Molecular Modeling of Dimetal Systems. Part 3. Dichromium Bonds

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Compounds containing dichromium bonds have been modeled in comparison with related dimolybdenum systems by molecular mechanics, in order to establish a sampling curve that reflects the functional relationship between characteristic bond length, r_o, harmonic force constant, k_r, and bond order, N, for all $Cr \overset{n}{-\!\!-} Cr$. Intersection of the sampling curve with any molecular-mechanics solution curve $\{k_r, r_o\}$, for dichromium compounds identifies an effective bond order for the Cr−Cr bond. By this approach the known flexibility of dichromium bonds of constant formal bond order was analyzed, and it was shown that the effective bond order is not a function of electron count only but also relates sensitively to both axial and equatorial ligation.

A large number of dichromium(II) compounds of the type illustrated in Figure 1, and all with the same formal bond order of 4, have been structurally characterized.[1] A surprising feature of this class of compound is the extreme variability in observed metal−metal bond length, reported over a range of 1.84 to 2.54 Å. This variability, not observed for corresponding molybdenum and tungsten compounds, raises a number of questions concerning the order of the dimetal bonds, and the effect of steric factors on their length. The observed bond length is found to be sensitive to the nature of X, Z, L, and R in Figure 1. When X and Z change from N,N to N,O to O,O, there is a gradual increase in Cr−Cr bond length, axial substitution invariably causes an increase in dimetal bond length, and for constant X,Z the lengthening of the Cr−Cr bond seems to correlate[2] with the basicity of the axial ligand, L. Although these trends clearly depend on electronic factors, steric contributions to the observed effects are by no means excluded. The question also remains whether bonds that vary over such a wide range can reasonably be considered to be of the same order.

One plausible strategy for comparing effective bond orders is to identify a number of situations where an authentic bond order, N, can be related to another more accessible parameter, to serve as a probe in the problematic situations. An attractive possibility is the harmonic force constant, k_r, of the dichromium bond, especially as used in conjunction with a characteristic bond length, r_o, in molecular mechanics. Once a functional relationship between N, k_r, and r_o has been established, effective bond orders can be obtained directly by structure modeling. However, because of bond variability only the bond order four can be assigned with any confidence to the so-called supershort Cr−Cr bonds.

To overcome this problem it was assumed that chromium and molybdenum are sufficiently alike to ensure that, if the functional relationship exists, it would be of the same form for the two elements. The relationship developed for molybdenum in two previous papers[3,4] reads
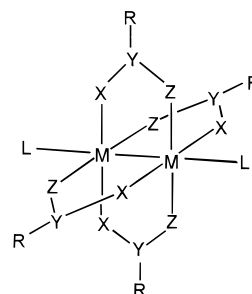
Figure 1. Molecular model for the simulation of dichromium(II) structures.

$$N = 0.9537k_r = 131.8r_o^{-5}$$

with (k_r, r_o) in units of (mdyne Å^{-1}, Å). It is therefore assumed that for dichromium bonds $N = cr_o^{-5} = bk_r$ and that the values of b and c are fixed by specifying $N = 4$ in the simulation of supershort bonds.

Dichromium Carboxylates

The possibility of multiple bonding between two chromium atoms was first recognized[5] in the structure of chromium acetate dihydrate with $d(Cr-Cr) = 2.36$ Å and with water in axial coordination. The bond length is even shorter[6] (2.29 Å) in crystals of the unsolvated complex, obtained by vacuum sublimation. However, the oxygen ligand atoms are situated in axial coordination positions with respect to neighboring molecules to form infinite chains of interconnected molecules. The structure type is therefore still the same as shown in Figure 1.

Many other $Cr_2(O_2CR)_4L_2$ compounds have been structurally investigated to analyze the response of the dichromium bond length to the nature and proximity of axial ligands, and the inductive character of the R group in the carboxylate ligand, $[RCO_2]^-$. The only two structural parameters that vary significantly are the Cr−Cr and Cr−L$_{ax}$ distances. The dichro-

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mium bond length varies between 2.21 and 2.54 Å compared to a variation of no more than 0.1 Å for comparable molybdenum compounds.[3]

All efforts to establish empirical relationships between dichromium bond length and other structural parameters have only been partially successful[2] which prompted this analysis in a bid to first classify the compounds in terms of effective bond orders.

Supershort Bonds

Another group of non-carboxylate dichromium compounds crystallize without axial ligands or intermolecular association and with $d(\text{Cr}-\text{Cr}) < 1.95$ Å, often referred to as supershort bonds. The bridging structure is the same as for the carboxylates, but the bridging groups are of the types $C \wedge O$, $N \wedge O$, $N \wedge N$, or the mixed $O \wedge O/C \wedge O$ type. The only carboxylate compound potentially of the same kind is $\text{Cr}_2(\text{O}_2\text{CMe})_4$ as studied by electron diffraction in the gas phase.[7] For the purpose of this analysis it was therefore assumed that, of the bridged compounds, only the supershort bonds may have order 4. To find a unique solution pair (k_r, r_o) for Cr $\overset{4}{-}$ Cr, the solution curves of the supershort bonds were compared with those for $\text{Cr}^{II}-\text{Cr}^{II}$ bonds not supported by bridging frameworks.

