Substituent effects on the physical properties of (μ-oxo)(μ-carboxylato)bis{tris(2-pyridylmethyl)aminechromium(III)} dimers

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Abstract

In order to document the influence of carboxylate substituents on the physical properties of $[(tmpa)Cr(\mu\text{-}O)(\mu\text{-}RCO_2)Cr(tmpa)]^{3+}$ dimers, electronic spectra, Cr(III,IV/III,III) half-wave reduction potentials, $\mu\text{-}OH^-$ ionization constants and antiferromagnetic coupling constants are reported for R = CH_2Cl, $CHCl_2$, $C(CH_3)_3$, $C(C_6H_5)_3$, 1-adamantyl and Ph-4-X (X = NMe_2, OH, OCH_3, CH_3, CF_3, F, Cl, CN, NO_2); tmpa = tris(2-pyridylmethyl)amine. Inductive effects of bridging benzoato *para* substituents are transmitted effectively to the $\mu\text{-}O^{2-}$ group in $[(tmpa)Cr(\mu\text{-}O)(\mu\text{-}4\text{-}X\text{-}PhCO_2)Cr(tmpa)]^{3+}$ dimers. A linear free energy relationship between $E_{1/2}$ Cr(III,IV/III,III) and $pK_a(Cr(\mu\text{-}OH)Cr)$ indicates a high degree of cooperativity among bridging oxo, complementary bridging and non-bridging ligands with regard to π-donation towards the Cr(III) centers. Trends in antiferromagnetic coupling constants are interpreted through the influence of configuration interaction between ligand- and metal-centered b_1 symmetry orbitals on the HOMO(b_1)–LUMO(a_2) singlet-triplet energy gap.

Introduction

The bioinorganic chemistry of oxo, carboxylato-bridged Fe [1, 2] and Mn [3] complexes has stimulated the investigation of these and related transition metal compounds [4–19]. Our interest in these species centers on the synergism between bridging oxo and carboxylato groups with regard to π-donation towards the metal centers. We have reported $[(tmpa)Cr(\mu\text{-}O)(\mu\text{-}RCO_2)Cr(tmpa)]^{3+}$ complexes having single oxo and carboxylato bridges in addition to tris(2-pyridylmethyl)amine N_4 donor sets; R = H, CH_3, C_6H_5 [20]. The acetate-bridged dimer has markedly non-equivalent Cr–O–Cr bond lengths of 1.79 and 1.85 Å, a CrOCr bond angle of 132° and unsymmetric tmpa ligation, i.e. one apical nitrogen atom is *trans* to $\mu\text{-}O^{2-}$ while the other is *trans* to a carboxylate O atom [20]. The Cr(III,IV/III,III) $E_{1/2}$ values of both $[(tmpa)Cr(\mu\text{-}O)(\mu\text{-}L)Cr(tmpa)]^{3+}$ and $[Cr(tmpa)L]_2O^{2+}$ complexes decrease linearly with increasing bridging oxo group basicity, suggesting that the HOMO energy rises according to the progression: $\mu\text{-}C_6H_5CO_2^- \approx \mu\text{-}HCO_2^- < \mu\text{-}CH_3CO_2^- \approx NCS^- < NCO^- \approx Cl^- < N_3^- \ll \mu\text{-}F^- < \mu\text{-}OH^-$ [21].

In order to further document the influence of carboxylate bridging groups on the electronic structure of Cr(III) dimers, we report here substituent effects on electronic and IR spectra, Cr(III,IV/III,III) half-wave reduction potentials, acid–base properties and magnetic susceptibilities of $[(tmpa)Cr(\mu\text{-}O)(\mu\text{-}RCO_2)Cr(tmpa)]^{3+}$ complexes, where R = CH_2Cl, $CHCl_2$, $C(CH_3)_3$, $C(C_6H_5)_3$, 1-adamantyl and Ph-4-X (X = NMe_2, OH, OCH_3, CH_3, CF_3, F, Cl, CN, NO_2).

