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Sensitivity of the Cr–Cr Quadruple Bond to Axial Interactions in Dichromium(II) Compounds

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Abstract: X-ray crystallographic studies have been made on five $Cr_2[RNC(O)R']_4L_2$-type compounds, R = C_6H_5, 2,6-$(CH_3)_2C_6H_3$; 4-$(Me_2N)C_6H_4$; R′ = CH_3, NHPh; L = THF, NC_5H_5, to determine the response of the Cr–Cr bond to the introduction and variation of axial ligands. The structures reported here are for the following compounds, where the numbers in parentheses are the lengths in Å of the Cr–Cr bond: $Cr_2[(4\text{-}Me_2N\text{-}C_6H_4)NC(O)CH_3]_4\cdot THF$ (**1**) (2.006 (2)); $Cr_2[(2,6\text{-xylyl})NC(O)CH_3]_4\cdot 3THF$ (**2**) (2.221 (3)); $Cr_2[(2,6\text{-xylyl})NC(O)CH_3]_4\cdot THF\cdot C_6H_5CH_3$ (**3**) (2.023 (1)); $Cr_2[PhNC(NHPh)O]_4\cdot 2THF\cdot C_6H_{14}$ (**4**) (2.246 (2)); $Cr_2[(2,6\text{-xylyl})NC(O)CH_3]_4\cdot 3NC_5H_5$ (**5**) (2.354 (5)). The Cr–Cr bond length is shown to be a sensitive function of both the number of axial ligands present and the donor ability of the axial ligands. Each THF molecule in the axial position is shown to cause an ~0.18-Å increase in the length of the Cr–Cr bond. The Cr–Cr bond length is also seen to increase by about 0.12 Å upon replacing two axial THF ligands by two pyridine ligands. The basic crystallographic data on the five compounds are as follows. **1**: space group, *C2/c*; $a = 21.254$ (4) Å, $b = 10.990$ (2) Å, $c = 20.733$ (4) Å, $\beta = 110.64$ (2)°, $Z = 4$. **2**: *Pbcn*; $a = 16.775$ (2) Å, $b = 19.736$ (3) Å, $c = 19.739$ (2) Å, $Z = 4$. **3**: *Pbcn*; $a = 16.806$ (2) Å, $b = 19.311$ (3) Å, $c = 14.887$ (3) Å, $Z = 4$. **4**: *Pccn*; $a = 24.813$ (5) Å, $b = 13.408$ (3) Å, $c = 18.631$ (3) Å, $Z = 4$. **5**: $P2_1/n$; $a = 17.374$ (4) Å, $b = 12.836$ (4) Å, $c = 23.603$ (6) Å, $Z = 4$. These structures are then compared with those of some 30 other quadruply bonded dichromium compounds with bridging ligand chains of the types O–C–O, N–C–O, N–C–N, N–N–N, C–C–O, and C–P–C, and certain trends in the Cr–Cr distance as these ligand types are changed are noted.

Introduction

The chemistry of compounds containing quadruple metal-metal bonds has developed rapidly since the recognition of the existence of the first such bond.[1] With several of the elements that have shown a consistent tendency to form such bonds, particularly molybdenum and rhenium, the structural patterns are relatively simple. In these cases, the central Mo_2^{4+} and Re_2^{6+} units appear to be structurally rigid and the observed variation in the metal-metal bond distance is relatively small. For example, Mo-Mo quadruple bond lengths range from 2.037 (3) Å in $Mo_2[(C_5NH_4)NC(O)CH_3]_4$[2] to 2.183 (2) Å in $Mo_2(C_3H_5)_4$[3] and the known range of Re-Re quadruple bonds is from 2.178 (1) Å in $Re_2Me_8^{2-}$ [4] to about 2.24 Å in several $Re_2Cl_8^{2-}$ salts.[5] With chromium, however, the situation is more complicated.

Quadruply bonded dichromium(II) compounds exhibit a unique variability of the Cr–Cr bond length, covering a range of more than 0.7 Å. The shortest distance, 1.828 (2) Å, is found in Cr_2[5-methyl-2-methoxyphenyl]$_4$, and the longest, 2.541 (1) Å, is found in $Cr_2(O_2CCF_3)_4(Et_2O)_2$.[7] Apart from the species $[Cr_2R_8]^{4-}$ (R = CH_3 or $^1\!/_2C_4H_8$)[8] and $Cr_2(C_3H_5)_4$[9] which contain nonbridging ligands, the numerous examples of $Cr_2(X\text{–}Y\text{–}Z)_4$ compounds can be divided into two distinctly different groups: (1) First there are the tetracarboxylato compounds which have Cr–Cr distances ranging from 2.283 (2) to 2.541 (1) Å;[7,10,11] the related $[Cr_2(CO_3)_4]^{4-}$ ion has a slightly shorter distance, 2.214 (1) Å.[11] All of these molecules have been found to be either disolvated, in which the solvent molecules, L, occupy the axial positions, $Cr_2(O_2CR)_4L_2$, or to have a structure in which the $Cr_2(O_2CR)_4$ units are arranged in infinite chains with intermolecular O···Cr axial distances of 2.22–2.44 Å.[7] (2) Then there are the compounds with "supershort" bonds,[12] i.e., $d_{Cr\text{–}Cr} \leq 1.90$ Å. These can generally be characterized as having ligands derived from weak acids and usually have the axial positions blocked as a result of intramolecular steric hindrance.[13]

The rather long metal-metal distances in the carboxylato series have provoked considerable controversy concerning the Cr–Cr bond order.[14,15] One early report even claimed that in $Cr_2(O_2CCH_3)_4(H_2O)_2$ and other carboxylato compounds there is no Cr–Cr bond.[14a] This, however, has been conclusively refuted[14b,15] by a later ab initio calculation that suggests that the Cr–Cr bond should have its maximum strength at a distance of ca. 2.40 Å.[14b] Later studies on the carboxylate series $Cr_2(O_2CR)_4L_2$, concerned with examining the factors contributing to the Cr–Cr bond, have shown that the variations of the Cr–Cr bond distance in this series cannot be accounted for solely by postulating linear and independent dependencies on the inductive effect of the R groups and the distance of the axial ligands.[11] Recent investigations designed to examine

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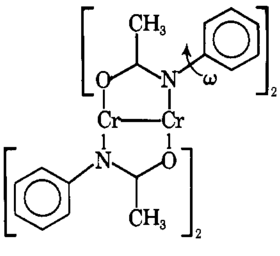
more fully the factors affecting the Cr-Cr bond length have reached a decisive stage with the synthesis and structural characterization of tetraacetanilidodichromium(II), $Cr_2[C_6H_5NC(O)CH_3]_4$.[12] The $PhNC(CH_3)O^-$ ligand is very similar to the acetate ion, $OC(CH_3)O^-$, the most conspicuous difference being the steric properties associated with the *N*-phenyl group that interfere with coordination of axial ligands under certain circumstances. This observation has led us to consider the possibility that the sharp dichotomy between the "supershort" and long Cr-Cr quadruple bonds is due primarily to the presence or absence of axial ligands, and thereby implying that an isolated $Cr_2(O_2CR)_4$ molecule should possess a Cr-Cr bond short enough to place it in the "supershort" category.[12] Experimental proof for this prediction still remains elusive. As a result, therefore, we have pursued another route in order to elucidate the role of axial coordination. It is evident from the ORTEP figure of $Cr_2[PhNC(O)CH_3]_4$[12] that the axial position is blocked because of the tilting of the phenyl ring with respect to the Cr_2NCO plane; the torsion angle ω is 48°. This observation led us to the conclusion that increasing this angle to $\omega = 90°$ would open up a "hole" in the axial position large enough to accommodate coordinating ligands. This would allow us, through substituting various axial ligands, to make a comparison between axially coordinated (or self-associated) or noncoordinated Cr_2^{4+} complexes of the same ligand type. This objective has been achieved by taking advantage of both steric and electronic factors: first, the introduction of two methyl groups into the 2 and 6 positions of the phenyl ring, which forces this ring to lie essentially perpendicular to the amide system because of steric interference; second, by introduction of the strongly donating $(CH_3)_2N$ group into the most sensitive 4 position of the aromatic ring. This also results in an increased torsional angle, because overlap between the now very electron-rich aromatic π system and the electron-rich amide anion system is disfavored. By the deliberate modification of the amidato ligands in the ways just described and with some good fortune in the choice of solvents and conditions of crystallization, we have succeeded in obtaining a number of compounds in which the number of axial ligands has been varied from zero to one to two, and in the case of two the identity of the ligand has been changed, all the while retaining the essential similarity of the four bridging amidato groups.



We report here the synthesis and crystal structures of four tetraamidatodichromium(II) compounds ($Cr_2[(4\text{-}Me_2N\text{-}C_6H_4)NC(O)CH_3]_4 \cdot THF$ (**1**). $Cr_2[(2,6\text{-xylyl})NC(O)CH_3]_4 \cdot 3THF$ (**2**), $Cr_2[(2,6\text{-xylyl})NC(O)CH_3]_4 \cdot THF$ $C_6H_5CH_3$ (**3**), and $Cr_2[PhNC(NHPh)O]_4 \cdot 2THF \cdot C_6H_{14}$ (**4**) having either one or two THF molecules in the axial positions) and of $Cr_2[(2,6\text{-xylyl})NC(O)CH_3]_4 \cdot 3NC_5H_5$ (**5**), which has pyridine molecules in the axial positions.

Experimental Section

p-(Dimethylamino)acetanilide was prepared from acetic anhydride and *N,N'*-dimethyl-*p*-phenylenediamine.[16a] It was recrystallized from ethanol-water and had a melting point of 130 °C. 2,6-Dimethylacetanilide was made from acetic anhydride and 2,6-xylidine.[16b] After recrystallization from ethanol the compound had the literature melting point at 176 °C. All manipulations were carried out under an atmosphere of dry argon.

Preparation of $Cr_2[(4\text{-}Me_2N\text{-}C_6H_4)NC(O)CH_3]_4 \cdot THF$ (1). A solution of 0.71 g (4 mM) of 4'-dimethylaminoacetanilide in 30 mL of THF was treated with 1 equiv of *n*-butyllithium in hexane to give the slightly soluble anion $[(4\text{-}Me_2N\text{-}C_6H_4)NC(O)CH_3]^-$. Dichromium tetraacetate (0.34 g, 1 mM) was then added and the mixture was stirred overnight. The orange solution, obtained after removal of amorphous lithium acetate, was slowly evaporated to dryness by a continuous flow of argon. Inspection of the resultant solid material under a microscope revealed a few crystals of sufficient size and quality for the structure determination.

