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Further Studies of Cr–Cr Bond Lengths in Quadruply Bonded Dinuclear Compounds

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X-ray crystallographic studies have been carried out on three compounds containing chromium–chromium quadruple bonds: $Cr_2(O_2CCH_3)_4(HO_2CCH_3)_2$, I, $Cr_2(O_2CCH_3)_4(C_5H_{11}N)_2$, II, and $[NH_4]_4[Cr_2(CO_3)_4(H_2O)_2](H_2O)_{1-2}$, III. The results, together with those on nine compounds in the literature, are sufficient to indicate a crude general relationship between the donor ability of the bridging ligands and the length of the quadruple Cr–Cr bond. This trend within dichromium(II) complexes bridged by O–C–O linkages is in keeping with the observation that the shortest quadruple Cr–Cr bonds are obtained with bridging ligands which are very good donors. Crystal data for I: $P2_1/n$, $a = 15.123$ (2) Å, $b = 7.775$ (1) Å, $c = 8.302$ (1) Å, $\beta = 102.80$ (1)°, $V = 952.0$ (4) Å^3, $Z = 2$. Crystal data for II: $C2/m$, $a = 15.989$ (2) Å, $b = 10.331$ (2) Å, $c = 8.035$ (1) Å, $\beta = 116.05$ (1)°; $V = 1192.4(6)$ Å^3, $Z = 2$. Crystal data for III: $P2_1/c$, $a = 6.949$ (2) Å, $b = 16.112$ (4) Å, $c = 7.737$ (2) Å, $\beta = 108.14$ (2)°, $V = 823.2$ (7) Å^3, $Z = 2$.

Introduction

Dichromium(II) compounds are unique among metal–metal quadruply bonded systems in the range of metal–metal distances they display and in the tendency of the metal atoms in neutral molecules to bind axial ligands, particularly when the ligands on the equatorial sites of the chromium are relatively weak donors. In the dirhenium(III) system, the neutral molecule $Re_2(O_2CPh)_2I_4$ shows no tendency to bind axial ligands.[1] The addition of two pyridine molecules to $Mo_2(O_2CCF_3)_4$ does occur (Mo–N = 2.548 (8) Å) but this causes an increase in the Mo–Mo distance of only 0.039 Å from 2.090[2] to 2.129 (2) Å.[3] Indeed, the extrema of known molybdenum–molybdenum quadruple bond distances cover a range of only 0.12 Å, from a high value of 2.183 (2) Å in $Mo_2(C_3H_5)_4$[4] to a low one of 2.064 (1) Å in $Mo_2(C_8H_9O_2)$.[5] In contrast to the molybdenum case, the span of chromium–chromium bond lengths is remarkable. Here, the known range is 0.71 Å, from a high of 2.541 (1) Å in $Cr_2(O_2CCF_3)_4(OEt_2)_2$[6] to a low of 1.830 (4) Å in $Li_6Cr_2(o\text{-}C_6H_4O)_4Br_2\cdot 6Et_2O$.[7] This flexibility of the Cr–Cr bond offers a valuable opportunity to study the factors which influence metal–metal multiple bonding, and we have, therefore, extended our investigations of tetra-μ-carboxylato-dichromium(II) complexes.

Our study of these compounds was initiated in response to the suggestion,[8] based on erroneous self-consistent field MO calculations, that $Cr_2(O_2CCH_3)_4(H_2O)_2$, despite its diamagnetism[9] and a measured Cr–Cr distance of only 2.362 (1) Å,[10] has no metal–metal bonding interaction whatsoever. Subsequent, more complete calculations have verified the chromium–chromium quadruple bond in the compound,[11,12] and it has been shown experimentally that removal of the axial water molecules causes a contraction of the Cr–Cr bond to 2.288 (2) Å.[13] We have shown in previous work that variations in Cr–Cr distances within the tetra-μ-carboxylato framework cannot be accounted for entirely by assuming a simple linear, independent relationship of d(Cr–Cr) with the inductive effects of the R groups in O_2Cr^- and with the distances to the axial ligand atoms, although a rough correlation with the latter certainly exists.[6] Since structures of several $Cr_2(O_2CH)_4$ complexes were already in hand,[6,14] the present work was carried out to provide information on $Cr_2(O_2CCH_3)_4$ derivatives so that comparisons between the formates and acetates could be made. We have also obtained the first bond distance information of high precision for a carbonato, $[Cr_2(O_2CO)_4L_2]^{4-}$, complex.

Experimental Section

Preparation. Reactions were conducted under an argon atmosphere. Crystals were examined under a layer of heavy, degassed mineral oil and mounted in glass capillaries with epoxy cement.

Anhydrous chromous acetate was prepared by a standard method.[15]

$Cr_2(O_2CCH_3)_4(HO_2CCH_3)_2$, I. To 1.0 g of $Cr_2(O_2CCH_3)_4$ was added 25 mL of glacial acetic acid. The mixture was stirred for 1 h and then filtered into a clean Schlenk tube. The stoppered tube was suspended in a Dewar vessel above ice. The product was obtained as well-formed red needles and blocks.

$Cr_2(O_2CCH_3)_4(C_5H_{11}N)_2$, II. To 1.0 g of $Cr_2(O_2CCH_3)_4$ was added 20 mL of neat piperidine previously dried over KOH. This mixture was stirred for 2 h, giving a deep red-purple solution. The solution was filtered into a flask and cooled slowly. The product formed as deeply colored leaflets and blocks. The majority of these were of poor quality, but a few of the leaflets possessed adequate thickness for X-ray diffraction studies. Oddly enough, attempts to crystallize the pyridine analogue of this compound failed because $Cr_2(O_2CCH_3)_4$ proved to be essentially insoluble in pyridine.

