Synthetic, structural and electrochemical studies of cationic chromium(VI) and molybdenum(VI) bis(imido) complexes supported by 1,4,7-triazacyclononane macrocycles

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Treatment of $[Cr(N^tBu)_2Cl_2]$ or $[Mo(N^tBu)_2Cl_2(dme)]$ with 1,4,7-triazacyclononane (tacn) in THF, followed by metathesis using $NaClO_4$ in aqueous medium, readily afforded $[M(tacn)(N^tBu)_2Cl]ClO_4$ (M = Cr **1** or Mo **2**); $[M(Me_3tacn)(N^tBu)_2Cl]Cl$ (M = Cr **3** or Mo **4**) were similarly prepared using the metal precursors and 1,4,7-trimethyl-1,4,7-triazacyclononane (Me_3tacn). Complexes **1**–**4** are resistant to hydrolysis, but do not mediate imido group transfer reactions. Distinctive UV-vis absorption bands are tentatively assigned to imido-to-metal LMCT transitions. The crystal structures of **1** and **2**·CH_3CN show that the 3 nitrogen atoms of tacn are not equidistant from the respective metal centres. A severely distorted imido moiety (imido angle 151.8(4)°) has been observed in the structure of **1** but not **2**·CH_3CN, and is attributed to steric and crystal packing factors rather than electronic effects. Metathesis of both chloride groups in **3** using AgOTf (OTf = SO_3CF_3) yielded $[Cr(Me_3tacn)(N^tBu)_2(OTf)]OTf$ **5**. The cyclic voltammograms of **1**–**5** in acetonitrile consist of a quasi-reversible couple (+0.86 to +1.20 V *vs.* $Cp_2Fe^{0/+}$) and an irreversible wave (−1.04 to −2.08 V *vs.* $Cp_2Fe^{0/+}$); the former couple is assigned to an imido-centred oxidation.

Introduction

Investigations into the co-ordination chemistry of the macro-cyclic facial triamine ligands 1,4,7-triazacyclononane (tacn) and 1,4,7-trimethyl-1,4,7-triazacyclononane (Me_3tacn) have demonstrated their ability to accommodate high- and low-valent metal centres.[1,2] This is particularly evident for electron-deficient metals in complexes with metal–ligand multiple bonds, and attention has been focused on the oxo moiety.[3–6] In Group 6, many monomeric di- and tri-oxo derivatives of Me_3tacn are stable to hydrolysis and undergo interesting reversible electron transfer reactions.[3a–d] Incorporation of the isolobal imido ligand into metal–tacn systems was only recently reported for titanium(IV),[7] rhenium-(V)[8] and -(VII)[9] species. Herein is described the convenient preparation of cationic chromium(VI) and molybdenum(VI) bis(imido) derivatives of tacn and Me_3-tacn, which are the first imido complexes of Group 6 to bear these tridentate azamacrocycles. Structural and electrochemical investigations have been undertaken which revealed some interesting observations.

Experimental

All reactions were performed under a nitrogen atmosphere using standard Schlenk techniques unless otherwise stated. All solvents were appropriately dried and distilled prior to use. The ^1H and ^{13}C NMR spectra were recorded on a Bruker 300 DPX FT-NMR spectrometer (ppm) using Me_4Si as internal standard, ^{19}F NMR spectra on a JEOL 270 FT-NMR spectrometer using trifluoroacetic acid as external reference, infrared spectra were obtained as Nujol mulls between KBr plates on a Bio Rad FT-IR spectrometer and fast atom bombardment (FAB) mass spectra on a Finnigan MAT 95 spectrometer using 3-nitrobenzyl alcohol matrix. Elemental analyses were performed by Butterworth Ltd., UK.

Cyclic voltammetry was performed using a Princeton Applied Research (PAR) Model 175 universal programmer, Model 173 potentiostat and Model 179 digital coulometer. The working electrode was edge plane pyrolytic graphite (EPG, Union Graphite). In acetonitrile, a Ag^+–Ag reference electrode was used but potentials are reported with respect to the Cp_2-$Fe^{0/+}$ couple in the same solution.

The compounds $[Cr(N^tBu)_2Cl_2]$,[10] $[Mo(N^tBu)_2Cl_2(dme)]$,[11] tacn[12] and Me_3tacn[13] were prepared by published procedures. **CAUTION:** perchlorate salts are potentially explosive and should be prepared in small quantities and handled with care.

