Thiocyanato and Azido Oxo-bridged Chromium(III) Dimers with Aromatic Diimine Ligands

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The spectroscopic, magnetic and electrochemical characteristics of four $[\{Cr(N\text{–}N)_2L\}_2O]^{2+}$ dimers are reported, where N–N = 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen) and $L^- = NCS^-$ or N_3^-. Electronic spectra are dominated by strong, diimine ligand-centred $\pi\text{–}\pi^*$ transitions, red-shifted on co-ordination to the chromium(III) centres. Strong antiferromagnetic coupling in $[\{Cr(bipy)_2(NCS)\}_2O][ClO_4]_2\cdot H_2O$ ($J = -247$ cm^{-1}) and $[\{Cr(phen)_2(NCS)\}_2O][ClO_4]_2\cdot H_2O$ ($J = -271$ cm^{-1}) indicates a diamagnetic ground state arising from $Cr(d_\pi)\text{–}O(p_\pi)\text{–}Cr(d_\pi)$ bonding within near-linear CrOCr units. An upper limit of 0 on pK_a for both $[\{Cr(N\text{–}N)_2(NCS)\}_2OH]^{3+}$ complexes reveals substantial bipy- and phen-promoted CrOCr π-bonding strength enhancements relative to the previously characterized $[\{Cr(tpma)(NCS)\}_2O]^{2+}$ dimer [tpma = tris(2-pyridylmethyl)amine]. Oxidative and reductive cyclic voltammograms of the $\mu\text{-}O^{2-}$ dimers have been determined in an effort to identify the highest occupied and lowest unoccupied molecular orbitals. Both magnetic and electrochemical findings suggest the splitting of formally non-bonding b_{2g} (highest occupied) and b_{1u} (lowest unoccupied) levels by virtue of π interactions with the diimine ligands.

The spectroscopy, photophysics, magnetism and electrochemistry of both mononuclear and dinuclear chromium(III) complexes with 2,2′-bipyridine (bipy) and 1,10-phenanthroline (phen) ligands have attracted considerable attention.[1–7] The μ-oxo $[(bipy)_2ORuORuO(bipy)_2]^{4+}$ complex and related species show considerable promise as catalysts for the oxidation of H_2O, Cl^- and organic substrates.[8–11] Oxo-bridged chromium(III) dimers with aromatic amine ligands {N_4 = tpma [tris(2-pyridylmethyl)amine], 2 bipy or 2 phen} may be prepared from the corresponding diols [equation (1)] where

$$(N_4)Cr(OH)_2Cr(N_4)^{4+} + 2\,L^- \longrightarrow L(N_4)CrOCr(N_4)L^{2+} + H_2O \quad (1)$$

L^- represents Cl^- or a pseudohalide ion.[12,13] The $[\{Cr(tpma)(NCS)\}_2O]^{2+}$ cation exhibits strong near-ultraviolet bands at 28 500 and 24 000 cm^{-1}, assigned to $e_u^* \longleftarrow e_g$ and $e_u^* \longleftarrow b_{2g}$ transitions within the pseudo-D_{4h} $Cr(d_\pi)\text{–}O(p_\pi)\text{–}Cr(d_\pi)$ manifold, and a $\mu\text{-}O^{2-}$ basicity indicative of moderately strong π bonding within the CrOCr core.[13] The magnetic susceptibility ($J = -255$ cm^{-1}) and electrochemistry [$E_{\frac{1}{2}}$ $Cr^{III,IV} \longrightarrow Cr^{III,III} = 1.17$ V *vs.* normal hydrogen electrode, 25 °C, $I = 0.1$ mol dm^{-3} (CH_3CN)] of this linear, centrosymmetric[12] dimer point to a $(e_u^b)^4(e_g)^4(b_{2g})^2$ π electronic configuration, based on the Dunitz and Orgel[14] molecular-orbital framework.

In order further to probe the electronic structures of CrOCr dimers, we report here the spectroscopic, magnetic and electrochemical properties of four $[L(N\text{–}N)_2CrOCr(N\text{–}N)_2L]^{2+}$ complexes, where N–N = bipy or phen and $L^- = NCS^-$ or N_3^-. The possibility that nominally non-bonding e_g and b_{2g} highest occupied molecular orbitals of $[\{Cr(tpma)L\}_2O]^{2+}$ will acquire substantial bonding character in the analogous complexes with strongly π-accepting bipy and phen ligands is of particular interest.

