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Rational Preparation and Structural Study of a Dichromium *o*-Oxyphenyl Compound: The Shortest Metal-to-Metal Bond Yet Observed

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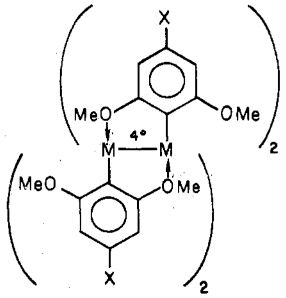
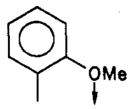
The compound $Li_6Cr_2(o\text{-}C_6H_4O)_4Br_2\cdot 6(C_2H_5)_2O$ has been prepared from $Cr_2(O_2CCH_3)_4$ and $Li_2C_6H_4O$ in diethyl ether by a method in which the formation of the extremely insoluble $Li_4Cr_2(o\text{-}C_6H_4O)_4\cdot 4(C_2H_5)_2O$ is avoided through addition of the stoichiometric quantity of LiBr to the reaction mixture. Soxhlet extraction then allows isolation of the crystalline compound, whose structure has been determined by X-ray crystallography to reveal the presence of $Cr_2(o\text{-}C_6H_4O)_4$ anions loosely associated with bromide ions. The Cr–Cr distance is 1.830 (4) Å which is shorter at the 99% confidence level than the shortest previously observed Cr–Cr bond, 1.847 (1) Å, in $Cr_2[2,6\text{-}(MeO)_2C_6H_4]_4$. The compound crystallizes in space group $C2/c$ with $a = 21.637$ (5) Å, $b = 14.734$ (3) Å, $c = 19.039$ (4) Å, $\beta = 73.33$ (2)°, and $Z = 4$. The structure was refined to $R_1 = 0.072$ and $R_2 = 0.090$ using 1548 reflections with $I > 3\sigma(I)$.

Introduction

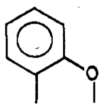
Our recent discovery[1-3] that compounds of the type I contain exceedingly short quadruple bonds between the metal atoms caused us to take an interest in the compounds, reported a few years earlier by Hein and Tille,[4] containing the related ligands II and III.



Ia:[1] M = M′ = Cr, X = H
Ib:[1] M = M′ = Mo, X = H
Ic:[2] M = M′ = Cr, X = OMe
Id:[3] M = Cr, M′ = Mo, X = H



II



III

The only chromium(II) compound containing ligand II that has been reported is $Cr_2(C_6H_4OMe)_4$. This was described[5,6] by Hein and Tille as a yellow, pyrophoric, microcrystalline solid, insoluble in all common solvents but slowly hydrolyzed by alcohol. The preparation and general properties of this rather intractable compound were subsequently confirmed by Sneeden and Zeiss.[7] We have also prepared this compound and find it to be as previously described. Efforts to obtain crystals suitable for structure analysis have so far failed.

Hein and Tille[5] also reported that from the reaction of lithium 2-lithiophenoxide, $Li_2C_6H_4O$, with $CrCl_3$ in 3.3/1 mol ratio they isolated a yellow-orange product of composition $Li_2Cr(C_6H_4O)_2\cdot LiBr\cdot 3(C_2H_5)_2O$. No comment or explanatory statement about the presence of bromine in the product was made. We presume that it was unintentionally introduced into the reaction mixture during the preparation of the $Li_2C_6H_4O$ reagent from $o\text{-}C_6H_4OH$ by lithiation with butyllithium, the latter having carried over bromine from its own precursor, butyl bromide. Whether Hein and Tille considered this so obvious as to require no comment we do not know. Contamination of the butyllithium reagent with LiBr does appear to have been a normal occurrence at that time.

Experimental Section

Preparation. All manipulations were conducted in an atmosphere of dry nitrogen. Lithium 2-lithiophenoxide, $Li_2C_6H_4O$, was prepared by the reaction of *o*-bromophenol with *n*-butyllithium (1.6 M in hexane).[8] LiBr was generated by the reaction of 1,2-dibromoethane with *n*-butyllithium.

Anhydrous chromium(II) acetate, $Cr_2(O_2CCH_3)_4$ (2.45 g, 7.25 mmol), was allowed to react with $Li_2C_6H_4O$ (29 mmol) and LiBr (1.26 g, 14.5 mmol) in 200 mL of diethyl ether. After being stirred for 12 h at room temperature, the reaction mixture was filtered. Repeated extraction of the solid residue in a Soxhlet apparatus with diethyl ether gave a yellow-orange crystalline product in about 25% yield.