Molecular Modeling

We propose to study the dichromium system by the same techniques used before for dimolybdenum.[3] Since the bridging framework for a given $(\text{X}-\text{Y}-\text{Z})^{-1}$ ligand is comparatively insensitive to changes in dimetal bond length its force field is assumed to be transferable and the only additional parameters required are for interactions involving chromium directly; these are shown in Table 1.

All structures were modeled according to the criteria stipulated before[3] and with the aim of establishing a solution curve $\{k_r, r_o\}$ for each compound of interest. The procedure is to vary one parameter and find the matching value of the second that correctly simulates the measured bond length at each step. The results for compounds with the supershort bond and for the $[\text{Cr}_2\text{Me}_8]^{4-}$ ion are shown in Figure 2. The slopes of the solution curves are all positive, which indicates that the dichromium bond is stretched from its electronic value to the observed distance by steric forces. An interesting separation into two or more families is immediately apparent, and a common bond order for all compounds would therefore not be appropriate. The logical conclusion is that of the bridged species, only the $C \wedge O$ and $N \wedge N$ types have the highest bond order and that the intersection of their solution curves with that of $[\text{Cr}_2\text{Me}_8]^{4-}$ defines the characteristic (k_r, r_o) pair for Cr $\overset{4}{-}$ Cr. Details are collated in Table 2 and Figure 3.

Slight stretching of the dichromium bond or opening of the $\text{Cr}-\text{Cr}-\text{X}_{br}$ angles can occur to accommodate the natural bite of the bidentate ligands. The opening is symmetrical for the $N \wedge N$ bridged compounds, but in the case of the $C \wedge O$ bridged compounds the excess bite is compensated for almost entirely by more obtuse $\text{Cr}-\text{Cr}-\text{O}_{br}$ angles (ca. 102°) compared to near-orthogonal $\text{Cr}-\text{Cr}-\text{C}_{br}$ (ca. 92°) angles. However, all $\text{Cr}-\text{Cr}-\text{X}_{br}$ angles are more obtuse (by ca. 3°) than the corresponding $\text{Mo}-\text{Mo}-\text{X}_{br}$ angles[3] due to the shorter $\text{Cr}-\text{Cr}$ and $\text{Cr}-\text{X}_{br}$ bonds.

Further evidence of steric crowding around Cr_2 is provided by the larger $\text{N}-\text{Cr}-\text{Cr}-\text{N}$ torsion angles in $\text{Cr}_2(\text{PhN}-\text{N}-\text{NPh})_4$ (10.4, 10.5, 12.9, and 14.8°) and $\text{Cr}_2(\text{DMF})_4$ (8.4 and 8.7°), compared to the near-eclipsing in the corresponding Mo_2

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Table 1. Force Field Parameters for Harmonic Distortions and Nonbonded Interactions Pertaining to Dichromium Compounds; Nonbonded parameters Are Constants That Define the Energy of Interaction as $V = cr^{-6} + ae^{-br}$

interaction	force constant (k_r/Å k_e/mdyne Å)	characteristic value (r_o/Å or θ/rad)
$\text{Cr}-\text{C}^{-1/2}$	2.08	2.18
$\text{Cr}-\text{N}_{br}$	0.84	2.03
$\text{Cr}-\text{O}_{br}$	0.84	1.97
$\text{Cr}-\text{C}_{br}$	2.08	2.05
$\text{C}_{br}-\text{O}(\text{CO}_3)$	3.00	1.26
$\text{C}_{ar}-\text{N}$	3.00	1.30
$\text{Cr}-\text{Br}_{ax}$	0.30	3.30
$\text{Cr}-\text{Cl}_{ax}$	0.20	3.20
$\text{Cr}-\text{O}_{ax}$	0.60	2.29
$\text{Cr}-\text{O}_{ax}$ (inter)	0.40	2.30
$\text{Cr}-\text{N}_{ax}{}^a$	0.70	2.32
$\text{Cr}-\text{N}_{ax}{}^b$	0.70	2.27
$\text{Cr}-\text{O}_{ax}$ (Et$_2$O)$_2$	0.60	2.22
$\text{Cr}-\text{N}_{ax}{}^c$	0.70	2.24
$\text{C}-\text{N}-\text{C}$	0.10	1.911
$\text{C}-\text{N}-\text{Lp}$	0.40	1.911
$\text{O}_{br}-\text{C}_{br}-\text{O}$	1.00	2.094
$\text{O}_{br}-\text{C}_{br}-\text{C}_{ar}$	1.00	2.094
$\text{C}-\text{C}-\text{Cl}$	0.65	1.911
$\text{H}-\text{C}-\text{Cl}$	0.52	1.911
$\text{Cr}-\text{O}-\text{Lp}$	0.40	1.911
$\text{Cr}-\text{O}-\text{C}$	0.20	1.911
$\text{C}-\text{O}-\text{C}$	0.10	1.911
$\text{C}-\text{O}-\text{Lp}$	0.40	1.911
$\text{C}_{ar}-\text{N}-\text{H}$	0.60	2.094
$\text{H}-\text{N}-\text{H}$	0.50	2.094
$\text{H}-\text{C}-\text{F}$	0.52	1.911
$\text{C}_{ar}-\text{N}-\text{C}$	0.20	2.094