Syntheses

$[Cr(tacn)(N^tBu)_2Cl]ClO_4$ 1. To a stirred solution of $[Cr(N^tBu)_2Cl_2]$ (0.14 g, 0.55 mmol) in THF (10 ml) at −30 °C was added tacn (0.07 g, 0.55 mmol) in THF (10 ml). A pale purple precipitate immediately appeared. The mixture was allowed to warm to room temperature and after 1 h the purple solid was collected and washed with Et_2O. The solid was then dissolved in deionised water and addition of a saturated aqueous solution of $NaClO_4$ yielded a dark red solid. This was washed with cold water, dried *in vacuo* for several hours and recrystallised using acetonitrile–Et_2O to afford red crystals (yield: 0.17 g, 68%). Calc. for $C_{14}H_{33}Cl_2CrN_5O_4$: C, 36.69; H, 7.26; N, 15.28. Found: C, 36.87; H, 7.48; N, 15.05%. IR $\tilde{\nu}$ cm^{-1}: 3261 (N–H), 1195 (Cr=N) and 1090 (Cl–O). MS (FAB, *m/z*): 358 [M⁺]. UV-vis (CH_3CN): λ_{max} 494 nm (ε 1140 dm^3 mol^{-1} cm^{-1}). ^1H NMR (CD_3CN): δ 1.45 (s, 18H, CMe_3), 2.73; 3.01; 3.1–3.4 (m, 12H, NCH_2), 3.69 (broad s, 2H, NH) and 5.20 (broad s, 1H, NH). ^{13}C NMR (CD_3CN): δ 27.9 (CMe_3), 45.3; 46.5; 52.4 (NCH_2) and 71.0 (CMe_3).

$[Mo(tacn)(N^tBu)_2Cl]ClO_4$ 2. The procedure for complex **1** was adopted using $[Mo(N^tBu)_2Cl_2(dme)]$ (0.21 g, 0.53 mmol) and tacn (0.07 g, 0.53 mmol). A yellow precipitate was afforded after 2 h. Addition of $NaClO_4$ in deionised water yielded a pale yellow solid which was recrystallised using acetonitrile–Et_2O to give yellow crystals (yield: 0.19 g, 72%). Calc. for $C_{14}H_{33}MoN_5O_4Cl_2$: C, 33.48; H, 6.62; N, 13.94. Found: C, 33.62; H,

6.70; N, 13.80%. IR $\tilde{\nu}$ cm^{-1}: 3252 (N–H), 1208 (Mo=N) and 1092 (Cl–O). MS (FAB, m/z): 404 [M$^+$]. UV-vis (CH$_3$CN): λ_{max} 294 nm (ε 2200 dm^3 mol^{-1} cm^{-1}). ^{1}H NMR (CD$_3$CN): δ 1.38 (s, 18H, CMe$_3$), 2.7–3.5 (m, 12H, NCH$_2$), 4.15 (broad s, 2H, NH) and 5.78 (broad s, 1H, NH). ^{13}C NMR (CD$_3$CN): δ 29.3 (CMe_3), 45.1; 46.4; 51.6 (NCH$_2$) and 70.7 (CMe_3).

[Cr(Me$_3$tacn)(N^{t}Bu)$_2$Cl]Cl 3. The ligand Me$_3$tacn (0.33 g, 1.9 mmol) in THF (10 ml) was added dropwise to a stirred solution of [Cr(N^{t}Bu)$_2$Cl$_2$] (0.51 g, 1.9 mmol) in THF (20 ml) at room temperature. The mixture gradually turned dark red with precipitation of a red solid. After 6 h the solid was collected, washed with Et$_2$O and dried *in vacuo*. Recrystallisation by diffusion of Et$_2$O into an acetonitrile solution afforded dark red crystals (yield: 0.59 g, 71%). Calc. for C$_{17}$H$_{39}$Cl$_2$CrN$_5$: C, 46.78; H, 9.01; N, 16.05. Found: C, 46.62; H, 9.29; N, 15.89%. IR $\tilde{\nu}$ cm^{-1}: 1183 (Cr=N). MS (FAB, m/z): 400 [M$^+$]. UV-vis (CH$_3$CN): λ_{max} 497 nm (ε 1080 dm^3 mol^{-1} cm^{-1}). ^{1}H NMR (CD$_3$CN): δ 1.62 (s, 18H, CMe$_3$), 2.71 (s, 6H, NMe), 2.8–3.3 (m, 12H, NCH$_2$) and 2.93 (s, 3H, NMe). ^{13}C NMR (CD$_3$CN): δ 31.3 (CMe_3), 51.4; 54.8; 56.3 (NCH$_2$), 62.0; 63.7 (NMe) and 85.0 (CMe_3).