Determination of Structure. A crystal with approximate dimensions 0.4 × 0.3 × 0.4 mm was placed in a capillary with epoxy cement. This was mounted on a Syntex $P\bar{1}$ automated diffractometer. Preliminary examination showed that the crystal belonged to the monoclinic system with cell dimensions $a = 21.637$ (5) Å, $b = 14.734$ (3) Å, $c = 19.039$ (4) Å, $\beta = 73.33$ (2)°, and $V = 5814$ (3) Å^3. The volume is consistent with the presence of four formula units, with mol wt = 1106.42 and $d_{calcd} = 1.26$ g cm^{-3}. Systematic absences were those for the space group $C2/c$ (No. 15).

Using molybdenum Kα radiation (λ 0.710 730 Å) with a graphite monochromator in the incident beam, data were collected at 22 ± 2 °C using the θ–2θ scan technique. Scans ranged from 1° above to 1° below the Kα_1, Kα_2 doublet, scan speeds ranged from 4.0° to 24.0°/min, and the scan to background time ratio was 0.5. The intensities of three standard reflections were monitored at regular intervals and showed only acceptably small random variations. The data in the range $0 < 2\theta \leq 45°$ were reduced[9] to $|F_o|^2$ values and those 1548 reflections with values greater than $3\sigma(|F_o|^2)$, where σ is based on counting statistics, were retained as observed and used to solve and refine the structure.[9] Absorption corrections were omitted ($\mu = 19.1$ cm^{-1}).

The chromium and bromine atoms were located using the Patterson function and all remaining atoms were then found by a sequence of refinement and difference map steps. In the final stages of refinement the Cr, Br, and phenoxy atoms were treated anisotropically while all others were treated isotropically. The final discrepancy indices were $R_1 = 0.072$ and $R_2 = 0.090$. The highest peak in a final difference map had an amplitude of 1.0 e/Å^3 and was so located as to have no evident structural significance. The vibrational amplitudes of several atoms in the ether molecules are quite large but we could not see any evidence that these atoms were actually disordered.

A list of the observed and calculated structure factors is available as supplementary material.

Results

Synthetic. The reaction of dichromium tetraacetate with lithium 2-lithiophenoxide in diethyl ether gives an insoluble yellow powder which we presume to be $Li_4Cr_2(2\text{-oxyphenyl})_4\cdot n\mathrm{Et_2O}$. The addition of LiBr to the reaction mixture increases the solubility of the product to the extent that it can be recrystallized by Soxhlet extraction. The yellow-orange crystalline product, $Li_6Cr_2(2\text{-oxyphenyl})_4Br_2(Et_2O)_6$, is apparently the same product previously reported by Hein and Tille.[5] Presumably, the addition of LiBr serves to disrupt some intermolecular bonding to give the more soluble material in which the individual dinuclear units are kept apart by the bromide ions.

Structural. The atomic positional coordinates and thermal vibrational parameters are listed in Table I. Interatomic distances and angles involving Cr or Li atoms are listed in Table II, while distances and angles within the ligands are given in Table III. The structure is illustrated in Figures 1

Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br(1)	0.18513 (9)	−0.0142 (1)	0.4862 (1)	0.00383 (5)	0.0062 (1)	0.00521 (7)	−0.0018 (1)	−0.00304 (9)	−0.0008 (2)
Cr(1)	0.2360 (1)	0.1938 (2)	0.4910 (1)	0.00192 (5)	0.0051 (1)	0.00224 (7)	−0.0003 (2)	−0.0006 (1)	0.0001 (2)
O(11)	0.1586 (4)	0.1703 (6)	0.5833 (4)	0.0020 (2)	0.0057 (6)	0.0023 (3)	0.0001 (7)	−0.0005 (4)	−0.0006 (8)
O(21)	0.2888 (4)	0.1094 (6)	0.5414 (5)	0.0027 (3)	0.0051 (6)	0.0031 (3)	0.0009 (7)	−0.0017 (5)	0.0012 (8)