Experimental

Reagent grade chemicals were used throughout. The complexes $[\{Cr(bipy)_2(NCS)\}_2O][ClO_4]_2\cdot H_2O$ **1** [ν_{max} 856s (CrOCr) and 2066s (CN) cm^{-1}], $[\{Cr(bipy)_2(N_3)\}_2O][ClO_4]_2\cdot H_2O$ **2** [ν_{max} cm^{-1} 836s (CrOCr) and 2059s (NN)], $[\{Cr(tpma)(OH)\}_2]Br_4\cdot 8H_2O$, $[(tpma)CrO(OH)Cr(tpma)][ClO_4]_3\cdot H_2O$ and dimers of the form $[\{Cr(tpma)L\}_2O][ClO_4]_2$ ($L^- = Cl^-$, NCS^-, NCO^-, CN^- or N_3^-) were prepared as before.[13,15] **CAUTION.** Chromium(III) perchlorates are potentially explosive and should be handled carefully in small quantities. All reported compounds were vacuum dried at room temperature for 8 h prior to analysis.

The complex $[\{Cr(phen)_2(NCS)\}_2O][ClO_4]_2\cdot H_2O$ **3** was prepared by refluxing $[\{Cr(phen)_2(OH)\}_2][ClO_4]_4\cdot 3H_2O$[15] (2.50 g, 1.91 mmol) with NaSCN (3.15 g, 38.9 mmol) in CH_3CN (125 cm^3) for 40 min, at which time the solution had changed from red to red-brown. Lithium perchlorate (20 g) and water (50 cm^3) were then added to the cooled reaction mixture following filtration to remove excess of NaSCN. A crude solid isolated subsequent to the evaporation of CH_3CN was washed with diethyl ether and recrystallized from aqueous $LiClO_4$. Yield: 1.72 g, 77% (Found: C, 51.00; H, 2.70; N, 11.85. $C_{50}H_{34}Cl_2Cr_2N_{10}O_{10}S_2$ requires C, 51.15; H. 2.90; N, 11.95%). ν_{max} 2066s (CN) cm^{-1}.

The complex $[\{Cr(phen)_2(N_3)\}_2O][ClO_4]_2\cdot 2H_2O$ **4** was synthesised by combining NaN_3 (2.10 g, 32.3 mmol) with $[\{Cr(phen)_2(OH)\}_2][ClO_4]_4\cdot 3H_2O$ (1.00 g, 0.763 mmol) in boiling water (200 cm^3) to which two drops of 1 mol dm^{-3} $HClO_4$ had been added to suppress ionization of the diol $\mu\text{-}OH^-$ groups. After 1 min, the dark brown product was quickly precipitated by the addition of solid $LiClO_4$, filtered off and washed with water and ether. Yield: 0.68 g, 77% (Found: C, 49.75; H, 2.85; N, 16.70. $C_{48}H_{36}Cl_2Cr_2N_{14}O_{11}$ requires C, 49.70; H, 3.15; N, 16.90%). ν_{max} 2054s (NN) cm^{-1}.

The complexes $[\{Cr(bipy)_2(NCS)\}_2OH][ClO_4]_3\cdot 2H_2O$ **5** and $[\{Cr(phen)_2(NCS)\}_2OH][ClO_4]_3\cdot H_2O$ **6** were isolated in near-quantitative yields from the addition of three drops of concentrated aqueous $HClO_4$ to **1** and **3** (0.1 g), respectively, dissolved in the minimum volume of CH_3CN. The products were precipitated and washed with ether [Found: C, 42.40; H, 2.80; N, 11.70. $C_{42}H_{21}Cl_3Cr_2N_{10}O_{15}$ **5** requires C, 42.15; H, 3.10; N, 11.70%); ν_{max} 2055s (CN) cm^{-1}. Found: C, 47.25; H, 2.70;

Table 1 Electronic spectra of oxo- and hydroxo-bridged chromium(III) dimers[a]

Complex	λ_{max}/nm	log ε
1	240	4.67
	301	4.72
2	246	4.69
	300	4.75
3	226	5.00
	271	4.89
4	224	5.06
	274	4.90
	536	2.40
5	310	4.63
	527	2.46
6	224	5.06
	270	4.84
	354	3.98
	529	2.34
$[\{Cr(bipy)_2(OH)\}_2]^{4+}$ [b]	310	4.62
	392	2.84
	533	2.04
$[\{Cr(bipy)_2O\}_2]^{2+}$ [c]	244	4.59
	301	4.72
$[\{Cr(phen)_2(OH)\}_2]^{4+}$	226	5.06
	276	4.91
	353	3.54
	538	2.04

[a] In CH_3CN solution unless otherwise stated; ε expressed in $dm^3\ mol^{-1}\ cm^{-1}$. [b] 5 mmol dm^{-3} $HClO_4$(aq). [c] 0.05 mol dm^{-3} NaOH(aq).