Nonbonded Parameters

	a (10^5 kJ mol^{-1})	b (Å^{-1})	c (10^2 Å^6 kJ mol^{-1})
Cr- - -Cr	4.113	3.28	13.25
Cr- - -O	8.946	3.89	13.37
Cr- - -H(Lp)	2.060	3.86	4.28
Cr- - -C	11.49	3.88	12.83
Cr- - -N	8.133	3.89	13.56
Cr- - -Br	2.101	3.02	49.52
Cr- - -Cl	7.104	3.51	34.58
Cr- - -F	4.202	3.90	8.01

^{a} L_{ax} = pyrazine, $2 - \text{CN} - \text{py}$, $4 - \text{CN} - \text{py}$, py. ^{b} $L_{ax} = 4 - \text{NH}_2 - \text{py}$, $4 - \text{CMe}_3 - \text{py}$, $4 - \text{NMe}_2 - \text{py}$. ^{c} $\text{O}_2\text{CR} = \text{O}_2\text{C(CF}_2\text{H)}$ and $L_{ax} = 4 - \text{NMe}_2 - \text{py}$.

compounds.[3] However these small rotations have no effect on the strength of the δ component of the quadruple Cr_2 bond, as previously demonstrated[3] for Mo_2.

The Cr_2 bond in $[\text{Cr}_2\text{Me}_8]^{4-}$ is sterically more congested than the analogous Mo_2 compound. This follows from the larger $\text{Cr}-\text{Cr}-\text{C}^{-1/2}$ angles and the stretched $\text{Cr}-\text{Cr}$ bond. The lengthening of the $\text{Cr}-\text{Cr}$ distance upon rotation around the dimetal bond is also more pronounced that for $[\text{Mo}_2\text{Me}_8]^{4-}$.

Dichromium Bond-Order Function

The region of overlap in Figure 3 defines an average (k_r, r_o) = (2.45 mdyne/Å, 1.79 Å) as the most likely values of the force constant and strain-free bond length of the quadruple dichromium bond. The rather low force constant would explain why dichromium bonds appear to be anomalously long when compared with their dimolybdenum analogues. The $r_o(\text{Mo})$: $r_o(\text{Cr})$ ratio of 1.13, however, comes close to the ratio of 1.1 between the covalent radii of the two metals.

Suitable data to compare the calculated force constant with vibrational frequencies are not available, but it is noted that a
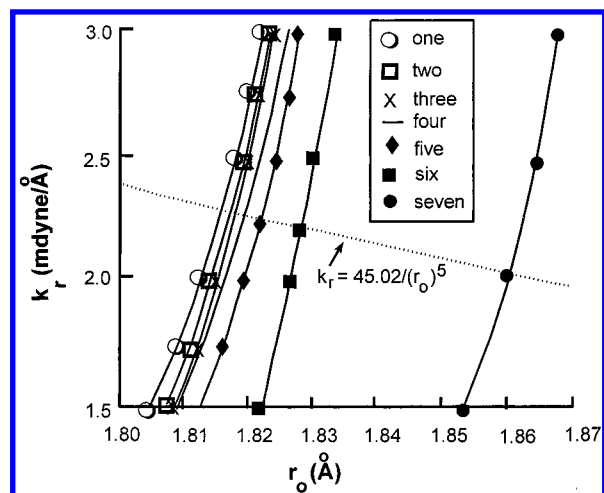
Figure 2. Molecular mechanics solution curves $\{k_r, r_o\}$ for the supershort Cr−Cr bonds.
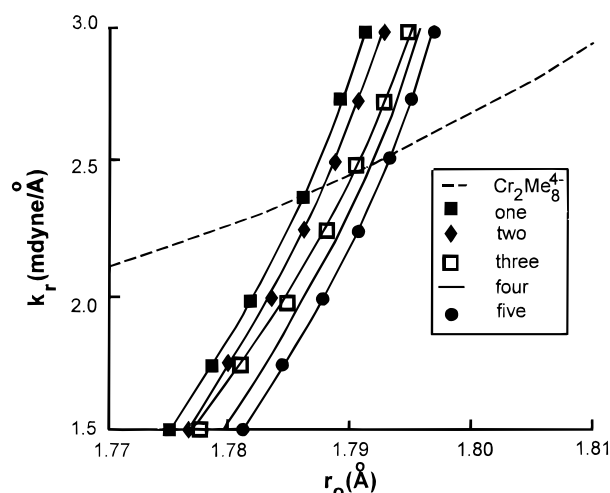
Figure 3. Molecular mechanics solution curves $\{k_r, r_o\}$ for quadruple Cr−Cr bonds.
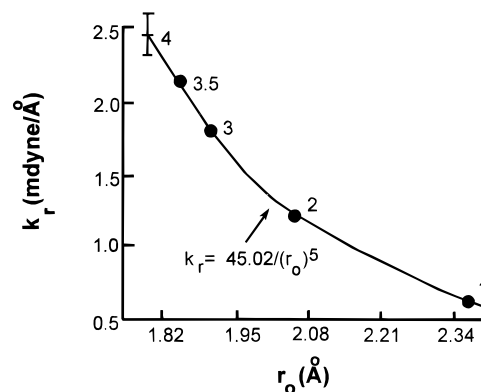
Table 2. Calculated and Observed Cr $\overset{4}{—}$ Cr Bond Lengths

