the principal axes of the $\tilde{g}$-tensor. Using this spin-Hamiltonian and assuming Lorentzian line shapes, we have obtained an excellent agreement between the experimental [Fig. 2(*a*)] and calculated [Fig. 2(*b*)] spectra for the following set of effective principal *g*-values and band halfwidths: $g_x' = 4.02$, $g_y' = 3.55$, $g_z' = 1.946$; $W_x = 15.0$ mT, $W_y = 22.5$ mT, $W_z = 10.0$ mT. The relationship between the effective and true principal *g*-factors is a function of the *a priori* unknown η-parameter which accounts for the departure from axial symmetry.** Since the observed EPR spectrum is practically axial it is reasonable to assume an axial true $\tilde{g}$-tensor as well. Under this assumption the following true *g*-values have been derived: $g_\parallel = 1.98$ and $g_\perp = 1.90$ with $\eta = 0.08(1)$. It is interesting that, while the $g_\parallel$-value is typical for a Cr³⁺ ion, the $g_\perp$-value departs from that of the free electron by more than what is usually observed for this paramagnetic entity. This could be attributed to an extra orbital contribution due to the ligand as a consequence of the covalent bonding.
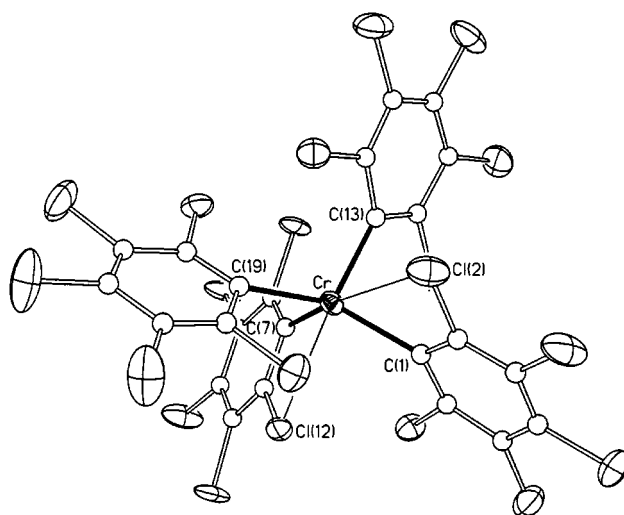
Fig. 1 Thermal ellipsoid diagram of the anion of **1**. Selected distances (pm) and angles (°): Cr–C(1) 213.7(11), Cr–C(7) 207.3(10), Cr–C(13) 208.1(10), Cr–C(19) 217.3(11), Cr–Cl(2) 300.1(4), Cr–Cl(12) 281.8(4); C(1)–Cr–C(7) 111.7(4), C(1)–Cr–C(13) 94.2(4), C(1)–Cr–C(19) 141.5(4), C(1)–Cr–Cl(2) 59.5(3), C(1)–Cr–Cl(12) 83.1(3), C(7)–Cr–C(13) 103.2(4), C(7)–Cr–C(19) 90.8(4), C(7)–Cr–Cl(2) 170.1(3), C(7)–Cr–Cl(12) 63.2(3), C(13)–Cr–C(19) 111.1(4), C(13)–Cr–Cl(2) 74.2(3), C(13)–Cr–Cl(12) 163.4(3), C(19)–Cr–Cl(2) 99.0(3), C(19)–Cr–Cl(12) 79.8(4), Cl(2)–Cr–Cl(12) 117.4(1).
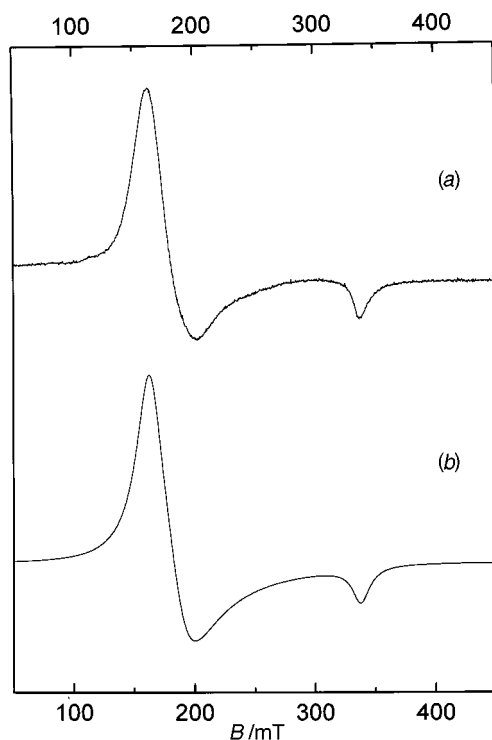
Fig. 2 EPR spectrum of a frozen CH_2Cl_2 solution of **1** at liquid nitrogen temperature (microwave frequency: 9.49 GHz): experimental (*a*) and calculated (*b*)