Preparation of $Cr_2[(2,6\text{-xylyl})NC(O)CH_3]_4 \cdot 3THF$ (2). A solution of $Li[(2,6\text{-xylyl})NC(O)CH_3]$ was prepared by dissolving 0.65 g (4 mmol) of 2',6'-dimethylacetanilide in 25 mL of THF and adding the corresponding amount of *n*-butyllithium in hexane. The presence of any excess *n*-BuLi is indicated by the appearance of a yellow tint in the reaction mixture. Anhydrous dichromium tetraacetate (0.34 g, 1 mmol) was added to this solution, and the darkening solution was stirred for 16 h at room temperature. Subsequent filtration gave an orange-brown solution. Slow evaporation of this solution using a continuous flow of argon produced a good crop of air-sensitive crystals with dimensions up to 1 mm. Mass spectroscopy of this compound revealed strong coordination of the solvent molecules. The loss of THF was not completed until 90 °C at 10^{-6} Torr. At 300 °C the molecular ion was observed with *m/e* 752.251 664 for the principal isotopic species. The calculated value for $C_{40}H_{48}N_4O_4Cr_2$ is 752.248 540.

Preparation of $Cr_2[(2,6\text{-xylyl})NC(O)CH_3]_4 \cdot THF \cdot C_6H_5CH_3$ (3). The tritetrahydrofuranate **2**, $Cr_2[(2,6\text{-xylyl})NC(O)CH_3]_4 \cdot 3THF$, obtained by the above procedure, was transferred into an evacuation tube and a vacuum of 10^{-2} Torr was applied. After a short time of evacuation at room temperature the color of the substance had changed from brown to yellow. Heating to 90 °C caused a further color change to whitish-gray. This material was dissolved in toluene and a hexane layer allowed to diffuse slowly into the toluene solution. This procedure yielded well-shaped brown crystals of **3** suitable for X-ray diffraction.

Preparation of $Cr_2[PhNC(NHPh)O]_4 \cdot 2THF \cdot C_6H_{14}$ (4). A solution of 0.85 g (4 mM) of carbanilide (*N,N'*-diphenylurea) in 35 mL of THF was heated with 1 equiv of *n*-butyllithium to produce the monoanion $[PhNC(NHPh)O]^-$. Anhydrous chromium acetate (0.34 g, 1 mM) was added to the solution, and the solution was stirred for 16 h at room temperature. Subsequent filtering yielded a brownish filtrate. Subsequent diffusion of a hexane layer into this solution yielded a considerable amount of green material (probably Cr(III)), but also some brown crystals. These rather air-sensitive crystals were found to be suitable for X-ray analysis and were found to contain THF as well as hexane.

Preparation of $Cr_2[(2,6\text{-xylyl})NC(O)CH_3]_4 \cdot 3NC_5H_5$ (5). A sample of **2**, pumped and heated as described above, was dissolved in neat pyridine to give a red solution. Slow evaporation of this solution under vacuum afforded an air-sensitive precipitate which was found to contain a few crystals of rather poor quality which were used for X-ray analysis. Numerous attempts to grow crystals of better quality were unsuccessful.

X-ray Crystallography. Compounds 1, 2, 4, and 5. Crystals of the compounds were transferred under a stream of dry argon to a Petri dish containing degassed mineral oil. The crystals were then examined under a microscope and a suitable crystal was selected. The crystal was then transferred to a slide on which there was a drop of epoxy cement. The crystal was coated with the epoxy, sucked up into a thin glass capillary, and mounted on a Syntex P1 automatic diffractometer. Lattice constants were obtained by carefully centering 15 reflections in the range $20° < 2\theta < 32°$ selected to give varied crystal orientations. The procedures preliminary to data collection have been described previously.[17]

Intensity data were collected using Mo Kα ($\lambda = 0.710\,73$ Å) radiation monochromatized in the incident beam with a graphite crystal. Data were collected in the range $0° < 2\theta \leq 45°$ at 22 ± 4 °C using the θ-2θ scan technique. Variable scan rates, 4-24° min^{-1}, were used with a scan range of K$\alpha_1 - 1.0°$ to K$\alpha_2 + 1.0°$ and a scan to background time ratio of 2. The intensities of three standard reflections were measured after every 97 reflections as a check on crystal and electronic stability. The usual Lorentz and polarization corrections were applied but absorption corrections were omitted.[18] The positions of the chromium atoms were found by the application of the MULTAN direct methods procedure.[18] The remaining nonhydrogen atoms were found from successive Fourier and difference syntheses. Full-matrix anisotropic least-squares refinement of the chromium atoms and the

Table IA. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Cr_2[(4-Me_2N-C_6H_4)NC(O)CH_3]_4 \cdot THF$ (**1**)

atom	x	y	z	$B(1,1)$	$B(2,2)$	$B(3,3)$	$B(1,2)$	$B(1,3)$	$B(2,3)$
Cr(1)	0.0000(0)	0.5933(2)	0.2500(0)	3.44(9)	2.18(8)	3.49(9)	0	0.82(7)	0
Cr(2)	0.0000(0)	0.7759(2)	0.2500(0)	3.16(8)	2.16(8)	3.28(9)	0	0.80(7)	0
O(1)	0.0596(3)	0.5662(5)	0.1965(3)	4.2(3)	2.6(3)	4.3(3)	0.4(2)	2.1(2)	0.1(2)
O(2)	−0.0812(3)	0.7934(5)	0.1651(3)	3.6(3)	2.4(3)	3.6(3)	−0.2(2)	0.7(2)	−0.5(2)
O(3)	0.0000(0)	0.9897(7)	0.2500(0)	3.0(4)	2.4(3)	4.3(4)	0	0.2(3)	0
N(1)	0.0616(3)	0.7710(6)	0.1906(4)	3.3(3)	2.3(3)	3.8(3)	−0.0(3)	1.6(2)	0.1(3)
N(2)	−0.0827(3)	0.5905(6)	0.1609(4)	3.2(3)	2.1(3)	3.5(3)	−0.1(3)	0.6(3)	−0.2(3)
N(3)	−0.1877(4)	0.1344(8)	0.0454(4)	4.2(2)	atom	x	y	z	$B(1,1)$
N(4)	0.1425(5)	1.2172(9)	0.1062(5)	6.0(2)	C(11)	−0.1087(4)	0.6947(8)	0.1355(5)	3.4(2)
C(1)	0.0799(5)	0.6641(9)	0.1761(5)	3.8(2)	C(12)	−0.1710(5)	0.7063(10)	0.0712(6)	4.9(2)
C(2)	0.1267(6)	0.6469(11)	0.1341(6)	5.8(3)	C(13)	−0.1114(4)	0.4766(8)	0.1288(5)	3.1(2)
C(3)	0.0839(4)	0.8793(8)	0.1668(5)	3.4(2)	C(14)	−0.0846(5)	0.4159(9)	0.0865(5)	4.1(2)
C(4)	0.1466(5)	0.9276(10)	0.2029(6)	4.8(2)	C(15)	−0.1087(4)	0.3018(8)	0.0584(5)	3.5(2)
C(5)	0.1661(6)	1.0400(11)	0.1818(6)	5.8(3)	C(16)	−0.1632(4)	0.2483(8)	0.0729(4)	3.0(2)
C(6)	0.1232(5)	1.1033(10)	0.1269(5)	4.5(2)	C(17)	−0.1906(5)	0.3091(9)	0.1151(5)	4.0(2)
C(7)	0.0599(5)	1.0560(10)	0.0903(5)	4.5(2)	C(18)	−0.1649(5)	0.4232(9)	0.1439(5)	4.0(2)
C(8)	0.0406(5)	0.9416(9)	0.1114(5)	3.8(2)	C(19)	0.0544(5)	1.0652(9)	0.2958(5)	4.1(2)
C(9)	0.0887(8)	1.2914(15)	0.0619(9)	9.2(4)	C(20)	−0.1563(5)	0.0663(10)	0.0043(6)	4.6(2)
C(10)	0.1948(8)	1.2830(16)	0.1616(9)	9.3(4)	C(21)	−0.2335(5)	0.0672(10)	0.0719(6)	5.2(3)
					C(22)	0.0379(6)	1.1945(12)	0.2655(8)	7.2(3)

[a] The form of the anisotropic thermal parameter is $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Table IB. Bond Distances for $Cr_2[(4-Me_2N-C_6H_4)NC(O)CH_3]_4 \cdot THF$ (**1**)

atoms	distance, Å	atoms	distance, Å
Cr(1)-Cr(2)	2.006(2)	O(1)-C(1)	2.284(8)
-O(1)	1.979(4)	O(2)-C(11)	1.281(7)
-N(2)	2.053(6)	O(3)-C(19)	1.467(8)
Cr(2)-O(2)	1.993(4)	N(1)-C(1)	1.306(8)
-O(3)	2.350(6)	-C(3)	1.432(8)
-N(1)	2.090(5)	N(2)-C(11)	1.300(8)
		-C(13)	1.448(8)

Table IC. Bond Angles for $Cr_2[(4-Me_2N-C_6H_4)NC(O)CH_3]_4 \cdot THF$ (**1**)

atoms	angle, deg	atoms	angle, deg
Cr(2)-Cr(1)-O(1)	98.6(1)	O(3)-Cr(2)-N(1)	91.5(1)
-N(2)	90.9(1)	-O(2)	84.5(1)
O(1)-Cr(1)-O(1)′	162.7(2)	Cr(1)-O(1)-C(1)	114.5(4)
-N(2)	90.4(2)	Cr(2)-O(2)-C(11)	116.6(4)
N(2)-Cr(1)-N(2)′	178.3(3)	C(19)-O(3)-C(19)	111.1(7)
O(2)-Cr(2)-O(2)′	168.9(2)	Cr(2)-N(1)-C(1)	117.3(4)
-N(1)	90.6(2)	-C(3)	122.3(4)
N(1)-Cr(2)-N(1)	177.1(3)	Cr(1)-N(2)-C(11)	117.2(4)
Cr(1)-Cr(2)-O(3)	179.97(4)	-C(13)	121.0(4)