$[NH_4]_4[Cr_2(CO_3)_4(H_2O)_2](H_2O)$, III. Crystals were grown in a silica gel medium according to techniques described by Henisch.[16] An aqueous solution of $Na_2SiO_3\cdot 9H_2O$ was neutralized with HCl and allowed to gel in a 2-cm diameter U-tube. An argon atmosphere was provided. A saturated $(NH_4)_2CO_3$ solution was floated on the surface of the gel in one leg of the U-tube, while the second leg was filled with a solution prepared by treating a saturated aqueous solution of $CrCl_3\cdot 6H_2O$ with amalgamated zinc. Diffusion was initially rapid and produced a thick layer of precipitate in the center of the U-tube within 1 day. Single crystals appeared after 3 days and attained dimensions of up to 2 mm after 2 weeks. Although the compound forms as a bright yellow powder with conventional synthetic techniques, the single crystals were pale orange-brown.

X-ray Data Collection. Data were collected at 21 ± 2° on a Syntex $P\bar{1}$ automated diffractometer using Mo Kα radiation with a graphite crystal monochromator in the incident beam. The automatic centering and indexing procedures used have been described previously.[17] All data were collected using the θ–2θ scan technique with a variable scan rate from 4.0 to 24.0°/min and a scan range from 2θ(Mo Kα_1) − 1.0° to 2θ(Mo Kα_2) + 1.0°. The intensities of 3 standard reflections measured after every 97 reflections showed no significant decay in any of the crystals used. Lorentz and polarization corrections were applied to the intensity data,[18] but absorption corrections were deemed unnecessary in view of the low linear absorption coefficients. Crystallographic data for the compounds, details of data collection and refinement, and the final R values are given in Table IV.

Solution and Refinement of the Structures.[18] The structures were solved from three-dimensional Patterson functions. In each case the geometry of the molecules is such that the centric Cr_2O_8 cores produce, through overlap of parallel interatomic vectors, sets of three orthogonal Patterson vectors from which the positions of the chromium atom and the bonded oxygen atoms could be determined. The positions of the carbon atoms in I and II or the carbonyl unit in III were then calculated, as well as the position of the axial oxygen or nitrogen atom. After these positions were refined in two cycles of full-matrix least squares, the positions of the remaining nonhydrogen atoms were found in a difference Fourier map in each case.

The refinement of I was completed by two cycles of full-matrix least squares using isotropic temperature factors followed by four cycles

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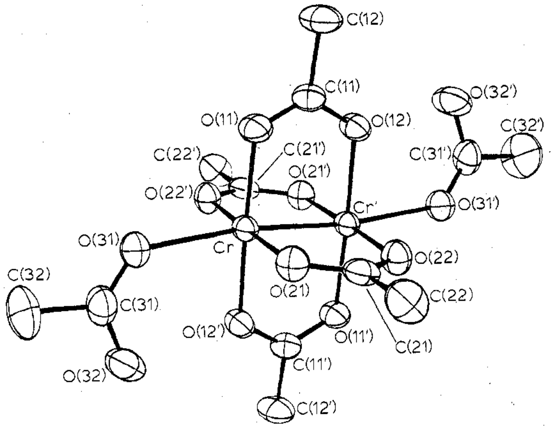

Figure 1. ORTEP view of $Cr_2(O_2CCH_3)_4(HO_2CCH_3)_2$, **I**, using 50% probability ellipsoids. Primed atoms are related to unprimed ones by inversion.

with anisotropic temperature factors. Most of the larger peaks in a final difference Fourier map were in regions where hydrogen atoms should reside.

The completion of the structure of II required the resolution of a space group ambiguity between *C*2/*m*, *Cm*, and *C*2. The Patterson function indicated the presence of a twofold axis and thereby ruled out *Cm*. The solution was begun in *C*2/*m*. A partial model with the unique atoms $Cr(O_2C_2)N$, corresponding to the molecular fragment $Cr_2(O_2CC)_4N_2$, behaved normally under refinement in *C*2/*m*, but the difference Fourier map based on these atoms revealed that the carbon atoms of the piperidine ring lay essentially upon the mirror plane. Since the saturated ring cannot be planar, the model was refined first in *C*2/*m* with the ring atoms disordered across the mirror plane and then in *C*2 with ordered atoms. The latter required the addition of a second (O_2CC) unit to complete the model in the lower symmetry space group. Despite the consequent increase in the number of variables, the discrepancy factor was larger in space group *C*2, indicating that *C*2/*m* was the better choice. In space group *C*2/*m*, the model was refined both with anisotropic temperature parameters for all atoms and with isotropic temperature factors for the ring carbons only. The Hamilton test[19] indicated that the use of anisotropic temperature factors for the disordered atoms was justified at the 99.5% confidence level. Despite the disorder in the piperidine ring, the nine largest peaks in the final difference Fourier map were clustered about the methyl carbon atom.

The initial difference Fourier map of III, based upon a partial model consisting of the 10 unique nonhydrogen atoms of the $[Cr_2(CO_3)_4(H_2O)_2]^{4-}$ anion, had three significant peaks. Since there was no straightforward method of distinguishing the oxygen atom of the water molecule from the two ammonium ion nitrogen atoms, all three atoms were temporarily treated as nitrogen atoms and refinement was continued. Refinement with anisotropic temperature factors for all atoms converged with discrepancy indices

$$R_1 = \Sigma||F_o| - |F_c||/|F_o| = 0.043$$

$$R_2 = [\Sigma w(||F_o| - |F_c||)^2/\Sigma w|F_o|^2]^{1/2} = 0.065$$

The function minimized during all least-squares refinements was $\Sigma w(|F_o| - |F_c|)^2$, where the weighting factor w equals $4F_o^2/\sigma(F_o^2)^2$. A value of 0.07 was used for p in the calculation of σ.[18] A second difference Fourier map gave reasonable positions for all 12 hydrogen atoms and thus permitted identification of the water oxygen atom. The hydrogen atoms were all arbitrarily assigned fixed isotropic temperature factors of 6.0. When the two protons of the uncoordinated water molecule refined to positions over 1.5 Å from the oxygen, they were discarded. Because of the behavior of these protons and because the published analytical data on the compound indicated that there should be less than two free water molecules per chromium dimer,[20] refinement was continued with the occupation factor for the water oxygen atom as a variable. The refinement converged with an occupation factor of 0.788 (8). A final difference Fourier map had among the largest peaks those due to the two protons omitted from the refinement. Since the hydrogen atoms already included had unequivocally identified the nitrogen atoms, no attempt was made to include the omitted ones in the model.