N, 10.85. $C_{50}H_{19}Cl_3Cr_2N_{10}O_{14}$ **6** requires C, 47.15; H, 2.75; N, 11.00%; ν_{max} 2042s (CN) cm^{-1}].

Determinations of electronic and infrared spectra (KBr pellet), magnetic susceptibilities (6–350 K) and cyclic voltammograms were carried out as before.[13] The model of an isolated Heisenberg dimer containing $S = \frac{3}{2}$ ions with interaction Hamiltonian $\mathscr{H} = -2JS_1\cdot S_2$ was used throughout,[13] and non-linear least-squares fits of magnetic susceptibility temperature dependences took into account a trace monomeric impurity (fraction ρ) with Weiss constant θ. Cyclic voltammograms were acquired with platinum button (oxidative sweeps) and hanging mercury drop (reductive sweeps) working electrodes; platinum and aqueous saturated calomel (0.1 mol dm^{-3} $NaNO_3$) auxiliary and reference electrodes, respectively, were used throughout. Solutions were purged with Ar to remove O_2 prior to the acquisition of reductive voltammograms. Peak potentials were referenced to the normal hydrogen electrode (NHE) by using hydroxyethylferrocene ($E_{\frac{1}{2}}$ = 402 mV *vs.* NHE) as an internal calibrant; $E_{\frac{1}{2}}$ was calculated as $(E_{pa} + E_{pc})/2$.

Results and Discussion

The syntheses of $[L(N_4)CrOCr(N_4)L]^{2+}$ complexes with N_4 = 2 bipy or 2 phen and L^- = NCS^- or N_3^- proceed in excellent yield according to reaction (1). Displacement of H_2O from $[\{Cr(bipy)_2(OH)\}_2]^{4+}$ and $[\{Cr(phen)_2(OH)\}_2]^{4+}$ by pseudohalide nucleophiles occurs readily only when the incoming group is thiocyanate or azide, however. Thus, unlike $[\{Cr(tpma)(OH)\}_2]^{4+}$, the bipy and phen diols do *not* follow reaction (1) when refluxed with salts of NCO^-, CN^- or Cl^- in CH_3CN solution. Also, different products may be isolated from aqueous and acetonitrile reaction mixtures. For example, $[\{Cr(phen)_2(N_3)\}_2O][ClO_4]_2\cdot 2H_2O$ is the preferred product when $[\{Cr(phen)_2(OH)\}_2]^{4+}$ reacts with NaN_3 in hot water, while a complex with empirical formula $Cr_2(phen)_4(N_3)_2(ClO_4)_4(CH_3CN)(H_2O)_2$ predominates when the same reactants are refluxed in CH_3CN.

The structural assignment of 2,2′-bipyridine complexes **1** and **2** to near-linear, oxo-bridged dimers follows from elemental analysis data, strong asymmetric CrOCr stretching bands near 850 cm^{-1},[12,13,16] and the isolation of μ-OH^- complex **5** upon protonation of **1** by $HClO_4$. As anticipated, **5** exhibits no strong infrared absorption in the 800–900 cm^{-1} region. Although 1,10-phenanthroline vibrations obscure this region within the infrared spectra of **3** and **4**, elemental analysis data and the synthesis of μ-OH^- derivative **6** provide reasonable support for the assignment of the former two complexes to the μ-O^{2-} class. The presence of two structurally equivalent NCS^- (N-bonded) or N_3^- ligands in complexes **1**–**6** is indicated by single, sharp CN or NN stretches between 2030 and 2070 cm^{-1}.