Experimental

Reagent grade chemicals and doubly or triply distilled water were used throughout. Sodium chloroacetate, sodium dichloroacetate, sodium trichloroacetate, sodium trimethylacetate hydrate, triphenylacetic acid, 1-adamantanecarboxylic acid and benzoic acid derivatives of the type $4\text{-}X\text{-}C_6H_4COOH$ (X = CH_3, CF_3, F, Cl, OH, OCH_3, CN, NO_2 and $N(CH_3)_2$) were used as supplied by Aldrich. Complexes of the form $[(tmpa)Cr(\mu\text{-}O)(\mu\text{-}RCO_2)Cr(tmpa)](ClO_4)_3 \cdot nH_2O$ were readily prepared as before [20] from the reactions of $[Cr(tmpa)(OH)]_2(ClO_4)_4 \cdot 4H_2O$ [22] with excess carboxylate incoming group (acetonitrile or methanol solvent). Free acids were neutralized with stoichiometric lithium hydroxide or triethylamine. Analytical data for the new $[(tmpa)Cr(\mu\text{-}O)(\mu\text{-}RCO_2)Cr(tmpa)](ClO_4)_3 \cdot nH_2O$ complexes are presented in Table 1.

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TABLE 1. Analytical data for $[(tmpa)Cr(\mu\text{-}O)(\mu\text{-}RCO_2)Cr(tmpa)](ClO_4)_3 \cdot nH_2O$ complexes

R	*n*	Yield (%)	Calc. (%)				Found (%)			
			Cr	C	H	N	Cr	C	H	N
CH_2Cl	4	93	8.93	39.19	3.98	9.62	9.01	39.15	3.33	9.42
$CHCl_2$	2	53	8.94	39.24	3.55	9.63	8.97	39.40	3.23	9.66
$C(CH_3)_3$	2	51	9.15	43.34	3.55	9.86	9.30	43.53	3.99	9.97
$C(C_6H_5)_3$	0	72	8.08	52.29	4.00	8.71	8.01	52.40	3.98	8.48
$C_{10}H_{15}$[a]	1	89	8.69	47.19	4.42	9.37	8.72	47.54	4.32	8.94
C_6H_4-4-NMe_2	2	56	8.67	45.07	3.87	10.51	8.74	44.81	3.71	10.34
C_6H_4-4-OH	4	70	8.61	42.75	4.09	9.27	8.53	43.47	3.69	8.99
C_6H_4-4-OCH_3	2	70	8.77	44.55	3.65	9.45	8.76	44.11	3.62	9.45
C_6H_4-4-CH_3	2	72	8.89	45.16	3.70	9.58	9.14	45.31	3.74	9.31
C_6H_4-4-CF_3	2	78	8.49	43.17	3.29	9.15	8.76	43.30	3.20	8.97
C_6H_4-4-F	2	75	8.86	43.98	3.43	9.54	8.99	44.05	3.44	9.43
C_6H_4-4-Cl	2	77	8.73	43.38	3.39	9.41	8.90	43.53	3.07	9.13
C_6H_4-4-CN	2	24	8.80	44.74	3.41	10.67	9.04	44.61	3.21	10.15
C_6H_4-4-NO_2	4	63	8.41	41.74	3.91	10.19	8.59	41.91	3.35	9.68

[a] 1-Adamantyl group.

$[(OH)(tmpa)Cr(\mu\text{-}O)Cr(tmpa)(Cl_3CCO_2)](ClO_4)_2$ was synthesized by refluxing $NaCl_3CCO_2$ (0.935 g, 5.04 mmol) with $[Cr(tmpa)(OH)]_2(ClO_4)_4 \cdot 4H_2O$ (0.598 g, 0.503 mmol) in 100 ml of CH_3CN for 1 h. The reaction mixture was filtered following evaporation to 50 ml and the filtrate was then combined with 2 g of $LiClO_4$ dissolved in 100 ml of water. A green microcrystalline product (0.398 g, 67%) was collected, washed with ether and air-dried. *Anal.* Calc. for $[(OH)(tmpa)CrOCr(tmpa)(Cl_3CCO_2)](ClO_4)_2$: Cr, 9.64; C, 42.30; H, 3.46; N, 10.38. Found: Cr, 9.69; C, 42.21; H, 3.60; N, 9.73%. Several attempts to prepare the analogous trifluoroacetate derivative were unsuccessful.