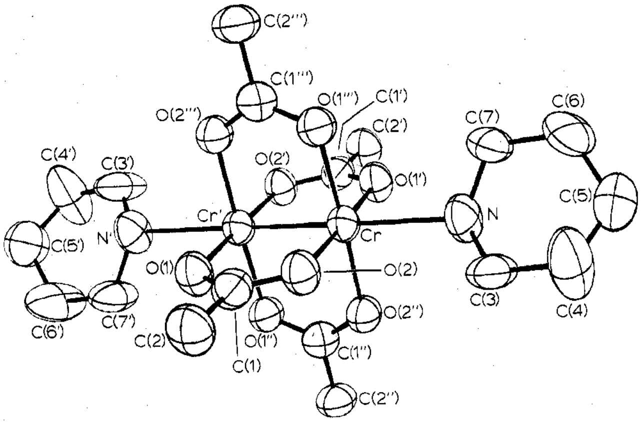

Figure 2. The $Cr_2(O_2CCH_3)_4(C_5H_{11}N)_2$, II, molecule using 50% probability ellipsoids. The singly primed atoms are related to unprimed ones by inversion. Doubly and triply primed atoms are related to unprimed and singly primed ones, respectively, by a mirror plane. Only one set of the disordered piperidine atoms is shown.

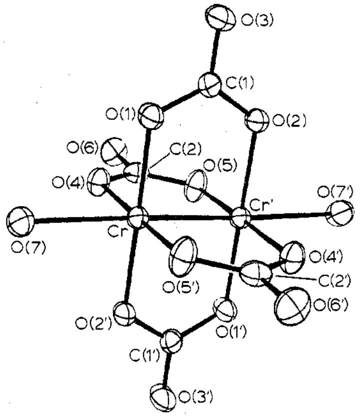

Figure 3. The $[Cr_2(CO_3)_4(H_2O)_2]^{4-}$ ion, from III, drawn with 50% probability ellipsoids. Primed and unprimed atoms are related by inversion.

Tables of calculated and observed structure factors are available for all three structures.[21]

Results

The crystallographic results are given in tables and figures numbered according to the compounds described. Tables IA–IIIA contain the thermal and positional parameters, Tables IB–IIIB give bond lengths and angles, and Figures 1, 2, and 3 illustrate the dinuclear units and the atom numbering schemes.

Each of the dinuclear units illustrated in Figures 1–3 is centrosymmetric. This is the only symmetry imposed crystallographically upon I and III, while the $Cr_2(O_2CCH_3)_4$ core of II has crystallographic 2/*m* symmetry. As the data in Tables IB–IIIB show, however, in each case the $Cr_2(O_2CR)_4$ portion of the dinuclear unit has virtual D_{4h} symmetry. These data also indicate that the Cr–O distances, exclusive of those involving the axial ligands, are the same in all three complexes. Thus, the average Cr–O distances are 2.016 Å in both I and II and 2.013 Å in III. Special features of the individual compounds will now be described.

$Cr_2(O_2CCH_3)_4(HO_2CCH_3)_2$, I. The structure of this molecular compound is adequately illustrated in Figure 1. The only unusual feature in the structure is an asymmetry of one of the bridging acetate ligands. The data in Table IB show that the C(11)–O(12) distance of 1.284 (5) Å is significantly greater than the C(11)–O(11) distance of 1.238 (5) Å. The proximity of O(32′) to O(12), 2.642 (5) Å, is readily evident in Figure 1, and it is presumed that the acidic proton on O(32′)

Table I

A. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Cr_2(O_2CCH_3)_4(HO_2CCH_3)_2$[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cr	0.06059 (5)	0.0744 (1)	−0.02794 (9)	0.00221 (3)	0.0083 (1)	0.0095 (1)	−0.0004 (1)	0.00174 (9)	0.0012 (2)
O(11)	0.1454 (2)	−0.1113 (5)	0.0849 (4)	0.0022 (2)	0.0115 (6)	0.0151 (6)	0.0006 (6)	0.0010 (5)	0.005 (1)
O(12)	0.0290 (2)	−0.2562 (5)	0.1372 (4)	0.0026 (2)	0.0102 (7)	0.0138 (6)	−0.0005 (6)	0.0013 (5)	0.006 (1)
O(21)	0.0742 (2)	0.1967 (5)	0.1890 (4)	0.0033 (2)	0.0113 (6)	0.0109 (5)	−0.0026 (6)	0.0022 (5)	−0.004 (1)
O(22)	−0.0436 (2)	0.0526 (5)	0.2424 (4)	0.0035 (2)	0.0119 (6)	0.0110 (5)	−0.0027 (6)	0.0035 (5)	−0.002 (1)
O(31)	0.1687 (2)	0.2542 (5)	−0.0934 (5)	0.0033 (2)	0.0131 (7)	0.0175 (6)	−0.0018 (6)	0.0056 (5)	0.004 (1)
O(32)	0.0912 (3)	0.4915 (5)	−0.1731 (6)	0.0050 (2)	0.0115 (7)	0.0277 (9)	0.0010 (7)	0.0057 (7)	0.011 (1)
C(11)	0.1142 (3)	−0.2367 (7)	0.1457 (6)	0.0028 (2)	0.0094 (9)	0.0105 (7)	0.0005 (9)	−0.0001 (7)	−0.001 (1)
C(12)	0.1777 (4)	−0.3728 (8)	0.2390 (8)	0.0038 (3)	0.0133 (10)	0.0191 (11)	0.0041 (10)	−0.0006 (10)	0.007 (2)
C(21)	0.0194 (4)	0.1621 (7)	0.2799 (6)	0.0043 (3)	0.0093 (9)	0.0096 (7)	0.0040 (9)	0.0014 (7)	0.002 (1)
C(22)	0.0324 (5)	0.2530 (8)	0.4463 (6)	0.0074 (4)	0.0137 (11)	0.0090 (7)	−0.0019 (11)	0.0035 (9)	−0.007 (2)
C(31)	0.1650 (4)	0.4027 (8)	−0.1384 (7)	0.0043 (3)	0.0143 (11)	0.0158 (9)	−0.0043 (9)	0.0065 (8)	−0.002 (2)
C(32)	0.2447 (5)	0.5038 (12)	−0.1660 (12)	0.0071 (4)	0.0223 (15)	0.0501 (21)	−0.0096 (13)	0.0208 (12)	0.009 (3)

