parameters (2 pages). Ordering information is given on any current masthead page.

References and Notes

(1) For recent reviews of compounds containing metal-to-metal multiple bonds, see F. A. Cotton, *Acc. Chem. Res.*, **11,** 225 (1978); M. H. Chisholm and F. A. Cotton, *ibid.*, **11,** 356 (1978); M. H. Chisholm, *Transition Met. Chem.*, (*Weinheim, Ger.*) **3,** 321 (1978).

(2) Potential catalytic implications of cluster chemistry have recently been discussed. See E. L. Muetterties, *Bull. Soc. Chim. Belg.*, **84,** 959 (1974); E. L. Muetterties, *Science*, **196,** 839 (1977); R. Ugo, *Catal. Rev.*, **11,** 225 (1975).

(3) For a classification of organometallic reactions, see C. A. Tolman *Chem. Soc. Rev.*, **1,** 337 (1972).

(4) M. H. Chisholm, F. A. Cotton, M. W. Extine, and B. R. Stults, *J. Am. Chem. Soc.*, **98,** 4477 (1976).

(5) Anal. Calcd: C, 29.93; H, 5.86. Found: C, 30.2; H, 5.96.

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(7) Cell constants: $a = 12.645$ (4), $b = 13.157$ (4), $c = 9.788$ (3) Å; $\alpha = 102.43$ (2), $\beta = 67.80$ (2), $\gamma = 101.05$ (2)°; $V = 1461.5$ (7) Å^3. The structure was solved in the centrosymmetric space group $P\bar{1}$. A total of 3782 unique data having $0° < 2\theta$ Mo Kα $< 45.0°$ were measured, of which those 2949 having $I > 3\sigma(I)$ were used in subsequent refinement. All atoms were refined to convergence utilizing anisotropic thermal parameters for the tungsten and oxygen atoms and isotropic thermal parameters for the carbon atoms. The final cycle of least-squares refinement, including the μ-H atoms, gave $R_1 = 0.037$ and $R_2 = 0.052$. A table of atomic positional and thermal parameters is available as supplementary material. See the paragraph at the end of the paper.

(8) We thank Professor Charles Gilvarg of the Department of Biochemistry Princeton University for his assistance and guidance in these experiments.

(9) This compound is obtained by reaction of $W_2(NMe_2)_6$ with Pr^{i}OH in pyridine; cf. M. Akiyama, M. H. Chisholm, F. A. Cotton, M. W. Extine, D. Little, and P. E. Fanwick, *Inorg. Chem.*, submitted for publication. The structure is analogous to that found for $Mo_2(OSiMe_3)_6(HNMe_2)_2$ by M. H. Chisholm, F. A. Cotton, M. W. Extine, and W. W. Reichert, *J. Am. Chem. Soc.*, **100,** 153 (1978).

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(12) A W═W bond with a length of 2.530 (2) Å has recently been reported by A. Bino, F. A. Cotton, Z. Dori, and J. C. Sekutowski, *Inorg. Chem.*, **17,** 2946 (1978). Re═Re bonds have long been known in $Re_3X_9L_3$-type compounds and have bond lengths of ~2.47 Å; cf. M. J. Bennett, F. A. Cotton, and B. M. Foxman, *Inorg. Chem.*, **7,** 1563 (1968), and earlier papers cited therein.

(13) We thank the Office of Naval Research and the National Science Foundation for support at Indiana and Princeton Universities and the Robert A. Welch Foundation for support at the Texas A&M University. M.H.C. was an Alfred P. Sloan Foundation Fellow, 1976–1978.

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The "Supershort" Chromium-to-Chromium Quadruple Bond: Its Occurrence in a Tetracarboxamidatodichromium(II) Compound

Sir:

Extensive studies on tetracarboxylatodichromium(II) compounds[1,2] have shown that they all have Cr-Cr distances in the range 2.29-2.53 Å.[3] The closely related $[Cr_2(CO_3)_4]^{4-}$ ion has a slightly shorter distance,[1c] 2.22 Å. These rather long distances have provoked controversy as to the Cr—Cr bond order.[4,5] On the other hand, there are a number of Cr_2 species in which the Cr—Cr distances are short enough that there has been no lack of agreement that they contain quadruple bonds. While two of these (with Cr—Cr distances in parentheses), namely, $[Cr_2(CH_3)_8]^{4-}$ (1.98 Å)[6] and $Cr_2(C_3H_5)_4$ (1.97 Å),[7] have been known for several years, they are so different, at least superficially, from the $Cr_2(O_2CR)_4$ type that their general significance is (or was) ambiguous. A distinct dichotomy was created with the discovery[8] of a series of compounds, beginning with **1**, of which those in Table I are representative. These contain ligands that are sterically and electronically similar to the carboxylato group, and yet they have vastly shorter Cr—Cr bonds, i.e., in a range ≤1.90 Å, which we informally designate *supershort*.[9]