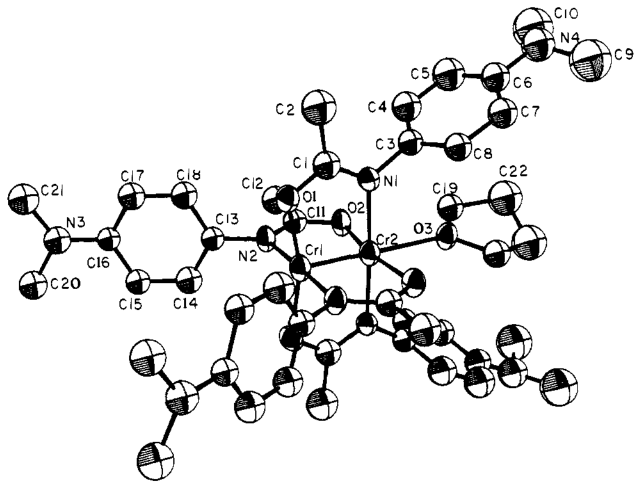


Figure 1. The molecular structure of compound **1**; each atom is represented by its ellipsoid of thermal vibration at the 50% probability level.

coordination sphere and isotropic refinement of the remaining nonhydrogen atoms yielded the crystallographic parameters shown in Table VI. The final discrepancy indices are defined by expressions

$$R_1 = (\sum||F_o| - |F_c||)/\sum|F_o|$$

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

The function $\sum w(|F_o| - |F_c|)^2$ was minimized with the weighting factor, w, equal to $4F_o^2/\sigma(F_o^2)^2$. Atomic scattering factors were these of Cromer and Waber.[19] Anomalous dispersion effects were also included for the chromium atoms.[20]

Compound 3. Crystals of this compound were transferred under a stream of dry argon to a Petri dish containing dry, degassed mineral oil, mounted in epoxy cement as already described and placed on an Enraf-Nonius CAD-4F automatic diffractometer. Intensity data were collected using Mo Kα radiation (λ = 0.710 73 Å) monochromatized by a graphic crystal in the incident beam. The takeoff angle of the X-ray tube was 2.80° and the temperature during data collection was 26 ± 2 °C. Twenty-five reflections in the range 12.5° < θ < 16° were located using the standard CAD-4 random automatic searching routine. These reflections were subsequently centered and used as the basis for the indexing, also using the standard CAD-4 indexing routine. The intensity data were collected in the range 0° < $2\theta \leq 45°$ with all reflections measured using an ω-2θ motion. The scan width for each reflection was measured with a preliminary scan rate of 20.12°/min. The scan rate for the final scan was calculated from the preliminary scan such that the ratio $I/\sigma(I)$ would be at least 20 and the maximum scan time would not exceed 30 s. If the preliminary scan gave $I/\sigma(I) > 20$, this measurement was used as the datum. The scan rates used varied from 20.12 to 2.51°/min. The width of the adjustable vertical aperture at the detector was given by (1.5 + tan θ) mm. The horizontal slit was 4 mm. Of the 96 steps in the profile scan, the first and last 16 steps were considered to be background. Intensities and standard deviations in the intensities were assigned as

$$I = [P - 2(B_1 + B_2)]S$$

$$\sigma I = [P + 4(B_1 + B_2)]^{1/2}S$$

where P is the gross peak intensity, B_1 and B_2 are the background intensities, and S is the scan rate. During data collection, three orientation standards as well as three intensity standards were measured every 100 reflections. The intensity standards showed no significant decrease throughout data collection. Lorentz and polarization corrections were applied, but no absorption correction was deemed necessary. The solution and refinement procedures were essentially those described above.

Table IIA. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Cr_2[(2,6\text{-xylyl})NC(O)CH_3]_4 \cdot 3THF$ (**2**)

atom	x	y	z	$B(1,1)$	$B(2,2)$	$B(3,3)$	$B(1,2)$	$B(1,3)$	$B(2,3)$
Cr(1)	0.0000(0)	0.2559(1)	0.2500(0)	2.8(1)	3.5(1)	3.6(1)	0	0.5(1)	0
Cr(2)	0.0000(0)	0.1434(1)	0.2500(0)	2.9(1)	3.6(1)	3.1(1)	0	0.1(1)	0
O(1)	−0.1100(4)	0.2600(4)	0.2010(5)	3.6(4)	3.7(4)	4.3(4)	−0.1(4)	0.7(4)	−0.4(4)
O(2)	0.0474(5)	0.1394(4)	0.1346(5)	3.7(4)	3.0(3)	3.3(4)	−0.1(3)	0.6(3)	0.5(3)
O(3)	0.0000(0)	0.0258(6)	0.2500(0)	4.7(3)					
O(4)	0.0000(0)	0.3734(6)	0.2500(0)	4.6(3)					
N(1)	−0.1167(6)	0.1454(5)	0.1951(6)	3.1(4)	3.7(4)	3.5(5)	0.1(4)	−0.6(4)	−0.3(4)
N(2)	0.0498(6)	0.2543(5)	0.1256(6)	3.9(5)	4.3(5)	3.1(5)	−0.3(4)	0.9(4)	1.1(4)
C(1)	−0.1469(7)	0.2053(6)	0.1827(7)	3.8(3)					
C(2)	−0.2308(8)	0.2152(7)	0.1411(9)	5.1(3)					
C(3)	−0.1584(7)	0.0848(6)	0.1723(8)	3.9(3)					
C(4)	−0.2059(9)	0.0536(7)	0.2315(9)	5.7(3)					
C(5)	−0.2424(9)	−0.0106(8)	0.2114(10)	6.7(4)					
C(6)	−0.2292(10)	−0.0377(8)	0.1357(10)	7.1(4)					
C(7)	−0.1856(9)	−0.0072(8)	0.0714(10)	6.6(4)					
C(8)	−0.1508(8)	0.0563(7)	0.0935(9)	4.9(3)					
C(9)	−0.2223(9)	0.0846(8)	0.3218(10)	6.3(4)					
C(10)	−0.1014(9)	0.0933(8)	0.0227(10)	6.0(4)					
C(11)	0.0624(7)	0.1942(6)	0.0941(8)	4.2(3)					
C(12)	0.1010(9)	0.1845(7)	0.0028(9)	5.4(3)					
C(13)	0.0705(8)	0.3136(7)	0.0794(8)	4.6(3)					
C(14)	0.1514(9)	0.3389(7)	0.0843(9)	5.2(3)					

atom	x	y	z	$B(1,1)$
C(15)	0.1705(9)	0.4006(8)	0.0394(9)	6.0(4)
C(16)	0.1124(10)	0.4319(8)	−0.0066(10)	7.2(4)
C(17)	0.0329(9)	0.4073(8)	−0.0136(10)	6.2(4)
C(18)	0.0137(8)	0.3472(6)	0.0281(9)	4.9(3)
C(19)	0.2157(9)	0.3019(8)	0.1338(9)	6.1(4)
C(20)	−0.0690(10)	0.3186(8)	0.0150(10)	6.5(4)
C(21)	0.0263(7)	−0.0148(7)	0.1777(9)	5.0(3)
C(22)	0.0186(14)	−0.0864(10)	0.2014(13)	11.7(7)
C(23)	−0.0662(9)	0.4156(7)	0.2242(9)	5.8(4)
C(24)	−0.0477(11)	0.4859(10)	0.2541(15)	10.5(6)
C(25)	0.5184(17)	0.2480(14)	0.3340(20)	6.1(7)
C(26)	0.4499(26)	0.2286(23)	0.3025(27)	11.2(13)
C(27)	0.4566(34)	0.1854(28)	0.3122(37)	16.3(19)
C(28)	0.5603(27)	0.1781(22)	0.2809(27)	11.2(13)
C(29)	0.5781(28)	0.2303(23)	0.2860(28)	11.9(14)

[a] The form of the anisotropic thermal parameter is $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Table IIB. Bond Distances for $Cr_2[(2,6\text{-xylyl})NC(O)CH_3]_4 \cdot 3THF$ (**2**)

atoms	distance, Å	atoms	distance, Å
Cr(1)-Cr(2)	2.221(3)	O(1)-C(1)	1.278(9)
-O(1)	2.001(6)	O(2)-C(11)	1.279(9)
-O(4)	2.318(9)	O(3)-C(21)	1.46(1)
-N(2)	2.129(7)	O(4)-C(23)	1.45(1)
Cr(2)-O(2)	1.984(6)	N(1)-C(1)	1.30(1)
-O(3)	2.321(8)	-C(3)	1.43(1)
-N(1)	2.141(7)	N(2)-C(11)	1.30(1)
		-C(13)	1.42(1)

Table IIC. Bond Angles for $Cr_2[(2,6\text{-xylyl})NC(O)CH_3]_4 \cdot 3THF$ (**2**)

atoms	angle, deg	atoms	angle, deg
Cr(2)-Cr(1)--O(1)	92.3(2)	O(2)-Cr(2)-O(2)′	175.5(3)
-O(4)	180.00(5)	-O(3)	87.7(2)
-N(2)	89.2(2)	-N(1)	89.8(2)
O(1)-Cr(1)-O(1)′	175.4(3)	O(3)-Cr(2)-N(1)	91.1(2)
-O(4)	87.7(2)	N(1)-Cr(2)-N(1)′	177.9(4)
-N(2)	90.4(2)	Cr(1)-O(1)-C(1)	120.0(6)
O(4)-Cr(1)-N(2)	90.8(2)	Cr(2)-O(2)-C(11)	120.1(6)
N(2)-Cr(1)-N(2)′	178.3(4)	Cr(2)-N(1)-C(1)	115.7(6)
Cr(1)-Cr(2)-O(2)	92.3(2)	-C(3)	122.2(6)
-O(3)	179.97(4)	C(1)-N(1)-C(3)	122.2(8)
-N(1)	88.9(2)	Cr(1)-N(2)-C(11)	115.2(6)
		-C(13)	123.7(6)
		C(11)-N(2)-C(13)	121.1(8)

Results

The tables and figures giving the results are numbered according to the compounds they describe. Thus, Tables IA-VA give the positional and thermal parameters for compounds **1-5**, and Tables IB-VB and IC-VC give those bond lengths and angles, respectively, that involve the Cr atoms and those atoms forming part of the coordination sphere. Tables including *all* bond lengths and angles are available as supplementary material. Each figure number (1-5) corresponds directly to the number assigned to the compound. The salient characteristics of each of the individual compounds will now be summarized.