B. Bond Distances (Å) and Angles (deg) for $Cr_2(O_2CCH_3)_4(HO_2CCH_3)_2$, I[b]

Distances

Cr–Cr′	2.300 (1)	Cr′–O(22)	2.002 (3)	O(21)–C(21)	1.267 (5)	C(11)–C(12)	1.521 (6)
Cr–O(11)	2.019 (3)	Cr–O(31)	2.306 (3)	O(22)–C(21)	1.263 (6)	C(21)–C(22)	1.526 (6)
Cr′–O(12)	2.027 (3)	O(11)–C(11)	1.238 (5)	O(31)–C(31)	1.211 (6)	C(31)–C(32)	1.498 (8)
Cr–O(21)	2.007 (3)	O(12)–C(11)	1.284 (5)	O(32)–C(31)	1.289 (6)	O(12)–O(32′)	2.642 (5)

Angles

Cr′–Cr–O(11)	90.0 (1)	Cr′–O(22)–C(21)	119.5 (3)	O(11)–Cr–O(12′)	117.5 (1)	O(21)–Cr–O(31)	89.3 (1)
Cr–Cr′–O(12)	87.6 (1)	Cr–O(31)–C(31)	131.6 (3)	O(21)–Cr–O(22′)	178.0 (1)	O(22′)–Cr–O(31)	92.7 (1)
Cr′–Cr–O(21)	89.1 (1)	O(11)–C(11)–C(12)	120.0 (4)	O(11)–Cr–O(21)	89.7 (1)	O(12)–C(11)–C(12)	117.4 (4)
Cr–Cr′–O(22)	88.9 (1)	O(21)–C(21)–C(22)	118.1 (4)	O(11)–Cr–O(22′)	90.2 (1)	O(22)–C(21)–C(22)	118.3 (4)
Cr′–Cr–O(31)	172.3 (1)	O(31)–C(31)–C(32)	124.3 (5)	O(12′)–Cr–O(21)	89.8 (1)	O(32)–C(31)–C(32)	111.8 (5)
Cr–O(11)–C(11)	119.5 (3)	O(11)–C(11)–O(12)	122.6 (4)	O(12′)–Cr–O(22)	90.3 (1)	O(31)–C(31)–O(32)	123.9 (4)
Cr′–O(12)–C(11)	120.4 (3)	O(21)–C(21)–O(22)	123.6 (4)	O(11)–Cr–O(31)	97.6 (1)	O(11)–O(12)–O(32′)	141.5 (3)
Cr–O(21)–C(21)	118.9 (3)	Cr–O(12)–O(32′)	97.2 (1)	O(12′)–Cr–O(31)	84.8 (1)	O(12)–O(32′)–C(31′)	137.6 (2)

[a] The form of the anisotropic thermal parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. [b] The atom numbering scheme is shown in Figure 1. Primed atoms are related to unprimed ones by inversion.

Table II

A. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Cr_2(O_2CCH_3)_4(C_5H_{11}N)_2$[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cr	0.06899 (8)	0.0[b]	0.1379 (2)	0.00405 (5)	0.0097 (1)	0.0157 (2)	0.0[b]	0.0050 (1)	0.0[b]
O(1)	−0.0117 (2)	0.1390 (4)	−0.2321 (5)	0.0049 (2)	0.0130 (5)	0.0195 (7)	−0.0012 (5)	0.0065 (5)	0.0042 (10)
O(2)	0.1196 (2)	0.1378 (4)	0.0300 (5)	0.0048 (2)	0.0115 (4)	0.0194 (6)	−0.0013 (5)	0.0065 (5)	0.0023 (9)
N	0.2003 (5)	0.029 (1)	0.420 (1)	0.0050 (4)	0.017 (2)	0.019 (1)	0.003 (1)	0.003 (1)	0.001 (3)
C(1)	0.0696 (3)	0.1795 (6)	−0.1319 (7)	0.0050 (2)	0.0101 (6)	0.0222 (9)	0.0012 (7)	0.0094 (7)	0.002 (1)
C(2)	0.1074 (4)	0.2858 (7)	−0.2096 (8)	0.0063 (3)	0.0140 (7)	0.0266 (11)	−0.0024 (8)	0.0130 (8)	0.007 (2)
C(3)	0.2845 (6)	0.0061 (42)	0.4214 (12)	0.0049 (4)	0.0334 (21)	0.0253 (17)	−0.0031 (38)	0.0093 (12)	0.026 (6)
C(4)	0.3697 (7)	−0.0129 (35)	0.6003 (15)	0.0055 (5)	0.0423 (27)	0.0299 (23)	0.0127 (31)	0.0043 (17)	−0.026 (7)
C(5)	0.3628 (8)	0.0179 (38)	0.7669 (17)	0.0069 (6)	0.0377 (31)	0.0286 (24)	−0.0094 (44)	0.0056 (20)	−0.007 (10)
C(6)	0.2705 (8)	−0.0158 (35)	0.7616 (13)	0.0077 (6)	0.0434 (29)	0.0228 (20)	−0.0014 (43)	0.0060 (18)	0.036 (6)
C(7)	0.1880 (6)	−0.0163 (29)	0.5792 (12)	0.0060 (4)	0.0337 (23)	0.0202 (16)	−0.0063 (30)	0.0081 (13)	0.019 (5)

