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Tetrakis-(2,4,6-trimethoxyphenyl)dichromium. A Homologous New Compound with an Exceedingly Short Bond

F. A. COTTON and M. MILLAR

Department of Chemistry, Texas A&M University, College Station, Texas 77843, USA

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We recently described the discovery and characterization of a compound, tetrakis-(2,6-dimethoxyphenyl)dichromium, $Cr_2(DMP)_4$, containing by far the shortest metal-to-metal bond, 1.847(1) Å known [1]. This is, in fact, the shortest of all homonuclear bonds in proportion to the size of the atoms involved as gauged by the Pauling R_1 radii. We considered it important to investigate the homogolous compound, $Cr_2[2,4,6\text{-}(MeO)_3C_6H_2]_4$, $Cr_2(TMP)_4$, for several reasons. One was simply to show the generality of the previous result provided that the essential 2,6-dimethoxyphenyl unit is present, and another was to see if the Cr–Cr bond would show sensitivity to a marked change in the π inductive character of the ligand. The 2,4,6-trimethoxyphenyl group is uniquely suited for this because (a) all ring positions available for lithiation are equivalent so that only one $(MeO)_3C_6H_2Li$ reagent can be formed, and (b) in the *para* position H is replaced by MeO which has fairly large negative σ_p and σ_p^+ values [2].

The 2,4,6-trimethoxyphenyl lithium reagent was prepared as described in the literature [3]. $Cr_2(TMP)_4$ was prepared in essentially the same way as $Cr_2(DMP)_4$ and has comparable physical and chemical properties.

It crystallizes in the monoclinic space group $P2_1/n$ with Z = 2 and the following cell dimensions: a = 11.075(3) Å, b = 14.279(3) Å, c = 11.748(2) Å, β = 91.07(2)°, V = 1857.6(7) Å^3.

Data were collected using MoKα radiation on a Syntex P$\bar{1}$ diffractometer. All computations were done on the PDP 11/45 computer at the Molecular Structure Corporation, College Station, Texas, using the Enraf–Nonius Structure determination package of Frenz and Okaya.

The structure was refined using those 1698 reflections in the range $0° < 2\theta \leqslant 45°$ for which $I > 3\sigma(I)$. The coordinates of the chromium atoms were located from a three dimensional Patterson map. A difference Fourier map revealed the positions of all the remaining non-hydrogen atoms. Final anisotropic refinement of all atoms excluding the methoxy carbon atoms gave residuals of R_1 = 0.066 and R_2 = 0.091.

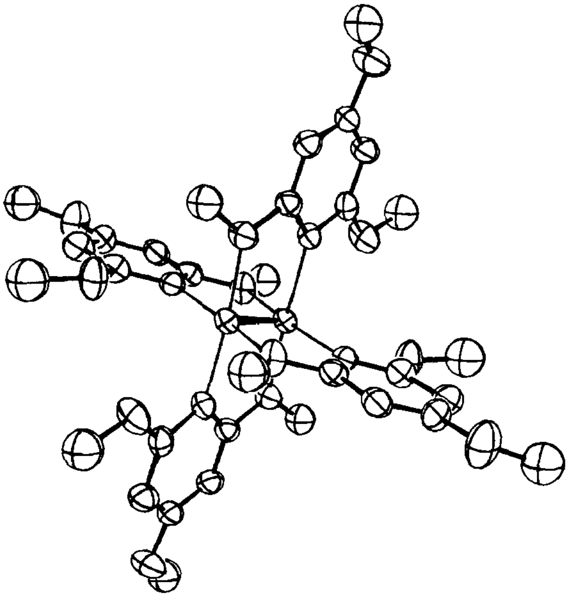

Fig. 1. An ORTEP view of $Cr_2(TMP)_4$. Each atom is represented by its ellipsoid of thermal vibration scaled to enclose 50% of the electron density.

TABLE I. Some Important Bond Lengths (Å) and Angles (Deg) in $Cr_2(TMP)_4$.

Cr–Cr	1.849(2)[a]	Cr–Cr–C	91.0 ± 0.3
Cr–C	2.061 ± 0.006[b]	Cr–Cr–O	101.8 ± 0.8
Cr–O	2.128 ± 0.001	Cr–Cr–C	93.1(2)
		C–Cr–O	166.2 ± 0.2
		C–Cr–O	91.2 ± 1.0
		O–Cr–O	81.8(2)

[a] Parentheses enclose esd's for unique parameters. [b] Error intervals are mean deviations from the mean obtained by averaging over several crystallographically independent values.

The structure is shown in Figure 1; some pertinent bond distances are listed in Table I. The centrosymmetric $Cr_2(TMP)_4$ dimer is structurally similar to the $Cr_2(DMP)_4$ complex. While the only crystallographic element of symmetry is the center of inversion at the midpoint of the Cr–Cr bond, the molecule has symmetry approximating very closely to $C_{2h}(2/m)$.

The Cr–Cr distance of 1.849(2) in $Cr(TMP)_4$ does not differ significantly from the corresponding distance in $Cr_2(DMP)_4$. This very short Cr–Cr distance is apparently unaffected by the change in the phenyl substituents. This result contrasts with the substantial variation in Cr–Cr distance observed in several $Cr_2(O_2CR)_4$ with R = H, CH_3, CF_3 [4].

The structure reported here confirms the existence of very short Cr–Cr quadruple bonds. The structural and electronic factors associated with and responsible for these exceedingly short metal–metal bonds are under active investigation.

References

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