The homoleptic tetraorganochromate(III) salt **1** is stable enough to allow its isolation and characterisation. This reasonable stability can be ascribed to the versatility of the C_6Cl_5-group which is able to act as a standard monodentate σ-aryl ligand as well as a poor didentate one depending on the electronic and steric demands of the metal centre. Further studies aimed at exploring the chemical reactivity and redox behaviour of the new compound **1** are in progress.

Notes and References

† The use of the very bulky bis(trimethylsilyl)methyl group has enabled Lappert and coworkers to isolate and characterise a highly unusual, coordinatively unsaturated neutral complex of formula $[CrR_3]$ (ref. 4).

‡ Hein and Schmiedeknecht reported on the synthesis of sodium and lithium tetraphenylchromate(III) salts, but the authors concluded that they were, in fact, solvent-stabilised species of formula $M[CrPh_4\cdot2dme]\cdot2dme$ (M = Na or Li; dme = 1,2-dimethoxyethane). The analogous thf-stabilised salts $MCrPh_4\cdot x$thf were too unstable to be isolated (ref. 7).

§ *Experimental procedure:* to a solution of LiC_6Cl_5 (*ca.* 34 mmol) in Et_2O (130 cm³) at −78 °C was added $[CrCl_3(thf)_3]$ (2.57 g, 6.85 mmol). The suspension was allowed to warm to −10 °C and after about 4 h of stirring, the by then violet solid was filtered and extracted in CH_2Cl_2 (60 cm³). The solvent in the extract was replaced by thf (20 cm³) and the slow diffusion of an *n*-hexane layer (60 cm³) into it at −30 °C yielded **1** as a violet solid in 57% yield. Anal. Found: C 36.21, H 2.02; $C_{40}H_{32}Cl_{20}CrLiO_4$ requires: C 35.73, H 2.40%. IR (KBr; cm⁻¹): 1321s, 1311s, 1281vs, 1219m, 1125m, 1059s [ν(COC)$_{asym}$], 1043vs [ν(COC)$_{asym}$], 915m, 887s [ν(COC)$_{sym}$], 822vs (C_6Cl_5: X-sensitive vibr.),[11] 667vs, 600w, 415m and 349m. MS (FAB−): *m/z* 1040 $[Cr(C_6Cl_5)_4]^-$ and 828 $[Cr(C_6Cl_5)_3Cl]^-$.

¶ *Crystal data* for **1**·0.5OEt₂·0.5C₆H₁₄: $C_{45}H_{44}Cl_{20}CrLiO_{4.5}$, $M = 1424.74$, monoclinic, $a = 4151.3(6)$, $b = 1288.25(10)$, $c = 2387.8(3)$ pm, $\beta = 117.324(12)°$, $U = 11.345(3)$ nm³, $T = 150(1)$ K, space group $C2/c$ (no. 15), graphite-monochromated Mo-Kα radiation, $\lambda = 71.073$ pm, $Z = 8$, $D_c = 1.668$ g cm⁻³, $F(000) = 5736$, violet, approx. crystal dimensions: 0.40 × 0.25 × 0.10 mm, μ(Mo-Kα) = 1.187 mm⁻¹, measured absorption correction based on ψ scans, transmission factors: 0.899–0.793; Enraf-Nonius CAD4 diffractometer, ω–θ scans, data collection range $4.0 < 2\theta < 50.0°$, +*h*, +*k*, ±*l*, three standard reflections showed no significant variation