[Mo(Me$_3$tacn)(N^{t}Bu)$_2$Cl]Cl 4. The procedure for complex **3** was adopted using Me$_3$tacn (0.40 g, 2.3 mmol) and [Mo(N^{t}Bu)$_2$-Cl$_2$]·dme (0.93 g, 2.3 mmol) to afford yellow crystals (yield: 0.83 g, 74%). Calc. for C$_{17}$H$_{39}$Cl$_2$MoN$_5$: C, 42.51; H, 8.18; N, 14.58. Found: C, 42.66; H, 8.39; N, 14.32%. IR $\tilde{\nu}$ cm^{-1}: 1198 (Mo=N). MS (FAB, m/z): 445 [M$^+$]. UV-vis (CH$_3$CN): λ_{max} 295 nm (ε 2050 dm^3 mol^{-1} cm^{-1}). ^{1}H NMR (CD$_3$CN): δ 1.45 (s, 18H, CMe$_3$), 2.86 (s, 6H, NMe), 2.8–3.4 (m, 12H, NCH$_2$) and 3.03 (s, 3H, NMe). ^{13}C NMR (CD$_3$CN): δ 29.9 (CMe_3), 50.9; 54.6; 56.2 (NCH$_2$), 60.1; 61.0 (NMe) and 72.9 (CMe_3).

[Cr(Me$_3$tacn)(N^{t}Bu)$_2$(OTf)]OTf 5. (OTf = SO$_3$CF$_3$). To a stirred solution of [Cr(Me$_3$tacn)(N^{t}Bu)$_2$Cl]Cl **3** (0.15 g, 0.35 mmol) in acetonitrile (20 ml) was added AgOTf (0.20 g, 0.77 mmol). A white precipitate formed immediately. After 12 h the dark red solution was filtered from the solid and all solvent was removed *in vacuo*. Extraction with CH$_2$Cl$_2$, followed by concentration and precipitation using Et$_2$O, gave a dark red crystalline solid (yield: 0.18 g, 77%). Calc. for C$_{19}$H$_{39}$CrF$_6$N$_5$O$_6$S$_2$: C, 34.39; H, 5.92; N, 10.55. Found: C, 34.51; H, 5.99; N, 10.37%. IR $\tilde{\nu}$ cm^{-1}: 1275, 1256, 1206, 1160 and 1030. MS (FAB, m/z): 514 [M$^+$]. UV-vis (CH$_3$CN): λ_{max} 478 nm (ε 1230 dm^3 mol^{-1} cm^{-1}). ^{1}H NMR (CD$_3$CN): δ 1.74 (s, 18H, CMe$_3$), 2.73 (s, 6H, NMe), 2.9–3.5 (m, 12H, NCH$_2$) and 2.94 (s, 3H, NMe). ^{13}C NMR (CD$_3$CN): δ 30.5 (CMe_3), 50.3; 53.9; 55.6 (NCH$_2$), 61.8; 63.8 (NMe) and 88.1 (CMe_3). ^{19}F NMR (CD$_3$CN): δ −78.9 and −121.1.

X-Ray crystallography

For data collection, a dark red (0.25 × 0.15 × 0.35 mm) or yellow (0.25 × 0.15 × 0.30 mm) crystal of complexes **1** and **2**·CH$_3$CN respectively was used on a MAR diffractometer with Mo-Kα radiation (λ = 0.71073 Å) at 301 K. The structures were solved by direct methods, expanded using Fourier techniques, and refined by full-matrix least squares using the software package TEXSAN[14] on a Silicon Graphics Indy computer. For **1** the perchlorate anion was disordered and the O atoms were placed at 7 positions with occupation numbers 1.00, 0.75, 0.25, 0.70, 0.30, 0.73 and 0.27 for O(1), O(2), O(2′), O(3), O(3′), O(4) and O(4′) respectively. The protons bonded to the tacn N atoms were located in the Fourier-difference map. In the least-squares refinement 22 non-H atoms were refined anisotropically, the O atoms of the perchlorate anion were refined isotropically, the positional parameters of the 3 located H atoms were refined, and 30 other H atoms at calculated positions with thermal parameters equal to 1.3 times that of the attached C atoms were