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
O(31)	0.0176 (6)	0.1042 (9)	0.5641 (7)	9.6 (4)	O(51)	0.1982 (6)	0.0048 (9)	0.6945 (7)	9.7 (4)
O(41)	0.3712 (6)	−0.0631 (10)	0.4284 (7)	9.9 (4)					

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(11)	0.1928 (6)	0.3212 (9)	0.6085 (7)	0.0026 (4)	0.0047 (9)	0.0025 (5)	0.0004 (10)	−0.0018 (7)	0.001 (1)
C(12)	0.1481 (7)	0.2459 (11)	0.6281 (7)	0.0023 (4)	0.0075 (10)	0.0022 (5)	0.0004 (11)	−0.0011 (7)	0.001 (1)
C(13)	0.0947 (7)	0.2482 (12)	0.6922 (7)	0.0023 (4)	0.0088 (11)	0.0021 (5)	−0.0005 (12)	−0.0005 (8)	0.002 (1)
C(14)	0.0872 (8)	0.3243 (12)	0.7389 (8)	0.0043 (5)	0.0098 (13)	0.0021 (5)	0.0046 (15)	−0.0017 (8)	−0.003 (1)
C(15)	0.1344 (8)	0.3956 (11)	0.7231 (9)	0.0037 (5)	0.0056 (10)	0.0061 (7)	−0.0008 (13)	−0.0032 (10)	−0.000 (2)
C(16)	0.3148 (7)	0.1088 (11)	0.3421 (8)	0.0028 (4)	0.0085 (11)	0.0024 (5)	0.0040 (12)	−0.0010 (7)	−0.002 (1)
C(21)	0.3258 (6)	0.2554 (9)	0.5650 (7)	0.0014 (4)	0.0033 (8)	0.0029 (5)	0.0009 (9)	0.0003 (7)	0.000 (1)
C(22)	0.3280 (6)	0.1632 (10)	0.5732 (7)	0.0019 (4)	0.0060 (9)	0.0033 (5)	0.0001 (10)	−0.0016 (7)	−0.004 (1)
C(23)	0.3652 (7)	0.1105 (2)	0.6094 (8)	0.0026 (4)	0.0083 (11)	0.0042 (6)	0.0018 (3)	−0.0030 (7)	0.000 (1)
C(24)	0.4015 (7)	0.1621 (12)	0.6461 (8)	0.0026 (4)	0.0097 (12)	0.0036 (5)	0.0012 (3)	−0.0022 (8)	−0.001 (2)
C(25)	0.4010 (8)	0.2572 (12)	0.6432 (8)	0.0031 (5)	0.0087 (12)	0.0040 (6)	0.0002 (13)	−0.0014 (9)	−0.002 (2)
C(26)	0.3623 (7)	0.3039 (11)	0.6040 (7)	0.0027 (4)	0.0070 (10)	0.0033 (5)	−0.0005 (12)	−0.0029 (7)	−0.002 (1)

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
C(31)	0.002 (1)	0.013 (2)	0.596 (2)	15.9 (10)	C(43)	0.356 (2)	−0.154 (3)	0.381 (2)	22.4 (15)
C(32)	0.012 (2)	−0.010 (2)	0.658 (2)	17.3 (11)	C(44)	0.348 (2)	−0.202 (3)	0.443 (2)	26.2 (18)
C(33)	−0.032 (1)	0.160 (2)	0.579 (2)	15.5 (10)	C(51)	0.201 (1)	0.040 (2)	0.762 (1)	13.0 (8)
C(34)	−0.015 (1)	0.246 (2)	0.549 (1)	13.8 (9)	C(52)	0.217 (1)	0.132 (2)	0.765 (1)	10.3 (6)
C(41)	0.441 (1)	−0.048 (2)	0.408 (2)	16.5 (10)	C(53)	0.192 (1)	−0.093 (2)	0.694 (2)	16.4 (10)
C(42)	0.461 (1)	0.035 (2)	0.414 (1)	12.3 (8)	C(54)	0.252 (2)	−0.128 (3)	0.657 (2)	19.3 (12)
Li(1)	0.111 (1)	0.132 (2)	0.525 (2)	6.0 (7)	Li(3)	0.308 (1)	0.035 (2)	0.459 (2)	6.4 (7)
Li(2)	0.205 (1)	0.070 (2)	0.605 (1)	5.4 (7)					

[a] The form of the anisotropic thermal parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