Electronic spectral data for the μ-O^{2-} and μ-OH^- dinuclear complexes are compared with those of their $(\mu\text{-}OH)_2$ precursors in Table 1. Spectra are dominated by strong, diimine ligand-centred π–π* transitions, observed at 235 (4.01), 280 (3.85) and 229 (4.68), 263 (log ε = 4.48) nm for free bipy and phen in CH_3OH solutions, respectively. In order of increasing energy, we assign the strongest ultraviolet features to bipy or phen $^1B_1 \longleftarrow {}^1A_1$ and $^1A_1 \longleftarrow {}^1A_1$ transitions,[17–19] red-shifted on co-ordination[19–21] to the chromium(III) centres; only the former band is well resolved in hydroxo-bridged $Cr(bipy)_2$ complexes. On this basis, the π–π* band energies of complexes **1**–**6** compare favourably with those of the diol precursors and monomeric Cr^{III}–bipy or -phen species.[7,18,22] The lowest-energy π–π* bands of oxo-bridged bipy complexes **1** and **2** are blue-shifted by *ca.* 1000 cm^{-1} relative to the corresponding hydroxo-bridged species, as expected on electrostatic grounds.[19] Consistent with our spectroscopic interpretation, the difference in energy between ligated diimine π–π* bands is essentially independent of bridging type for both bipy and phen dinuclear chromium(III) complexes.

Although visible metal-to-ligand change-transfer (m.l.c.t.) bands are commonly observed for d^6, low-spin diimine complexes,[23,24] such transitions are evidently obscured by the intense $^1B_1 \longleftarrow {}^1A_1$ π–π* band in the present series of dinuclear chromium(III) complexes. Unfortunately, the distinctive near-ultraviolet features (330–420 nm) of the CrOCr chromophore are also unobservable for $L(N_4)CrOCr(N_4)L^{2+}$ dimers containing 2,2′-bipyridine or 1,10-phenanthroline. Thus, the observation of $e_u{}^* \longleftarrow e_g$ and $e_u{}^* \longleftarrow b_{2g}$ transitions near 350 and 420 nm, respectively, supported a molecular-orbital analysis of $Cr(d_\pi)$–$O(p_\pi)$–$Cr(d_\pi)$ bonding in $[\{Cr(tpma)L\}_2O]^{2+}$ species,[13] for which the pyridyl π–π* transition is well separated from the features of interest. Near-ultraviolet spectrophotometric titrations of $[\{Cr(bipy)_2(NCS)\}_2O]^{2+}$ and $[\{Cr(phen)_2(NCS)\}_2O]^{2+}$ were attempted in order to determine the pK_a values of their conjugate hydroxo-bridged acids, an indirect measure of CrOCr π-bonding strength.[13] Both μ-O^{2-} dimers are very weakly basic in water, such that ⩽50% protonation was observed even in 1.0 mol dm^{-3} HNO_3 (25 °C). An upper limit of 0 may therefore be placed on the pK_a values of **5** and **6**, revealing ⩾10^2-fold bipy- and phen-promoted acidity enhancements relative to $[\{Cr(tpma)(NCS)\}_2OH]^{3+}$ (pK_a = 2.05, 25 °C, I = 0.1 mol dm^{-3}).[13] Considering that pK_a (μ-OH^-) should increase with decreasing π-bonding strength in the CrOCr unit,[13,25] we conclude that π bonding mediated by the bridging oxo function is dramatically enhanced by the more potent π-accepting, strong-field bipy and phen ligands. Indeed, pK_a is inversely related to 10 *Dq* in $[Cr(tpma)L]_2O^{2+}$ complexes, ranging from 4.25 (L^- = N_3^-) to 0.64 (L^- = CN^-), reflecting the ability of strong-field ligands to bring e_u (D_{4h}) metal $[d_{xz,yz}(1) + d_{xz,yz}(2)]$ and oxo (p_x, p_y) symmetry orbitals into closer energetic proximity.[13]

Magnetic parameters derived from the temperature-dependent magnetic susceptibilities of complexes **1** and **3** (Figs 1 and 2) are compared with those of $[\{Cr(tpma)(NCS)\}_2O][ClO_4]_2\cdot H_2O$ in Table 2. All three compounds exhibit very strong antiferromagnetic coupling indicative of diamagnetic ground states. The singlet–triplet gaps ($-2J$) of **1** (494 cm^{-1}), **3** (542 cm^{-1}) and

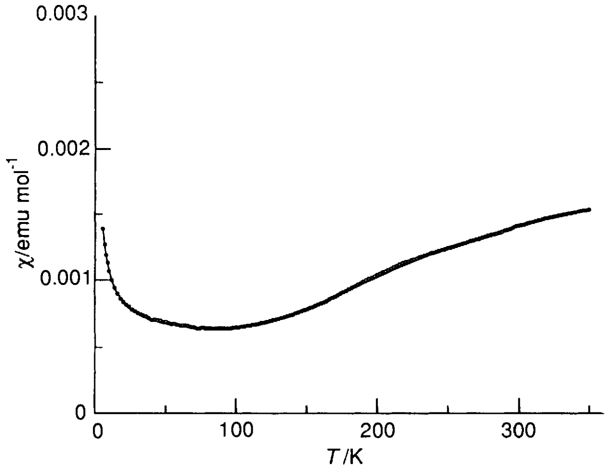

Fig. 1 Plot of magnetic susceptibility *vs.* temperature for $[\{Cr(bipy)_2(NCS)\}_2O][ClO_4]_2{\cdot}H_2O$ **1**. The solid line corresponds to the non-linear least-squares fit of the data (emu = SI × $10^6/4\pi$)