not refined. For **2**·CH$_3$CN all 29 non-H atoms were refined anisotropically, the positional parameters of the three protons bonded to the tacn nitrogen atoms located in the Fourier-difference map were refined, and the other 33 H atoms at calculated positions with thermal parameters equal to 1.3 times that of the attached C atoms were not refined. Crystal data for **1** and **2**·CH$_3$CN are listed in Table 1.

CCDC reference number 186/1591.

Results

Synthesis and characterisation

Treatment of [Cr(N^{t}Bu)$_2$Cl$_2$] or [Mo(N^{t}Bu)$_2$Cl$_2$(dme)] with tacn in THF, followed by metathesis using NaClO$_4$ in *aqueous* medium, readily affords the perchlorate complexes [M(tacn)-(N^{t}Bu)$_2$Cl]ClO$_4$ (M = Cr **1** or Mo **2**) as purple or yellow precipitates respectively in good yields (≈70%). Indeed, **1** and **2** are stable for over 4 weeks in air and water. Similarly, the air-stable compounds [M(Me$_3$tacn)(N^{t}Bu)$_2$Cl]Cl (M = Cr **3** or Mo **4**) are prepared using the metal precursors and Me$_3$tacn (Scheme 1),
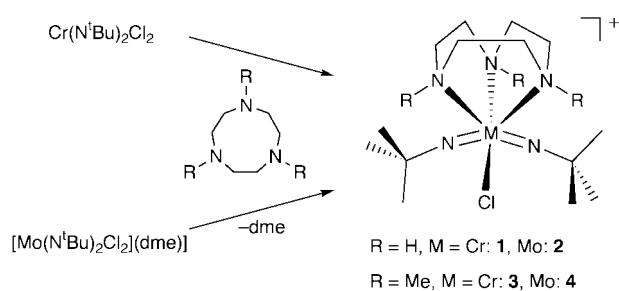
Scheme 1

although the reaction times are longer due to greater steric exertion by the trimethyl-substituted azacycle.

Complexes **1**–**4** exhibit equivalent imido moieties and a 2:1 ratio of resonances for the NR groups of the macrocycles by ^{1}H spectroscopy. This is in accordance with the presence in solution of a mirror plane through the chloride and one triamine nitrogen atom, bisecting the imido–metal–imido angle. The broad signals for the amine hydrogens of the tacn ligand are shifted significantly downfield (δ 3.69, 5.20 for **1**; 4.15, 5.78 for **2**). The FAB mass spectra for **1**–**4** clearly reveal the isotopic cluster of peaks corresponding to the respective parent cationic species. While the yellow molybdenum complexes **2** and **4** absorb at λ_{max} 295 nm in the UV-vis spectra, the dark red chromium analogues **1** and **3** display red-shifted absorption bands at λ_{max} 494–497 nm. In the light of the reported reaction of [Cr(N-^{t}Bu)$_2$(terpy)][BF$_4$]$_2$ (terpy = 2,2′:6′,2″-terpyridine) with PMe$_3$ to yield phosphinimines,[15] the imido group transfer capability of the compounds herein was investigated. However, **1**–**4** displayed no reactivity with styrene, cyclohexene or trimethylphosphine in acetonitrile.