Table II. Interatomic Distances (Å) and Bond Angles (deg) Involving Metal Atoms

Cr–Cr′	1.830 (4)	Cr–Li(1)	2.75 (2)
Cr–Br	3.266 (2)	Cr–Li(2)	2.72 (2)
Cr–O(11)	2.079 (7)	Cr–Li(3)	2.78 (2)
Cr–O(21)	2.098 (8)	Br–Li(1)	2.66 (2)
Cr–C(11)	2.082 (12)	Br–Li(2)	2.72 (2)
Cr–C(21)	2.074 (12)	Br–Li(3)	2.66 (2)
Li(1)–O(11)	1.80 (2)	Li(1)–O(31)	1.99 (2)
Li(2)–O(11)	1.90 (2)	Li(2)–O(51)	1.93 (2)
Li(2)–O(21)	1.95 (2)	Li(3)–O(41)	1.96 (2)
Li(3)–O(21)	1.87 (2)		
Cr–Cr–Br	170.7 (1)	Br–Cr–C(11)	92.4 (2)
Cr–Cr–O(11)	102.8 (3)	Br–Cr–C(21)	93.0 (2)
Cr–Cr–O(21)	101.4 (3)	Cr–O(11)–C(12)	109.7 (7)
Cr–Cr–C(11)	93.9 (4)	Cr–O(22)–C(22)	109.6 (8)
Cr–Cr–C(21)	93.8 (4)	Br–Li(1)–Cr	74.4 (6)
O(11)–Cr–O(21)	85.8 (3)	Br–Li(2)–Cr	73.1 (5)
C(11)–Cr–C(21)	89.3 (4)	Br–Li(3)–Cr	73.8 (6)
C(11)–Cr–O(21)	89.7 (4)	O(11)–Li(1)–O(31)	123 (1)
C(11)–Cr–O(11)	163.2 (4)	O(11)–Li(2)–O(21)	92 (1)
C(21)–Cr–O(11)	90.8 (3)	O(11)–Li(2)–O(51)	132 (1)
C(21)–Cr–O(21)	164.8 (4)	O(21)–Li(2)–O(51)	122 (1)
Br–Cr–O(11)	70.8 (2)	O(21)–Li(3)–O(41)	130 (1)
Br–Cr–O(21)	71.9 (2)		

and 2. Figure 1 shows the central $Cr_2(C_6H_4O)_4Br_2$ unit, while Figure 2 shows all of the surrounding Li, Br, and diethyl ether atoms with only a portion of the $Cr_2(C_6H_4O)_4$ unit so as to avoid excessive overlap of atoms; only the Cr atoms and the C–C–O chains bridging the pair Cr atoms are included.

The formula units are located on crystallographic inversion centers and are therefore rigorously centrosymmetric. The $Cr_2(C_6H_4O)_4$ units are discrete and each one is enveloped by the remaining components of the formula unit. The Br^- ions lie approximately along extensions of the Cr–Cr axes but at such a great distance, 3.266 (2) Å, that they are only very weakly, if at all bonded.

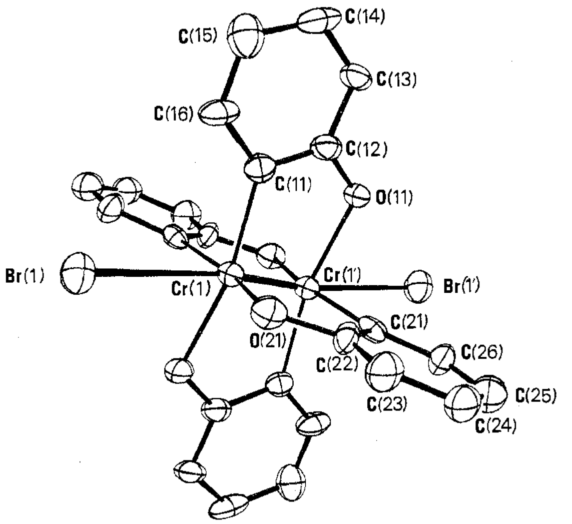


Figure 1. The central, $Cr_2(C_6H_4O)_4Br_2$ portion of the structure. Each atom is represented by its thermal vibration ellipsoid scaled to enclose 30% of its electron density. The numbering scheme is defined. There is a center of inversion at the midpoint of the Cr–Cr bond which relates primed and unprimed atoms with the same number.

