rigidity imposed by such etheno bridges is well-known to increase the chelating tendencies of multidentate ligands relative to their flexible, ethano-bridged analogues.[30] Complex **8** is to our knowledge the first homoleptic zinc enolate.

The thermal dehydrogenation of **7** to **8** is a novel (and unanticipated) metal enolate synthesis. In a possibly related observation, Mazdiyasni reported several years ago[31] that the synthesis of "Y(O-*i*-Pr)$_3$"[32] from yttrium metal and refluxing 2-propanol was under some conditions accompanied by the formation of Y[OC(=CH$_2$)Me]$_3$. However, it was not shown (or claimed) that the enolate was derived from the alkoxide. The driving force for the **7** to **8** conversion is unknown, but it may be the thermodynamic stability of the chelated, mononuclear structure as discussed above. The mechanisms by which alkoxides undergo thermal decomposition have not been widely studied, but a number of pathways are apparently operative, which depend on the metal and the nature of the alkoxide substituents.[7c,13b,31,33] The dehydrogenation identified here may depict an early stage in some alkoxide-decomposition processes.

Our soluble zinc(II) dialkoxides hydrolyze rapidly to afford amorphous, hydrated zinc oxide powders. However, compound **1** and acetone react to give transparent gels, which afford amorphous, hydrated zinc oxide upon drying.[15a] The cohydrolyses of zinc(II) and copper(II) or copper(I) alkoxides lead to Zn/Cu oxides that are catalytically active for carbon monoxide hydrogenation to methanol.[15b] The details of these studies will be described in future publications. In conclusion, the zinc(II) dialkoxides provided herein should be ideal precursors for a wide range of experiments aimed at ZnO fabrication.

Acknowledgment. We are grateful to Washington University and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support. Washington University's X-Ray Crystallography Facility was funded by the NSF Chemical Instrumentation Program (Grant CHE-8811456). The Washington University High-Resolution NMR Service Facility is funded in part by NIH Biomedical Research Support Shared-Instrument Grant 1 S10 RR02004 and a gift from the Monsanto Co. W.E.B. thanks Professors J. R. Bleeke (Washington University) and K. G. Caulton (Indiana University) for helpful discussions.

Supplementary Material Available: Listings of crystallographic data collection parameters, equivalent isotropic thermal parameters, bond distances, bond angles, calculated hydrogen atom parameters, and anisotropic thermal parameters (11 pages); tables of observed and calculated structure factors (28 pages). Ordering information is given on any current masthead page.

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(30) King, R. B.; Eggers, C. A. *Inorg. Chim. Acta* **1968**, *2*, 33. (b) King, R. B.; Houk, L. W.; Kapoor, P. N. *Inorg. Chem.* **1969**, *8*, 1792. (c) King, R. B. *J. Coord. Chem.* **1971**, *1*, 67.

(31) Mazdiyasni, K. S.; Lynch, C. T.; Smith, J. S. *Inorg. Chem.* **1966**, *5*, 342.

(32) Poncelet, O.; Sartain, W. J.; Hubert-Pfalzgraf, L. G.; Folting, K.; Caulton, K. G. *Inorg. Chem.* **1989**, *28*, 263.

(33) (a) Bradley, D. C.; Faktor, M. M. *J. Appl. Chem.* **1959**, *9*, 435. (b) Bradley, D. C.; Faktor, M. M. *J. Chem. Soc., Faraday Trans.* **1959**, *55*, 2117. (c) Jeffries, P. M.; Girolami, G. S. *Chem. Mater.* **1989**, *1*, 8. (d) Stecher, H. A.; Sen, A.; Reingold, A. L. *Inorg. Chem.* **1989**, *28*, 3280. (e) Duesler, E.; Hampden-Smith, M. J.; Smith, D. E.; Huffman, J. C. *Abstracts of Papers*, 197th National Meeting of the American Chemical Society, Dallas, TX; American Chemical Society: Washington, DC, 1989; INOR-29.

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Synthesis, Structure, and Physical Properties of (μ-Oxo)(μ-carboxylato)bis{(tris(2-pyridylmethyl)amine)chromium(III)} Complexes

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Three μ-oxo–μ-carboxylato-bridged complexes of the form [(tmpa)Cr(O)(RCO$_2$)Cr(tmpa)]$^{3+}$ (R = H, CH$_3$, C$_6$H$_5$; tmpa = tris(2-pyridylmethyl)amine) have been prepared and characterized through measurements of electronic and infrared spectra, ionization constants of conjugate hydroxy-bridged acids, magnetic susceptibility temperature dependences, and cyclic voltammograms. A perchlorate salt of the methyl derivative, [(tmpa)Cr(O)(CH$_3$CO$_2$)Cr(tmpa)](ClO$_4$)$_3$ (Cr$_2$Cl$_3$O$_{15}$N$_8$C$_{38}$H$_{39}$·0.7H$_2$O), crystallizes in the monoclinic system (space group $P2_1/c$ (No. 14)), with a = 10.509 (5) Å, b = 21.040 (16) Å, c = 20.724 (7) Å, β = 98.46 (4°), and V = 4532 (4) Å^3; Z = 4. The Cr–O–Cr core is characterized by nonequivalent Cr–O bond distances of 1.789 (9) and 1.853 (9) Å, a bond angle of 131.9° and trans influences toward Cr–N bonds of 0.054 and 0.034 Å, respectively. Linear correlations of free carboxylic acid pK_a values with both the pK_a's of [(tmpa)Cr(OH)(RCO$_2$)Cr(tmpa)]$^{4+}$ species and the antiferromagnetic coupling constants of [(tmpa)Cr(O)(RCO$_2$)Cr(tmpa)]$^{3+}$ dimers demonstrate that enhanced Cr–O(carboxylate) bond strengths, linked to increasing RCO$_2^-$ nucleophilicity, occur at the expense of π-bonding within the CrOCr bridging unit. Electronic spectra and one-electron oxidation waves of the μ-oxo–μ-carboxylato dimers are consistent with expectations when a linear (D_{4h}) CrOCr complex is bent to pseudo-C_{2v} symmetry with some retention of π-bonding.

Introduction

The unusual lability of a bridging hydroxy group in [(tmpa)Cr(OH)$_2$Cr(tmpa)]$^{4+}$ (tmpa = tris(2-pyridylmethyl)amine)[1] and related dihydroxo-bridged chromium(III) dimers with aromatic amine ligands led to our recent synthesis of LN$_4$CrOCrN$_4$L^{2+} linear μ-oxo complexes,[2] where L$^-$ = NCS$^-$, NCO$^-$, N$_3^-$, CN$^-$, and Cl$^-$. An early attempt to extend this series with L$^-$ = acetate showed that μ-OH$^-$ displacement proceeds readily in the presence of a carboxylate incoming group, but the product contains only one CH$_3$CO$_2^-$ ion per dinuclear Cr unit.[2] A very different synthetic route featuring carboxylate-induced aggregation of monomer units yields [L$_2$Cr$_2$(μ-OH)(μ-CH$_3$CO$_2$)$_2$]$^{3+}$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane), characterized by weak antiferromagnetic coupling between the triply-bridged Cr(III) centers (J = −15.5 cm^{-1}).[3,4] Reversible ionization of the μ-OH function accompanied by enhancement of ΔE(singlet–triplet) has recently been established for the [L$_2$M$_2$(μ-OH)(μ-CH$_3$CO$_2$)$_2$]$^{3+}$ series of

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(1) Gafford, B. G.; Holwerda, R. A. *Inorg. Chem.* **1989**, *28*, 60.