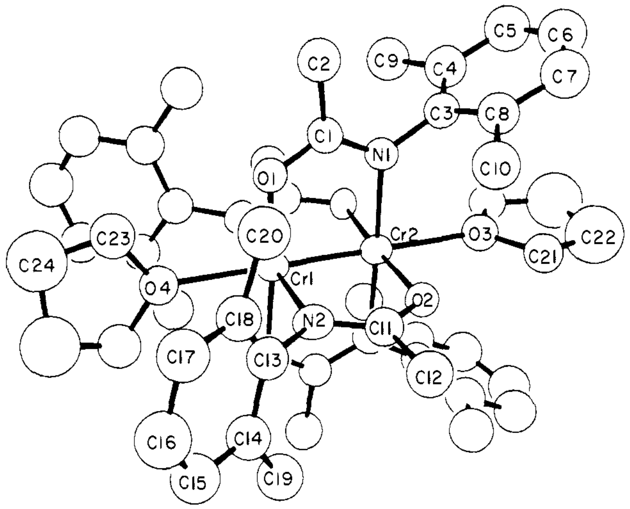


Figure 2. The molecular structure of compound **2**.

$Cr_2[(4\text{-}Me_2N\text{-}C_6H_4)NC(O)CH_3]_4 \cdot THF$ (1). The structure was solved in the space group *C*2/*c*. Each molecule resides on a crystallographic twofold axis coincident with the Cr-Cr bond. There is an axially coordinated THF molecule (Cr-O = 2.350 (6) Å) at one end only and the Cr-Cr distance is 2.006 (2) Å. The phenyl groups are approximately perpendicular to the O-Cr_2-N planes with the average dihedral angle between the O-Cr_2-N plane and the plane of the phenyl rings being 81.7°. Since the axial THF molecule lies on the C_2 axis, it is forced by symmetry to adopt the twist conformation as opposed to the half-chair conformation.

$Cr_2[(2,6\text{-xylyl})NC(O)CH_3]_4 \cdot 3THF$ (2). The structure was solved in the orthorhombic space group *Pbcn*. As in **1**, each molecule resides on a crystallographic C_2 axis of rotation coincident with the metal-metal bond. The Cr-Cr bond length is 2.221 (3) Å, and there is a THF molecule coordinated to each chromium atom at distances of 2.318 (9) and 2.321 (8) Å. The phenyl dihedral angle between the plane of the phenyl rings and the O-Cr_2-N planes is 88°. As in **1**, the axial THF molecules lie on the twofold axis and as a result adopt the twist

Table IIIA. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Cr_2[(2,6\text{-xylyl})NC(O)CH_3]_4\cdot THF\cdot C_6H_5CH_3$ (**3**)

atom	*x*	*y*	*z*	*B*(1,1)	*B*(2,2)	*B*(3,3)	*B*(1,2)	*B*(1,3)	*B*(2,3)
Cr(1)	0.5000(0)	0.24553(7)	0.2500(0)	2.54(6)	2.47(6)	2.31(6)	0	−0.12(6)	0
Cr(2)	0.5000(0)	0.35031(7)	0.2500(0)	2.66(6)	2.67(6)	2.75(6)	0	−0.31(7)	0
O(1)	0.5450(3)	0.3610(2)	0.1281(3)	3.7(2)	2.7(2)	2.9(2)	−0.4(2)	−0.2(2)	−0.0(2)
O(2)	0.6093(2)	0.2390(2)	0.3026(3)	3.0(2)	3.5(2)	2.9(2)	0.1(2)	−0.4(2)	−0.3(2)
O(3)	0.5000(0)	0.1256(3)	0.2500(0)	3.6(3)	2.7(2)	4.3(3)	0	0.3(3)	0
N(1)	0.5478(3)	0.2452(2)	0.1197(4)	3.5(3)	2.3(2)	2.3(2)	0.0(2)	0.1(2)	−0.1(2)
N(2)	0.6141(3)	0.3553(3)	0.3047(4)	3.0(2)	2.6(2)	2.9(3)	0.3(2)	−0.7(2)	0.0(2)
C(1)	0.5598(4)	0.3055(3)	0.0836(4)	3.1(3)	3.5(3)	2.8(3)	−0.8(3)	−0.2(3)	−0.3(3)
C(2)	0.5912(5)	0.3145(4)	−0.0123(5)	6.9(5)	4.4(4)	3.2(4)	−1.2(3)	1.7(3)	−0.0(3)
C(3)	0.5691(4)	0.1836(3)	0.0692(4)	4.6(3)	3.9(3)	1.8(3)	−0.6(3)	0.8(3)	−0.1(3)
C(4)	0.5136(4)	0.1514(4)	0.0168(5)	4.4(4)	4.4(3)	2.8(3)	−0.7(3)	0.3(3)	−1.2(3)
C(5)	0.5340(5)	0.0890(4)	−0.0277(6)	8.2(5)	5.6(4)	3.8(4)	−1.1(4)	1.7(4)	−1.3(4)
C(6)	0.6108(6)	0.0618(4)	−0.0199(6)	8.4(6)	5.5(4)	5.0(5)	−0.5(4)	1.4(5)	−1.2(4)
C(7)	0.6678(5)	0.0948(4)	0.0319(6)	6.9(5)	4.5(4)	4.4(4)	−0.7(4)	2.0(4)	−1.3(4)
C(8)	0.6462(4)	0.1589(4)	0.0763(5)	3.9(3)	4.4(4)	3.1(3)	0.3(3)	1.0(3)	0.1(3)
C(9)	0.7107(5)	0.1972(4)	0.1265(6)	3.9(3)	5.9(4)	5.7(5)	−0.1(4)	0.2(4)	−0.6(4)
C(10)	0.4317(5)	0.1805(4)	0.0025(6)	5.5(4)	6.6(4)	4.4(4)	−0.4(4)	−0.5(4)	−1.0(4)
C(11)	0.6466(4)	0.2954(3)	0.3212(5)	3.0(3)	3.7(3)	3.0(3)	−0.6(3)	−0.3(3)	−0.7(3)
C(12)	0.7284(4)	0.2861(4)	0.3634(6)	2.9(3)	4.2(4)	6.1(4)	0.0(3)	−2.0(3)	−0.5(4)
C(13)	0.6561(4)	0.4180(3)	0.3227(5)	2.1(3)	3.1(3)	4.7(4)	−0.5(3)	−1.3(3)	−0.4(3)
C(14)	0.7059(4)	0.4468(3)	0.2563(6)	3.5(3)	3.7(3)	6.0(4)	−0.8(3)	−1.4(4)	0.3(4)
C(15)	0.7402(5)	0.5124(4)	0.2700(7)	4.7(4)	5.3(4)	7.6(6)	−0.8(3)	−2.2(4)	0.1(4)
C(16)	0.7282(5)	0.5460(4)	0.3514(7)	5.8(5)	3.8(4)	10.9(7)	0.5(4)	−3.7(4)	−0.9(5)
C(17)	0.6832(5)	0.5161(4)	0.4199(6)	5.0(4)	4.9(4)	8.7(6)	0.4(3)	−2.3(4)	−1.6(4)
C(18)	0.6464(4)	0.4507(3)	0.4061(5)	3.9(3)	3.9(3)	5.1(4)	0.4(3)	−2.1(3)	−1.5(3)
C(19)	0.6004(5)	0.4194(5)	0.4823(6)	7.0(5)	8.1(5)	3.7(4)	−1.1(4)	0.2(4)	−1.3(4)
C(20)	0.7232(5)	0.4098(5)	0.1706(6)	7.9(5)	7.7(5)	4.3(4)	−3.1(4)	1.2(4)	−0.8(4)
C(21)	0.5672(4)	0.0822(3)	0.2773(6)	3.7(3)	2.5(3)	7.0(5)	1.2(3)	−1.2(3)	−0.1(3)
C(22)	0.4545(5)	0.0102(4)	0.2544(6)	5.7(4)	3.6(3)	6.8(5)	−0.3(3)	−0.8(5)	0.6(4)
C(23)	0.5000(0)	0.4467(9)	0.7500(0)	11.7(6)					
C(24)	0.5000(0)	0.3761(8)	0.7500(0)	8.2(4)					
C(25)	0.4297(7)	0.3346(5)	0.7664(7)	7.9(3)					
C(26)	0.4332(8)	0.2659(6)	0.7694(9)	9.9(3)					
C(27)	0.5000(0)	0.2236(10)	0.7500(0)	10.7(5)					

[a] The form of the anisotropic thermal parameter is $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Table IIIB. Bond Distances for $Cr_2[(2,6\text{-xylyl})NC(O)CH_3]_4\cdot THF\cdot CH_3C_6H_5$ (**3**)

atoms	distances, Å	atoms	distances, Å
Cr(1)-Cr(2)	2.023(1)	O(2)-C(11)	1.287(5)
-O(2)	2.000(3)	O(3)-C(21)	1.46(5)
-O(3)	2.315(4)	N(1)-C(1)	1.299(6)
-N(1)	2.099(4)	-C(3)	1.451(6)
Cr(2)-O(1)	1.977(3)	N(2)-C(11)	1.303(6)
-N(2)	2.086(4)	-C(13)	1.426(6)
O(1)-C(1)	1.283(5)	C(1)-C(2)	1.532(7)

Table IIIC. Bond Angles for $Cr_2[(2,6\text{-xylyl})NC(O)CH_3]_4\cdot THF\cdot CH_3C_6H_5$ (**3**)

atoms	angle, deg	atoms	angle, deg
Cr(2)-Cr(1)-O(2)	93.6(1)	Cr(2)-O(1)-C(1)	117.4(3)
-N(1)	90.2(1)	Cr(1)-O(2)-C(11)	118.6(3)
O(2)-Cr(1)-O(2)′	172.8(2)	C(21)-O(3)-C(21)	110.2(5)
-N(1)	90.6(2)	Cr(1)-N(1)-C(1)	116.0(3)
N(1)-Cr(1)-N(1)′	179.6(2)	-C(3)	125.2(3)
O(3)-Cr(1)-O(2)	86.4(1)	C(1)-N(1)-C(3)	118.8(4)
-N(1)	89.8(1)	Cr(2)-N(2)-C(11)	114.7(3)
Cr(1)-Cr(2)-O(1)	95.97(9)	-C(13)	124.6(3)
-N(2)	92.6(1)	C(11)-N(2)-C(13)	120.8(4)
O(1)-Cr(2)-O(1)′	168.1(2)	O(1)-C(1)-N(1)	120.3(5)
-N(2)	90.1(2)	-C(2)	117.0(4)
N(2)-Cr(2)-N(2)′	174.7(2)	N(1)-C(1)-C(2)	122.7(5)

conformation. The remaining THF molecule occupies a lattice position between the dimers. This THF molecule also resides on a twofold axis, but appears to be extremely disordered, and its exact location and orientation could not be determined. Since the position of this THF molecule is of little importance to us and repeated efforts to refine it failed, we decided to simply use the top five peaks that appeared in the difference map in this region of space in order to account for the electron density present. These positions, which were off the C_2 axis, were half-weighted and refined isotropically. Although the resulting positions made no sense chemically, they did help to lower the residuals. This type of extreme disordering of lattice THF molecules is not uncommon.