The locations of the lithium ions are reasonable electrostatically. Each one is coordinated by an ether oxygen atom and by a bromide ion. Two of them, Li(1) and Li(3), are also coordinated by one phenoxy oxygen atom, while Li(2) is close to two phenoxy oxygen atoms.

Discussion

As expected, the key structural feature is the $Cr_2(C_6H_4O)_4^{4-}$ anion. Each Cr atom is bonded to two phenyl carbon atoms and two oxygen atoms in a cis arrangement. This leads to overall virtual symmetry of C_{2h} although the only crystallo-

Table III. Interatomic Distances (Å) and Bond Angles (deg) within Ligands

A. In C_6H_4O

O(11)-C(12)	1.38 (1)	O(21)-C(22)	1.42 (1)
C(11)-C(12)	1.45 (2)	C(21)-C(22)	1.37 (2)
C(11)-C(16)	1.37 (2)	C(21)-C(26)	1.42 (2)
C(12)-C(13)	1.42 (2)	C(22)-C(23)	1.43 (2)
C(13)-C(14)	1.41 (2)	C(23)-C(24)	1.41 (2)
C(14)-C(15)	1.44 (2)	C(24)-C(25)	1.40 (2)
C(15)-C(16)	1.40 (2)	C(25)-C(26)	1.45 (2)
C(12)-C(11)-C(16)	117 (1)	C(22)-C(21)-C(26)	113 (1)
C(11)-C(12)-C(13)	122 (1)	C(21)-C(22)-C(23)	130 (1)
C(12)-C(13)-C(14)	119 (1)	C(22)-C(23)-C(24)	115 (1)
C(13)-C(14)-C(15)	120 (1)	C(23)-C(24)-C(25)	121 (1)
C(14)-C(15)-C(16)	119 (1)	C(24)-C(25)-C(26)	121 (1)
C(15)-C(16)-C(11)	123 (1)	C(25)-C(26)-C(21)	121 (1)
C(11)-C(12)-O(11)	119 (1)	C(21)-C(22)-O(21)	118 (1)

B. In Ether Molecules

O(31)-C(31)	1.47 (3)	O(41)-C(41)	1.45 (3)	O(51)-C(51)	1.40 (2)
O(31)-C(33)	1.32 (3)	O(41)-C(43)	1.70 (4)	O(51)-C(53)	1.46 (3)
C(31)-C(32)	1.32 (3)	C(41)-C(42)	1.31 (3)	C(51)-C(52)	1.41 (3)
C(33)-C(34)	1.39 (3)	C(43)-C(44)	1.35 (4)	C(53)-C(54)	1.40 (3)
C(31)-O(31)-C(33)	114 (2)	C(41)-O(41)-C(43)	109 (2)	C(51)-O(51)-C(53)	114 (2)
O(31)-C(31)-C(32)	123 (3)	O(41)-C(41)-C(42)	117 (2)	O(51)-C(51)-C(52)	118 (2)
O(31)-C(33)-C(34)	112 (2)	O(41)-C(43)-C(44)	87 (3)	O(51)-C(53)-C(54)	107 (3)

Table IV. Mean Distances and Angles in the Title Compound and Related DMP Complexes[a]

	M-M, Å	x(M-M-C),[a] deg	x(M-M-O),[a] deg
$Li_6Cr_2(2\text{-oxyphenyl})_4Br_2(Et_2O)_6$	1.830 (4)	93.9 ± 0.4	102.1 ± 0.7
$Cr_2(DMP)_4$[b]	1.847 (1)	91.1 ± 0.3	101.7 ± 0.4
$Mo_2(DMP)_4$[b]	2.064 (1)	91.1 ± 0.5	96.2 ± 0.1
$V_2(DMP)_4$[c]	2.200 (2)	91.7 ± 0.2	92.1 ± 0.1

[a] Averaged according to virtual symmetry. Error intervals are mean deviations from the mean. [b] From ref 1. [c] F. A. Cotton and M. Miller, *J. Am. Chem. Soc.*, **99**, 7886 (1977).

graphically rigorous symmetry element is an inversion center at the midpoint of the Cr–Cr quadruple bond. The arrangement of C and O atoms about the M_2 core is the same one found previously[1,2] in $M_2(DMP)_4$ (DMP = 2,6-dimethoxyphenyl, M = Cr, Mo) and $Cr_2(TMP)_4$ (TMP = 2,4,6-trimethoxyphenyl). It appears that there is a consistent preference for having M–O and M–C bonds trans to each other. This could be a manifestation of the well-known strong trans effect of metal–carbon bonds. A comparable trans geometry occurs in tris(2-dioxolanophenyl)chromium(III) where only the *fac* isomer is observed.[10] A trans effect of the M–C bonds could also help to account for the fact that the M–O bonds in all the compounds of this type are as long as, or longer, than the Cr–C bonds.