Crystal structures

The molecular structures of complexes **1** and **2**·CH$_3$CN have been determined by X-ray crystallography; selected bond lengths and angles are collected in Table 2. The molybdenum atom in **2** resides in a distorted octahedral environment (Fig. 1). The Mo(1)–N(1) and Mo(1)–N(2) distances of 1.739(3) and 1.752(3) Å are similar to the Mo–N (imido) contacts in the related complex [MoTp*(N^{t}Bu)$_2$Cl] (Tp* = tris(3,5-dimethylpyrazolyl)hydroborate).[16] The imido angles at N(1) and N(2) (171.1(3) and 161.5(3)° respectively) are typical for linear imido groups with bulky substituents. The three N(tacn) atoms are not equidistant from the metal centre as a result of the greater *trans* influence of the imido ligand compared to the chloride group. The range of Mo–N (tacn) distances [2.201(3)–
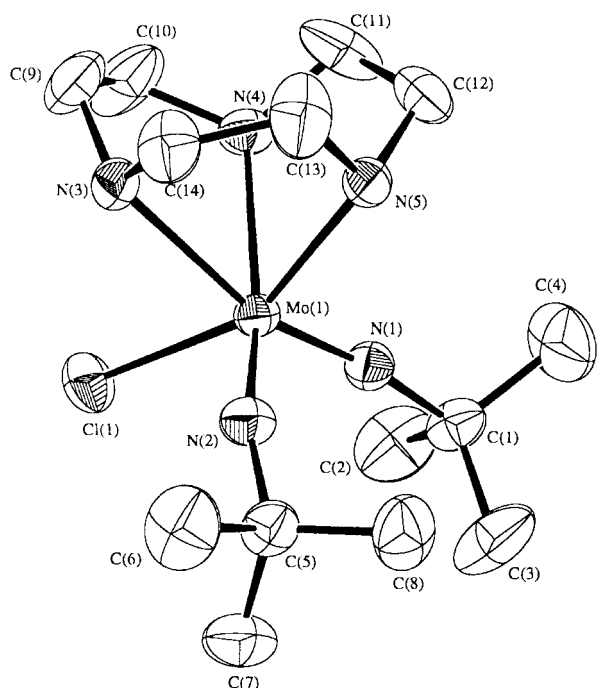
Fig. 1 Perspective view of the cation in complex **2**·CH₃CN (40% probability ellipsoids, H atoms omitted for clarity).
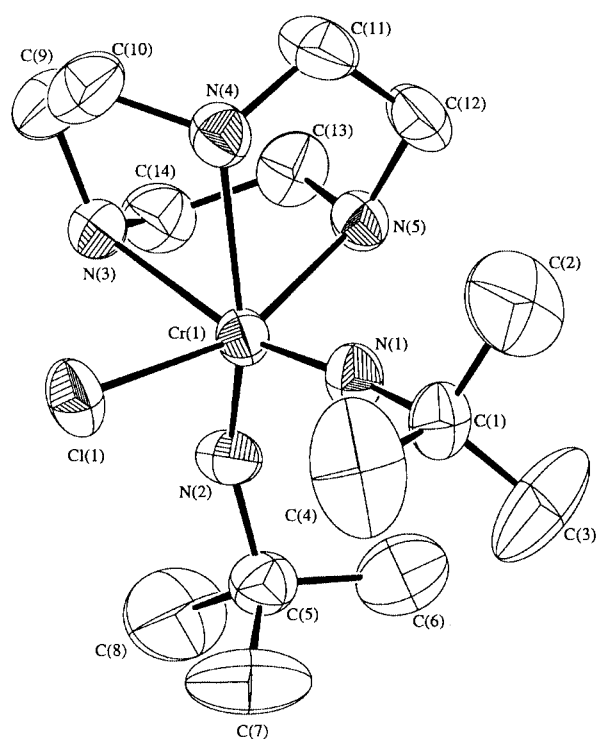

Fig. 2 Perspective view of the cation in complex **1**. Details as in Fig. 1.

Formula	$C_{14}H_{33}Cl_2CrN_5O_4$	$C_{16}H_{36}Cl_2MoN_6O_4$
M	458.35	543.34
Crystal system	Monoclinic	Triclinic
Space group	$C2/c$ (no. 15)	$P\bar{1}$ (no. 2)
a/Å	24.831(3)	8.858(2)
b/Å	14.095(2)	11.325(3)
c/Å	15.185(3)	13.209(3)
α/°	—	84.04(2)
β/°	122.73(2)	79.19(2)
γ/°	—	83.13(2)
V/Å³	4470(2)	1249(1)
Z	8	2
D_c/g cm⁻³	1.362	1.444
μ/cm⁻¹	7.77	7.69
No. unique data	6671	4346
No. observed data [$I > 3\sigma(I)$]	3877	3744
R, R'	0.065, 0.087	0.037, 0.049
Residual ρ/e Å⁻³	+0.55, −0.44	+0.54, −0.48

Table 2 Selected bond distances (Å) and angles (°)