B. Bond Distances (Å) and Angles (deg) for $Cr_2(O_2CCH_3)_4(C_5H_{11}N)_2$, II[c]

Distances

Cr′–Cr	2.342 (2)	O(1)–C(1)	1.263 (5)	N–C(3)	1.40 (2)	C(5)–C(6)	1.50 (4)
Cr′–O(1)	2.020 (3)	O(2)–C(1)	1.267 (5)	C(3)–C(4)	1.48 (1)	C(6)–C(7)	1.48 (1)
Cr–O(2)	2.012 (3)	C(1)–C(2)	1.514 (6)	C(4)–C(5)	1.43 (4)	C(7)–N	1.45 (2)
Cr–N	2.338 (7)						

Angles

Cr–Cr′–O(1)	87.8 (1)	Cr–N–C(7)	113.7 (9)	O(1)–Cr′–O(1″)	90.6 (2)	O(1″)–Cr–N	84.6 (3)
Cr′–Cr–O(2)	89.0 (1)	N–C(3)–C(4)	119 (1)	O(2)–Cr–O(2″)	90.0 (2)	O(2)–Cr–N	88.9 (3)
Cr′–Cr–N	171.9 (4)	C(3)–C(4)–C(5)	119 (1)	O(1′)–Cr–O(2″)	89.6 (1)	O(2″)–Cr–N	98.6 (3)
Cr′–O(1)–C(1)	120.4 (3)	C(4)–C(5)–C(6)	114 (4)	O(1′)–Cr–O(2)	176.7 (1)	O(1)–C(1)–O(2)	123.4 (4)
Cr–O(2)–C(1)	119.4 (3)	C(5)–C(6)–C(7)	118 (1)	O(1′)–Cr–N	95.1 (3)	O(1)–C(1)–C(2)	117.6 (4)
Cr–N–C(3)	114.6 (8)	C(6)–C(7)–N	118 (1)			O(2)–C(1)–C(2)	119.0 (4)
		C(7)–N–C(3)	113 (2)				

[a] The form of the anisotropic thermal parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. [b] Values required by the atom position. [c] The atom numbering scheme is shown in Figure 2. Primed atoms are related to unprimed ones by inversion. Doubly and triply primed ones are related to unprimed and singly primed ones, respectively, by a mirror plane.

participates in hydrogen bonding to O(12), leading to localization of π-bonding electron density in the C(11)–O(11) bond. Indeed, the asymmetry about C(11) is almost as great as that about C(31).

$Cr_2(O_2CCH_3)_4(C_5H_{11}N)_2$, II. This compound, too, consists of molecular units, the structure of which is shown in Figure 2. The disorder of the piperidine molecule across the mirror plane causes the six ring atoms to have rather large tem-

Table III

A. Positional and Thermal Parameters and Their Estimated Standard Deviations for $[NH_4]_4[Cr_2(CO_3)_4(H_2O)_2](H_2O)_{1-2}$[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cr	−0.10446 (7)	0.01724 (3)	0.07680 (6)	0.00785 (8)	0.00145 (2)	0.00637 (7)	0.00009 (8)	0.0053 (1)	−0.00016 (7)
O(1)	0.0815 (3)	−0.0328 (2)	0.3064 (3)	0.0108 (4)	0.00257 (10)	0.0080 (3)	0.0028 (4)	0.0090 (6)	0.0017 (3)
O(2)	0.2926 (3)	−0.0674 (2)	0.1518 (3)	0.0114 (5)	0.00323 (11)	0.0071 (4)	0.0046 (4)	0.0063 (6)	0.0002 (4)
O(3)	0.3718 (4)	−0.0960 (2)	0.4468 (3)	0.0189 (6)	0.00429 (13)	0.0088 (4)	0.0103 (5)	0.0072 (8)	0.0032 (4)
O(4)	0.0442 (3)	0.1256 (2)	0.1476 (3)	0.0137 (5)	0.00163 (9)	0.0115 (4)	−0.0011 (4)	0.0109 (7)	−0.0022 (3)
O(5)	0.2487 (3)	0.0921 (2)	−0.0128 (3)	0.0161 (5)	0.00229 (10)	0.0145 (4)	−0.0038 (4)	0.0201 (7)	−0.0038 (4)
O(6)	0.2939 (4)	0.2099 (2)	0.1422 (4)	0.0163 (6)	0.00170 (9)	0.0161 (5)	−0.0034 (4)	0.0075 (9)	−0.0030 (4)
O(7)	−0.3296 (3)	0.0554 (2)	0.2261 (3)	0.0097 (5)	0.00468 (14)	0.0111 (4)	0.0009 (4)	0.0083 (7)	−0.0036 (4)
O(8)	−0.0904 (7)	0.2606 (3)	0.2755 (7)	0.0229 (11)	0.00620 (23)	0.0336 (11)	0.0032 (8)	0.0076 (18)	−0.0146 (8)
N(1)	0.5814 (5)	0.2228 (2)	−0.0446 (4)	0.0232 (8)	0.0024 (1)	0.0155 (6)	−0.0006 (5)	0.018 (1)	−0.0018 (5)
N(2)	0.2278 (5)	0.3835 (2)	0.0580 (5)	0.0249 (8)	0.0026 (1)	0.0197 (6)	0.0057 (6)	0.026 (1)	0.0038 (5)
C(1)	0.2500 (5)	−0.0657 (2)	0.3033 (4)	0.0129 (7)	0.0016 (1)	0.0078 (5)	0.0022 (5)	0.005 (1)	−0.0001 (5)
C(2)	0.1980 (5)	0.1434 (2)	0.0927 (5)	0.0105 (7)	0.0018 (1)	0.0082 (5)	−0.0004 (5)	0.003 (1)	0.0012 (5)