in intensity; 10 103 intensity data collected, 9956 unique ($R_{int} = 0.0887$) which were used in all calculations. The structure was solved by Patterson and Fourier methods and refined anisotropically (except for the solvent atoms) by full-matrix least squares on F^2 (program SHELXL 93; ref. 12) to final values of $R_1 = 0.0870$ [for 4366 data with $I > 2\sigma(I)$] and $wR_2 = 0.2324$ (all data) for 635 parameters; GOF = 1.037, maximum $\Delta/\sigma = 0.001$, maximum $\Delta\rho = 1063$ e nm⁻³ (−1053 e nm⁻³) located very near the chromium atom. Hydrogen atoms were set geometrically. The weighting scheme was $w = [\sigma^2(F_o^2) + (0.0590P)^2 + 115.07P]^{-1}$, where $P = (1/3)[\max\{F_o^2,0\} + 2F_c^2]$. CCDC 182/936.

‖ EPR data were taken on a Varian E-112 spectrometer working in the X-band. The magnetic field was measured with a Bruker ER035M gaussmeter. The diphenylpicrylhydrazyl resonance signal [$g = 2.0037(2)$] was used to determine the microwave frequencies. The program WIN-EPR SimFonia (supplied by Bruker) was used to perform the simulation. In the calculations, the following interpolating halfwidth formula was used: $W^2(l_x,l_y,l_z) = W_x^2 l_x^2 + W_y^2 l_y^2 + W_z^2 l_z^2$.

** The relevant spin Hamiltonian for the paramagnetic centre in **1** [Cr^{III}, d³, $S = 3/2$] should read:

$$H = \mu_B\boldsymbol{B}\cdot\tilde{\boldsymbol{g}}\cdot\boldsymbol{S} + \boldsymbol{S}\cdot\tilde{\boldsymbol{D}}\cdot\boldsymbol{S}$$

where μ_B is the Bohr magneton. The first term accounts for the electronic Zeeman interaction and the second one for the zero field splitting. In the principal axes of the $\tilde{\boldsymbol{D}}$-tensor, the latter term is given by

$$\boldsymbol{S}\cdot\tilde{\boldsymbol{D}}\cdot\boldsymbol{S} = D[\{S_z^2 - \tfrac{1}{3}S(S+1)\} + \eta(S_x^2 - S_y^2)]$$

where η can always be set to a value of $< 1/3$ by an appropriate choice of principal axes. In the absence of any applied magnetic field, the quartet corresponding to the ($S = 3/2$)-system splits into two doublets separated by $\Delta_o = 2D(1 + 3\eta^2)^{\frac{1}{2}}$, which can be treated independently if Δ_o is greater than the Zeeman energy. Moreover, for low values of the rhombic parameter, the only transition actually observed is the one among the states of the $S = \pm 1/2$ doublet. Under these conditions, the initial $S = 3/2$ problem reduces to a quasi-axial $S = 1/2$ spin system, with the spin Hamiltonian given in eqn. (1). If the principal axes of the $\tilde{g}$- and $\tilde{D}$-tensors coincide the relationship between the effective (g_i') and the principal (g_i) true g-factors is given by

$$g_x' = g_x (1 + \cos 2\beta + \sqrt{3}\sin 2\beta)$$
$$g_y' = g_y (1 + \cos 2\beta - \sqrt{3}\sin 2\beta)$$
$$g_z' = g_z(2\cos 2\beta - 1),$$

where $\tan 2\beta = (\sqrt{3})\eta$.

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