(2) Gafford, B. G.; O'Rear, C.; Zhang, J. H.; O'Connor, C. J.; Holwerda, R. A. *Inorg. Chem.* **1989**, *28*, 1720.

(3) Chaudhuri, P.; Winter, M.; Küppers, H.-J.; Wieghardt, K.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1987**, *26*, 3302.

(4) Reber, C.; Güdel, H. U.; Buijs, M.; Wieghardt, K.; Chaudhuri, P. *Inorg. Chem.* **1988**, *27*, 2115.

0020-1669/90/1329-4652$02.50/0

complexes (M = Mo, Ru).[5,6] (μ-Carboxylato)(μ-hydroxo)bis{bis(ethylenediamine)chromium(III)} salts with acetate, formate, and glycinate bridging groups were prepared by extended heating of the carboxylic acids with the *meso*-bis(ethylenediamine)chromium diol, but rapid base-assisted carboxylate bridge cleavage prevented the isolation of the corresponding μ-oxo–μ-carboxylato species in the solid state.[7] Facile interconversions between bridging acetato and oxo or hydroxo ligands are well-documented for Mn(III)[8-10] and Fe(III)[11-13] dinuclear complexes.

We report here the synthesis of dinuclear $[(\text{tmpa})\text{Cr(O)}(\text{RCO}_2)\text{Cr}(\text{tmpa})]^{3+}$ cations with R = H, CH_3, and C_6H_5, the first structurally characterized complexes with a strongly bent Cr–O–Cr group. The proposed (μ-O)(μ-RCO_2) bridging is supported by an X-ray crystallographic study of the μ-acetato dimer, and the impact of a bent Cr–O–Cr unit on the spectroscopic, acid–base, electrochemical, and magnetic properties of these compounds is described.

Experimental Section

Reagent grade chemicals and doubly or triply distilled water were used throughout. Determinations of electronic and infrared spectra, magnetic susceptibilities (6–300 K), ionization constants, and cyclic voltammograms were carried out as before.[2] The model of an isolated Heisenberg dimer containing $S = {}^3/_2$ ions with interaction Hamiltonian $\mathbf{H} = -2JS_1{\cdot}S_2$ was used throughout. The susceptibility (χ') based on the model is [14]

$$\chi' = \frac{Ng^2\mu_B{}^2}{kT}\,\frac{2e^{2J/kT} + 10e^{6J/kT} + 28e^{12J/kT}}{1 + 3e^{2J/kT} + 5e^{6J/kT} + 7e^{12J/kT}} \qquad (1)$$

$$\chi_m = \chi'(1 - \rho) + Ng^2\mu_B{}^2S(S + 1)\rho/3k(T - \Theta) + \text{TIP} \qquad (2)$$

where all of the parameters have their usual meaning. Taking into account the possibility of monomeric impurities that obey the Curie–Weiss expression, the magnetic data were fit to relationship 2 by a nonlinear least-squares procedure that weights the data so the percent difference deviation is minimized; ρ and Θ represent the impurity fraction and the Weiss constant, respectively. Fits were not improved by the introduction of a molecular field correction, and antiferromagnetic coupling constants were not changed appreciably upon treating g as a constant (1.98) rather than a free-floating variable.

The kinetics of $[(\text{tmpa})\text{Cr(O)}(\text{CH}_3\text{CO}_2)\text{Cr}(\text{tmpa})]^{3+}$ generation from the reaction of acetate ion with $[(\text{tmpa})\text{Cr(O)(OH)Cr}(\text{tmpa})]^{3+}$ (0.245 mM, perchlorate salt)[1] was studied at 336 nm in 1 cm cells thermostated to 25.0 °C. Methanolic solutions contained pseudo-first-order excesses of $\text{LiOAc}{\cdot}2\text{H}_2\text{O}$ (0.0250–0.500 M) and sufficient LiBr to maintain a constant ionic strength of 0.5 M. Preliminary studies showed that methanolic LiOAc induces partial ionization of $[\text{Cr}(\text{tmpa})\text{OH}]_2{}^{4+}$ to $[(\text{tmpa})\text{Cr(O)(OH)Cr}(\text{tmpa})]^{3+}$, making it necessary to use the latter in kinetic studies to assure that the reactant is in a single ionization state. Blank experiments proved that LiBr is unreactive toward $[(\text{tmpa})\text{Cr(O)(OH)Cr}(\text{tmpa})]^{3+}$. Rate constants ($k_{obsd}$) were derived from the linear least-squares slopes of first-order analytical plots and are reported as the mean of at least three determinations.

Synthesis of $[(\text{tmpa})\text{Cr}(\mu\text{-O})(\mu\text{-RCO}_2)\text{Cr}(\text{tmpa})](\text{ClO}_4)_3$ Complexes. The synthetic route to $[(\text{tmpa})\text{Cr}(\mu\text{-O})(\mu\text{-CH}_3\text{CO}_2)\text{Cr}(\text{tmpa})](\text{ClO}_4)_3$ is representative of the methods employed for all three μ-carboxylato complexes (R = H, CH_3, C_6H_5). $[(\text{tmpa})\text{Cr(OH)}_2\text{Cr}(\text{tmpa})](\text{ClO}_4)_4{\cdot}4\text{H}_2\text{O}$[1] (1.00 g, 0.841 mmol) was dissolved in 100 mL of hot CH_3CN and refluxed with $NaCH_3CO_2$ (2.29 g, 16.8 mmol) for 1 h. Evaporation to 50 mL followed the removal of excess sodium acetate by filtration. $LiClO_4$ (1.0 g) dissolved in 50 mL of water was then added, affording a dark green product and virtually colorless supernatant upon slow evaporation. The crude product was recrystallized once from 700 mL of H_2O by slowly adding $LiClO_4$ until precipitation commenced and then digesting the stirred solution at 5 °C for 1 h. Recrystallized material was filtered off, washed twice with cold triply distilled water, and air-dried. Yield: 0.81 g (91%). Anal. Calcd for $[(\text{tmpa})\text{Cr(O)}(\text{CH}_3\text{CO}_2)\text{Cr}(\text{tmpa})](\text{ClO}_4)_3$: Cr, 9.83; C, 43.14; H, 3.72; N, 10.59. Found: Cr, 9.72; C, 43.09; H, 3.61; N, 10.44. IR: $\nu_{as}(\text{CO}_2^-) = 1549\ \text{cm}^{-1}$; $\nu_s(\text{CO}_2^-) = 1443\ \text{cm}^{-1}$. Anal. Calcd for $[(\text{tmpa})\text{Cr(O)}(\text{HCO}_2)\text{Cr}(\text{tmpa})](\text{ClO}_4)_3$: Cr, 9.96; C, 42.56; H, 3.57; N, 10.73. Found: Cr, 9.94; C, 42.46; H, 3.54; N, 10.80. IR: $\nu_{as}(\text{CO}_2^-) = 1561\ \text{cm}^{-1}$; $\nu_s(\text{CO}_2^-) = 1369\ \text{cm}^{-1}$. Anal. Calcd for $[(\text{tmpa})\text{Cr(O)}(\text{C}_6\text{H}_5\text{CO}_2)\text{Cr}(\text{tmpa})](\text{ClO}_4)_3{\cdot}2\text{H}_2\text{O}$: Cr, 8.99; C, 44.67; H, 3.92; N, 9.69. Found: Cr, 9.01; C, 44.81; H, 3.62; N, 9.76. IR: $\nu_{as}(\text{CO}_2^-) = 1527\ \text{cm}^{-1}$; $\nu_s(\text{CO}_2^-) = 1413\ \text{cm}^{-1}$.