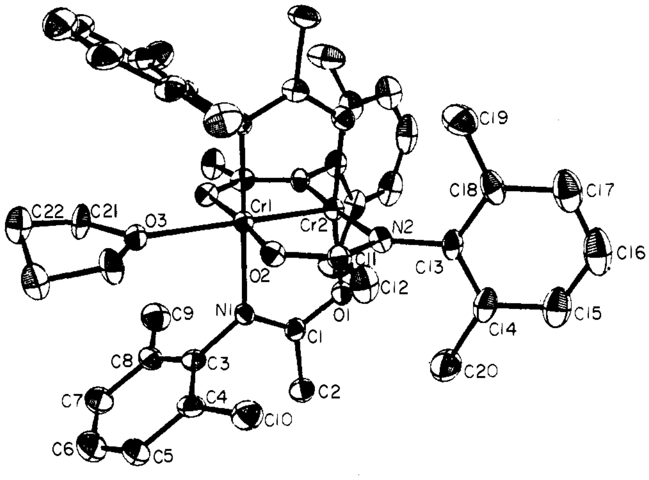


Figure 3. The molecular structure of compound **3**.

$Cr_2[(2,6\text{-xylyl})NC(O)CH_3]_4\cdot THF\cdot C_6H_5CH_3$ (3). This struc-

Table IVA. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Cr_2[PhNC(NHPh)O]_4{\cdot}2THF{\cdot}C_6H_{14}$ (**4**)

atom	*x*	*y*	*z*	*B*(1,1)	*B*(2,2)	*B*(3,3)	*B*(1,2)	*B*(1,3)	*B*(2,3)
Cr(1)	0.23320(6)	0.3278(1)	0.58298(9)	2.96(6)	2.70(6)	4.34(7)	0.26(6)	−0.02(9)	−0.09(9)
O(1)	0.1993(3)	0.4914(5)	0.5794(4)	5.0(4)	2.9(3)	6.2(4)	0.6(3)	−0.5(4)	−0.5(3)
O(2)	0.2868(3)	0.3794(5)	0.6533(4)	3.9(3)	3.3(3)	5.5(4)	0.3(3)	−1.7(3)	−0.0(3)
O(3)	0.3252(3)	0.2058(5)	0.5135(4)	4.0(3)	2.5(3)	4.4(4)	0.8(3)	0.5(3)	0.8(3)
N(1)	0.3175(3)	0.2199(5)	0.6660(5)	3.8(4)	2.4(4)	4.5(5)	0.2(3)	0.3(4)	−0.4(4)
N(2)	0.3554(4)	0.3508(6)	0.7338(5)	5.2(4)	2.8(4)	6.3(5)	−0.3(4)	−1.8(5)	−0.5(4)
N(3)	0.2870(3)	0.3575(6)	0.4992(5)	2.8(4)	2.6(3)	5.1(5)	1.0(3)	0.6(4)	0.6(4)
N(4)	0.3645(3)	0.3118(6)	0.4344(5)	3.5(4)	4.1(4)	4.4(5)	0.6(3)	0.9(4)	1.0(4)

atom	*x*	*y*	*z*	*B*(1,1)
C(2)	0.2238(5)	0.5769(10)	0.6160(7)	5.8(3)
C(3)	0.1820(7)	0.6619(12)	0.5994(9)	9.0(5)
C(4)	0.1549(6)	0.6326(10)	0.5292(7)	6.5(3)
C(5)	0.1510(5)	0.5181(9)	0.5389(6)	4.8(3)
C(6)	0.3188(4)	0.3173(8)	0.6822(6)	3.9(2)
C(7)	0.3572(4)	0.1510(7)	0.6931(6)	3.5(2)
C(8)	0.3400(5)	0.0772(8)	0.7384(6)	4.7(3)
C(9)	0.3783(5)	0.0026(10)	0.7619(7)	6.2(3)
C(10)	0.4308(6)	0.0085(10)	0.7374(7)	6.4(3)
C(11)	0.4482(5)	0.0851(10)	0.6935(8)	6.0(3)
C(12)	0.4103(4)	0.1583(8)	0.6703(6)	4.7(3)
C(13)	0.3658(4)	0.4516(8)	0.7523(6)	3.7(2)
C(14)	0.3876(5)	0.4693(9)	0.8198(7)	4.8(3)
C(15)	0.3998(5)	0.5677(10)	0.8397(7)	5.6(3)
C(16)	0.3913(5)	0.6470(9)	0.7955(7)	6.0(3)
C(17)	0.3700(6)	0.6283(11)	0.7276(8)	6.8(4)
C(18)	0.3563(5)	0.5293(10)	0.7038(7)	6.1(3)
C(19)	0.3245(4)	0.2906(7)	0.4844(6)	3.5(2)
C(20)	0.2893(4)	0.4519(8)	0.4625(6)	3.8(2)
C(21)	0.3275(5)	0.5231(9)	0.4849(7)	4.8(3)
C(22)	0.3282(6)	0.6187(11)	0.4481(8)	6.7(3)
C(23)	0.2924(6)	0.6367(11)	0.3937(8)	6.8(4)
C(24)	0.2538(6)	0.5686(11)	0.3721(8)	7.0(4)
C(25)	0.2517(5)	0.4708(8)	0.4087(6)	4.8(3)
C(26)	0.4132(4)	0.2598(7)	0.4246(6)	3.3(2)
C(27)	0.4333(4)	0.1878(8)	0.4713(6)	4.0(2)
C(28)	0.4844(5)	0.1435(9)	0.4543(7)	5.2(3)
C(29)	0.5113(5)	0.1674(10)	0.3930(7)	6.0(3)
C(30)	0.4921(5)	0.2398(10)	0.3463(7)	5.8(3)
C(31)	0.4414(5)	0.2867(9)	0.3604(7)	4.9(3)
C(32)	0.5164(10)	0.4639(18)	0.5126(16)	16.5(9)
C(33)	0.5194(11)	0.5644(23)	0.4217(15)	18.7(10)
C(34)	0.4880(16)	0.6386(29)	0.3951(22)	25.2(15)

[a] The form of the anisotropic thermal parameter is $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Table IVB. Bond Distances for $Cr_2[PhNC(NHPh)O]_4{\cdot}2THF{\cdot}C_6H_{14}$ (**4**)

atoms	distance, Å	atoms	distance, Å
Cr(1)-Cr(1)	2.246(2)	O(1)-C(2)	1.47(1)
-O(1)	2.350(5)	-C(5)	1.46(1)
-O(2)	1.992(5)	O(2)-C(6)	1.269(9)
-O(3)	1.995(5)	O(3)-C(19)	1.260(9)
-N(1)	2.094(7)	N(1)-C(6)	1.34(1)
-N(3)	2.092(6)	N(3)-C(19)	1.322(9)

Table IVC. Bond Angles for $Cr_2[PhNC(NHPh)O]_4{\cdot}2THF{\cdot}C_6H_{14}$ (**4**)

atoms	angle, deg	atoms	angle, deg
Cr(1)′-Cr(1)-O(1)	178.2(2)	N(1)-Cr(1)-N(3)	173.1(2)
-O(2)	94.3(2)	Cr(1)-O(1)-C(2)	124.6(5)
-O(3)	93.4(2)	-C(5)	122.5(4)
-N(1)	86.5(2)	C(2)-O(1)-C(5)	112.8(6)
-N(3)	86.6(2)	Cr(1)-O(2)-C(6)	117.9(5)
O(1)-Cr(1)-O(2)	86.2(2)	Cr(1)′-O(3)-C(19)	118.2(5)
-O(3)	86.1(2)	Cr(1)′-N(1)-C(6)	118.5(6)
-N(1)	95.2(2)	-C(7)	118.3(4)
-N(3)	91.7(2)	C(6)-N(1)-C(7)	122.0(7)
O(2)-Cr(1)-O(3)	172.2(2)	O(3)-C(19)-N(3)	122.1(8)
-N(1)	91.2(2)	Cr(1)-N(3)-C(19)	118.4(6)
-N(3)	90.0(2)	O(2)-C(6)-N(1)	122.0(8)
O(3)-Cr(1)-N(1)	88.5(2)	N(1)-C(6)-N(2)	118.9(8)
-N(3)	91.3(2)		

ture was similarly solved in the orthorhombic space group *Pbcn*. Each molecule again has a crystallographic twofold axis coincident with the metal–metal bond. The Cr–Cr bond length, 2.023 (1) Å, is nearly identical with that observed in **1** (i.e., 2.006 (2) Å). The structure is essentially identical with that of **2** except for the loss of one THF molecule from the axial position. As in **1** and **2**, the phenyl groups are approximately perpendicular to the O–Cr_2–N planes, the average dihedral angle being 88.3°. The axial THF molecule again adopts the twist configuration since it resides on the twofold axis. The toluene molecule also sits on the twofold axis occupying a position between the dimers.

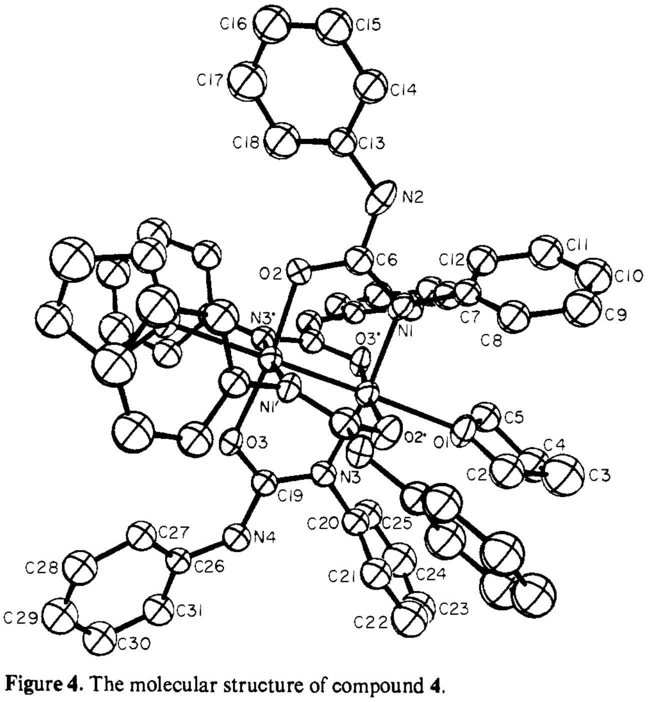


Figure 4. The molecular structure of compound **4**.