Complex 1

Cr(1)–Cl(1)	2.326(2)	Cr(1)–N(1)	1.639(4)
Cr(1)–N(2)	1.674(4)	Cr(1)–N(3)	2.238(4)
Cr(1)–N(4)	2.304(4)	Cr(1)–N(5)	2.093(4)
N(1)–C(1)	1.434(6)	N(2)–C(5)	1.429(7)
N(3)–C(9)	1.490(8)	C(9)–C(10)	1.484(9)
Cl(1)–Cr(1)–N(1)	92.5(1)	Cl(1)–Cr(1)–N(2)	97.9(1)
N(1)–Cr(1)–N(2)	107.4(2)	N(1)–Cr(1)–N(3)	164.8(2)
N(1)–Cr(1)–N(4)	92.3(2)	N(1)–Cr(1)–N(5)	97.6(2)
N(3)–Cr(1)–N(4)	72.7(2)	N(3)–Cr(1)–N(5)	77.2(2)
Cr(1)–N(1)–C(1)	173.2(4)	Cr(1)–N(2)–C(5)	151.8(4)

Complex 2·CH₃CN

|			
Mo(1)–Cl(1)	2.4087(9)	Mo(1)–N(1)	1.739(3)
Mo(1)–N(2)	1.752(3)	Mo(1)–N(3)	2.367(3)
Mo(1)–N(4)	2.381(3)	Mo(1)–N(5)	2.201(3)
N(1)–C(1)	1.450(4)	N(2)–C(5)	1.443(4)
N(3)–C(9)	1.470(5)	C(9)–C(10)	1.459(7)
Cl(1)–Mo(1)–N(1)	98.05(9)	Cl(1)–Mo(1)–N(2)	98.9(1)
N(1)–Mo(1)–N(2)	107.0(1)	N(1)–Mo(1)–N(3)	160.5(1)
N(1)–Mo(1)–N(4)	90.3(1)	N(1)–Mo(1)–N(5)	97.7(1)
N(3)–Mo(1)–N(4)	70.5(1)	N(3)–Mo(1)–N(5)	73.9(1)
Mo(1)–N(1)–C(1)	171.1(3)	Mo(1)–N(2)–C(5)	161.5(3)

Electrochemistry

The electrochemical studies on complexes **1–4** by cyclic voltammetry in acetonitrile are summarised in Table 3. The cyclic voltammogram of **2** is shown in Fig. 3. An irreversible wave is observed at considerably more negative potentials for the molybdenum species **2** and **4** (−2.02 to −2.08 V *vs.* Cp₂Fe⁰/⁺) than for the chromium analogues **1** and **3** (−1.06 to −1.29 V). The irreversibility implies the unstable nature of the reduced d¹ metal species. The irreversible wave at +0.66 V for the chloride salts **3** and **4** is assigned to the oxidation of the chloride counter anion because the cyclic voltammogram for ammonium chloride gives an identical wave at the same potential.

The d⁰ complexes **1–4** display a quasi-reversible couple (+0.86 V for **1**, up to +1.20 V *vs.* Cp₂Fe⁰/⁺ for **4**; independent of scan rate from 50 to 200 mV s⁻¹; ΔE_p range 70–90 mV). To dismiss a co-ordinated chloride-centred oxidation, we prepared the triflate complex [Cr(Me₃tacn)(NᵗBu)₂(OTf)]OTf **5** (OTf = SO₃CF₃) by metathesis of both chloride groups in [Cr(Me₃-tacn)(NᵗBu)₂Cl]Cl **3** using AgOTf. Indeed, the cyclic voltammogram of **5** reveals a quasi-reversible couple at +0.96 V. The peak current is comparable to that of the Cp₂Fe⁰/⁺ couple at the same concentration under identical conditions; hence a

2.381(3) Å] are longer than those in [Re(tacn)(NPh)(OH)-(PPh₃)][ClO₄]₂ [2.14(1)–2.20(1) Å].[8]

X-Ray crystal analysis has revealed that the chromium complex **1** (Fig. 2) is structurally related to **2**. The Cr–N (tacn) bonds differ noticeably [2.093(4)–2.304(4) Å] as in **2** but are shorter due to the smaller radius of the chromium(VI) ion. It is apparent from the Cr–N (imido) distances of 1.639(4) and 1.674(4) Å (typically 1.54–1.65 Å for bis(imido)chromium(VI) species [10,15,17–19]) and the Cr–N (imido)–C angles of 173.2(4) and 151.8(4)° for N(1) and N(2) respectively that the latter imido moiety is severely distorted. Importantly, this feature is not observed in the structure of **2**.