Table I. Crystallographic Data for (μ-Oxo)(μ-acetato)bis{(tris(2-pyridylmethyl)amine)chromium(III)} Perchlorate

formula: $Cr_2Cl_3O_{15}N_8C_{38}H_{39}{\cdot}0.7H_2O$	$\mu = 7.59\ \text{cm}^{-1}$
fw = 1070.74	$\lambda = 0.71073$ Å
space group: $P2_1/c$ (No. 14)	tot. no. of reflcns: 4724
a = 10.509 (5) Å	tot. indep reflcns: 4210
b = 21.040 (16) Å	no. of reflcns used in refin: 4210
c = 20.724 (7) Å	
β = 98.46 (4)°	no. of reflcns with $F_o{}^2 > 0$: 3349; $R_F = 0.158$
V = 4532 (4) Å^3	
$\rho_{calc} = 1.57\ \text{g cm}^{-3}$	no. of reflcns with $F_o{}^2 > 3\sigma(F_o{}^2)$: 1611; $R_F = 0.081$
Z = 4	
T = 22 °C	

X-ray Diffraction Studies of $[(\text{tmpa})\text{Cr}(\mu\text{-O})(\mu\text{-CH}_3\text{CO}_2)\text{Cr}(\text{tmpa})](\text{ClO}_4)_3$. The crystal used in the X-ray diffraction studies was grown by slow evaporation of an acetonitrile/diethyl ether solution. The thickest crystal that we could find, about 0.07 × 0.23 × 0.29 mm, was glued to a glass fiber with epoxy cement and used for all experiments. Preliminary oscillation and Weissenberg photographs showed that it was single. It was then transferred to a CAD-4 diffractometer and unit cell dimensions and an orientation matrix were calculated from the setting angles of 2θ reflections with $8° < 2\theta < 21°$. (25 reasonably strong reflections at higher 2θ were identified later, but their profiles were so broad that they could not be centered satisfactorily.) Intensities were measured to $2\theta = 40°$, the effective limit of observable data; three check reflections showed no decay. Systematic absences were removed, the 154 multiply measured reflections were merged (goodness-of-fit for merging, 1.04), and coordinates for the two chromium atoms were provided by MULTAN; the remaining atoms were found by successive structure factor-Fourier cycles. When all of the expected atoms had been located, least-squares refinement was begun, first with isotropic B's and then with anistropic U_{ij}'s for Cr, Cl, and the perchlorate O atoms. Hydrogen atoms were introduced at calculated positions (C–H = 0.95 Å), with those of the methyl group disordered between two half-populated sets 60° apart; they were assigned isotropic B's 20% larger than their attached carbon atoms. Their parameters were not refined, but they were repositioned several times during the refinements.

These first refinements led to large U's for the ClO_4^- oxygen atoms, particularly three of those attached to Cl1; this perchlorate was then modeled with one fully populated, anisotropic oxygen position and two sets of three half-populated, isotropic oxygen positions. In addition, a persistent peak in difference maps was presumed to represent a water molecule, hydrogen bonded to two perchlorate oxygen atoms O14 in symmetry-related anions; it was included in the refinement, with a population parameter (final value, 0.73 (3)). In the final cycle, no parameter shifted by as much as 0.1 esd. Crystallographic data and refinement details are summarized in Table I. Final atom coordinates and isotropic displacement parameters are given in Table II; anisotropic U_{ij}'s and assigned hydrogen parameters are included in the supplementary material. Calculations were done with the CRYM crystallographic computing system and ORTEP. Scattering factors and corrections for anomalous dispersion were taken from a standard reference.[15] The absorption correction was negligibly small ($\mu r_{max} = 0.15$; see supplementary Table S1). The function minimized in the full-matrix least squares was $\sum w(F_o{}^2 - F_c{}^2)^2$, where $w = \sigma^{-2}(F_o{}^2)$. Variances of the individual reflections were assigned on the basis of the counting statistics plus an additional term, $0.014I^2$; variances of merged reflections were obtained from standard propagation of error plus another additional term, $0.014\langle I\rangle^2$. The final

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(5) Wieghardt, K.; Bossek, U.; Neves, A.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1989**, *28*, 432.

(6) Neubold, P.; Wieghardt, K.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1989**, *28*, 459.

(7) Springborg, J.; Toftlund, H. *Acta Chem. Scand., Ser. A* **1979**, *33*, 31.

(8) Wieghardt, K.; Bossek, U.; Zsolnai, L.; Huttner, G.; Blondin, G.; Girerd, J.-J.; Babonneau, F. *J. Chem. Soc., Chem. Commun.* **1987**, 651.

(9) Wieghardt, K.; Bossek, U.; Ventur, D.; Weiss, J. *J. Chem. Soc., Chem. Commun.* **1985**, 347.

(10) Wieghardt, K.; Bossek, U.; Bonvoisin, J.; Beauvillain, P.; Girerd, J.-J.; Nuber, B.; Weiss, J.; Heinze, J. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1030.

(11) Armstrong, W. H.; Lippard, S. J. *J. Am. Chem. Soc.* **1983**, *105*, 4837.

(12) Armstrong, W. H.; Spool, A.; Papaefthymiou, G. C.; Frankel, R. B.; Lippard, S. J. *J. Am. Chem. Soc.* **1984**, *106*, 3653.

(13) Wieghardt, K.; Pohl, K.; Gebert, W. *Angew. Chem., Int. Ed. Engl.* **1983**, *95*, 739.

(14) O'Connor, C. J. *Prog. Inorg. Chem.* **1982**, *29*, 203.

(15) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, 1974; Vol. IV, pp 71, 149.

Table II. Final Parameters for (μ-Oxo)(μ-acetato)bis{(tris(2-pyridylmethyl)amine)chromium(III)} Perchlorate (x, y, z, and $U_{eq}{}^a \times 10^4$)