molecule	calcd/Å	obsd/Å	ref	figure label
$[Cr_2Me_8]^{4-}$	1.982	1.980(1)	8	
$Cr_2(DMP)_4{}^a$	1.847	1.847(1)	9, 10	two
$[Cr_2Me_8]^{4b}$	1.847	1.849(2)	10, 11	two
$Cr_2(2MeO\text{-}5MeC_6H_3)_4$	1.830	1.828(2)	12	one
$Cr_2(PhN\text{−}N\text{−}NPh)_4$	1.858	1.858(1)	13	4
$Cr_2(MAP)_4{}^c$	1.870	1.870(3)	14	five
$Cr_2(DMF)_4{}^d$	1.930	1.930(2)	15	three
$[Cr_2(o\text{−}C_6H_4O)_4(Br_2)]^{6-}$	1.831	1.830(4)	16	one

^{a} 2,6-Dimethoxyphenyl. ^{b} 2,4,6-Trimethoxyphenyl. ^{c} 6-Methyl-2-aminopyridine. ^{d} Dimethylformamide.

pure Cr $\overset{4}{—}$ Cr stretching frequency of 400 cm^{-1} is predicted. It could be more than coincidence that SCF calculations indicate[17]

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Figure 4. Relationship between harmonic force constant and characteristic bond length which defines a sampling curve for dichromium compounds of different order, as $N = 73.51/r_o{}^5$.

Table 3. Calculated and Observed Cr−Cr Bond Lengths in Bridged Compounds with Bond Orders Less than 4

$(X\text{−}Z\text{−}Y)_n$	$(L_{ax})_2$	calcd/Å	obsd/Å	ref	figure label
$(PhN\text{−}C(Me)\text{-}O)_4$	−	1.871	1.873(1)	18, 19	three
$(MHP)_4{}^a$	−	1.890	1.889(1)	20	one
$(DMHP)_4{}^b$	−	1.903	1.907(3)	21	one
$[(2,6\text{-xylyl})N\text{−}C(Me)\text{−}O]_4$	−	1.938	1.937(2)	22	two
$(2,6\text{-xylyl})N\text{−}C(Me)\text{−}O]_4$	CH_2Cl_2	1.950	1.949(2)	23	five
$(2,6\text{-xylyl})N\text{−}C(Me)\text{−}O]_4$	CH_2Br_2	1.958	1.961(2)	22	four
$(CHP)_4{}^c$	−	1.957	1.955(2)	24	four
$(o\text{-}Bu^tOC_6H_4)_2(O_2CMe)_2$	−	1.863	1.862(1)	25	six
$O_2CMe)_4$	−	1.96	1.96(1)	7	seven

^{a} 6-Methyl-2-hydroxypyridine. ^{b} 2,4-Dimethyl-6-hydroxypyrimidine. ^{c} 6-Chloro-2-hydroxypyridine.

quadruple bonds not to occur at interatomic distances of more than 1.80 Å.

Substitution of the estimated (k_r, r_o) pair into the general expressions

$$N = cr_o{}^a = bk_r, \, a \text{ (assumed)} = -5,$$

yields $k_r = 45.02 r_o{}^{-5}$

$$N = 1.633 k_r = 73.51 r_o{}^{-5}$$

and the sampling curve shown in Figures 2 and 4. We propose to term the constant c the "index of inflexibility", which has the value of 137.4 for the less flexible dimolybdenum bond.[4]

Details of the modeling of other bridged structures are shown in Table 3 and Figure 5. Intersection with the sampling curve suggests at least three different bond orders, and these correspond neatly with the N∧O, C∧O/O∧O, and O∧O classes of compound, respectively.

The results are summarized in Table 4 and Figure 6. The inference that effective bond order depends on the nature of the bridging ligands is inescapable. If this relates to the electron density at the dichromuim center, as modified by the X−Y−Z bridging group, donor ability is modeled to decrease in the order C∧O = N∧N > N∧O> (O∧O/C∧O) > O∧O. This is also the sequence expected in terms of electronegativities or acidity, which decreases in the order OH > NH > CH.