Table 3 Electrochemical data[a]

Complex	E°/V vs. $\mathrm{Cp_2Fe^{0/+}}$	
	Oxidation	Reduction
1 [Cr(tacn)(N^{t}Bu)$_2$Cl]ClO$_4$	+0.86 (q)	−1.29 (i)
2 [Mo(tacn)(N^{t}Bu)$_2$Cl]ClO$_4$	+0.99 (q)	−2.08 (i)
3 [Cr(Me$_3$tacn)(N^{t}Bu)$_2$Cl]Cl	+1.09 (q), +0.66 (i)[b]	−1.06 (i)
4 [Mo(Me$_3$tacn)(N^{t}Bu)$_2$Cl]Cl	+1.20 (q), +0.66 (i)[b]	−2.02 (i)
5 [Cr(Me$_3$tacn)(N^{t}Bu)$_2$(OTf)]OTf	+0.96 (q)	−1.04 (i)

q = Quasi-reversible ($E_{\frac{1}{2}}$), i = irreversible. [a] Recorded in acetonitrile at 100 mV s^{-1}, 0.1 mol dm^{-3} [^{n}Bu$_4$N][PF$_6$] as supporting electrolyte. [b] Cl$^-$ oxidation.
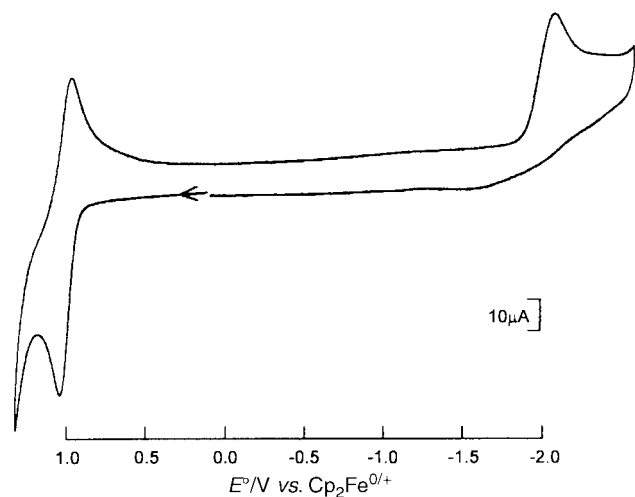
Fig. 3 Cyclic voltammogram of complex **2** in acetonitrile at 100 mV s^{-1} with 0.1 mol dm^{-3} [^{n}Bu$_4$N][PF$_6$] as supporting electrolyte.

one-electron process is implied. Given the +6 oxidation state of the metals and the electrochemically inert nature of tacn/Me$_3$tacn, the couple is ascribed to an imido-centred oxidation (see Discussion).

Discussion

The stability of the d^0 bis(imido) complexes **1**–**4** with respect to hydrolysis allows for convenient experimental manipulations. Their resistance to hydrolysis is notable since d^0 imido species of the Group 4–6 transition metals are typically unstable in the presence of air and moisture. The titanium(IV) mono(imido) analogues [Ti(L)(N^{t}Bu)Cl$_2$] (L = tacn or Me$_3$tacn) are also reported to be mildly air- and moisture-sensitive.[7a] First, high-valent titanium species are generally more oxophilic than Group 6. Chromium(VI) and molybdenum(VI) ions are more electronegative than Ti^{IV}, hence metal–imido interactions are more covalent for Group 6 metals. For Ti^{IV} electrons are relatively localised on the imido nitrogen atom which becomes more susceptible to electrophilic attack by protons. In addition, we also suggest that the highly congested co-ordination spheres in **1**–**4** (see Crystal structures), arising from the spatially demanding nature of tacn/Me$_3$tacn and the two N^{t}Bu moieties, present hydrophobic barriers which provide protection from hydrolysis. Unlike the cyclopentadienyl ligand, these purely σ-donating triamines do not compete with imido groups for pπ $\longrightarrow$ dπ donation to metal centres, and their ability to accommodate metal centres in high oxidation states is again illustrated.

