vector). If the motion of the molecule is that of an isotropic rotor, we should have the same value of $N \times T_1$ for each carbon atom, but this is not strictly the case. Discrepancies may be attributed to anisotropy of the overall motion for the rigid part of the molecule and/or to internal motion of the tolyl or phenyl group (Table VI). Differences in absolute values of mean T_1 between the three complexes are related to differences in solubility.

Nevertheless, rotation of the phenyl or tolyl group about the C–N bond should decrease τ_{eff} for the off-axis carbon atoms relative to the value for the tertiary carbon atoms situated on the rotation axis as can be seen by comparing their relaxation time ratios ρ (Table VI).

If we postulate that, in solution, rotation is rigorously prevented for [Ir(sal-*o*-tol)(cod)] then the same would be true for [Ir(salanil)(cod)], [Ir(sal-*m*-tol)(cod)], and the N-bonded phenyl ring in [Ir(salabp)(cod)] for which we have similar ρ values. For this latter compound, however, the free rotation of the terminal phenyl is clearly demonstrated by a significantly greater ρ value. We cannot exclude a limited libration motion of the tolyl or phenyl group around the C–N axis in these compounds, but we can reject the hypothesis of a rapid rotation as a cause of the equivalence of the carbon atoms of the cyclooctadiene in[Ir(sal-*m*-tol)(cod)]. Perhaps the methyl group in the meta position is not sufficient to destroy the local symmetry of these atoms.

The long T_1 values measured for methyl groups indicates in each case a very fast reorientation around their axes.

Acknowledgment. The authors wish to thank Professor R. Chevalier for providing facility for X-ray measurements.

Registry No. **1**, R = H, 32761-45-8; **1**, R = 2-CH_3, 68868-44-0; **1**, R = 3-CH_3, 77662-13-6; **1**, R = 4-C_6H_5, 77662-14-7; [Ir(OCH_3)(cod)]$_2$, 33087-83-1.

Supplementary Material Available: Listings of root-mean-square amplitudes of vibration and structure factor amplitudes (22 pages). Ordering information is given on any current masthead page.

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Tetraamidodichromium(II) Compounds and Their Dihalomethane Adducts. Structures of $Cr_2[(2,6\text{-xylyl})NC(CH_3)O]_4\cdot 1.5C_6H_5CH_3$ and $M_2[(2,6\text{-xylyl})NC(CH_3)O]_4\cdot 2CH_2Br_2$, M = Cr, Mo

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Received September 11, 1980

The structures of the compounds $Cr_2[(2,6\text{-xylyl})NC(CH_3)O_4]\cdot 1.5C_6H_5CH_3$ (**1**) and $M_2[(2,6\text{-xylyl})NC(CH_3)O]_4\cdot 2CH_2Br_2$, M = Cr (**2**) and Mo (**3**), are reported. Compound **1** crystallizes in the monoclinic space group $P2_1/c$ and has crystallographic parameters a = 16.219 (2) Å, b = 15.290 (2) Å, c = 19.360 (2) Å, β = 92.21 (1)°, V = 4798 (2) Å^3, and Z = 4. The Cr–Cr bond length is 1.937 (2) Å, and the average Cr–O and Cr–N distances are 1.957 (5) and 2.078 (9) Å, respectively. Associated with each molecule are 1.5 $C_6H_5CH_3$ molecules, one of which occupies a general position within the cell and the other is disordered on an inversion center. Compounds **2** and **3** crystallize in the orthorhombic space group *Pccn* with eight molecules per unit cell. The unit cell constants for the Cr and Mo compounds, respectively, are a = 31.107 (5), 31.300 (4) Å, b = 15.852 (2), 15.944 (3) Å, c = 18.321 (3), 18.378 (2) Å, V = 9034 (4), 9171 (4) Å^3, and Z = 8. Each molecule resides on a general position within the unit cell. The Cr–Cr and Mo–Mo distances are 1.961 (4) and 2.085 (2) Å, respectively. The average M–O and M–N distances are 1.97 (1) and 2.08 (1) Å, and 2.12 (1) and 2.20 (2) Å for the Cr and Mo compounds, respectively. The two CH_2Br_2 moieties occupy positions along the axial extensions of the M–M bonds with M–Br distances of 3.554 (5) and 3.335 (4) Å for the Cr compound and 3.544 (4) and 3.390 (3) Å for the molybdenum compound. The Cr–Cr bond distance in **1** requires revision of our earlier conclusions concerning the extent of axial interactions in **2** and its previously described CH_2Cl_2 analogue.

Introduction

The effect of axial coordination on the metal–metal bond length in quadruply bonded dichromium(II) compounds has been a subject of investigation in our laboratory for the past few years.[1-3] Unlike the dimolybdenum(II) analogues, the quadruply bonded dichromium(II) compounds are unusually good electron-pair acceptors and form bis-axial adducts very easily even with relatively weak Lewis bases, unless the approach of such donor molecules toward the axial site is sterically prohibited. Another interesting difference which makes the chromium compounds unique is the sensitivity of the chromium–chromium quadruple bond length toward the extent of such axial coordination.[1,3] The precise reasons for this qualitative difference in behavior of the Cr–Cr and Mo–Mo quadruple bonds is still under study, but the different energies of the M–M σ and σ^* orbitals[4] as well as the very shallow potential energy curve[5] for $Cr_2(O_2CH)_4$ are probably key factors.