Even in the absence of axial ligands it therefore follows that integral bond orders at the dichromium center will be the exception rather than the rule. Although this may be difficult to rationalize in terms of popular models of multiple bonding it is readily understood if bond order is formulated in terms of
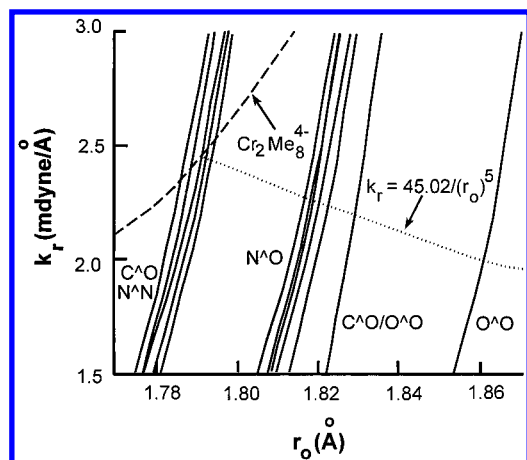
Figure 5. Molecular mechanics solution curves $\{k_r, r_o\}$ for the Cr—Cr bonds of different order, less than 4.
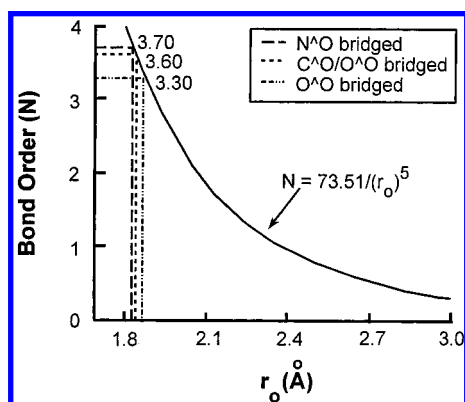

Figure 6. Derivation of bond orders for the (N∧O)$_4$-, [(C∧O)$_2$ (O∧O)$_2$] and (O∧O)$_4$-bridged dichromium bonds from the general sampling curve.

Table 4. Effective Bond Orders, Force-Field Parameters, and Harmonic Stretching Frequencies for Bridged Dichromium Compounds

(X−Y−Z)$_n$	(k_r, r_o)	N	ν/cm^{-1}
(C−C−O)$_4$			
(N−N−N)$_4$	2.45, 1.79	4	400
(N−C−N)$_4$			
(N−C−O)$_4$	2.26, 1.82	3.70	384
(C−C−O)$_2$(O−C−O)$_2$	2.21, 1.83	3.60	380
(O−C−O)$_4$	2.02, 1.86	3.30	363

the screening of internuclear repulsion[26] rather than simple electron counts.

These conclusions are not without experimental support, for instance the photoelectron spectra, which differ for carboxylates of molybdenum and chromium[27] but correspond[28] for Mo$_2$-(MHP)$_4$ and Cr$_2$(MHP)$_4$. It is a simple bond-order effect. Whereas only the molybdenum carboxylates are of order 4, the latter pair both have quadruple bonds.

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Effect of Axial Ligands

A large number of compounds with formal dichromium quadruple bonds weakened by axial ligation have been characterized. It is generally agreed that donation into d$z^2\sigma^*$ antibonding orbitals is responsible for the weakening, and by comparison of the molecular mechanics solution curves of these compounds, through the general sampling curve, effective bond orders have now been obtained. The results are shown in Figures 7−12, and summarized in Table 5.

It is noted that the dichromium bond in amidato compounds, which is invariably less than 1.96 Å, is stretched by an average 0.3 Å on axial ligation. The results are shown in Figure 7. The CrOC$_2$ fragment of the axial THF was modeled with sp^2 geometry and both lone pairs contributing to antibonding. The overall effect is a reduction in the effective dichromium bond order from 3.7 by about 1.5 units.

The effect of axial coordination in carboxylato-bridged compounds is even more pronounced with an increase of 0.6 Å in Cr—Cr bond length. The results of modeling a large number of these compounds are shown in Figures 8−12.

The results for axial oxygen donors are in Figure 8. The bond orders are invariably less than for gaseous Cr$_2$(O$_2$CMe)$_4$ with N = 3.30. As noted before[40] for other low-order bonds, the observed bond lengths are less than the characteristic strain-free values, r_o. The solution curves have negative slopes, and the bridging structure actually compresses the central bonds toward a suitable bite of ideally about 2.2 Å. Bulky groups in axial position counteract this compression.

The tabulated frequencies are predictions based on the estimated values of harmonic force constants only and could serve as a guide in future spectroscopic assignments. The calculated bond order of 0.5 for Cr$_2$(O$_2$CCF$_3$)(Et$_2$O)$_2$ is in accord with the experimentally observed paramagnetism (μ_{eff} = 0.85 μ_B at 25°) and indicates that the derived bond orders make chemical sense.

There is no obvious, simple relationship between the electronic properties of axial ligands and dichromium bond orders, since these are also affected by the bridging ligands. Clear trends, however, emerge in groups of compounds with a constant bridging structure and different axial ligands, as presented in Figures 9−12. The pK_a of the bridging carboxylic acid provides a useful index for comparison of bond order dependence on coordination effects, as shown in Figure 13. Derivatives of the same bridging acid have the same ordinate and compounds with the same axial ligand can be grouped on straight lines of constant slope. The complementary plot of protonated base pK_a values for axial ligands (L), against dichromium bond order, is shown in Figure 14 for compounds Cr$_2$(O$_2$CR)$_4$L$_2$. As the bridging

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(40) Boeyens, J. C. A.; Cotton, F. A.; Han, S. *Inorg. Chem.* **1985**, *24*, 1750.