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
H(1)	−0.431 (7)	0.061 (4)	0.175 (6)	6.0000 (0)	H(14)	0.489 (8)	0.254 (3)	−0.158 (7)	6.0000 (0)
H(2)	−0.336 (8)	0.072 (4)	0.341 (7)	6.0000 (0)	H(21)	0.214 (8)	0.328 (3)	0.075 (7)	6.0000 (0)
H(11)	0.672 (8)	0.247 (3)	0.016 (8)	6.0000 (0)	H(22)	0.362 (8)	0.392 (3)	0.061 (7)	6.0000 (0)
H(12)	0.622 (7)	0.186 (4)	−0.079 (6)	6.0000 (0)	H(23)	0.164 (8)	0.396 (3)	−0.007 (7)	6.0000 (0)
H(13)	0.502 (7)	0.210 (4)	0.017 (7)	6.0000 (0)	H(24)	0.167 (8)	0.407 (3)	0.113 (7)	6.0000 (0)

B. Bond Distances (Å) and Angles (deg) for $[NH_4]_4[Cr_2(CO_3)_4(H_2O)_2](H_2O)_{1-2}$, III[b]

Distances

Cr–Cr′	2.214 (1)	Cr–O(4)	2.016 (3)	O(1)–C(1)	1.292 (4)	O(5)–C(2)	1.285 (5)
Cr–O(1)	2.011 (2)	Cr′–O(5)	2.012 (3)	O(2)–C(1)	1.296 (4)	O(3)–C(1)	1.266 (4)
Cr′–O(2)	2.012 (2)	Cr–O(7)	2.300 (3)	O(4)–C(2)	1.299 (5)	O(6)–C(2)	1.256 (4)

Angles

Cr′–Cr–O(1)	91.44 (7)	O(4)–Cr–O(7)	90.2 (1)	O(1)–Cr–O(2′)	179.4 (1)	O(1)–C(1)–O(2)	119.3 (3)
Cr–Cr′–O(2)	89.09 (7)	O(5′)–Cr–O(7)	89.6 (1)	O(4)–Cr–O(5′)	178.4 (1)	O(4)–C(2)–O(5)	118.8 (3)
Cr′–Cr–O(4)	89.81 (8)	Cr–O(1)–C(1)	119.0 (2)	O(1)–Cr–O(4)	88.5 (1)	O(1)–C(1)–O(3)	120.3 (3)
Cr–Cr′–O(5)	90.45 (8)	Cr′–O(2)–C(1)	121.2 (2)	O(1)–Cr–O(5′)	90.0 (1)	O(2)–C(1)–O(3)	120.4 (3)
Cr′–Cr–O(7)	177.75 (9)	Cr–O(4)–C(2)	120.5 (2)	O(2′)–Cr–O(4)	91.6 (1)	O(4)–C(2)–O(6)	120.1 (3)
O(1)–Cr–O(7)	90.8 (1)	Cr′–O(5)–C(2)	120.3 (2)	O(2′)–Cr–O(5′)	89.9 (1)	O(5)–C(2)–O(6)	121.1 (3)
O(2′)–Cr–O(7)	88.7 (1)						

[a] The form of the anisotropic thermal parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. [b] The atom numbering scheme is shown in Figure 3. Primed atoms are related to unprimed ones by inversion.

Table IV. Crystallographic Data for the Three Compounds

Parameter	Compound		
	I, $Cr_2(O_2CCH_3)_4(HO_2CCH_3)_2$	II, $Cr_2(O_2CCH_3)_4(C_5H_{11}N)_2$	III, $[NH_4]_4[Cr_2(CO_3)_4(H_2O)_2](H_2O)_{1-2}$
Space group	$P2_1/n$	$C2/m$	$P2_1/c$
a, Å	15.123 (2)	15.989 (2)	6.949 (2)[a]
b, Å	7.775 (1)	10.331 (2)	16.112 (4)[a]
c, Å	8.302 (1)	8.035 (1)	7.737 (2)[a]
β, deg	102.80 (1)	116.05 (1)	108.14 (2)[a]
V, Å^3	952.0 (4)	1192.4 (6)	823.2 (7)
d_X, g/cm^3	1.61	1.42	1.90
Z	2	2	2
Formula wt	460.28	510.47	470.23
Cryst size, mm	0.3 × 0.3 × 0.3	0.1 × 0.3 × 0.5	0.2 × 0.2 × 0.45
μ, cm^{-1}	12.48	9.94	14.66
Range of 2θ, deg	0–55	0–50	0–50
No. unique data	1434	1125	1511
No. data, $F_o^2 > 3\sigma(F_o^2)$	1072	728	1113
No. variables	118	97	149
R_1[b]	0.043	0.058	0.033
R_2[b]	0.068	0.078	0.044
Esd	1.571	1.693	1.014
Largest peak, e/Å^3 [c]	0.97	1.89	0.53

[a] These values differ substantially from those reported in ref 24. [b] The discrepancy factors are defined in the text. [c] Largest peaks in the final difference Fourier map.

perature factors and there is considerable scatter of bond distances and angles in the ring.

$[NH_4]_4[Cr_2(CO_3)_4(H_2O)_2](H_2O)_{1-2}$, III. For this ionic compound, Figure 3 presents only the anionic fragment. The data in Table IIIB show that the anion is an extremely regular unit, with only a very small variation among chemically equivalent bond lengths and angles.