atom	x	y	z	U_{eq} or B, Å^2
Cr1	2733 (2)	1413 (1)	7456 (1)	612 (7)
Cr2	1904 (2)	2585 (1)	6401 (1)	693 (8)
O1	2972 (8)	2014 (4)	6831 (4)	4.8 (2)^b
O2	1065 (9)	1693 (5)	7629 (5)	6.2 (3)^b
O3	353 (9)	2312 (5)	6757 (5)	6.7 (3)^b
C37	212 (15)	2003 (8)	7264 (8)	6.6 (4)^b
C38	−1142 (16)	2012 (8)	7478 (8)	8.1 (5)^b
N1	4485 (10)	1000 (6)	7412 (6)	5.2 (3)^b
C1	4445 (14)	759 (7)	6754 (8)	6.0 (4)^b
C2	3138 (14)	477 (7)	6501 (7)	4.8 (4)^b
C3	2937 (16)	−6 (8)	6040 (8)	7.2 (4)^b
C4	1731 (18)	−171 (8)	5811 (8)	7.9 (5)^b
C5	704 (15)	100 (8)	6035 (8)	7.4 (4)^b
C6	990 (15)	551 (7)	6520 (8)	6.0 (4)^b
N2	2165 (11)	745 (5)	6750 (5)	4.6 (3)^b
C7	4710 (14)	454 (8)	7896 (8)	6.9 (4)^b
C8	3687 (13)	349 (7)	8305 (7)	4.4 (3)^b
C9	3814 (14)	−121 (8)	8788 (8)	6.3 (4)^b
C10	2800 (14)	−213 (7)	9125 (7)	5.6 (4)^b
C11	1721 (14)	141 (7)	8971 (7)	5.7 (4)^b
C12	1631 (13)	594 (7)	8498 (7)	4.9 (4)^b
N3	2635 (10)	713 (5)	8161 (5)	4.5 (3)^b
C13	5453 (13)	1501 (7)	7596 (7)	5.7 (4)^b
C14	5108 (15)	1906 (7)	8132 (7)	5.4 (4)^b
C15	5984 (15)	2281 (8)	8540 (9)	7.5 (5)^b
C16	5534 (18)	2643 (9)	9003 (9)	8.8 (5)^b
C17	4291 (17)	2671 (8)	9054 (8)	7.5 (5)^b
C18	3428 (14)	2308 (7)	8642 (8)	5.8 (4)^b
N4	3814 (10)	1929 (5)	8182 (5)	4.6 (3)^b
N5	691 (12)	3261 (6)	5867 (7)	6.5 (3)^b
C19	1465 (17)	3675 (8)	5462 (9)	7.9 (5)^b
C20	2803 (15)	3471 (8)	5505 (8)	5.7 (4)^b
C21	3627 (17)	3786 (8)	5110 (8)	7.6 (5)^b
C22	4841 (16)	3568 (8)	5161 (8)	6.9 (4)^b
C23	5310 (15)	3103 (8)	5591 (8)	6.6 (4)^b
C24	4454 (15)	2809 (7)	5959 (7)	6.1 (4)^b
N6	3231 (12)	3001 (6)	5917 (6)	5.8 (3)^b
C25	−310 (16)	2896 (9)	5454 (9)	7.8 (5)^b
C26	236 (17)	2386 (9)	5137 (9)	7.9 (5)^b
C27	−118 (17)	2122 (9)	4524 (10)	9.1 (5)^b
C28	487 (19)	1625 (9)	4317 (10)	9.5 (6)^b
C29	1526 (18)	1339 (9)	4699 (10)	8.8 (5)^b
C30	1919 (15)	1615 (8)	5320 (8)	6.8 (4)^b
N7	1299 (12)	2082 (6)	5540 (6)	6.0 (3)^b
C31	175 (17)	3640 (9)	6344 (10)	9.3 (5)^b
C32	1157 (18)	3784 (9)	6951 (9)	8.0 (5)^b
C33	1242 (19)	4300 (9)	7361 (10)	9.4 (5)^b
C34	2215 (20)	4380 (9)	7830 (9)	9.1 (5)^b
C35	3236 (17)	3964 (9)	7934 (9)	8.6 (5)^b
C36	3100 (15)	3461 (8)	7468 (8)	6.1 (4)^b
N8	2118 (12)	3331 (6)	7045 (6)	5.9 (3)^b
Ow^c	4123 (25)	559 (13)	4547 (14)	21.4 (17)^b
Cl1	8071 (5)	688 (3)	9141 (3)	859 (17)
O4	8975 (11)	460 (8)	9624 (7)	1685 (64)
O5A^d	8118 (31)	348 (17)	8589 (19)	12.8 (11)^b
O6A^d	8743 (24)	1275 (13)	8997 (13)	10.0 (7)^b
O7A^d	6800 (21)	718 (13)	9226 (10)	6.8 (6)^b
O5B^d	7285 (25)	1147 (12)	9323 (11)	7.9 (7)^b
O6B^d	7261 (26)	112 (15)	9077 (14)	11.3 (8)^b
O7B^d	8266 (24)	769 (15)	8485 (15)	9.0 (8)^b
Cl2	7312 (6)	1295 (3)	2614 (4)	1073 (21)
O8	8060 (18)	779 (10)	2502 (9)	2247 (85)
O9	7951 (15)	1586 (7)	3133 (8)	1729 (65)
O10	6180 (14)	1017 (8)	2728 (9)	2078 (76)
O11	7083 (20)	1675 (8)	2094 (10)	2725 (100)
Cl3	7069 (8)	1169 (4)	5706 (4)	1306 (25)
O12	7940 (19)	1354 (9)	5383 (10)	2680 (88)
O13	6559 (19)	1593 (9)	5995 (11)	2481 (97)
O14	6080 (26)	901 (16)	5374 (11)	3346 (143)
O15	7454 (22)	720 (13)	6105 (16)	3339 (142)

^{a} $U_{eq} = {}^1/_3\sum_i\sum_j[U_{ij}(a^*_i a^*_j)(\vec{a}_i\cdot\vec{a}_j)]$. ^{b} Isotropic displacement parameter, B. ^{c} Population, 0.73 (3). ^{d} Population, 0.5 (assumed).

value of the goodness of fit, $[\sum w(F_o{}^2 - F_c{}^2)^2/(n - p)]^{1/2}$, was 1.55 for n = 4210 total reflections and p = 352 parameters.

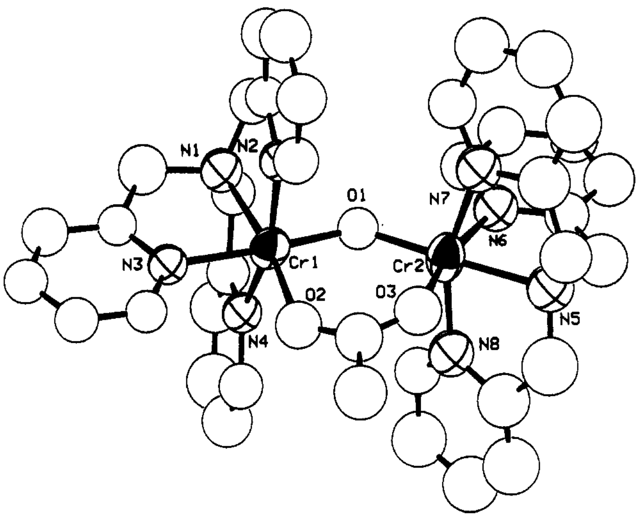

Figure 1. ORTEP drawing of the $[(tmpa)Cr(O)(CH_3CO_2)Cr(tmpa)]^{3+}$ cation with 50% thermal ellipsoids. Hydrogen atoms have been omitted.

Table III. Principal Distances (Å) and Angles (deg) in (μ-Oxo)(μ-acetato)bis{(tris(2-pyridylmethyl)amine)chromium(III)} Perchlorate

	Distances		
Cr1–O1	1.853 (9)	Cr2–N5	2.112 (13)
Cr2–O1	1.789 (9)	Cr2–N6	2.032 (12)
Cr1–O2	1.931 (10)	Cr2–N7	2.093 (13)
Cr2–O3	1.970 (10)	Cr2–N8	2.050 (13)
Cr1–N1	2.050 (12)	O2–C37	1.265 (19)
Cr1–N2	2.054 (11)	O3–C37	1.264 (19)
Cr1–N3	2.087 (11)	C37–C38	1.55 (2)
Cr1–N4	2.056 (11)		
	Angles		
O1–Cr1–O2	98.2 (4)	O1–Cr2–N6	96.3 (5)
O1–Cr1–N1	92.4 (4)	O1–Cr2–N7	100.0 (4)
O1–Cr1–N2	91.3 (4)	O1–Cr2–N8	100.9 (5)
O1–Cr1–N3	174.9 (4)	O3–Cr2–N5	85.6 (5)
O1–Cr1–N4	92.0 (4)	O3–Cr2–N6	167.3 (5)
O2–Cr1–N1	169.3 (5)	O3–Cr2–N7	90.4 (5)
O2–Cr1–N2	99.5 (4)	O3–Cr2–N8	89.8 (5)
O2–Cr1–N3	86.9 (4)	N5–Cr2–N6	81.7 (5)
O2–Cr1–N4	97.0 (4)	N5–Cr2–N7	79.0 (5)
N1–Cr1–N2	81.2 (4)	N5–Cr2–N8	80.0 (5)
N1–Cr1–N3	82.5 (4)	N6–Cr2–N7	86.6 (5)
N1–Cr1–N4	81.5 (4)	N6–Cr2–N8	88.5 (5)
N2–Cr1–N3	88.7 (4)	N7–Cr2–N8	158.9 (5)
N2–Cr1–N4	162.5 (4)	O3–C37–O2	127.1 (15)
N3–Cr1–N4	86.6 (4)	C38–C37–O2	115.8 (14)
O1–Cr2–O3	96.4 (4)	C38–C37–O3	117.1 (14)
O1–Cr2–N5	177.8 (5)		