Electronic (CH_3CN solution) and IR (KBr pellet) spectra were acquired on Shimadzu UV-260 and Perkin-Elmer model 1600 instruments, respectively. Spectrophotometric titrations of aqueous solutions (371 nm; 25.0 °C, $I = 0.1$ M ($NaNO_3$)), cyclic voltammetric measurements on acetonitrile solutions (Pt button working electrode; 25.0 °C, $I = 0.1$ M ($N(n\text{-}C_4H_9)_4ClO_4$)) and magnetic susceptibility measurements (4–300 K) were performed and interpreted as previously described [20, 21].

Results and discussion

Oxo, carboxylato dimers of the type $[(tmpa)Cr(\mu\text{-}O)(\mu\text{-}RCO_2)Cr(tmpa)]^{3+}$ are easily prepared in good yields by the displacement of H_2O from a dihydroxo-bridged precursor (eqn. (1)). Electronic spectra and carboxylate stretching frequencies are reported in Table 2. Excellent correlations of $\nu_{as}(CO_2^-)$ with RCOOH pK_a [23] pertain for dimers with both aliphatic and aromatic substituents (Fig. 1), consistent with expectations for isostructural compounds. Small energy differences between $\nu_{as}(CO_2^-)$ and $\nu_s(CO_2^-)$ support this conclusion [20]. A significant exception is $R = CCl_3$, for which $\nu_{as}(CO_2^-)$ is much smaller than anticipated on the basis of CCl_3COOH acidity. The trichloroacetate complex is best formulated as $[(OH)(tmpa)Cr(\mu\text{-}O)Cr(tmpa)(CCl_3CO_2)]^{3+}$ in view of the analytical data and other anomalies in its physical properties (*vide infra*); the weakly basic $CCl_3CO_2^-$ anion is thought to function as a monodentate rather than a bridging ligand.

$$[(tmpa)Cr(OH)_2Cr(tmpa)]^{4+} + RCO_2^- \longrightarrow$$
$$[(tmpa)Cr(O)(RCO_2)Cr(tmpa)]^{3+} + H_2O \quad (1)$$

Electronic spectra of $[(tmpa)Cr(\mu\text{-}O)(\mu\text{-}RCO_2)Cr(tmpa)]^{3+}$ dimers are essentially independent of the R group; very modest variations in peak positions and band intensities were observed. The $(b_1)^2(a_1)^2(b_2)^2(a_2)^2(b_1)^2$ (C_{2v}) π-electronic configuration was proposed for these complexes, leaving non-bonding a_2 in addition to a_1 and b_1 π-antibonding levels unoccupied [20]; $b_1(HOMO) = Cr\ d_{xy}(1) + d_{xy}(2)$, $a_2(LUMO) = Cr\ d_{xy}(1) - d_{xy}(2)$. Four allowed UV–Vis transitions are predicted: ${}^1B_2 \leftarrow {}^1A_1$ ($a_2 \rightarrow b_1$), ${}^1B_2 \leftarrow {}^1A_1$ ($b_2 \rightarrow a_1$), ${}^1A_1 \leftarrow {}^1A_1$ ($b_1 \rightarrow b_1$) and ${}^1B_1 \leftarrow {}^1A_1$ ($b_1 \rightarrow a_1$). We assign these transitions to strong bands observed in the vicinity of 336, 371, 390 (often poorly-resolved) and 420 nm, respectively. In addition, the lowest-energy d–d transition is observed near 565 nm. The $[(tmpa)Cr(\mu\text{-}O)(\mu\text{-}RCO_2)Cr(tmpa)]^{3+}$ dimers reversibly protonate to give $[(tmpa)Cr(\mu\text{-}OH)(\mu\text{-}RCO_2)Cr(tmpa)]^{4+}$ conjugate acids having pK_as between 0.46 ($R = CHCl_2$) and 2.21 ($R = Ph\text{-}4\text{-}OH$) (Table 3). Consistent with our previous findings, electronic spectra of the $\mu\text{-}OH^-$ complexes

TABLE 2 Electronic and IR spectroscopy of $[(\mathrm{tmpa})\mathrm{Cr}(\mu\text{-O})(\mu\text{-RCO}_2)\mathrm{Cr}(\mathrm{tmpa})]^{3+}$ dimers[a]