The most important aspect of this structure is the exceedingly short Cr–Cr quadruple bond distance, 1.830 (4) Å, which is even shorter than those previously found in $Cr_2(DMP)_4$, 1.847 (1) Å, and $Cr_2(TMP)_4$, 1.849 (1) Å. The Cr–Cr quadruple bond reported here is, in fact, the shortest metal-to-metal distance yet observed in any compound.

Prior to our work on these compounds with Cr–Cr distances <1.85 Å, two principal classes of quadruply bonded dichromium compounds were known: (1) the many carboxylates, which possess relatively weak and long bonds, in the range 2.28–2.54 Å,[11] and (2) the smaller class of organometallic complexes with Cr–Cr bond lengths in the range 1.95–2.00 Å, such as $Cr_2(CH_3)_8{}^{4-}$ [12] and $Cr_2(allyl)_4$.[13] This enormous range of variation in the length of the Cr–Cr quadruple bond has not been found with other metals, and an understanding of all the electronic and structural factors that affect the Cr–Cr distance is yet to be obtained.

As to what factors are responsible for these extremely short Cr–Cr distances, we can at least eliminate a few. The overall charge is clearly not crucial, since the bonds are extremely short in both $Cr_2(DMP)_4$ and $Cr_2(2\text{-oxyphenyl})_4{}^{4-}$. There is also evidence against the idea that these 2-oxyphenyl type ligands sterically constrain the metal atoms to such a short internuclear distance, since, as indicated in Table IV, much longer distances occur in similar compounds with other metals. It may also be noted that the shorter the M–M distance, the more obtuse is the M–M–O angle since the M–M–C angles are always close to 90°. Presumably, with extremely short M–M distances, the five-membered rings actually become strained, which is quite the opposite of the idea that the ligands have a steric preference for the short M–M distances.

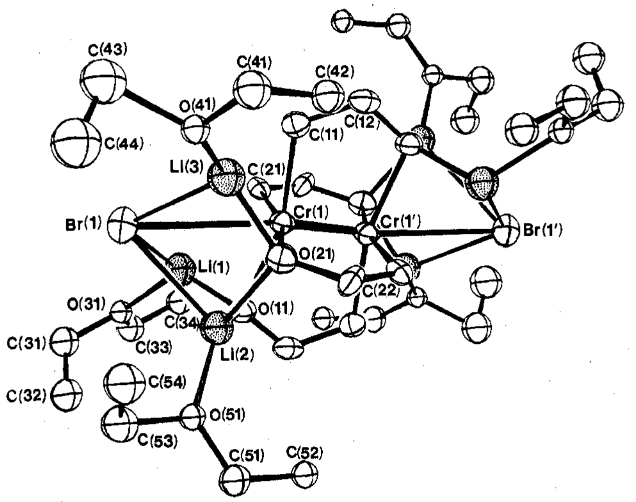


Figure 2. A drawing showing all of the lithium (stippled), bromine, and diethyl ether atoms that surround the central portion, of which only the two Cr atoms and the four C–C–O chains are shown. Atoms are represented by their ellipsoids or spheres of thermal motion with those of the ether atoms enclosing 10% and the others 30% of the electron density.

The effect of axial ligands on M–M distances has been well documented in connection with $Cr_2(O_2CR)_4$,[11] $Mo_2(O_2CR)_4$,[14] and $Re_2Cl_8^{2-}$[15] and naturally requires consideration here. In the $M_2(DMP)_4$ and $M_2(TMP)_4$ molecules the axial positions are rather effectively blocked by the uncoordinated methoxy groups and there is no axial coordination whatever. However, in the present case, no such blocking occurs, and there are Br^- ions along the axial directions, but these Br^- ions remain very distant. This could, of course, be due simply to the fact that the anionic $[Cr_2(C_6H_4O)_4]^{4-}$ unit as a whole repels the Br^- ions. In other words, the axial positions might be protected electrostatically though not sterically. Thus, we do not yet know what, if any, role axial ligands, or their absence, have to play in these compounds with exceedingly short Cr–Cr bonds.