Table 5. Bridged Dichromium Compounds with Axial Ligands

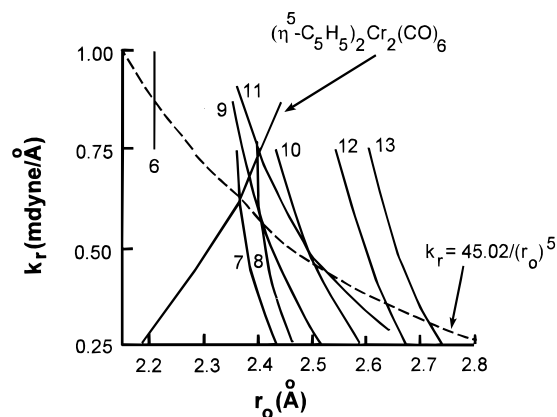| bridging ligand	$(L_{ax})_n$	d_{calcd} (Å)	d_{obsd} (Å)	Cr−L (Å)	N	ν (cm^{-1})	label	ref
(4NMe$_2$−C$_6$H$_4$)N$^-$C(Me)-O	(THF)$_1$	2.006	2.006(2)	2.350(6)	2.36	307	1	29
(2,6 xylyl)N−C(Me)-O	(THF)$_1$	2.022	2.023(1)	2.315(4)	2.30	303	2	29
				2.318(9)				
(2,6 xylyl)N−C(Me)-O	(THF)$_2$	2.220	2.221(3)	2.321(8)	2.19	296	3	29
FHP^a	(THF)$_1$	2.151	2.150(2)	2.266(6)	2.19	296	4	30
PhN−C(NHPh)-O	(THF)$_2$	2.246	2.246(2)	2.350(5)	2.03	285	5	31
(O$_2$CR)$_4$	(H$_2$O)$_2$							
R = carbonate (O)	(sp^2)	2.214	2.214(1)	2.300(3)	1.39	236	6	32
biph	(inter)$_1$^{b}	2.349	2.348(2)	2.309(5)	1.00	200	7	33
Me	(inter)$_1$^{c}	2.286	2.288(2)	2.327	0.91	191	9	34
CMe	(inter)$_1$^{c}	2.390	2.388(4)	2.44(1)	0.92	193	8	35
Me	(H$_2$O)$_2$		2.362(1)					
	(sp^3)	2.360		2.272	0.75	173	11	36−38
biph	(THF)$_2$		2.316(3)					
	(sp^3)	2.316		2.275(6)	0.71	168	10	33
CF$_2$H	(Et$_2$O)$_2$							
	(sp^2)	2.490	2.490(3)	2.233(6)	0.58	151	12	2
CF$_3$	(Et$_2$O)$_2$	2.541	2.541(1)	2.244(3)	0.50	142	13	35
CMe$_3$	2-CNpy	2.327	2.327(1)	2.388(4)	0.86	186		2
CMe$_3$	4-CNpy	2.335	2.335(1)	2.334(2)	0.85	184		2
CMe$_3$	py	2.358	2.359(3)	2.325(8)	0.77	175		2
CMe$_3$	4-NH$_2$py	2.380	2.379(1)	2.282(2)	0.68	166		2
Me	pyrazine^d	2.295	2.295(2)	2.31(1)	0.87	186		39
Me	4-CNpy	2.315	2.315(2)	2.327(4)	0.84	182		2
Me	py	2.370	2.369(2)	2.335(5)	0.76	175		39
Me	4-NHMe$_2$py	2.410	2.411(1)	2.279(4)	0.66	162		2
H	4-CNpy	2.385	2.385(3)	2.34(1)	0.81	179		32
H	py	2.408	2.408(1)	2.308(3)	0.73	169		35
H	4-NMe$_2$py	2.443	2.443(1)	2.270(4)	0.62	158		2
CH$_2$Cl	4-CNpy	2.408	2.408(4)	2.23(2)	0.77	175		2
Me/CH$_2$Cl	py	2.369	2.367(2)	2.336(6)	0.73	169		2
CF$_2$H	4-CMe$_3$py	2.514	2.514(1)	2.277(9)	0.66	164		2
CF$_2$H	4-NMe$_2$py	2.500	2.500(1)	2.246(9)	0.58	151		2