R	UV–Vis λ_{max} (nm) (ϵ_{max} (M^{-1} cm^{-1}))		IR (CrOCr dimer) (cm^{-1})	
	CrOCr dimer	Cr(OH)Cr dimer	$\nu_{as}(CO_2^-)$	$\nu_s(CO_2^-)$
$(C_6H_5)_3C$	256 (22500) 289, sh (5130) 337 (4960) 371 (3470) 421 (1470) 566 (210) 611 (190)	264 (18500) 393 (220) 514 (312)	1553	1391
$(CH_3)_3C$	255 (20400) 289, sh (5140) 337 (5020) 371 (3250) 391, sh (2400) 418 (2190) 565 (235)	263 (22200) 389 (264) 514 (340)	1534	1428
CH_2Cl	255 (21400) 289, sh (5240) 336 (5720) 371 (3180) 392 (2820) 398, sh (2520) 565 (223)	263 (18100) 386 (246) 509 (330)	1580	1440
$CHCl_2$	256 (21400) 289, sh (5550) 336 (6070) 355, sh (3690) 371 (3620) 421 (1660) 564 (237) 601 (224)	264 (16900) 387 (230) 509 (318)	1617, sh	1421
CCl_3[b]	253 (21200) 292 (4500) 336, sh (3570) 372 (2840) 394, sh (2460) 437 (2250) 564 (190)	263 (16700) 384 (235) 511 (319)	1534	1349
$C_{10}H_{15}$[c]	256 (21200) 289 (4990) 337 (4850) 371 (3230) 390, sh (2350) 419 (2140) 565 (210)	263 (17500) 388 (240) 514 (326)	1526	1415
Ph-4-NMe_2	253 (23300) 298, sh (13700) 354 (29000) 422, sh (3310) 570 (276)	260 (29300) 380 (290) 511 (348)	1491	1399
Ph-4-OCH_3	257 (30000) 288 (22200) 335 (5260) 367, sh (3300) 389, sh (2580) 419 (2280) 566 (281)	262 (26600) 316 (17300) 379 (863) 513 (361)	1518	1406

(*continued*)

TABLE 2. (*continued*)

R	UV–Vis λ_{max} (nm) (ϵ_{max} (M^{-1} cm^{-1}))		IR (CrOCr dimer) (cm^{-1})	
	CrOCr dimer	Cr(OH)Cr dimer	$\nu_{as}(CO_2^-)$	$\nu_s(CO_2^-)$
Ph-4-CH_3	256 (36000) 336 (5350) 370, sh (3310) 391 (2730) 407, sh (2550) 420 (2470) 566 (246)	265 (25700) 291, sh (13500) 374 (385) 514 (360)	1522	1412
Ph-4-OH	257 (32000) 286 (21600) 334 (5210) 367, sh (3220) 391, sh (2440) 419 (2150) 566 (217)	262 (28300) 315 (16600) 378 (802) 515 (332)	1509	1406
Ph-4-Cl	255 (39000) 337 (5310) 369, sh (3090) 392 (2690) 406, sh (2540) 418, sh (2420) 564 (240)	265 (28600) 287 (15200) 379 (319) 513 (333)	1527	1419
Ph-4-F	252 (32900) 337 (5260) 371, sh (3050) 393 (2760) 406, sh (2600) 419, sh (2480) 567 (228)	264 (27100) 379 (284) 514 (342)	1528	1413
Ph-4-CF_3	236 (33800) 286, sh (8410) 336 (5690) 363, sh (3780) 370 (3570) 420 (2040) 565 (323)	258 (30100) 385 (281) 513 (349)	1542	1421
Ph-4-NO_2[d]	258 (35000) 336 (6120) 370, sh (3560) 420 (1910) 566 (222)	265 (33000) 380 (332) 513 (318)	1550	1414
Ph-4-CN[e]	254, sh (24100) 287, sh (7350) 337 (5270) 370 (3380) 419 (1890)	259 (25800) 383 (275) 511 (346)	1528	1412

[a] Spectra of CrOCr dimers and Cr(OH)Cr protonation products recorded in acetonitrile and water, respectively, at ambient temperature. Extinction coefficients expressed per mole of dimer. [b] $[(OH)(tmpa)Cr(\mu\text{-}O)Cr(tmpa)(CCl_3CO_2)]^{3+}$ complex; carboxylate group is not bridging. [c] R = 1-adamantyl. [d] N–O stretch observed at 1345 cm^{-1}. [e] C≡N stretch observed at 2228 cm^{-1}.