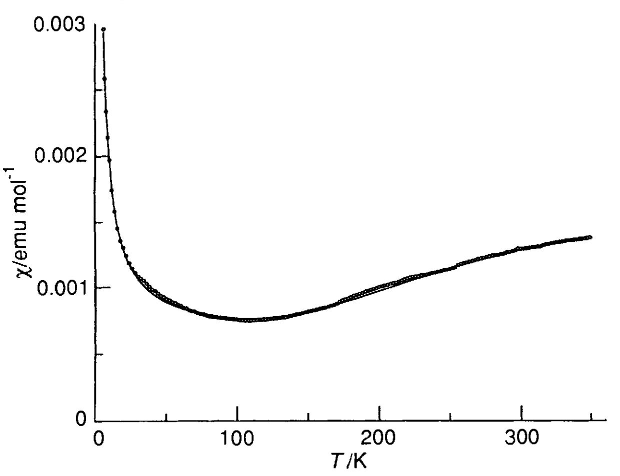

Fig. 2 Plot of magnetic susceptibility *vs.* temperature for $[\{Cr(phen)_2(NCS)\}_2O][ClO_4]_2{\cdot}H_2O$ **3**. The solid line corresponds to the non-linear least-squares fit of the data

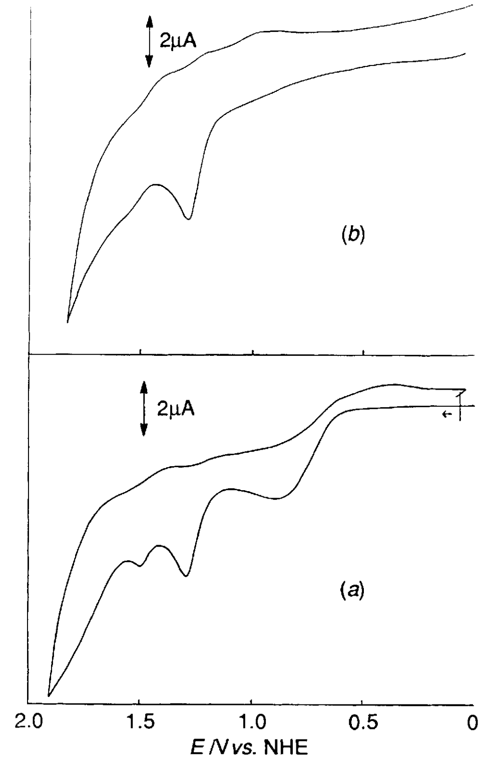

Fig. 3 Cyclic voltammograms of $[\{Cr(N_4)(NCS)\}_2O][ClO_4]_2$ complexes with $N_4 = (bipy)_2$ (*a*) and $(phen)_2$ (*b*); 0.5 mmol dm^{-3} electroactive solute, 25 °C, $I = 0.1$ mol dm^{-3} $NBu_4ClO_4(CH_3CN)$, platinum working electrode, sweep rate 50 mV s^{-1}

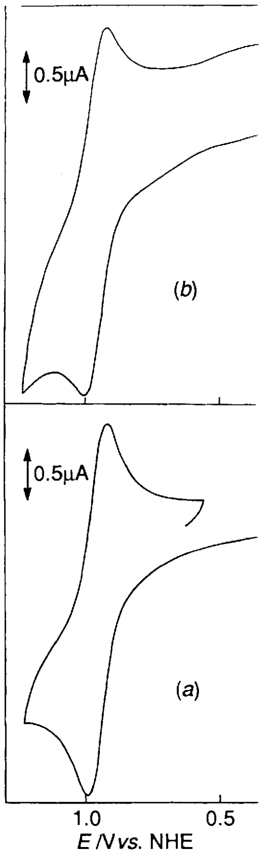

Fig. 4 Cyclic voltammograms of $[\{Cr(N_4)(N_3)\}_2O][ClO_4]_2$ complexes. Details as in Fig. 3