A view of a complete unit cell of III is presented in the stereoscopic projection in Figure 4. This drawing includes the eight anions centered at the cell vertices, the two anions centered in the *bc* faces of the cell, and all of the ammonium ions and uncoordinated water molecules contained in the cell. Hydrogen bonding contacts are represented by light lines. All of the hydrogen bonds drawn in Figure 4 are between atoms

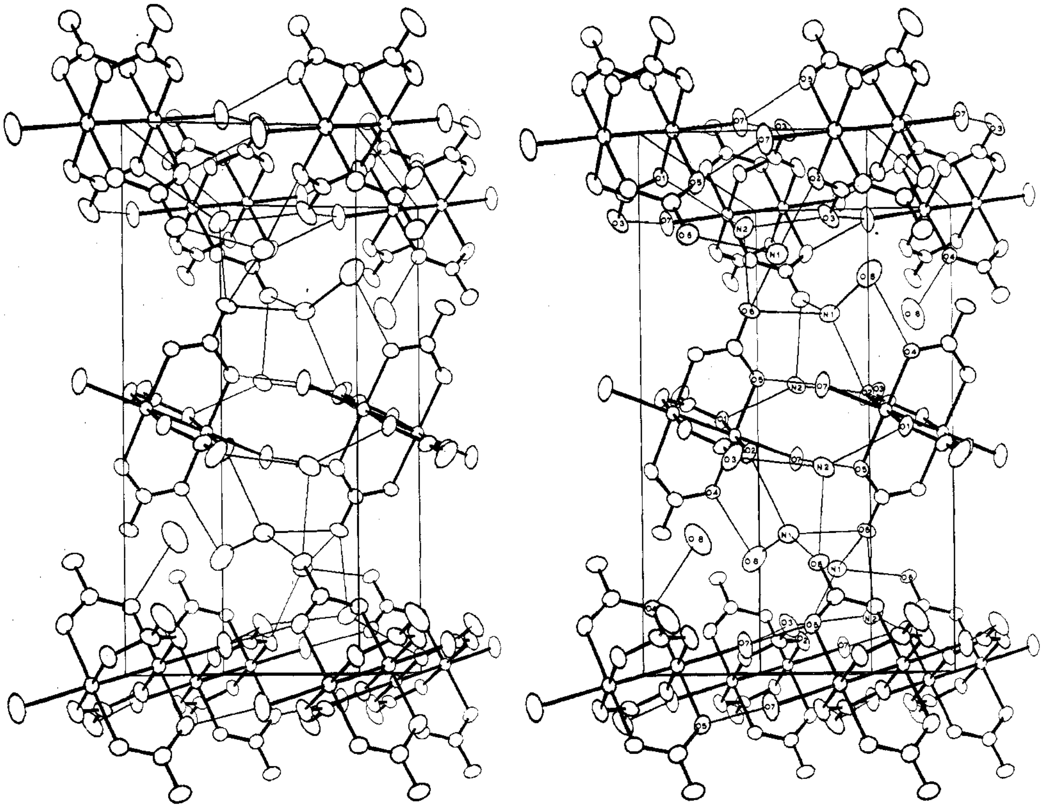

Figure 4. Stereoscopic projection of the unit cell of $(NH_4)_4[Cr_2(CO_3)_4(H_2O)_2](H_2O)_{1-2}$, III. The atoms which participate in hydrogen bonding are numbered, but the hydrogen atoms are omitted for clarity. Hydrogen bonds are represented by light lines.

separated by less than 3.0 Å, and in each case a hydrogen atom with approximately linear bonding (X–H–Y > 150°) was identified between the two atoms shown connected by the hydrogen bond. Of the 10 hydrogen atoms included in the model, all but H(23) participate in hydrogen bonding. One of the unrefined atoms on O(8) also forms a hydrogen bond. From Figure 4 it can be seen that the crystal is built up of sheets of anions in the *ab* plane. The bonding between anions within a sheet is made up of hydrogen bonds from O(7) to O(3) and O(5) as well as linkages through the ammonium ions, while bonding between sheets is restricted to hydrogen bonding through the ammonium ion hydrogen atoms.

There is no obvious reason for apparent partial occupancy of O(8). The published formula[20] for this compound was based upon the water content of the isomorphous potassium salt and would require O(8) to have 50% occupancy. The 78.8 (8)% occupancy obtained by refinement is presumably higher than the actual value, because of omission of the O(8) hydrogen atoms from the model, but an error of almost 30% is improbable. On the other hand, there is no apparent reason for any vacancy at all. There are no unusually short interatomic contacts involving O(8), and the equivalent O(8) atoms are separated by 3.88 Å. Briefly, the results here support vacancies in the O(8) sites but suggest no rationalization of them.

The only previous structure of a tetracarbonatodichromium(II) complex, that of the magnesium salt, was reported with a discrepancy factor (of undefined form) of 0.11, using isotropic temperature factors.[22] Since error estimates were included with neither atomic positions nor the bond lengths and angles, the reliability of that report could not be accurately judged. The study of III is, therefore, valuable in providing accurate data on the carbonato-type complex.

Discussion

In complexes of the general formula $Cr_2(O_2CR)_4L_2$, the only two structural parameters which vary significantly are the chromium–chromium distance and the chromium–axial ligand distance. Since the chromium–axial ligand bonding uses, to some extent, the same chromium d_{z^2} orbital that is the principal contributor to the chromium-chromium σ bond, the presence of axial ligands tends to weaken the chromium–chromium bond. In Figure 5, we present a plot of Cr–Cr distance vs. Cr–axial ligand distance for 12 tetra-μ-carboxylato-dichromium(II) complexes as well as for the carbonato complex, III. The figure makes it quite clear that these two structural parameters are related in only a very imprecise way. The best straight line, determined by a linear least-squares fit of the 13 points in the plot, has a slope of −0.19; the slope is −0.25 if the point for R = CMe_3 is omitted. There is, of course, no reason to prefer a linear relationship over a nonlinear one even over the ranges plotted and, in any case, a function extrap-