^{a} 6-Fluoro-2-hydroxypyridine. ^{b} Dimer of Cr$_2$(O$_2$biphenyl)$_4$ dimers. ^{c} Intermolecular axial O-donation from neighboring molecule. ^{d} Bifunctional pyrazine forms a 1:1 complex with Cr$_2$(OAc)$_4$ linking the Cr$_2$ units into chains.
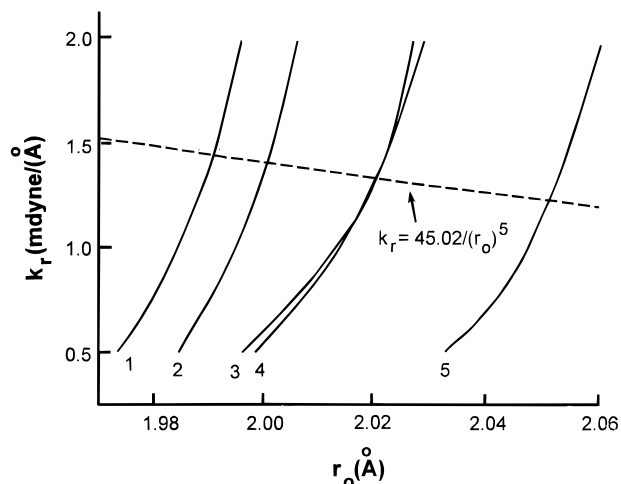
Figure 7. Molecular mechanics solution curves for the dichromium bonds spanned by N∧O ligands in the presence of axially coordinated THF.

Figure 8. Molecular mechanics solution curves for the carboxylato-bridged Cr−Cr bond with O-donor axial ligands. Intersection of the solution curve for a possible dichromium single bond is shown.

group becomes a weaker electron donor the Lewis acidity of the dichromium bond toward a given axial ligand, increases, causing a decrease in bond order. These changes are virtually constant between different bridging groups, irrespective of the axial donor.

For a given bridging group the estimated bond orders therefore change as a linear function of axial σ donor ability and for the same axial ligand, bond order depends on the acidity of the bridging group. Judging by the slopes of the relevant plots, changes in bond order are actually more sensitive to the nature of the bridging groups. O-donation by intermolecular association has a smaller effect on bond order than weak axial donors and the dimeric [Cr$_2$(O$_2$Cbiph)$_4$]$_2$ has a stronger dimetal bond than compounds with intermolecular association at both ends of the Cr$_2$ bonds.

The carbonate bridge represents one extreme of bridging donor strength. The axial water molecules donate two lone pairs

each to the Cr atoms, and yet this molecule has the strongest Cr−Cr bond. This demonstrates the decisive role of the bridging group. The strongly donating (CO$_3$)$^-$ reduces the effect of axial donation to even less than intermolecular association. At the other extreme where R = CF$_3$ and planar Et$_2$O groups are axially coordinated, the weakest Cr−Cr bond is observed.

Effective dichromium bond order depends in summary on the interplay between the electronic properties of the bridging and axial ligands, in terms of which all of Table 5 can be rationalized.

Dichromium Single Bond

The only unsupported dichromium compound of formal bond order less than 4, is[41] (η^5-C$_5$H$_5$)$_2$Cr$_2$(CO)$_6$. Molecular modeling requires a special procedure, described before for the molybdenum analogue,[4] with special values of the force field

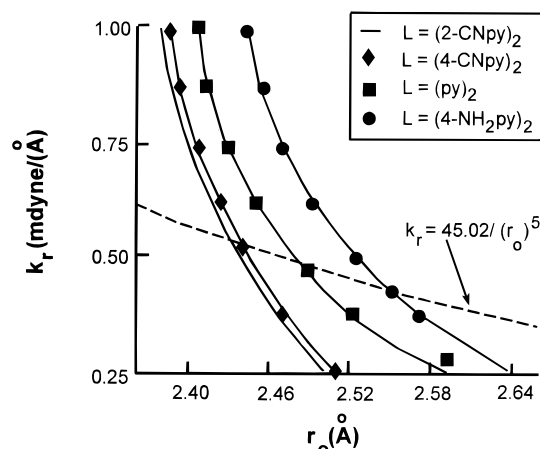(41) Adams, R. D.; Collins, D. E.; Cotton, F. A. *J. Am. Chem. Soc.* **1974**, *96*, 749.

Figure 9. Molecular mechanics solution curves for $Cr_2(O_2CCMe_3)_4L_2$ with pyridine or substituted pyridine as axial donors.

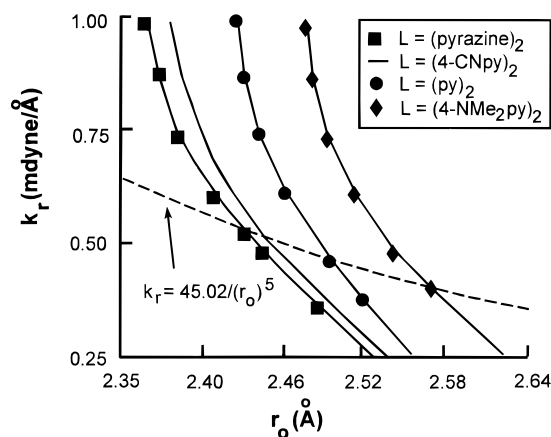**Figure 10.** Molecular mechanics solution curves for $Cr_2(O_2CMe)_4L_2$ with N-donor axial ligands.