(Table 2) feature the two lowest-energy d–d bands of the d^3 configuration (blue-shifted from the μ-O^{2-} spectra). The third d–d band is obscured by a strong pyridyl π–π^* transition. Although the spectrum of $[(OH)(tmpa)Cr(\mu\text{-}O)Cr(tmpa)(CCl_3CO_2)]^{3+}$ bears a superficial resemblance to those of the RCO_2^--bridged dimers, its ${}^1B_1 \leftarrow {}^1A_1$ transition is red-shifted to 437 nm and the ${}^1B_2 \leftarrow {}^1A_1$ (336 nm) band is significantly weaker. Furthermore, the μ-O^{2-} group of the trichloroacetate complex is more basic than those of other dimers which contain both oxo and carboxylate ligands by 4 to 6 orders of magnitude.

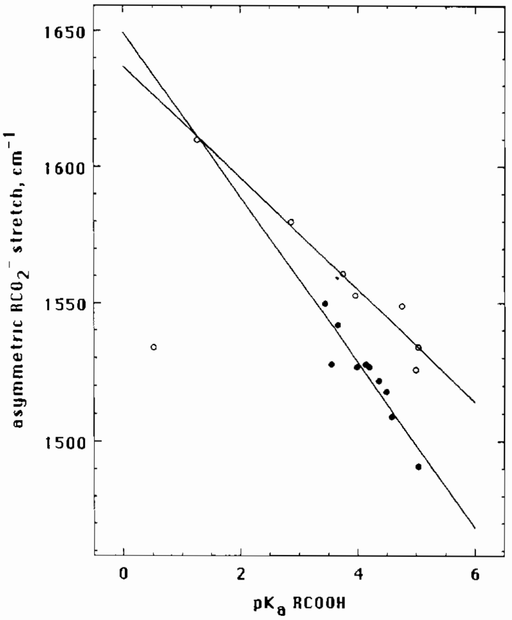

Fig. 1. Correlations of $\nu_{as}(CO_2^-)$ (Table 2) with pK_as for $[(tmpa)Cr(\mu\text{-}O)(\mu\text{-}RCO_2)Cr(tmpa)]^{3+}$ dimers with aliphatic (○) and aromatic (●) carboxylate substituents. Low-lying point for $R = CCl_3$ excluded from the least-squares fit Data for $R = H$, CH_3 and C_6H_5 from ref. 20.

A plot of μ-OH^- pK_a versus Hammett σ_p [23] is linear (correlation coefficient = 0.998) for all aromatic R groups considered, yielding a slope (ρ) of -0.81 ± 0.02 only slightly different from that characteristic of the parent benzoic acids (-1.00). Inductive effects of phenyl *para* substituents are transmitted effectively to the μ-O^{2-} group in $[(tmpa)Cr(\mu\text{-}O)(\mu\text{-}4\text{-}X\text{-}PhCO_2)Cr(tmpa)]^{3+}$ dimers, implying that pπ-donation from μ-RCO_2^- to Cr(III) occurs at the expense of Cr(dπ)–O(pπ)–Cr(dπ) bonding [20]. Analogous synergism between M–L and M–M bond strengths has been reported for $M_2(RCO_2)_4L_2$ dimers (M = Cr, Rh) [24].

Half-wave Cr(III,IV/III,III) reduction potentials based on quasi-reversible ($\Delta E_p = 70$–90 mV) one-electron oxidation waves are summarized in Table 3 along with magnetic parameters derived from fits of magnetic susceptibility temperature dependences to the Heisenberg exchange model for $S = 3/2$ centers. Figure 2 presents an updated plot of Cr(III,IV/III,III) $E_{1/2}$ versus pK_a(Cr(μ-OH)Cr), including all (tmpa)CrOCr(tmpa) dimers for which both of these parameters are available. The revised least-squares relationship: $E_{1/2} = 1.41 - 0.10(pK_a)$ V (correlation coefficient = 0.992) is in excellent agreement with that reported previously [21], and a fit including only the RCO_2^- complexes ($E_{1/2} = 1.39 - 0.092(pK_a)$ V) is identical to within experimental uncertainty. Thus, for both singly- and doubly-bridged dimers in this series, the energy of the highest occupied molecular orbital ($b_{2g}(D_{4h})$ or $b_1(C_{2v})$) correlates extremely well with CrOCr π-bonding