Results

The preparations of $[(tmpa)Cr(\mu\text{-}O)(\mu\text{-}RCO_2)Cr(tmpa)]^{3+}$ dimers (R = H, CH_3, C_6H_5) proceed with greater than 90% yields according to eq 3 in refluxing acetonitrile. These syntheses may

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

also be accomplished in methanol, but formation of $[(tmpa)Cr(O)(RCO_2)Cr(tmpa)]^{3+}$ is favored only slightly over decomposition to $[Cr(tmpa)(OH)]_2{}^{4+}$ in aqueous solution.

Structure of the $[(tmpa)Cr(\mu\text{-}O)(\mu\text{-}CH_3CO_2)Cr(tmpa)]^{3+}$ Cation. The results of the crystal-structure study are less precise than usual, because of the relatively small number of data with $F_o{}^2 > 3\sigma(F_o{}^2)$ (the crystal was small and its reflections broad), the large displacement factors of all the atoms, and the disorder associated with the water molecules and the perchlorate ions. Nevertheless, the main structural features of the cation are quite clear (Figure 1). Principal bond lengths and angles are summarized in Table III. The two chromium atoms are linked by an oxo and an acetato bridge; the tmpa ligands complete distorted

Table IV. Physical Properties of [(tmpa)Cr(μ-O or μ-OH)(μ-RCO$_2$)Cr(tmpa)]$^{3+/4+}$ Complexes

bridging groups	λ_{max},[a] nm (ϵ, M^{-1} cm^{-1})	$E_{1/2}$,[b] V	pK_a[c]
O^{2-}, CH$_3$COO$^-$	562 (200) 419 (1780) 388, sh (2070) 372 (2890) 336 (4090) 256 (20 600)	1.17	
OH$^-$, CH$_3$COO$^-$	510 (300) 386 (224) 264 (18 000)		2.20
O^{2-}, HCOO$^-$	563 (217) 419 (2050) 388, sh (2240) 372 (3600) 336 (5460) 256 (21 900)	1.21	
OH$^-$, HCOO$^-$	508 (310) 386 (230) 264 (17 000)		1.69
O^{2-}, C$_6$H$_5$COO$^-$	566 (225) 419 (2330) 388, sh (2540) 371 (3450) 337 (5440) 251 (35 200)	1.22	
OH$^-$, C$_6$H$_5$COO$^-$	512 (335) 382 (266) 263 (29 000)		1.88

[a] Electronic spectra of oxo- and hydroxo-bridged complexes measured at ambient temperature in CH$_3$CN and H$_2$O, respectively. Extinction coefficients are expressed per mole of dimer. [b] One-electron oxidation half-wave potential (vs SHE) calculated as (E_{pa} + E_{pc})/2 (Pt working electrode) at a sweep rate of 50 mV/s (25.0 °C, 0.1 M tetrabutylammonium perchlorate supporting electrolyte in CH$_3$CN solution). Uncertainty estimated at ±0.01 V. [c] K_a (ionization constant of bridging hydroxo group) derived from spectrophotometric titrations on buffered (5 mM) aqueous solutions (Figure 2) (25.0 °C, I = 0.1 M (NaNO$_3$)). Uncertainty estimated at ±0.02 pK_a unit.

octahedral coordination around the Cr's. As expected on steric grounds,[16] the tertiary N atom of one tmpa group, N5, is trans to the bridging oxo group while that of the other tmpa ligand, N1, is trans to a carboxylate oxygen, O2.

The Cr–O bonds to the oxo bridge are appreciably shorter than those to the acetate; moreover, they are distinctly nonequivalent (1.789 (9) and 1.853 (9) Å). In contrast, the singly bridged ion [(SCN)(tmpa)Cr]$_2$O^{2+} is centrosymmetric, with equal Cr–O distances of 1.801 (4) Å;[17] the centrosymmetric, doubly bridged species [(tmpa)Cr(OH)$_2$(tmpa)]$^{4+}$ shows Cr–O distances, 1.937 (8) and 1.959 (8) Å, that are nearly equal.[1] The Cr–O(acetato) bonds are also somewhat unequal, at 1.931 (10) and 1.970 (10) Å, and the Cr–N distances cover a relatively large range, from 2.032 (12) to 2.093 (13) Å. Much of the variation in the Cr–N distances can be attributed to the trans influence of the bridging oxo group, and the lengths of the Cr–O(acetato) bonds are inversely related to the lengths of the corresponding Cr–O(oxo) bonds.

Electronic Spectra, Magnetic Susceptibilities, Ionization Constant Determinations, and Electrochemical Measurements. Electronic spectra of [(tmpa)Cr(O)(RCO$_2$)Cr(tmpa)]$^{3+}$ dimers with R = H, CH$_3$ and C$_6$H$_5$ are strikingly similar in acetonitrile solution (Table IV). The characteristic features include intense, sharp bands at 23 900, 26 900, and 29 700 cm^{-1} plus a d–d transition ($^4T_2 \leftarrow {}^4A_2$) near 17700 cm^{-1}. On acidification, these green complexes reversibly form red [(tmpa)Cr(μ-OH)(μ-RCO$_2$)Cr(tmpa)]$^{4+}$ conjugate acids. Spectrophotometric titrations in the pH 0–5 range (Figure 2) afforded ionization constants and d–d band positions of the protonation products (Table IV). Ionization constants of these [(tmpa)$_2$Cr$_2$(μ-RCO$_2$)(μ-OH)]$^{4+}$ dimers are larger than those of analogous, unstable bis(ethylenediamine) complexes (p$K_a \approx$ 12)[7] by 10 orders of magnitude. Magnetic parameters for the μ-oxo–μ-carboxylato complexes derived from

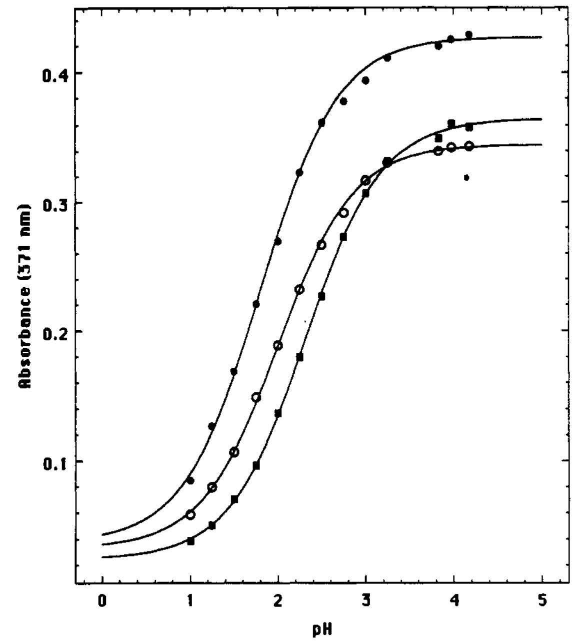

Figure 2. Spectrophotometric titrations of [(tmpa)Cr(O)(RCO$_2$)Cr(tmpa)]$^{3+}$ complexes with R = H (●, 0.266 mM), CH$_3$ (■, 0.246 mM), and C$_6$H$_5$ (○, 0.221 mM) at 25.0 °C, I = 0.1 M (NaNO$_3$), and 1 cm path length.