$Cr_2[PhNC(NHPh)O]_4{\cdot}2THF{\cdot}C_6H_{14}$ (4). The structure was solved in the orthorhombic space group *Pccn*. Each molecule resides on a twofold axis of symmetry, but in this case the twofold axis bisects the Cr–Cr bond and passes midway between the PhNC(NHPh)O ligands. As a result, the bridge atoms are not restricted by symmetry to an eclipsed configuration. They do, in fact, adopt a slightly staggered configuration, with a torsional angle of ca. 7.2° about the Cr–Cr bond. This is the first time such a twist has been observed in a quadruply bonded dichromium compound. The Cr–Cr bond length

Table VA. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Cr_2[(2,6\text{-xylyl})NC(O)CH_3]_4 \cdot 3NC_5H_5$ (**5**)

atom	*x*	*y*	*z*	*B*(1,1)	*B*(2,2)	*B*(3,3)	*B*(1,2)	*B*(1,3)	*B*(2,3)
Cr(1)	0.9872(2)	0.3061(3)	0.1606(2)	5.3(2)	2.0(2)	3.1(2)	−0.1(2)	−0.6(2)	0.1(2)
Cr(2)	0.9914(2)	0.4344(3)	0.2319(2)	5.2(2)	1.5(2)	3.9(2)	−0.2(2)	−0.6(2)	0.2(2)
O(1)	0.9795(9)	0.197(1)	0.2207(7)	4.9(4)					
O(2)	0.9939(9)	0.418(1)	0.1026(6)	4.5(4)					
O(3)	0.8758(9)	0.442(1)	0.2295(6)	4.2(4)					
O(4)	1.1031(8)	0.426(1)	0.2330(6)	3.6(4)					
N(1)	0.979(1)	0.308(2)	0.2913(8)	5.1(5)					
N(2)	0.998(1)	0.541(1)	0.1658(8)	3.8(5)					
N(3)	0.860(1)	0.322(2)	0.1618(8)	5.2(6)					
N(4)	1.111(1)	0.301(2)	0.1660(8)	5.2(6)					
N(5)	0.979(1)	0.182(2)	0.0902(9)	6.7(6)					
N(6)	0.998(1)	0.564(2)	0.3048(9)	5.2(5)					
C(1)	0.983(1)	0.211(2)	0.274(1)	4.5(7)					
C(2)	0.975(1)	0.117(2)	0.313(1)	4.4(7)					
C(3)	0.971(1)	0.328(2)	0.354(1)	4.2(6)					
C(4)	1.056(2)	0.335(2)	0.383(1)	7.5(9)					
C(5)	1.039(1)	0.361(2)	0.446(1)	4.8(7)					
C(6)	0.971(2)	0.386(2)	0.461(1)	6.2(8)					
C(7)	0.897(2)	0.364(3)	0.438(1)	9.0(10)					
C(8)	0.904(1)	0.343(2)	0.376(1)	5.0(7)					
C(9)	0.834(2)	0.325(3)	0.345(1)	8.7(10)					
C(10)	1.121(1)	0.323(2)	0.357(1)	5.2(7)					
C(11)	0.997(1)	0.519(2)	0.111(1)	4.8(7)					
C(12)	1.004(1)	0.586(2)	0.061(1)	5.2(7)					
C(13)	1.008(2)	0.659(2)	0.178(1)	6.7(9)					
C(14)	0.931(1)	0.708(2)	0.184(1)	5.6(7)					
C(15)	0.950(2)	0.821(3)	0.198(1)	10.7(11)					
C(16)	1.011(2)	0.860(3)	0.208(1)	8.6(10)					
C(17)	1.080(2)	0.810(3)	0.197(1)	10.2(11)					
C(18)	1.083(2)	0.695(2)	0.181(1)	6.8(8)					
C(19)	1.146(2)	0.643(3)	0.171(1)	8.4(10)					
C(20)	0.861(2)	0.673(2)	0.175(1)	6.8(8)					
C(21)	0.829(1)	0.389(2)	0.195(1)	4.1(6)					
C(22)	0.750(1)	0.408(2)	0.198(1)	4.9(7)					
C(23)	0.815(1)	0.266(2)	0.118(1)	4.7(7)					
C(24)	0.793(2)	0.160(3)	0.138(1)	9.2(10)					
C(25)	0.742(2)	0.105(3)	0.096(1)	8.8(10)					
C(26)	0.730(2)	0.152(2)	0.043(1)	6.9(9)					
C(27)	0.755(2)	0.245(3)	0.028(2)	10.8(12)					
C(28)	0.795(1)	0.311(2)	0.069(1)	5.2(7)					
C(29)	0.821(2)	0.422(3)	0.052(1)	7.7(9)					
C(30)	0.809(2)	0.121(2)	0.198(1)	7.3(9)					
C(31)	1.148(2)	0.366(2)	0.202(1)	5.5(7)					
C(32)	1.232(1)	0.374(2)	0.207(1)	5.4(7)					
C(33)	1.157(1)	0.232(2)	0.131(1)	5.3(7)					
C(34)	1.174(2)	0.257(2)	0.078(1)	7.7(9)					
C(35)	1.220(2)	0.186(3)	0.043(1)	11.2(12)					
C(36)	1.238(2)	0.087(3)	0.074(2)	10.5(11)					
C(37)	1.224(2)	0.063(3)	0.126(1)	9.8(11)					
C(38)	1.174(2)	0.132(3)	0.164(1)	8.1(9)					
C(39)	1.155(2)	0.109(2)	0.222(1)	7.9(9)					
C(40)	1.163(2)	0.364(3)	0.054(1)	9.3(10)					
C(41)	0.961(2)	0.207(3)	0.037(1)	7.6(9)					
C(42)	0.933(2)	0.135(3)	−0.005(1)	9.8(11)					
C(43)	0.912(2)	0.023(3)	0.009(2)	13.2(14)					
C(44)	0.929(2)	−0.001(3)	0.066(2)	12.3(13)					
C(45)	0.971(2)	0.074(3)	0.105(2)	10.8(12)					
C(46)	1.064(2)	0.595(2)	0.320(1)	7.1(9)					
C(47)	1.070(2)	0.689(3)	0.360(1)	9.4(10)					
C(48)	1.006(2)	0.731(3)	0.375(1)	9.2(10)					
C(49)	0.937(2)	0.706(3)	0.359(1)	10.3(11)					
C(50)	0.939(2)	0.602(3)	0.322(1)	7.9(10)					
C(51)	0.373(2)	0.468(3)	0.065(2)	12.8(13)					
C(52)	0.400(2)	0.568(3)	0.048(1)	10.2(11)					
C(53)	0.402(2)	0.585(3)	−0.005(1)	10.6(11)					
C(54)	0.394(2)	0.522(3)	−0.050(2)	13.9(14)					
C(55)	0.388(2)	0.417(3)	−0.032(2)	11.0(12)					
C(56)	0.370(2)	0.398(3)	0.024(2)	11.3(12)					

[a] The form of the anisotropic thermal parameter is $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Table VB. Bond Distances for $Cr_2[(2,6\text{-xylyl})NC(O)CH_3]_4 \cdot 3NC_5H_5$ (**5**)

atoms	distance, Å	atoms	distance, Å
Cr(1)-Cr(2)	2.354(5)	O(1)-C(1)	1.28(2)
-O(1)	2.00(1)	O(2)-C(11)	1.31(2)
-O(2)	1.99(1)	O(3)-C(21)	1.33(2)
-N(3)	2.21(2)	O(4)-C(31)	1.32(2)
-N(4)	2.15(2)	N(1)-C(1)	1.31(2)
-N(5)	2.31(2)	N(2)-C(11)	1.32(2)
Cr(2)-O(3)	2.01(1)	N(3)-C(21)	1.29(2)
-O(4)	1.94(1)	N(4)-C(31)	1.35(2)
-N(1)	2.16(2)	N(6)-C(46)	1.26(2)
-N(2)	2.08(2)	-C(50)	1.21(2)
-N(6)	2.40(2)		

Table VC. Bond Angles for $Cr_2[(2,6\text{-xylyl})NC(O)CH_3]_4 \cdot 3NC_5H_5$ (**5**)

atoms	angle, deg	atoms	angle, deg
Cr(2)-Cr(1)-O(1)	89.2(4)	O(4)-Cr(2)-N(1)	92.9(5)
-O(2)	89.2(4)	-N(2)	89.0(5)
-N(3)	87.0(4)	O(4)-Cr(2)-N(6)	89.4(6)
-N(4)	87.6(5)	N(1)-Cr(2)-N(2)	171.7(7)
-N(5)	178.3(5)	-N(6)	93.5(6)
O(1)-Cr(1)-O(2)	178.3(6)	N(2)-Cr(2)-N(6)	94.6(6)
-N(3)	88.9(5)	Cr(1)-O(1)-C(1)	126.7(1.4)
-N(4)	90.6(5)	Cr(1)-O(2)-C(11)	127.7(1.3)
-N(5)	91.2(6)	Cr(1)-O(3)-C(21)	126.7(1.2)
O(2)-Cr(1)-N(3)	90.5(5)	Cr(1)-O(4)-C(31)	128.4(1.3)
-N(4)	89.9(5)	Cr(2)-N(1)-C(1)	120.6(1.4)
-N(5)	90.3(6)	Cr(2)-N(2)-C(11)	126.5(1.4)
N(3)-Cr(1)-N(4)	174.7(7)	Cr(1)-N(3)-C(21)	120.0(1.4)
-N(5)	91.3(6)	Cr(1)-N(4)-C(31)	119.1(1.4)
N(4)-Cr(1)-N(5)	94.0(6)	Cr(1)-N(5)-C(41)	121.9(1.7)
Cr(1)-Cr(2)-O(3)	89.5(4)	O(1)-C(1)-N(1)	117(2)
-O(4)	89.5(4)	O(3)-C(21)-N(3)	117(2)
-N(1)	86.3(5)	O(1)-C(11)-N(2)	111(2)
-N(2)	85.7(4)	O(4)-C(31)-N(4)	115(2)
-N(6)	178.9(5)		
O(3)-Cr(2)-O(4)	179.0(5)		
-N(1)	87.1(5)		
-N(2)	90.8(5)		
-N(6)	91.6(6)		

is 2.246 (2) Å and the Cr-O_{ax} distances, which are required to be equal crystallographically, have lengths of 2.350 (6) Å.