TABLE 3. Magnetic susceptibility, spectrophotometric titration and cyclic voltammetric data for $[(tmpa)Cr(\mu\text{-}O)(\mu\text{-}RCO_2)Cr(tmpa)]^{3+}$ dimers[a]

R	*g*	*J* (cm^{-1})	*zJ'* (cm^{-1})	*TIP* (cgsu)	Impurity (%)	pK_a[b]	$E_{1/2}$ (V) vs. NHE[c]
H	2.16	−93.0	0	6.6×10^{-4}	0.25	1.69	1.21
CH_3	2.00	−50.3	0	6.5×10^{-5}	2.54	2.20	1.17
CH_2Cl	2.00	−76.5	26.7	2.3×10^{-3}	0.82	1.56(3)	1.25
$CHCl_2$	2.00	−98.2	38.8	2.6×10^{-4}	0.50	0.46(7)	1.33
CCl_3[d]	2.00	−30.7	−6.9	5.3×10^{-4}	0.00	5.95(3)	0.83
$C(CH_3)_3$						1.24(9)	1.26
$C(C_6H_5)_3$							1.34
$C_{10}H_{15}$[e]						1.41(6)	1.25
Ph	2.11	−75.4	0	1.1×10^{-3}	0.21	1.88	1.22
Ph-4-NMe_2	2.00	−66.0	6.5	1.4×10^{-3}	1.30		1.13[f]
Ph-4-OCH_3	2.00	−66.3	2.5	1.1×10^{-3}	1.05	2.11(4)	1.21
Ph-4-CH_3	2.00	−68.3	6.3	1.2×10^{-3}	0.82	1.98(5)	1.23
Ph-4-Cl	2.00	−69.0	7.6	1.5×10^{-3}	1.08	1.68(5)	1.23
Ph-4-F	2.00	−72.0	7.2	1.5×10^{-3}	0.91	1.82(3)	1.25
Ph-4-CF_3	2.00	−88.9	19.8	1.3×10^{-3}	0.59	1.46(5)	1.25
Ph-4-CN	2.00	−83.4	6.3	5.2×10^{-3}	2.56		1.28
Ph-4-OH						2.21(4)	1.23
Ph-4-NO_2						1.26(8)	1.28

[a] Magnetic, electrochemical and spectrophotometric titration data for R = H, CH_3 and Ph from ref. 20. [b] Corresponds to μ-OH^--to-μ-O^{2-} acid ionization, 25.0 °C, $I = 0.1$ M ($NaNO_3$). Standard deviations derived from non-linear least-squares fits of spectrophotometric titration data are shown in parentheses. [c] Half-wave reduction potential for $[(tmpa)Cr(\mu\text{-}O)(\mu\text{-}RCO_2)Cr(tmpa)]^{4+/3+}$ couple at 25.0 °C in CH_3CN with 0.1 M $N(n\text{-}C_4H_9)_4ClO_4$ supporting electrolyte. Uncertainty estimated at ±0.01 V. [d] $[(OH)(tmpa)Cr(\mu\text{-}O)Cr(tmpa)(CCl_3CO_2)]^{3+}$ complex; carboxylate group is not bridging. [e] R = 1-adamantyl group. [f] Irreversible anodic wave also observed at 1.28 V.