The distinguishing UV-vis absorption band for the d^0 complexes **1**–**5** can clearly be assigned to ligand-to-metal charge transfer (LMCT) transitions. An imido-to-metal LMCT assignment is tentatively proposed; chloride-to-metal LMCT is disregarded since the chloro species **1** and **3** and the chloro-free

complex **5** absorb at similar energies. The absorption bands for the chromium(VI) derivatives **1**, **3** and **5** (λ_{max} 478–497 nm) are significantly red-shifted from the molybdenum(VI) species **2** and **4** (λ_{max} 295 nm). Like the electrochemical data, this reflects the greater tendency for high-valent chromium compounds to undergo reduction. It is pertinent to correlate the λ_{max} values for the chromium(VI) complexes to the LMCT absorption of CrO$_4^{2-}$ at 373 nm. The imido-to-chromium(VI) transitions appear at lower energies as anticipated in view of the established superior π-donating ability of the imido moiety compared to the oxo ligand.

Compared with [Cr(N^{t}Bu)$_2$(terpy)][BF$_4$]$_2$,[15] the absence of imido group transfer activity by complexes **1**–**4** may be ascribed to the congested nature of the saturated metal centres, and this is further increased by the facially bound macrocyclic ligands. Electronically, the singly charged metal centres and the imido nitrogen atoms in **1**–**4** are rendered less electrophilic with respect to substrate interaction. In addition, there is no reversible couple between 0 and −1.0 V vs. $\mathrm{Cp_2Fe^{0/+}}$ for **1**–**4**, in contrast to [Cr(N^{t}Bu)$_2$(terpy)][BF$_4$]$_2$ (−0.74 V).[15] A correlation between redox potential and reactivity has been suggested for Cr-mediated oxo transfer processes.[20] Hence the magnitude of the reduction potential for **1**–**4** presumably makes them unsuitable for imido group transfer reactions, since they are sufficiently stabilised with respect to reduction by the ligand systems present.

A greatly distorted imido angle at N(2) [151.8(4)°] is revealed in the structure of the chromium derivative **1** but not **2**·CH$_3$CN. Whether this constitutes a truly bent sp^2-hybridised imido arrangement is debatable. Strongly bent imido ligands are very rarely encountered in the literature.[21] The angle at a linear imido group is flexible and has been crystallographically shown to fluctuate between 150 and 180°.[19] While anticipated differences in the *trans* influence[21a] of the two imido moieties upon the Cr–N (tacn) distances is observed (*trans* to 'distorted' imido Cr(1)–N(4) 2.304(4) Å; *trans* to 'normal' imido Cr(1)–N(3) 2.238(4) Å), the N(2) angle in **1** nevertheless approaches the lower limit for a linear imido ligand. We therefore favour the explanation that steric and/or crystal packing forces rather than electronic effects are primarily responsible, especially since the imido groups in the molybdenum congener are 'normal'. A congested co-ordination sphere around the chromium centre can be inferred from the inter-imido N(1)–Cr(1)–N(2) angle of 107.4(2)°, which compares with that of 115.6(6)° in [Cr(N^{t}Bu)$_2$(terpy)][BF$_4$]$_2$.[15] The corresponding angle in complex **2** [107.0(1)°] is similar to that in **1**, but the greater bond distances around the molybdenum atom ease repulsion between the sterically demanding ligands so that highly distorted imido moieties are not observed in **2**.

Although numerous reports on the electrochemistry of imido complexes have appeared,[15,22] accounts of reversible oxidation at imido moieties are sparse. Recent studies by McCleverty and co-workers[23] described the electrochemistry of the molybdenum(VI) complexes [Mo(O)(Tp*)Cl(NC$_6$H$_4$X)] (X = NH$_2$, NMe$_2$, or N=Mo(O)(Tp*)Cl), where reversible one-electron oxidation couples at +0.73 to +0.96 V vs. $\mathrm{Cp_2Fe^{0/+}}$ in CH$_2$Cl$_2$ were assigned to occur at the arylimido ligand *via* generation of a stable quinonoidal fragment. Significantly these oxidation potentials are comparable with those for **1**–**5** (+0.86 to +1.20 V vs. $\mathrm{Cp_2Fe^{0/+}}$). Although the imido substituent in the present work cannot afford similar stabilisation, we suggest that the imido-based oxidation assignment is reasonable considering the nucleophilicity of the imido nitrogen, the multiple bond nature (bond order > 2) of the metal–imido interaction and, crucially, the well known stability conferred by the triamine macrocycles.

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