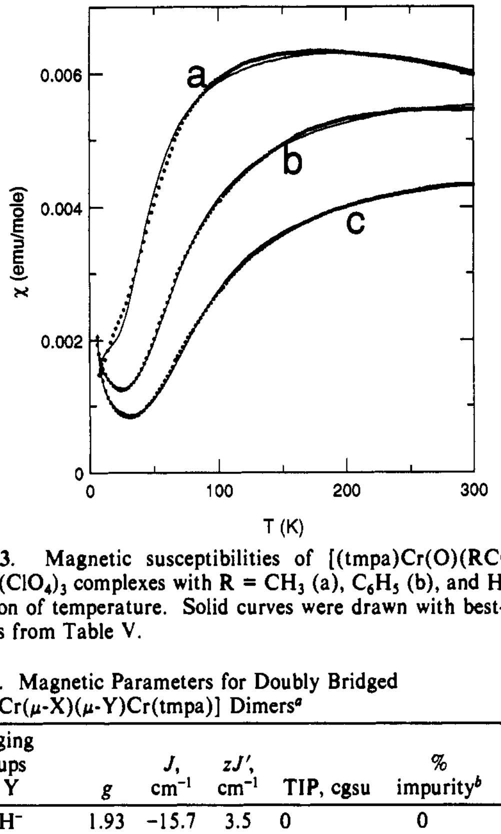

Figure 3. Magnetic susceptibilities of [(tmpa)Cr(O)(RCO$_2$)Cr(tmpa)](ClO$_4$)$_3$ complexes with R = CH$_3$ (a), C$_6$H$_5$ (b), and H (c) as a function of temperature. Solid curves were drawn with best-fit parameters from Table V.

Table V. Magnetic Parameters for Doubly Bridged [(tmpa)Cr(μ-X)(μ-Y)Cr(tmpa)] Dimers[a]

bridging groups X, Y	g	J, cm^{-1}	zJ', cm^{-1}	TIP, cgsu	% impurity[b]	θ, deg
OH$^-$, OH$^-$	1.93	−15.7	3.5	0	0	0
O^{2-}, OH$^-$	2.16	−68.5	7.2	3.8 × 10^{-4}	0.15	−0.936
O^{2-}, HCO$_2^-$	2.16	−93.0	0	6.6 × 10^{-4}	0.25	2.134
O^{2-}, CH$_3$CO$_2^-$	2.00	−50.3	0	6.5 × 10^{-5}	2.54[c]	
O^{2-}, C$_6$H$_5$CO$_2^-$	2.11	−75.4	0	1.1 × 10^{-3}	0.21	1.055

[a] Entries for OH$^-$, OH$^-$ and O^{2-}, OH$^-$ bridging groups from ref 2. Uncertainty in J is estimated at ±3%. [b] Impurity assumed to be monomeric unless otherwise stated. [c] Best fit of magnetic susceptibility temperature dependence achieved by presuming the presence of a dimeric impurity with J = −4.2 cm^{-1}.

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(16) Hodgson, D. J.; Zietlow, M. H.; Pedersen, E.; Toftlund, H. *Inorg. Chim. Acta* **1988**, *149*, 111.

(17) Gafford, B. G.; Holwerda, R. A.; Schugar, H. J.; Potenza, J. A. *Inorg. Chem.* **1988**, *27*, 1127.

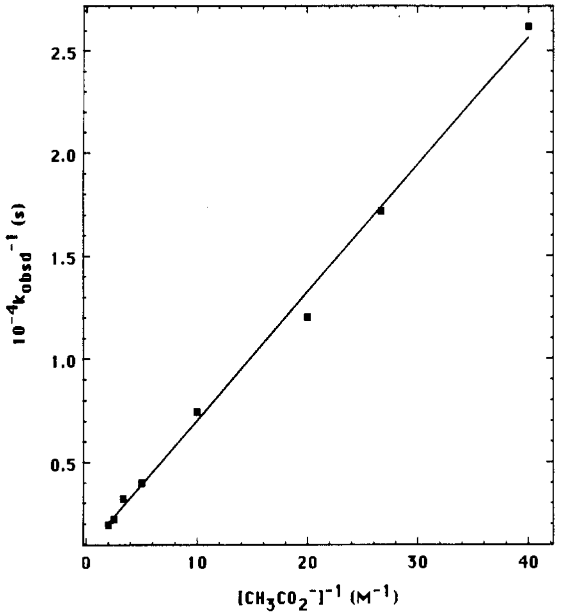

Figure 4. Correlation of k_{obsd}^{-1} with $[CH_3CO_2^-]^{-1}$ for the anation reaction of acetate ion with $[(tmpa)Cr(O)(OH)Cr(tmpa)]^{3+}$ in methanol solutions (25.0 °C, $I = 0.5$ M (LiOAc/LiBr)).

fits of magnetic susceptibility temperature dependences (Figure 3) to the Heisenberg exchange model for $S = {}^3/_2$ ions are compared in Table V with previous findings on $[Cr(tmpa)(OH)]_2^{4+}$ and $[(tmpa)Cr(O)(OH)Cr(tmpa)]^{3+}$. Cyclic voltammetry of $[(tmpa)Cr(O)(RCO_2)Cr(tmpa)]^{3+}$ species at a Pt working electrode in acetonitrile solution revealed quasi-reversible, one-electron oxidation waves in the 1.17–1.22 V (vs SHE) interval (Table IV), characterized by peak-to-peak separations of 70–75 mV at a sweep rate of 50 mV/s and i_a/i_c peak current ratios of 1.0. These large $E_{1/2}$ values contrast strongly with that of –0.09 V vs SHE reported for a $(\mu\text{-}O)(\mu\text{-}CH_3CO_2)_2$-dimolybdenum(III) complex, which undergoes facile aerobic oxidation to the corresponding Mo(III,IV) mixed-valence dimer.[5]

Kinetics of $[(tmpa)_2Cr_2(\mu\text{-}O)(\mu\text{-}CH_3CO_2)]^{3+}$ Formation. An exploratory kinetic study of the reaction between acetate ion and $[(tmpa)Cr(O)(OH)Cr(tmpa)]^{3+}$ was carried out at 25.0 °C in methanol ($I = 0.5$ M, LiOAc/LiBr). In the presence of excess OAc^-, quantitative conversions to $[(tmpa)Cr(O)(OAc)Cr(tmpa)]^{3+}$ were observed and first-order plots were found to be linear over greater than 3 half-lives of the anation reaction. A double inverse plot of k_{obsd}^{-1} vs $[OAc^-]^{-1}$ is linear (Figure 4), suggesting that an intermediate complex or activated intermediate mechanism may pertain.[18] The saturation rate constant (intercept^{-1}) is $(1.3 \pm 0.5) \times 10^{-3}$ s^{-1}, and intercept/slope = 1.24 ± 0.04 M^{-1}.