$[\{Cr(tpma)(NCS)\}_2O]^{2+}$ (510 cm^{-1}) are significantly larger than that of $[\{Cr(NH_3)_5\}_2O]^{2+}$ (450 cm^{-1}),[26] in which the ammonia ligands contribute to the σ bonding only. Since antiferromagnetic coupling in bent μ-oxo- and μ-hydroxo-chromium(III) species is typically smaller than that reported here by an order of magnitude,[6,25,27] our magnetic findings are consistent with a $(e_u^b)^4(e_g)^4(b_{2g})^2$ ground state arising from near-linear CrOCr bridging in compounds **1**–**4**. We note, however, that the finding of a diamagnetic ground term does not constitute proof of a 180° CrOCr bond angle.

The CrOCr b_{2g} $[d_{xy}(1) + d_{xy}(2)]$ and b_{1u} $[d_{xy}(1) - d_{xy}(2)]$ π molecular orbitals are expected to be approximately degenerate and non-bonding in the absence of Cr–Cr δ bonding and Cr d_π interactions with non-bridging ligands.[13,28] The magnetic susceptibility findings demonstrate that the lowest-lying triplet excited state falls substantially higher in energy than the singlet ground term, however. Considering that $t_{2g}(O_h)$ ligand π-symmetry orbitals transform as $e_g + b_{2g}$ in the approximate D_{4h} symmetry of $[(N_4)N'Cr]_2O^{2+}$ dimers, both the Cr e_g and b_{2g} levels presumably engage in back-bonding with low-lying π* levels of aromatic amine ligands, leaving only the b_{1u} molecular orbital as rigorously non-bonding. In this way, the mixing of ligand character into the primarily metal-centred b_{2g} molecular orbital could account for its preferential stabilization relative to the b_{1u} level. Indeed, lifting of the b_{2g}, b_{1u} degeneracy by anisotropic π donation from terminal oxo groups and bending of the bridging unit is well documented for RuORu dimers.[11,29–31] Bond length comparisons provide additional evidence that electrons placed in e_g, b_{2g} and b_{1u}

Table 2 Magnetic parameters for $[(SCN)(N_4)CrOCr(N_4)(NCS)][ClO_4]_2$ complexes *

Complex	g	J/cm^{-1}	Temperature-independent paramagnetism/cgsu	% impurity	θ
$[\{Cr(tpma)(NCS)\}_2O][ClO_4]_2 \cdot H_2O$	2.15	−255	1.7×10^{-5}	0.09	0.252
$[\{Cr(bipy)_2(NCS)\}_2O][ClO_4]_2 \cdot H_2O$	2.09	−247	5.6×10^{-4}	0.30	−1.784
$[\{Cr(phen)_2(NCS)\}_2O][ClO_4]_2 \cdot H_2O$	2.02	−271	6.3×10^{-4}	0.71	0.233

* Data for tpma complex from ref. 13.

Table 3 Electrochemistry of oxo-bridged chromium(III) dimers[a]

Complex	E_{pa}	E_{pc}	ΔE_p[b]/mV	$E_{\frac{1}{2}}$[c]/V *vs.* NHE
	V *vs.* NHE			
1		−1.43(sh)		
	−1.32(sh)	−1.31		
	−1.10	−1.18	80	−1.14
	−0.60(br)	−1.02		
	0.89	0.38		
	1.29			
	1.50			
2	−1.16	−1.24	80	−1.20
	−0.77(br)	−1.04		
	0.99	0.91	80	0.95
3	−1.19	−1.31	120	−1.25
	−1.11	−1.17	60	−1.14
	−0.77	−1.02		
	1.29			
4	1.00	0.92	80	0.96
$[\{Cr(tpma)(NCS)\}_2O]^{2+}$		−1.59		
		−1.35		
				1.17[d]
$[\{Cr(tpma)(N_3)\}_2O]^{2+}$	−1.82	−1.96	140	−1.89
		−1.82		
		−1.56		
		−1.41		
				0.96[d]
$[\{Cr(tpma)(NCO)\}_2O]^{2+}$	−1.88	−1.97	110	−1.93
		−1.51		
				1.02[d]
$[\{Cr(tpma)(CN)\}_2O]^{2+}$	−1.84	−1.89	50	−1.87
		−1.53		
				1.17[d]
$[\{Cr(tpma)Cl\}_2O]^{2+}$	−1.82	−1.90	80	−1.86
		−1.59		
				1.03[d]
$[\{Cr(tpma)(OH)\}_2]^{4+}$	−1.80	−1.88	80	−1.84
		−1.62		
$[Cr(tpma)O(OH)Cr(tpma)]^{3+}$	−1.82	−1.91	90	−1.87
		−1.54		
		−1.31		