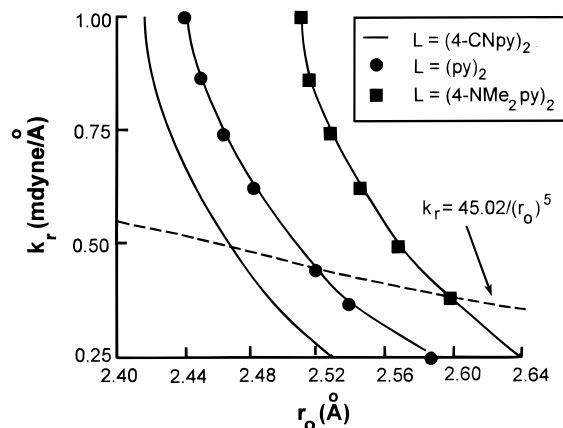**Figure 11.** Molecular mechanics solution curves for $Cr_2(O_2CH)_4L_2$ with pyridine or substituted pyridine as axial donors.

Figure 12. Molecular mechanics solution curves for $Cr_2(O_2CR)_4L_2$ with N-donor axial ligands.

Figure 13. Relationship between pK_a (RCO_2H) and bond order for dichromium carboxylates with N-donor axial ligands.

Figure 14. Relationship between pK_a (axial ligand) and bond order for $Cr_2(O_2CR)_4L_2$ compounds with axial N donors.

parameters (k_r/mdyne Å^{-1}, r_o/Å) for the bonds $Cr-CO$ (2.08, 1.85) and $Cr-cen$ (15.0, 1.84).

The solution curve is shown in Figure 8, intersecting the sampling curve at (k_r, r_o) = (0.61, 2.36) with a calculated bond length of 3.283 Å, compared to 3.281(1) Å, observed. This corresponds exactly to the bond order, $N = 1.00$.

It is interesting to analyze the bond stretching in terms of the severe steric crowding of the dichromium center, but of much more importance is the correct prediction of the single-bond order on the hand of the sampling curve, derived from
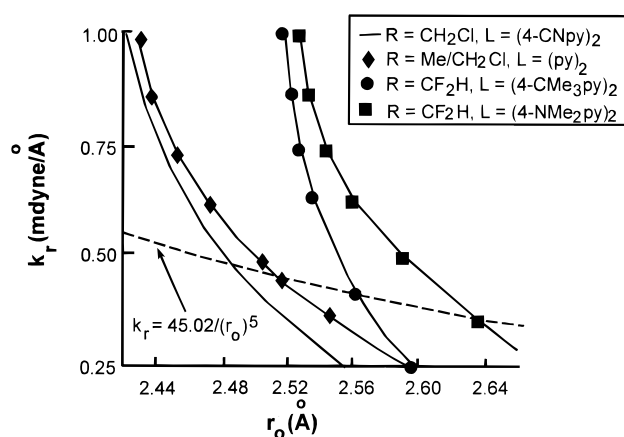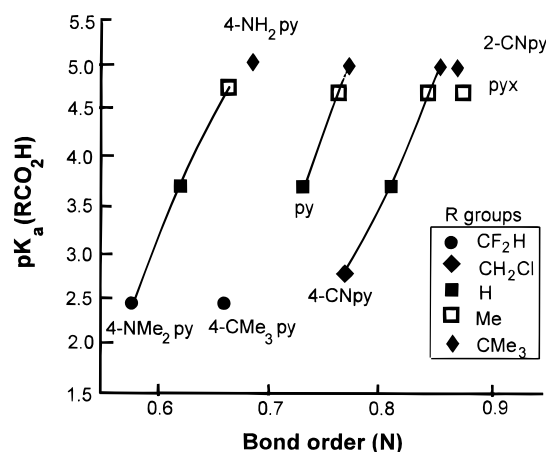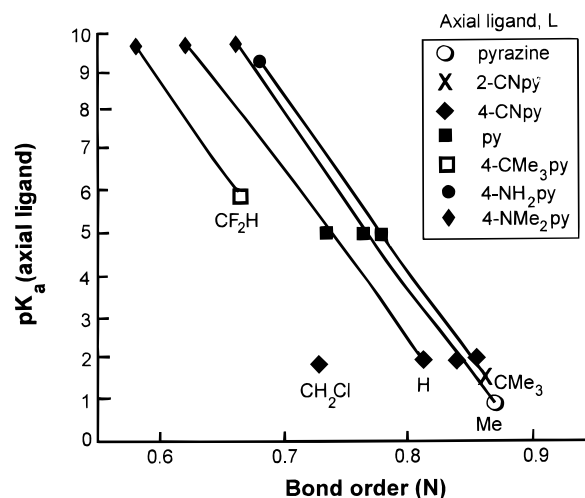
the results obtained with the more rigid dimolybdenum compounds. The entire procedure therefore appears to be self consistent, and the predicted bond orders for dichromium compounds are in good logical order. However, as correctly pointed out by one of the referees, the degree of self-consistency could be happenstance and the interpretation, although reasonable is not unassailable.