Discussion

Although crystallographic data are presented for only the acetato complex, there is little doubt that the formato and benzoato dimers also exhibit μ-oxo–μ-carboxylato bridging. Indeed, the separation between antisymmetric and symmetric carboxylato stretching frequencies ($\Delta\nu$) provides a sensitive measure of ligation type, decreasing in the following order: monodentate bound carboxylate > free carboxylate > bidentate or bridged carboxylate.[7] The $[(tmpa)Cr(O)(RCO_2)Cr(tmpa)](ClO_4)_3$ complexes exhibit $\Delta\nu$ values (192 cm^{-1} for R = H vs 235 cm^{-1} ($NaHCO_2$); 106 cm^{-1} for R = CH_3 vs 153 cm^{-1} ($NaCH_3CO_2$); 114 cm^{-1} for R = C_6H_5 vs 138 cm^{-1} ($NaC_6H_5CO_2$)) comparable to those reported previously for $[(en)_2Cr(OH)(RCO_2)Cr(en)_2]^{4+}$ (R = H, CH_3) and a variety of other carboxylate-bridged compounds.[6,7]

In previous studies of $[L(tmpa)Cr]_2O^{2+}$ complexes, pK_a values of the corresponding hydroxo-bridged dimers were utilized as a measure of π-bonding strength within the linear CrOCr unit.[2] Thus, a CrOCr dimer with strong Cr(dπ)–O(pπ)–Cr(dπ) bonding should resist protonation, giving rise to a comparatively low pK_a value provided that the inductive electronic influences of other bridging and nonbridging ligands are small. On this basis, the acidities of $[(tmpa)Cr(OH)(RCO_2)Cr(tmpa)]^{4+}$ dimers are surprisingly large, rivaling that of $[(NCS)(tmpa)Cr]_2OH^{3+}$ (pK_a = 2.05, 25 °C, $I = 0.1$ M).[2] In contrast, the first ionization constant of $[Cr(tmpa)(OH)]_2^{4+}$ (pK_{a1} = 7.50)[1] is smaller by more than 5 orders of magnitude. This observation, coupled with extensive similarities[2] between the electronic spectra, magnetic susceptibilities, and electrochemistries of the $[L(tmpa)Cr]_2O^{2+}$ and $[(tmpa)Cr(O)(RCO_2)Cr(tmpa)]^{3+}$ families, indicates that substantial π-bonding persists in the latter complexes despite a ca. 50° decrease in the CrOCr bond angle from 180°.

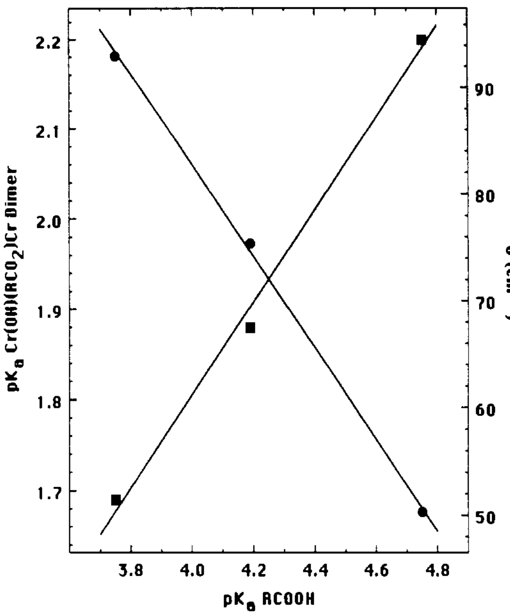

Figure 5. Correlations of $[(tmpa)Cr(OH)(RCO_2)Cr(tmpa)]^{4+}$ pK$_a$ (25 °C) values (■, left-hand axis) and $[(tmpa)Cr(O)(RCO_2)Cr(tmpa)](ClO_4)_3$ -J parameters (●, right-hand axis) with free carboxylic acid pK_a (25 °C) values (from ref 19).

Figure 5 presents linear correlations of free carboxylic acid pK_a values with both the pK's of $[(tmpa)Cr(OH)(RCO_2)Cr(tmpa)]^{4+}$ species and antiferromagnetic coupling constants of $[(tmpa)Cr(O)(RCO_2)Cr(tmpa)]^{3+}$ dimers. The pK_a (μ-OH$^-$) linear free energy relationship is characterized by a least-squares slope and intercept of 0.51 and –0.25 (correlation coefficient = 0.997), respectively, indicating moderately effective transmission of RCO_2^- group basicity to the μ-O^{2-} function in $[(tmpa)Cr(O)(RCO_2)Cr(tmpa)]^{3+}$ complexes. Enhanced Cr–O(carboxylate) bond strengths linked to increasing RCO_2^- nucleophilicity evidently occur at the expense of π-bonding within the CrOCr bridging unit. The related decreasing trend in -J with increasing pK_a (RCOOH) (slope = –43 cm^{-1}, intercept = 254 cm^{-1}; correlation coefficient = 0.999) supports this hypothesis, assuming that antiferromagnetic exchange is mediated primarily by the bridging oxo function. The extraordinarily good correlation of pK_a with -J based on only three points should be interpreted cautiously pending the completion of a more thorough test with additional carboxylate bridging groups.[20]

The sensitivity of J to the basicity of the bridging carboxylate group is strikingly high, considering the similarity of antiferromagnetic coupling constants in dihydroxo- and dialkoxo-bridged chromium(III) dimers.[21] When the magnetic behaviors of μ-oxo-μ-carboxylato complexes are compared with that of $[(tmpa)Cr(O)(OH)Cr(tmpa)]^{3+}$ (Table V), however, it is apparent

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(18) Gafford, B. G.; Holwerda, R. A. *Inorg. Chem.* **1990**, *29*, 233.

(19) *CRC Handbook of Chemistry and Physics*, 60th ed.; CRC Press: Boca Raton, FL, 1980.

(20) Tekut, T.; Holwerda, R. A. Investigation in progress.

(21) Hodgson, D. In *Magneto-Structural Correlations in Exchange Coupled Systems*; Willett, R. D., Ed.; Reidel: Dordrecht, The Netherlands, 1985; p 497.

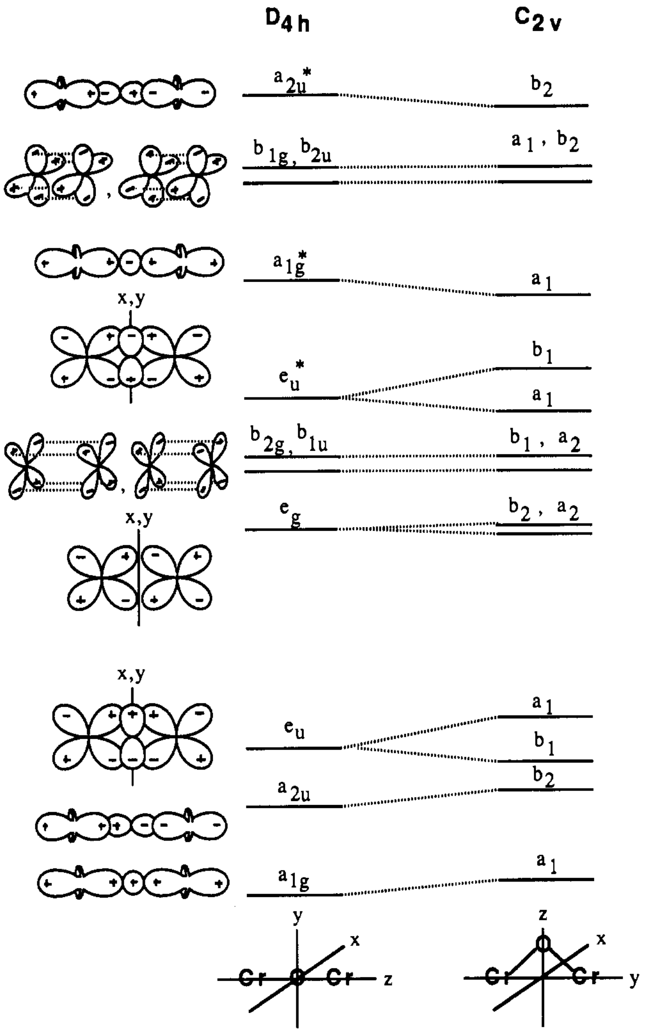

Figure 6. Qualitative π molecular orbital energy correlation scheme for the bending of a linear (D_{4h}) CrOCr complex to effective C_{2v} symmetry.