[a] At 25.0 °C, 0.1 mol dm^{-1} $NBu_4ClO_4(CH_3CN)$, 0.5 mmol dm^{-3} electroactive solute. Negative and positive E_{pa} and E_{pc} values derived from cathodic (mercury drop working electrode) and anodic (platinum working electrode) sweeps, respectively, commencing near E(SCE). [b] Peak-to-peak separation of quasi-reversible wave. [c] Half-wave potential of quasi-reversible couple, calculated as $(E_{pa} + E_{pc})/2$. [d] Corresponds to one-electron oxidation wave, from ref. 13.

molecular orbitals of the MOM π manifold are not all rigorously non-bonding.[32]

In order further to probe the relative energies and electronic characteristics of both highest occupied and lowest unoccupied molecular orbital levels, reductive and oxidative processes of Cr^{III}–O–Cr^{III} dimers with bipy, phen and tpma non-bridging ligands were elucidated by cyclic voltammetry. Cathodic and anodic peak potentials and half-wave potentials of reversible processes are summarized in Table 3 for studies carried out at 25 °C in 0.1 mol dm^{-3} NBu_4ClO_4 (CH_3CN). All reported half-wave potentials were shown to be independent of sweep rate in the 50–300 mV s^{-1} interval. Previous studies of $[\{Cr(tpma)L\}_2O]^{2+}$ dimers revealed reversible, one-electron oxidation waves in the $E_{\frac{1}{2}}$ = 0.96–1.17 V *vs.* NHE interval, defined by the N_3^- and NCS^- complexes, respectively.[13] Cyclic voltammograms initiated anodically for **1**–**4** (platinum working electrode, 0 to +1.8 V range) are compared in Figs. 3 and 4. Thiocyanate complexes **1** and **3** exhibit totally irreversible anodic waves at E_{pa} = 1.29 V, in contrast to the reversible $[\{Cr(tpma)(NCS)\}_2O]^{2+}$ voltammogram with $E_{\frac{1}{2}}$ = 1.17 V. Considering that $[(NCS)(tpma)Cr^{III}OCr^{IV}(tpma)(NCS)]^{3+}$ is susceptible to intra-complex redox decay on the 1 h time-scale,[13] it appears likely that the analogous bipy and phen chromium(III,IV) products undergo accelerated decay through internal NCS^- oxidation on a much faster time-scale. In any case, the shift in E_{pa} from 1.21 (tpma) to 1.29 V (bipy and phen) confirms the prediction of b_{2g} molecular-orbital stabilization by strong π-acid ligands. The least sterically crowded dimer, $[\{Cr(bipy)_2(NCS)\}_2O]^{2+}$, exhibits a unique, broad oxidative feature near 0.89 V, suggesting that NCS^- ligands may be accessible to direct oxidation in this complex.

In contrast to the thiocyanate complexes, azido oxo-bridged dimers **2** and **4** show quasi-reversible one-electron oxidation waves at potentials more negative by 0.3 V. To within experimental uncertainty, $E_{\frac{1}{2}}$ values of the tpma, bipy and phen azido μ-O^{2-} dimers are identical at 0.96 ± 0.01 V. The fact that E_{pa} (N_3^-) $\ll$ E_{pa} (NCS^-) for all three $[Cr(N_4)L]_2O^{2+}$ series prompted us to re-evaluate pseudohalide effects on previously reported $[\{Cr(tpma)L\}_2O]^{2+}$ oxidation half-wave potentials (Table 3). Considering that the preferred resonance forms of N_3^- (N=N=N) and NCS^- (N≡C–S) possess two and one lone pair on the N donor atom, respectively, the former is expected to function as a more potent π-donor ligand towards the chromium(III) centre. Indeed, symmetry-allowed overlaps between N($2p_{\pi}$) donor and Cr b_{2g} acceptor orbitals are expected to drive the highest occupied molecular orbital to higher energy, counteracting in part the influence of aromatic amine π acceptors. According to this hypothesis, halide and pseudohalide π-donor strengths in the tpma μ-oxo dimers increase with *decreasing* $E_{\frac{1}{2}}$: $CN^- \approx NCS^- \ll Cl^- < NCO^- < N_3^-$. This ranking is in reasonable accord with both the spectrochemical series,[33] $Cl^- < N_3^- < NCO^- < NCS^- < CN^-$, in which π donation attenuates ligand-field strength, and π-donor strength assessments based on the reduction of carbonyl stretching frequencies in compounds of the type *trans*-$[ML(CO)(PPh_3)_2]$.[34] This remarkable sensitivity of $Cr^{III,IV} \longrightarrow Cr^{III,III}$ $E_{\frac{1}{2}}$ values to the donor characteristics of a single pseudohalide group per Cr atom is undoubtedly magnified by the synergistic influence of the aromatic amine ligands.[35]