It is pertinent to note that a "naked" Cr_2 species has been observed in an argon matrix[16] and possibly in the thermal decomposition of $Cr(CO)_6$.[17] If the species Cr_2 has been correctly identified as such under the latter conditions, it can be inferred from its rotational energy levels that the Cr–Cr distance is 1.71 Å. The bond in this case might, as suggested for Mo_2,[18] be of order 6.

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Registry No. $Li_6Cr_2(o\text{-}C_6H_4O)_4Br_2\cdot 6(C_2H_5)_2O$, 66323-53-3; $Cr_2(O_2CCH_3)_4$, 15020-15-2.

Supplementary Material Available: A listing of structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

References and Notes

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Notes

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Conformation of Triangular Peroxo d^0 Metalloporphyrins

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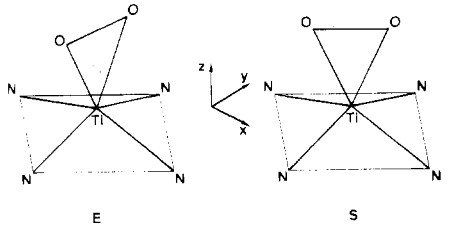
The detailed nature of the bonding of molecular oxygen to transition-metal complexes has been a subject of increasing interest because it represents a basic step in the function of oxygen carrying and activating metalloproteins in biological systems.[2] Recently, x-ray structures have been reported for titanium[3,4] and molybdenum[5] porphyrin complexes containing dioxygen ligands. It has been found that the MO_2 system adopts a triangular edge-on structure, the dioxygen moiety eclipsing two opposite nitrogens of the macrocycle. In the case of the bis(dioxygen)molybdenum complex each N–N diagonal is eclipsed by a dioxygen unit, one above the molecular plane and the other below. Dynamic NMR measurements on the titanium complex[4] support the view that these features of the solid-state structures are not imposed by crystal packing constraints but rather that they reflect the preferential conformation of the isolated molecules. The aim of this paper is to present a qualitative theoretical model to account for the preferential conformation of these edge-on adducts.

We start with the interaction of a diatomic O_2 with a pyramidal TiN_4 fragment. On the basis of the assumptions previously made by Hoffmann, Chen, and Thorn[6] the orbitals of the metal and of the dioxygen ligand to be taken into account are the four d orbitals of the metal, z^2, xy, xz, and yz, and the $3\sigma_g$, π_u, and π_g levels of the ligand. The ligand contributions and core levels are omitted as well as the high-lying levels σ_u and $x^2 - y^2$.



In the complex, the two conformations E (eclipsed) and S (staggered) belong to the C_{2v} point group. The fundamental difference appears in the fact that the plane containing the metal and the O_2 moiety is the yz plane in E whereas it bisects the xz, yz dihedron in S. Then, the constitutive orbitals of the fragments are distributed among the different irreducible representations as shown in Table I. Indices $\parallel$ and $\perp$ characterize the π orbitals parallel and perpendicular to the z axis, respectively. According to experimental data[3,4] the complex is best described by a peroxotitanium(IV) electronic structure. The number n of electrons to be placed in the molecular levels of the complex are given for each symmetry besides the corresponding label.

Let us now focus on what is changed in going from one conformation to the other. It appears clearly that for B_1 and B_2 representations all interactions are retained along the deformation coordinate since the symmetry-adapted orbitals of the $[TiN_4]_S$ fragment can be deduced from those of $[TiN_4]_E$ by a unitary transformation in the subspace of the degenerate levels of the metal. As concerns the A_1 representation, interactions between z^2 and the $3\sigma_g$ and $\pi_u^{\parallel}$ orbitals are invariant during the rotation around the z axis, the orbitals being themselves symmetric with respect to the rotation axis. The supplementary interaction between xy and the $3\sigma_g$ and $\pi_u^{\parallel}$ orbitals which appears in S is small as a consequence of the large energy gap between the metal and diatomic levels and the weakness of their mutual overlaps.[6] The deciding difference can be found in the A_2 representation. In E, interaction

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