Table I. Representative Dichromium(II) Compounds Having Supershort Bonds and Their Cr—Cr Bond Lengths

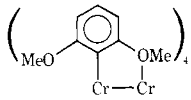
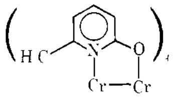
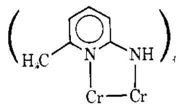
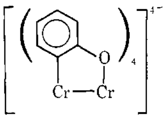
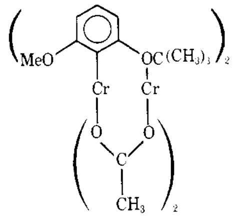
compd	no.	bond length, Å	ref
	**1**	1.85	8a
	**2**	1.89	8b
	**3**	1.87	8c
	**4**	1.83	8d
	**5**	1.86	8e

Table II. Some Bond Distances (Ångstroms) and Angles (Degrees) in $Cr_2[PhNC(CH_3)O]_4$

Cr—Cr	1.873 (7)	Cr′-Cr-O	98.0 (2)
Cr—N	2.06 (1)	Cr′-Cr-N	92.5 (3)
Cr—O	1.97 (1)		

Our attempts to identify the ligand properties responsible for the occurrence of supershort $\mathrm{Cr}\overset{4}{—}\mathrm{Cr}$ bonds have involved, inter alia, the following steps. (1) Compounds of type **2** (Table I) showed that the presence of Cr—C bonds is not critical, and compound **3** shows that Cr—O bonds are not essential. In short, no one type of ligand atom, C, N, or O, is critical. (2) Compound **5** showed that four noncarboxylato ligands are not necessary. (3) Compound **4** showed that it is not necessary for the Cr_2L_4 species to be a neutral molecule. (4) The one remaining common feature of all of the compounds in Table I with supershort $\mathrm{Cr}\overset{4}{—}\mathrm{Cr}$ bonds, namely, the incorporation of some ligand atoms in aromatic rings, was recently shown not to be essential by the discovery of supershort bonds in the compounds $Cr_2[(CH_2)_2P(CH_3)_2]_4$ (1.89 Å)[10] and $Cr_2(PhNNNPh)_4$ (1.86 Å).[11]

We report here a further crucial experimental step, perhaps the penultimate one, in achieving an understanding of what causes (or allows) the formation of supershort $\mathrm{Cr}\overset{4}{—}\mathrm{Cr}$ bonds. We have prepared the first carboxamido-bridged dichromium compound, viz., $Cr_2[RC(O)NR']_4$ with R = CH_3 and R′ =

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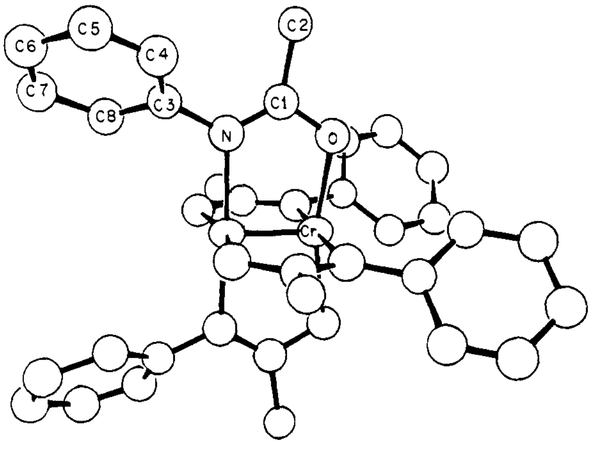

Figure 1. The structure of the $Cr_2[CH_3C(O)NPh]_4$ molecule. Some bond distances and angles are given in Table II.

C_6H_5, and determined its structure X-ray crystallographically.[12] The molecular structure is shown in Figure 1 and some important distances and angles are listed in Table II. The molecule has crystallographic $\bar{4}$ (S_4) symmetry, which means that there is only one crystallographically distinct ligand. The Cr—Cr distance, 1.873 (4) Å, is well down into the supershort range.