Reductive cyclic voltammograms of the Cr^{III}–O–Cr^{III} dimers (mercury drop working electrode, 0 to −2.2 V range) are considerably more complex than their oxidative counterparts. Nevertheless, the data (Table 3) confirm our prediction that linear oxo-bridged dimers, bent μ-hydroxo species and monomeric chromium(III) analogues should be reduced at comparable potentials. Thus, the non-bonding b_{1u} lowest unoccupied molecular orbital is considered to be electronically equivalent to the $3d_{xy}$ orbital of a chromium(III) monomer. Thiocyanato dimers **1** and **3** exhibit dominant, quasi-reversible one-electron chromium(III,II) reduction waves with $E_{\frac{1}{2}} = -1.14$ V *vs.* NHE, in close proximity to that of azido dimer **2** at −1.20 V. In all cases, this primary feature is preceded by adsorption pre-waves whose intensities decrease strongly in steady-state voltammograms. Half-wave reduction potentials of **1**, **2** and **3** in dmf (−1.13, −1.22 and −1.14 V; 25 °C, 0.1 mol dm^{-3} NBu_4ClO_4) are essentially identical to the results in CH_3CN. A second quasi-reversible wave observed for **3** at $E_{\frac{1}{2}} = -1.25$ V shifts to −1.29 V ($\Delta E_p = 70$ mV) in dimethylformamide (dmf). Comparable monomers, $[Cr(bipy)_2(NCS)_2]^+$ [$E_{\frac{1}{2}} = -1.017$, −1.196 V *vs.* sodium chloride saturated calomel electrode, (SSCE), 0.4 mol dm^{-3} $Na(O_3SCF_3)$ in dmf] and $[Cr(phen)_2(NCS)_2]^+$ [$E_{\frac{1}{2}} = -1.022$, −1.185 V *vs.* SSCE, 0.8 mol dm^{-3} $Na(O_3SCF_3)$ in dmf][7], also exhibit two closely spaced reduction waves at potentials similar to those reported here for **1**–**3**. In contrast, free 2,2′-bipyridine is reduced at much more negative potentials [$E_{\frac{1}{2}} = -2.10$, −2.66 V *vs.* saturated calomel electrode (SCE), 0.1 mol dm^{-3} NBu_4ClO_4 in dmf][36] while $[Cr(bipy)_3]^{3+}$ ($E_{\frac{1}{2}} = -0.212$, −0.720, −1.285, −1.913 V *vs.* Ag–AgCl, 0.1 mol dm^{-3} NEt_4BF_4 in CH_3CN) and related $[Cr(diimine)_3]^{3+}$ monomers are typically reduced in four reversible one-electron steps, the last of which populates a ligand π* level.[37]

Unfortunately, no reversible chromium(III) reduction waves were observed in cyclic voltammograms of $[\{Cr(tpma)L\}_2O]^{2+}$ dimers. Totally irreversible cathodic features were observed between −1.5 and −1.6 V *vs.* NHE for all tpma complexes; adsorption pre-waves appeared for $L^- = N_3^-$ and NCS^-. There is no apparent relationship between E_{pc} and pseudohalide π-acceptor strength. The negative shift in E_{pc} of the tpma complexes relative to the first reversible waves of bipy and phen dimers is consistent with the greater capacity of conjugated pyridyl ligands to delocalize electron density from the Cr atom, however. The quasi-reversible wave with $E_{\frac{1}{2}}$ near −1.9 V in $[\{Cr(tpma)L\}_2O]^{2+}$ reductive voltammograms may be attributed to tpma ligand reduction. There is very little difference among the cyclic voltammograms of $[\{Cr(tpma)L\}_2O]^{2+}$, $[\{Cr(tpma)(OH)\}_2]^{4+}$ and $[(tpma)CrO(OH)Cr(tpma)]^{3+}$, verifying that these data are not informative with regard to the electronic structure of μ-O^{2-} dimers.

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