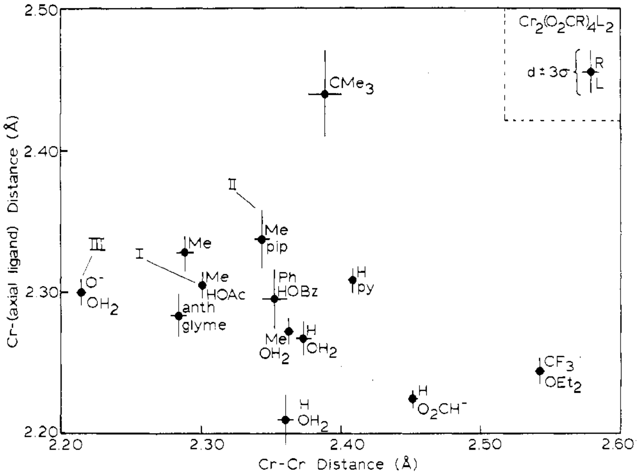

Figure 5. Plot of Cr–Cr bond distances vs. Cr–L_{ax} distances for 12 $Cr_2(O_2CR)_4L_2$ compounds and $[Cr_2(CO_3)_4(H_2O)_2]^{4-}$. Compounds I–III are identified on the figure, and the labeling scheme is shown in the upper right corner. Literature data are from ref 6, 10, 13, and 14.

olating to $d(\text{Cr–Cr}) = 0$ can have no physical meaning. One would, however, expect a negative slope to obtain regardless of the details of the relationship.

We have now obtained data on a sufficient number of crystals to recognize some groupings of compounds with the same bridging carboxylates. For the acetates, we have I and II, where the axial ligands are HO_2CCH_3 and $C_5H_{11}N$, respectively, the hydrated acetate,[10] and the anhydrous acetate.[13] These four compounds appear in Figure 5 as a cluster of points around a $d(\text{Cr–Cr})$ of about 2.32 Å. The surprising member of this group is the piperidine complex. One might have expected that piperdine, which is a much stronger base than either water or acetic acid, would bind fairly tightly to the chromium and give a Cr–Cr bond length of 2.4 Å or more. Experimentally, it binds at a rather long distance and gives a Cr–Cr bond even shorter than that found in the hydrate. It may be noted that the three acetate compounds in which the axial ligating atom is oxygen come close to defining a straight line.

The formato complexes behave in much the same manner as the acetates. Again there are four points in Figure 5, clustered loosely about a $d(\text{Cr–Cr})$ of about 2.40 Å, but even for the three with axial oxygen atoms there is no uniform trend. The compound with the axial nitrogen ligand is again above the other three, as with the acetates.

A trend that does emerge from the data in Figure 5 is that the Cr–Cr bond lengthens as the acids from which the bridging ligands are derived become stronger, although, as with the correlation of Cr–Cr and Cr–L_{ax} distances, this trend is imprecise. Trifluoroacetic acid is by far the strongest acid used, and hence $O_2CCF_3^-$ is the poorest donor of the bridging ligands. The Cr–Cr bond in $Cr_2(O_2CCF_3)_4(OEt_2)_2$ is 0.09 Å longer than any other yet measured. Formic acid has a pK_a of 3.75, benzoic acid a pK_a of 4.19, and acetic acid a pK_a of 4.75. The four formate derivatives have generally longer Cr–Cr bonds than the four acetates, and the one benzoate lies roughly between the two groups. To place the carbonate on the same scale as the carboxylates, one should perhaps consider as the parent acid the $HOCO_2^-$ anion, from which CO_3^{2-} is produced by loss of a single proton. The pK_a of this process is 10.25, and indeed the Cr–Cr bond in the $[Cr_2(CO_3)_4(H_2O)_2]^{4-}$ anion is significantly shorter than that in any of the carboxylates. In this argument, just as in the distance vs. distance plot, the one datum that stands out is that of $Cr_2(O_2CCMe_3)_4$. The pK_a of 5.03 for HO_2CCMe_3 would lead one to predict a Cr–Cr bond length of 2.28 ± 0.04 Å, instead of the observed 2.388 (4) Å. Our present state of knowledge simply does not permit the rationalization of this datum with any model we can devise.

The observation that the Cr–Cr bond in $Cr_2(O_2CR)_4L_2$ generally shortens as the carboxylate ligands become better donors appears to be consistent with knowledge of other chromium(II) complexes containing very different ligands. It is perhaps instructive to note that dimers of the type $Cr_2X_8^{4-}$ have not yet been obtained for the rather weakly donating halides, while the $Cr_2(CH_3)_8^{4-}$ ion has a Cr–Cr bond length of 1.980 (5) Å in the presence of strongly donating methide ligands.[23] Similarly, the shortest Cr–Cr bonds yet obtained occur in complexes where the ligands are both bridging and strongly donating.[5,7]

As we have shown thus far, these Cr–Cr bond lengths do not correlate simply and completely with the two most obvious variables, i.e., the Cr–axial bond length and the inductive effect of the R group. There are only two additional parameters that would appear relevant, and we are not yet prepared to address these in detail. The first additional parameter would be to replace the Cr–axial ligand bond length with an explicit measure of orbital overlap. It is logical to presume, for example, that one could attain good overlap between the chromium d_{z^2} orbitals and nitrogen lone pairs at a slightly greater distance than between chromium d_{z^2} and oxygen lone pairs because the nitrogen lone pairs would be less tightly bound. Some degree of variation in the spatial extension of the Cr d_{z^2} orbitals would, of course, be expected as a function of the inductive character of the R groups.

Finally, we cannot discount the possible effects of packing forces, but neither can we explicitly introduce them. The calculations of Benard and Veillard[12] indicate that the Cr–Cr bond strength in these compounds may be a very shallow function of bond distance, thus suggesting relatively easy extension or compression as a result of intermolecular forces. We have no way of knowing how much of the scatter which remains after allowing for the effects of metal-to-axial ligand binding and R-group electronegativity may be due to such forces. There is no reason to suppose that all of the scatter can be so explained, but neither is there any compelling evidence that it cannot.

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Registry No. I, 15225-50-0; II, 66197-70-4; III, 66197-71-5.

Supplementary Material Available: A table of distances and angles involving hydrogen atoms in compound III and tables of observed and calculated structure factors for the three compounds (15 pages). Ordering information is given on any current masthead page.

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