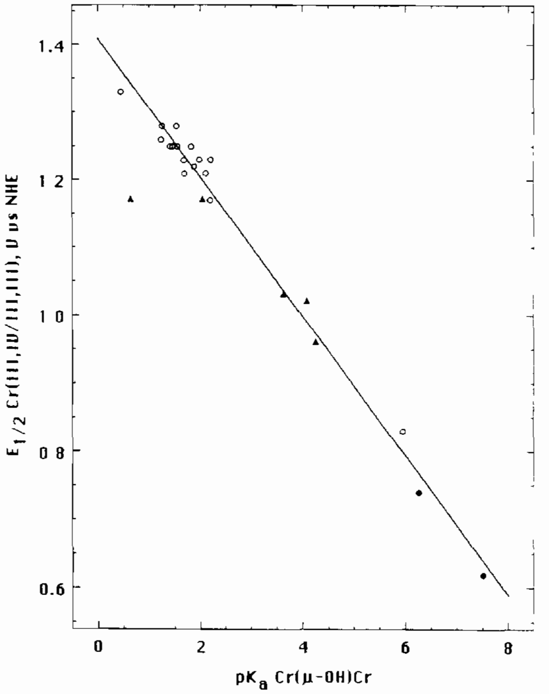

Fig. 2. Linear free energy relationship between one-electron oxidation and protonation reactions of (tmpa)Cr dimers with oxo and carboxylato ligands (○, Table 3), $[Cr(tmpa)L]_2O^{2+}$ dimers (▲, L = NCS^-, NCO^-, N_3^-, Cl^-, CN^-) and $[(tmpa)Cr(O)(L)Cr(tmpa)]^{3+}$ dimers (●, L = OH^-, F^-). Low-lying L = CN^- point excluded from the least-squares fit. All data not reported in this work from ref 21 Conditions: 25 0 °C, $I = 0$ 1 M for both reactions. Half-wave potentials and μ-OH^- ionization constants measured in acetonitrile and water, respectively

strength, as measured by $pK_a(Cr(\mu\text{-}OH)Cr)$. It should be noted that the trichloroacetate complex falls close to the correlation line defined by the bridging carboxylate species, even though its $E_{1/2}$ and pK_a values separately diverge considerably from the norm for μ-RCO_2^- donors. Assuming that HOMO destabilization originates primarily from configuration interaction with the b_1 π-donor orbitals of both bridging and non-bridging ligands, a scale of increasing π-donor effectiveness may be established according to decreasing $E_{1/2}$. The generality of this linear free energy relationship between one-electron oxidation and protonation reactions over seven orders of magnitude in μ-OH^- group acidity lends considerable support to a unified molecular orbital interpretation of physical properties for both linear and bent CrOCr dimers. Furthermore, the $E_{1/2}$-pK_a correlation offers quantitative evidence for cooperativity among bridging oxo, complementary bridging and non-bridging ligands with regard to π-donation towards the Cr(III) centers. Of particular significance is the placement of bridging carboxylate ligands at the low end of the π-donor effectiveness ranking, regardless of R group.

Spiccia *et al.* recently reviewed the magnetochemistry of oxo- and hydroxo-bridged dinuclear chromium(III) complexes, concluding that antiferromagnetic coupling constants increase with decreasing Cr···Cr distance (especially below 2.8 Å), increasing Cr–O–Cr bond angle and decreasing Cr-bridging O bond length [25]. Having successfully accounted for both spectroscopic and electrochemical characteristics of CrOCr dimers in molecular orbital terms [20, 26, 27], we are inclined to relate antiferromagnetic coupling constants to the HOMO(b_1)–LUMO(a_2) singlet–triplet energy gap, i.e. $-2J = E(a_2) - E(b_1)$. Provided that the a_2 LUMO is truly non-bonding [20] and given no significant variation in the CrOCr bond angle, it is anticipated that the singlet–triplet gap will be particularly sensitive to the configuration interaction between ligand- and metal-centered b_1 symmetry orbitals whose marked influence on the HOMO energy has already been discussed. In fact, $-2J$ generally increases with electron-withdrawing capacity of the carboxylate substituent and decreasing π-donor effectiveness of the μ-RCO_2^- ligand, as expected on the basis of our configuration interaction criterion. To be specific, a comparison of magnetic parameters within the series: R = CH_3, CH_2Cl, $CHCl_2$ and R = Ph-NMe_2 ($\sigma_p = -0.83$), Ph-H ($\sigma_p = 0$), Ph-CF_3 ($\sigma_p = +0.54$) is instructive. Finally, the failure of the $CCl_3CO_2^-$ complex to follow the magnetochemical pattern established by the μ-$CH_3CO_2^-$, μ-$CH_2ClCO_2^-$ and μ-$CHCl_2CO_2^-$ dimers (more negative J with increasing methyl chlorination) provides yet another indication that trichloroacetate is not a bridging ligand, allowing greater flexibility in the CrOCr angle; J for $[(OH)(tmpa)Cr(O)Cr(tmpa)(CCl_3CO_2)](ClO_4)_2$ falls between those of $[Cr(tmpa)(OH)]_2(ClO_4)_4 \cdot 4H_2O$ (-15.7 cm^{-1}) and $[(tmpa)Cr(O)(OH)Cr(tmpa)](ClO_4)_3 \cdot H_2O$ (-68.5 cm^{-1}) [26].

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