that there is very little difference between the *J* values associated with the O^{2-}, $C_6H_5CO_2^-$ and O^{2-}, OH^- bridging combinations in spite of the considerable basicity difference between the free benzoate and hydroxide ligands. According to the Glerup–Hodgson–Pedersen model,[21] the singlet–triplet gap (−2J) in hydroxo- and oxo-bridged Cr(III) dimers should increase with decreasing M–O–M (ϕ) and dihedral (θ, bridging OH^-) angles. Accordingly, it appears likely that the Cr–O–Cr angles in [(tmpa)Cr(O)(RCO_2)Cr(tmpa)]$^{3+}$ complexes decrease in the following order: R = H > C_6H_5 > CH_3 (131.9°). The $-J$ vs pK_a intercept is in close proximity to the antiferromagnetic coupling constants characteristic of [L(tmpa)Cr]$_2$O^{2+} complexes ($-J$ = 255 (NCS^-) and 290 (CN^-) cm^{-1}; ϕ = 180°)[2], consistent with expectations when the competition between carboxylate and oxide oxygen 2p orbitals for overlap with Cr dπ symmetry orbitals is eliminated.

A qualitative, one-electron molecular orbital scheme (Figure 6) illustrates the expected correlation of energy levels when a linear (D_{4h}) CrOCr complex[2] is bent with some retention of π-bonding, as in the present series of [(tmpa)Cr(O)(RCO_2)Cr(tmpa)]$^{3+}$ ions. Pseudo-C_{2v} symmetry is presumed, and the possibility of carboxylate oxygen pπ–chromium dπ orbital overlap is not taken into account explicitly. It should be noted, however, that a b_1 π-symmetry orbital based on the carboxylate oxygen atoms ($p_x(1) + p_x(2)$) in the C_{2v} coordinate system) will provide a pathway for carboxylate-to-chromium π-donation by interacting with the two Cr-centered b_1 MO's. The properties of [L(tmpa)CrOCr(tmpa)L]$^{2+}$ dimers are consistent with the π electronic configuration $(e_u)^4(e_g)^4(b_{2g})^2$. In similar fashion, the $(b_1)^2(a_1)^2(b_2)^2(a_2)^2(b_1)^2$ ground-state configuration may be reconciled with the electronic spectra and electrochemical behaviors of the [(tmpa)Cr(O)(RCO_2)Cr(tmpa)]$^{3+}$ family. It is anticipated that decreasing the Cr–O–Cr bond angle will destabilize Cr(dπ)–O(pπ) overlap in the plane defined by the CrOCr unit (*yz*) to a larger extent than in the perpendicular direction (*xy*), accounting for the ordering of a_1 and b_1 levels originating from the degenerate e_u and e_u^* sets of bonding and antibonding orbitals, respectively. The energies of approximately nonbonding e_g, b_{2g}, and b_{1u} (D_{4h}) levels should be affected little by such bending.

The intense 28 400-cm^{-1} band exhibited by all [L(tmpa)Cr]$_2$O^{2+} dimers has been assigned as a MLCT transition $(e_g–e_u^*)^2$. Similarly, the strong 26 900- and 29 700-cm^{-1} features of the [(tmpa)Cr(O)(RCO_2)Cr(tmpa)]$^{3+}$ complexes, located 1400 cm^{-1} lower and higher in energy than the reference e_g–e_u^* band, most logically correspond to symmetry-allowed b_2–a_1 and a_2–b_1 excitations, respectively. Thus, the appearance of two near-ultraviolet features is attributed primarily to the symmetry-required splitting of the π-antibonding level on lowering from point group D_{4h} to C_{2v}. The weaker 24 000 cm^{-1} b_{2g}–e_u^* feature of the [L(tmpa)Cr]$_2$O^{2+} species[2] is mimicked by the 23 900 cm^{-1} transition (b_1–a_1) of all three oxo, carboxylato-bridged complexes.

The reversible, one-electron oxidation waves of [(tmpa)Cr(O)(RCO_2)Cr(tmpa)]$^{3+}$ dimers with half-wave potentials in the 1.17–1.22 V interval (vs SHE) closely resemble the $E_{1/2}$ = 0.96–1.17 V oxidations reported previously[2] for [L(tmpa)Cr]$_2$O^{2+} dimers with L^- = NCS^-, NCO^-, N_3^-, CN^-, and Cl^-. This reversibility suggests the loss of a nonbonding electron, most likely from the b_1 (HOMO) level derived from b_{2g} (D_{4h}). The insensitivity of $E_{1/2}$ to pK_a (RCOOH) is a further indication that the ionized electron does not contribute significantly to CrOCr π-bonding. This conclusion is supported by the strong dependence of $E_{1/2}$ on pK_a (RCOOH) for oxidations of [L_2Ru_2(μ-O)(μ-RCO_2)$_2$]$^{2+}$ complexes (L = 1,4,7-trimethyl-1,4,7-triazacyclononane), which are thought to lose a π-antibonding electron when reaching the Ru(III,IV) oxidation state.[6]

Exploratory kinetic measurements on the anation of [(tmpa)Cr(O)(OH)Cr(tmpa)]$^{3+}$ by acetate ion indicate that k_{obsd} saturates at high [OAc^-], although the saturation limit could not be closely approached within the experimentally accessible concentration range. For this reason, the reported limiting rate constant of 1.3×10^{-3} s^{-1} carries a necessarily high uncertainty. Nevertheless, the proximity of this rate constant to literature values for the cleavage of a single hydroxo bridge in related $N_4Cr(OH)_2CrN_2^{4+}$ diols (k(25 °C) = (0.12–6.9) × 10^{-3} s^{-1}; N_4 = four NH_3 or two en)[22] makes feasible a mechanism (eq 4) featuring

$$CH_3OH + [(tmpa)Cr(\mu\text{-}O)(\mu\text{-}OH)Cr(tmpa)]^{3+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [(OH)(tmpa)CrOCr(tmpa)(CH_3OH)]^{3+}$$

$$[(OH)(tmpa)CrOCr(tmpa)(CH_3OH)]^{3+} + OAc^- \xrightarrow{k_2} [(tmpa)Cr(\mu\text{-}O)(\mu\text{-}OAc)Cr(tmpa)]^{3+} + OH^- + CH_3OH \quad (4)$$

a singly oxo-bridged intermediate. On this basis, $k_1 = 1.3 \times 10^{-3}$ s^{-1} and k_2/k_{-1} = 1.24 M^{-1} provided that the product of the k_1 step may be treated as a steady-state intermediate. Our hypothesis that the limiting rate should be independent of the incoming carboxylate anion is being tested in continuing kinetic studies.[20]

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Supplementary Material Available: Tables SI–SIV, listing a structure determination summary for [(tmpa)Cr(μ-O)(μ-CH_3CO_2)Cr(tmpa)](ClO_4)$_3$·0.7H_2O, assigned hydrogen parameters, anisotropic displacement parameters, and complete bond lengths and angles (9 pages); Table SV, listing observed and calculated structure factors (17 pages). Ordering information is given on any current masthead page.

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(22) Christensson, F.; Springborg, J. *Acta Chem. Scand., Ser. A* **1982**, *36*, 21.