As in the other compounds studied, the phenyl groups attached to the bridging nitrogen atoms are approximately perpendicular to the Cr-N-C plane, the average dihedral angle being 76.2°. The phenyl groups of the -NHPh group point away in each case from the phenyl group attached to the coordinated nitrogen atom within the same ligand, and are twisted away from the bridging *N*-phenyl group of the adjacent ligand to minimize steric repulsions between the two phenyl rings. Again, the axial THF ligands are observed to adopt the twist conformation. A molecule of what is believed to be hexane also occupies the free space between the dichromium molecules.

$Cr_2[(2,6\text{-xylyl})NC(O)CH_3]_4 \cdot 3NC_5H_5$ (5). This structure was solved in the monoclinic space group $P2_1/n$. The dinuclear molecules occupy general positions within the cell and as a

Table VI. Crystallographic Data

parameter	1	2	3	4	5
space group	*C*2/*c*	*Pbcn*	*Pbcn*	*Pccn*	*P*2$_1$/*n*
a, Å	21.254(4)	16.775(2)	16.806(2)	24.813(5)	17.374(4)
b, Å	10.990(2)	19.736(3)	19.311(3)	13.408(3)	12.836(4)
c, Å	20.733(4)	15.739(2)	14.887(3)	18.631(3)	23.603(6)
β, deg	110.64(2)	90.0	90.0	90.0	90.69(3)
$\alpha = \gamma$, deg	90.0	90.0	90.0	90.0	90.0
V, Å^3	4531.8(2.8)	5210.7(2.2)	4831.4(2.3)	6198.4(3.6)	5263.4(4.2)
d_x, g/cm^3	1.297	1.235	1.261	1.264	1.249
Z	4	4	4	4	4
formula wt	885.01	969.17	917.09	1179.37	990.15
crystal size, mm	0.30 × 0.25 × 0.30	0.50 × 0.50 × 0.50	0.40 × 0.40 × 0.40	0.30 × 0.30 × 0.50	0.30 × 0.25 × 0.30
μ, cm^{-1}	5.555	4.902	5.214	4.267	4.846
2θ range, deg	0-45	0-45	0-45	0-45	0-45
no. data, $F_o^2 > 3\sigma(F_o^2)$	1771	1422	1719	1811	1922 ($F_o^2 > 2\sigma(F_o^2)$)
no. of variables	148	167	264	205	283
R_1	0.083	0.088	0.061	0.083	0.125
R_2	0.111	0.114	0.082	0.104	0.133
esd	2.217	2.306	2.091	1.983	2.414

result have no crystallographically imposed symmetry. The Cr-Cr bond length of 2.354 (5) Å is comparable to the 2.369 (2) Å distance found in $Cr_2(O_2CCH_3)_4 \cdot 2NC_5H_5$.[21] This is the longest distance so far observed for N-C-O bridged compounds. The Cr-N_{ax} axial distances are 2.31 (2) and 2.40 (2) Å, respectively, and are quite comparable to the corresponding distances, 2.335 (5) and 2.308 (3) Å, in $Cr_2(O_2CCH_3)_4 \cdot 2NC_5H_5$[21] and $Cr_2(O_2CH)_4 \cdot 2NC_5H_5$,[7] respectively. The phenyl groups are rotated approximately perpendicular to the O-Cr_2-N plane; the average dihedral angle is approximately 88°. Owing to the poor quality of the crystal used, and the consequent lack of sufficient data to refine the structure adequately, the remaining heavy-atom positions are relatively imprecise. As a result, the associated distances and angles vary over a considerable range. Fortunately the metal-metal distance could be reliably determined, and is the only distance of importance to the arguments presented here anyway.

Discussion

Comparison of the Structures. The five structures reported in this paper together with that of $Cr_2(PhNC(O)CH_3)_4$ reported previously[12] display several interesting trends when compared, as they are in Table VII.

It should be noted that in all six compounds the essential geometry and symmetry of the central $Cr_2(RNC(O)R')_4$ unit is the same. The four ligands are so arranged that each chromium atom is bonded to two nitrogen atoms and two oxygen atoms and these are arranged in a trans manner. Thus, the central unit has idealized D_{2d} symmetry.

The most important trend is the increase in Cr-Cr distance as the number of axial ligands increases. This is shown by the results for the first five compounds in Table VII.

As noted before,[12] the $PhNC(O)CH_3^-$ ligand is very similar to a carboxyl group both sterically and electronically, but gives rise to a dichromium compound with a Cr-Cr distance enormously shorter than that in any $Cr_2(O_2CR)_4$ or $Cr_2(O_2CR)_4L_2$ compound. We have suggested that the main cause of this huge difference is the absence of axial coordination in the $PhNC(O)CH_3$ compound. Our new results provide striking and systematic evidence to confirm that suggestion. We have examined two compounds in which there is one coordinated ligand, THF, and find that these have Cr-Cr distances approximately 0.15 Å longer than that in $Cr_2(PhNC(O)CH_3)_4$. We then have two compounds in which there are two coordinated THF molecules, one at each end. In these the Cr-Cr distances are 0.35-0.38 Å greater than in $Cr_2(PhNC(O)CH_3)_4$.

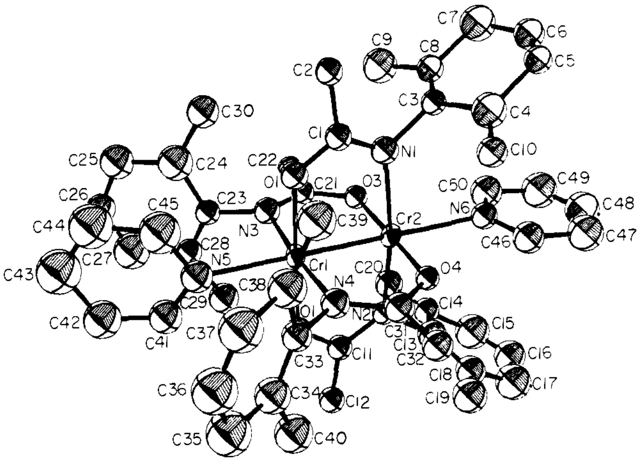


Figure 5. The molecular structure of compound 5.

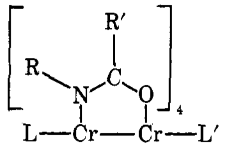
It is notable that the small changes in R in the first pair, and in both R and R′ in the second pair, are associated with only small differences in the Cr-Cr bond lengths. Two things seem clear: First, for a given type of bridging ligand, namely, $RNC(O)R'^-$, the Cr-Cr distance is very sensitive to the number of axial ligands but comparatively insensitive to changes in R and R′. Second, for a given axial ligand, namely, THF, the increase in the Cr-Cr distance is roughly linear in the number of axial ligands.

The second trend clearly shown in Table VII is that the more basic the axial ligands, the more they lengthen the Cr-Cr distance. For the compound with two axial pyridine ligands the Cr-Cr distance is about 0.12 Å greater than for the compounds in which the axial ligands are THF.

A third trend, which may be less important, but not unimportant, is that coordination of an axial ligand to a chromium atom increases the lengths of the bonds it forms to the four atoms of the bridging ligands. This increase can be seen not only in comparing molecules that have no axial ligands with those that have two, but in comparing one chromium atom with the other in those molecules that have an axial ligand at only one end. The increases in Cr-N and Cr-O distances upon introduction of the axial ligand are about 0.02-0.03 Å for the former and about 0.08 Å for the latter.

The axial ligands we have used in this work are practically pure σ donors. We would, therefore, expect that they affect the Cr-Cr quadruple bond primarily by introducing electrons into the d_{z^2}-$d_{z^2}\sigma^*$ component of that bond. This first-order effect

Table VII. Key Bond Distances (Å) in Dichromium Aminato Compounds



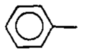
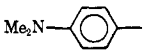
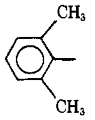
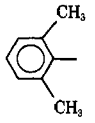
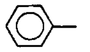
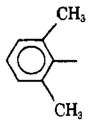
R	R'	L, L'	d_{Cr-Cr}	d_{Cr-L}	LCr-O	LCr-N	Cr-O	Cr-N
	CH_3	—, —	1.873(4)				1.97(1)	2.06(1)
	CH_3	THF, —	2.006(2)	2.350(6)	1.993(4)	2.090(5)	1.979(4)	2.053(6)
	CH_3	THF, —	2.023(1)	2.315(4)	2.000(3)	2.099(4)	1.977(3)	2.086(4)
	CH_3	THF, THF	2.221(3)	2.318(9) 2.321(8)	1.99(1)	2.135(7)		
	NHPh	THF, THF	2.246(2)	2.350(5)	1.994(4)	2.093(6)		
	CH_3	py, py	2.354(5)	2.31(2) 2.40(2)	2.00(1)	2.18(3)		

Figure 6. A plot of Cr–Cr quadruple bond distances (ordinate) for various types of bridging bidentate ligands. (ax) in columns 1 and 2 indicate that axial ligands are present. Compound numbers correspond to those in Table VIII.

could, of course, be accompanied by second-order effects stemming less directly from the addition of negative charge to the metal atoms. It is also to be expected that, just as the Cr–Cr σ bonding is weakened by donation into the main, outwardly projecting lobes of the d_{z^2} orbitals, so too would the metal-ligand σ bonding be weakened, and, as noted, this is also observed.