The occurrence of a supershort $Cr\overset{4}{—}Cr$ bond in a compound where the ligands are so similar to RCO_2 prompts the following observations. The most conspicuous difference between $CH_3C(O)NPh^-$ and $CH_3CO_2^-$ is the steric difference between PhN and O. The PhN groups make it impossible for the $Cr_2[CH_3C(O)PhN]_4$ to associate with each other through intermolecular O···Cr axial bonds, or to accommodate separate donor molecules as axial ligands, whereas *every* known tetracarboxylato Cr_2 molecule is either a disolvate with axial ligands, $Cr_2(O_2CR)_4L_2$, or has a structure in which the $Cr_2(O_2CR)_4$ molecules are arranged in infinite chains with intermolecular O···Cr axial distances of 2.22–2.44 Å. In nearly every other compound with a supershort $Cr\overset{4}{—}Cr$ bond the ligands prevent both axial coordination by separate donors or intermolecular association via axial bonds. In compound **4**, it is possible that, even if purely steric forces preclude axial coordination, the fact that the complex is very negatively charged renders it unattractive to donor molecules. This may also be true of the $[Cr_2(CH_3)_8]^{4-}$ ion. In any case, it is a fact that there *are no axial bonds* in *any* of the compounds with supershort bonds and there *are axial* bonds in *every one* of the compounds with Cr—Cr bonds as long as or longer than 2.22 Å.

We must, therefore, consider very seriously the possibility that the dichotomy of supershort and long $Cr\overset{4}{—}Cr$ bonds is due solely to the absence or presence of axial ligands. For $Mo\overset{4}{—}Mo$ and $Re\overset{4}{—}Re$ bonds it is known[13] that axial coordination causes slight lengthening of the bonds; it is likely that $Cr\overset{4}{—}Cr$ bonds are far more sensitive in this respect.

We feel that the electronic similarity of some ligands, especially $(PhN)OCCH_3^-$, to $O_2CCH_3^-$ is so great that the most crucial question about Cr_2^{4+} complexes is now set out in the starkest terms: Does the Cr—Cr quadruple bond length depend primarily upon nothing more than the presence or absence of axial ligands (which means that an isolated $Cr_2(O_2CR)_4$ molecule should have a Cr—Cr bond length ≤1.90 Å) or does a set of *four* O_2CR^- ligands have some special electronic property causing the Cr—Cr quadruple bond to be long and weak?

To answer this question, the ultimate experimental step must be to observe a $Cr_2(O_2CR)_4$ molecule in the absence of any significant axial bonding. There would appear to be only two practical ways to do this. One is to devise some kind of R group capable of suitably enshrouding the molecule; the other is to conduct an electron diffraction measurement of the Cr—Cr bond length in the gas phase. Both of these approaches are being actively pursued.

Should it turn out that the Cr—Cr bonds in $Cr_2(O_2CR)_4$ molecules free of axial bonds are supershort, the ab initio theoretical treatment of these substances will once again be in profound difficulties, since, after first predicting that no Cr—Cr bond exists,[4a] it currently asserts that such a bond has its maximum strength at a distance of ~2.40 Å.[4b]

Supplementary Material Available: Table of atomic positional and thermal parameters (1 page). Ordering information is given on any current masthead page.

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(2) The carbamato complex, $Cr_2(O_2CNEt_2)_4$, is also in this category: M. H. Chisholm, F. A. Cotton, M. W. Extine, and D. C. Rideout, *Inorg. Chem.*, **17,** 3536 (1978).

(3) Although virtually all the Cr—Cr distances pertinent to this discussion are known to within a few 0.001 Å, we shall state them all to only the nearest 0.01 Å since this conveys all the accuracy necessary in the present context.

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(9) The choice of 1.90 Å as a line of demarcation, though somewhat arbitrary, is not entirely so. For one thing, it does in fact constitute that approximate upper limit of bond lengths in all of the compounds that we wish to deal with. For another, a distance of ~1.90 Å (actually 1.89 Å to be exact) corresponds to the formal shortness ratio[8a] of 0.80, below which no metal–metal bonds (or *any others* save N≡N and C≡C) except these particular Cr—Cr bonds have ever been observed.

(10) F. A. Cotton, B. E. Hanson, and G. W. Rice, *Angew. Chem.*, **90,** 1015 (1978).

(11) F. A. Cotton, G. W. Rice, and J. C. Sekutowski, *Inorg. Chem.*, **18,** 1143 (1979).

(12) This yellow compound crystallizes in space group $I\bar{4}$ with $a = 12.724$ (3) Å, $c = 9.253$ (2) Å and $Z = 2$. The structure was solved and refined straightforwardly by conventional Patterson and Fourier methods. A detailed report will be published later. A table of atomic positional and thermal parameters is available as supplementary material. See the paragraph at the end of the paper.

(13) F. A. Cotton and W. T. Hall, *Inorg. Chem.*, **16,** 1867 (1977).

(14) (a) We thank the National Science Foundation for financial support. (b) W.K. is the holder of a Liebig stipend from the Verband der Chemischen Industrie.

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