Comparisons with Other Cr–Cr Compounds. In a study of the dichromium(II) carboxylates, $Cr_2(O_2CR)_4 \cdot L_2$, a relation between the Cr–Cr bond length and the donor strength of the bridging ligand was proposed,[11] and it was suggested that the pK_α of the corresponding acid might be an appropriate measure of the donor strength of the bridging ligand.[11] On this basis weak acids yield strongly donating anionic ligands and strong acids weakly donating anionic ligands. Within the carboxylate series $Cr_2(O_2CCF_3)_4(Et_2O)_2$[7] contains the most weakly donating anion, $CF_3CO_2^-$, and has the longest Cr–Cr bond. There may well be a synergic effect here with the electron-withdrawing character of the CF_3 causing increased donation by the axial oxygen atoms of the Et_2O ligands. The

Table VIII. Summary of the Cr-Cr Bond Distances in Neutral Dichromium(II) Complexes[a]

compd	compd. no.	bridge type	d_{Cr-Cr}	ref
$Cr_2(O_2CCF_3)_4(Et_2O)_2$	**8**	O-C-O	2.541(1)	7
$Cr_3(O_2CH)_6(H_2O)_2$	**9**	O-C-O	2.451(1)	7
$Cr_2(O_2CH)_4(NC_5H_5)_2$	**10**	O-C-O	2.408(1)	7
$Cr_2(O_2CCMe_3)_4$	**11**	O-C-O	2.388(4)	7
$Cr_2(O_2CCH_3)_4(H_2O)_2$	**12**	O-C-O	2.3855(5)	32
$Cr_2(O_2CH)_4(H_2O)_2$	**13**	O-C-O	2.373(2)	35
$Cr_2(O_2CCH_3)_4(NC_5H_5)_2$	**14**	O-C-O	2.369(2)	21
$Cr_2(O_2CCH_3)_4(H_2O)_2$	**15**	O-C-O	2.362(1)	33
$Cr_2(O_2CH)_4(H_2O)_2$	**16**	O-C-O	2.360(2)	35
$Cr_2[(2,6\text{-xylyl})NC(O)CH_3]_4(NC_5H_5)_3$	**5**	N-C-O	2.354(5)	this work
$Cr_2(O_2CPh)_4(HO_2CPh)_2$	**17**	O-C-O	2.352(3)	7
$Cr_2(O_2CCH_3)_4(NC_5H_{11})_2$	**18**	O-C-O	2.342(2)	11
$Cr_2(O_2CC_{12}H_9)_4(THF)_2$	**19**	O-C-O	2.316(3)	30
$Cr_2(O_2CCH_3)_4(HO_2CCH_3)_2$	**20**	O-C-O	2.300(1)	11
$Cr_2(O_2CCH_3)_4(N_2C_4H_4)_2$	**21**	O-C-O	2.295(5(	12
$Cr_2(O_2CCH_3)_4$	**22**	O-C-O	2.288(2)	34
$Cr_2(O_2CC_{14}H_9)_4(DME)_2$	**23**	O-C-O	2.283(2)	7
$Cr_2[PhNC(NHPh)O]_4 \cdot 2THF \cdot C_6H_{14}$	**4**	N-C-O	2.246(2)	this work
$Cr_2[(2,6\text{-xylyl})NC(O)CH_3]_4 \cdot 3THF$	**2**	N-C-O	2.221(3)	this work
$[NH_4]_4[Cr_2(CO_3)_4(H_2O)_2](H_2O)_{1-2}$[b]	**24**	O-C-O	2.214(1)	11
$Cr_2[(2,6\text{-xylyl})NC(O)CH_3]_4 \cdot THF \cdot C_6H_5CH_3$	**3**	N-C-O	2.023(1)	this work
$Cr_2[(4\text{-}Me_2N\text{-}C_6H_4)NC(O)]_4 \cdot THF$	**1**	N-C-O	2.006(2)	this work
$Cr_2(chp)_4$	**25**	N-C-O	1.955(2)	31
$Cr_2(dmhp)_4 \cdot O_3C_6H_4$	**26**	N-C-O	1.907(3)	28
$Cr_2(mhp)_4 \cdot CH_2Cl_2$	**27**	N-C-O	1.898(3)	28
$Cr_2(mhp)_4 \cdot CH_2Cl_2$	**28**	N-C-O	1.889(1)	27
$Cr_2[CH_3C(O)NPh]_4$	**6**	N-C-O	1.873(7)	12
$Cr_2(map)_4 \cdot THF$	**29**	N-C-N	1.870(3)	25
$Cr_2(PhN_3Ph)_4$	**30**	N-N-N	1.858(1)	26
$Cr_2[2,4,6\text{-}(MeO)_3C_6H_2]_4$	**31**	C-C-O	1.849(2)	37
$Cr_2[2,6\text{-}(MeO)_2C_6H_3]_4$	**32**	C-C-O	1.847(2)	38
$Cr_2[(MeN)_2CPh]_4$	**33**	N-C-N	1.843(2)	24
$Li_6Cr_2(o\text{-}C_6H_4O)_4Br_2 \cdot 6(C_2H_5)_2O$	**34**	C-C-O	1.830(4)	36
$Cr_2(2\text{-}MeO\text{-}5Me\text{-}C_6H_3)_4$	**35**	C-C-O	1.828(2)	6
$Cr_2[(CH_2)_2P(CH_3)_2]_4$	**36**	C-P-C	1.895(3)	39

[a] Abbreviations used; Hchp = 2-hydroxo-6-chloropyridine; Hdmhp = 2,4-dimethyl-6-hydroxopyrimidine; Hmhp = 2-hydroxo-6-methylpyridine; Hmap = 2-amino-6-methylpyridine. [b] Though not a neutral complex, this is included here for completeness.

remaining carboxylato complexes have Cr-Cr bond lengths ranging from 2.28 to 2.41 Å[22] which are observed to be distributed roughly according to the pK_a of the corresponding acids, which range from 3.65 for anthracene-9-carboxylic acid to 5.03 for pivalic acid. The pK_a approximation does not explain every detail of the bond-length variations in the carboxylato series since there are different axial ligands present and steric factors such as those in the pivalato or 9-anthryl compounds obviously add further complications. On the other hand, the pK_a of HCO_3^- is 10.25 and accordingly the Cr-Cr bond length in the carbonato complex $[Cr_2(CO_3)_4(H_2O)_2]^{4-}$ was found to be significantly shorter, 2.214 (1) Å, than those in all the known carboxylato species.[11]

The idea that the donor strength of the bridging ligands may have a significant influence on the metal-metal bond length has led us to survey the large number of compounds with bridged Cr-Cr quadruple bonds. The results are tabulated in Table VIII and summarized in Figure 6; the numbers in Figure 6 are the compound numbers used in Table VIII. We have found that the compounds can be conveniently arranged in a sequence according to the ligand donor strengths. To a first approximation the donor strengths of the bridging ligands are likely to be mainly a function of the kind of atoms (i.e., C, N, or O) in the 1 and 3 positions of the bridge, with the acidity decreasing in the order OH > NH > CH and the donor strengths of the corresponding anions increasing in the order $O^- < N^- < C^-$. Figure 6 shows that the strongest donors (i.e., those derived from the very weak acids) are the *m*-dimethoxyphenyl (dmp) derivatives[6,13a,23] and these have the shortest M-M bonds. These derivatives have C-C-O bridges and have an average Cr-Cr distance of d_{Cr-Cr} = 1.838 Å. Complexes with the less basic N-C-N[24,25] (or N-N-N)[26] bridging group have somewhat longer Cr-Cr distances, d_{Cr-Cr} = 1.857 Å. The compound with the most basic *N,N'*-dialkylamidinato ligand, $[MeNC(Ph)NMe]^-$, has the shortest Cr-Cr bond length of this series, d_{Cr-Cr} = 1.843 (2) Å.[24] This distance is slightly shorter, even, than the Cr-Cr bond distance in the dmp complex, $Cr_2(dmp)_4$.[23] Compounds with N-C-O bridging ligands (without interference of axial ligands) have still longer Cr-Cr bond lengths, d_{Cr-Cr} = 1.892 Å. Ligands with N-C-O bridges are either of the amide[12] or the 2-hydroxypyridine[27,28] type, the pK_a of 2-hydroxypyridine being 11.62.[29] It is noteworthy that the ylido complex $Cr_2[(CH_2)_2P(CH_3)_2]_4$ can also be included in this series. The Cr-Cr bond length, d_{Cr-Cr} = 1.895 (2) Å, is very short and there is no axial coordination despite the absence of "blocking groups" in the axial position.

The sequence shown in Figure 6 prompts us to engage in a little speculation about the Cr-Cr bond length of an isolated tetracarboxylatodichromium(II), $Cr_2(O_2CR)_4$, molecule in the absence of axial interactions. It seems apparent, from the considerations above, that such a species would have d_{Cr-Cr} > 1.90 Å, but probably not larger than ~2.0 Å.

Another line of reasoning leading to a similar estimate is as follows. It we take compound 19 in Table VIII, which is the only carboxylato compound having axial THF ligands (the acid here is 2-phenylbenzoic acid) and deduct 0.35 Å from its Cr–Cr distance of 2.32 Å, we obtain a projected value of 1.97 Å for the $Cr_2(O_2CC_{12}H_9)_4$ molecule.

Returning to Figure 6 we observe that within any given ligand group the variation of the Cr–Cr bond due to electronic factors resulting from changes in the substituents on the ligands is relatively small. In the carboxylates these factors are somewhat enhanced by the fact that as the Cr–Cr bond gets longer it becomes more labile and, therefore, more sensitive to such changes as ligand substitution and axial ligand interactions. Overall, however, the effects are still relatively small compared to effects due to the axial ligands. The above is also true if we compare compounds having comparable axial ligands, such as $Cr_2[OC(R)O]_4{\cdot}L_2$ and $Cr_2[OC(R)NR]_4{\cdot}L_2$, where L = py and THF. Two carboxylato complexes with axial pyridine are known, the formate with $d_{Cr-Cr} = 2.408$ (2) Å[7] and the acetate with $d_{Cr-Cr} = 2.369$ (2) Å.[21] The latter is very similar in length to the 2.354 (5) Å distance reported here for $Cr_2[(2,6\text{-xylyl})NC(O)CH_3]_4{\cdot}3NC_5H_5$. With respect to THF the amide species **2** and **4** have $d_{Cr-Cr} = 2.221$ (3) and 2.246 (2) Å, respectively, whereas the comparable carboxylate $Cr_2(O_2CC_{12}H_{19}){\cdot}2THF$ has $d_{Cr-Cr} = 2.316$ (3) Å. Although the impact of electronic effects on the metal-metal bond appears to be small in comparison to the effect arising from axial coordination, this influence may be somewhat greater than previously supposed.[31]

Taken together, then, the results and conclusions presented above make it evident that the metal-metal bond lengths in Cr_2^{4+} compounds are affected by two important factors: the major one is the extent of axial coordination and a lesser one is the donor strength of the bridging ligands.

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Supplementary Material Available: Tables of observed and calculated structure factors for the five compounds and complete tables IB-VB and IC-VC giving all of the bond lengths and angles (56 pages). Ordering information is given on any current masthead page.

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