We recently reported an example of what was believed to be significant axial donation from a chlorine atom in CH_2Cl_2 to a chromium atom of $Cr_2[(2,6\text{-xylyl})NC(CH_3)O]_4$.[2] In the crystal a CH_2Cl_2 molecule was found at each axial position of the dichromium molecule, with Cl···Cr distances of 3.354 (3) and 3.58 (1) Å. Although even the shorter of these two contacts would not in itself have constituted sufficient evidence for postulating a Cl→Cr donor bond, the additional observation of a Cr–Cr distance equal to 1.949 (2) Å was also invoked. It was noted that this is considerably greater than

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Table I. Crystallographic Parameters

parameter	1	2	3
space group	$P2_1/c$	$Pccn$	$Pccn$
a, Å	16.219 (2)	31.107 (5)	31.300 (4)
b, Å	15.290 (2)	15.852 (2)	15.944 (3)
c, Å	19.360 (2)	18.321 (3)	18.378 (2)
α, deg	90.0	90.0	90.0
β, deg	92.21 (1)	90.0	90.0
γ, deg	90.0	90.0	90.0
V, Å^3	4798 (2)	9034 (4)	9171 (4)
Z	4	8	8
fw	891.06	1100.54	1188.42
cryst size, mm	0.35 × 0.30 × 0.35	0.25 × 0.35 × 0.30	0.20 × 0.25 × 0.20
μ, cm^{-1}	5.215	42.987	42.779
2θ range, deg	0–45	0–45	0–45
no. of data	7059	6504	6614
$F_o^2 > 3\sigma(F_o^2)$	2492	1592	1516
no. of variables	487	255	275
R_1	0.067	0.099	0.062
R_2	0.084	0.104	0.071
esd	2.218	2.428	1.778
d_X, g/cm^3 (calcd)	1.234	1.618	1.721
diffractometer	CAD-4F	CAD-4F	CAD-4F
transmission factors, %			
min		47.81	93.5
max		99.92	97.82
av		68.64	95.32

the Cr–Cr distance in $Cr_2[PhNC(CH_3)O]_4$, viz., 1.873 (3) Å,[6] and it was assumed that no significant difference in Cr–Cr bond lengths was to be expected between $Cr_2[PhNC(CH_3)O]_4$ and $Cr_2[(2,6\text{-xylyl})NC(CH_3)O]_4$. A direct comparison of the latter with its CH_2Cl_2 adduct was precluded by the failure of all attempts to obtain the unsolvated 2,6-xylyl compound in crystalline form.

Recently, while trying to synthesize the triethylamine adduct, we succeeded, quite accidentally, in isolating the compound $Cr_2[(2,6\text{-xylyl})NC(CH_3)O]_4{\cdot}1.5C_6H_5CH_3$, in which the chromium atoms have no axial ligands. In line with our continuing study of the sensitivity of the Cr–Cr bond toward aliphatic halogen atoms, we have also prepared the methylene bromide adduct of $Cr_2[(2,6\text{-xylyl})NC(CH_3)O]_4$. We now wish to report in detail the structure of the parent compound $Cr_2[(2,6\text{-xylyl})NC(CH_3)O]_4{\cdot}1.5C_6H_5CH_3$ (**1**) and the CH_2Br_2 adduct $Cr_2[(2,6\text{-xylyl})NC(CH_3)O]_4{\cdot}2CH_2Br_2$ (**2**). For comparison we have also examined the analogous molybdenum compound $Mo_2[(2,6\text{-xylyl})NC(CH_3)O]_4{\cdot}2CH_2Br_2$ (**3**).

Experimental Section

2,6-Dimethylacetanilide, prepared[7] from acetic anhydride and 2,6-dimethylaniline, was recrystallized from methanol and its purity checked by elemental analysis and melting point (176 °C). Dibromo- and diiodomethane (Aldrich Chemical Co.) were dried over molecular sieves and degassed with nitrogen. Other solvents were dried and distilled under nitrogen shortly before being used. The following reactions were all run in an atmosphere of nitrogen.

$Cr_2[(2,6\text{-xylyl})NC(CH_3)O]_4{\cdot}1.5C_6H_5CH_3$ (1). A solution of Li[(2,6-xylyl)NC(CH_3)O] was prepared by dissolving 0.65 g (4 mmol) of 2,6-dimethylacetanilide in 25 mL of THF and adding an equivalent amount (2.5 mL of a 1.6 M solution) of *n*-butyllithium in hexane. After the mixture was stirred for about 1 h, 0.34 g (1 mmol) of anhydrous dichromium(II) tetraacetate was added to it, and stirring was continued overnight (~10 h). The deep orange solution was filtered and the solvent stripped under vacuum. The brown residue was heated at 130 °C under a vacuum of 10^{-2} torr for 6 h when it turned to gray-white powder. This was dissolved in 25 mL of toluene. The yellow solution was filtered quickly and about 0.5 mL (3 mmol) of triethylamine was added to the filtrate. This yellow solution was then kept at about −5 °C for 7 days, during which time large orange crystals formed. Elemental analysis was consistent with $Cr_2C_{40}H_{48}N_4O_4$ plus 1 or 2 C_7H_8 but not with additional nitrogen as would be required by the presence of coordinated triethylamine. The mass spectrum showed the presence of toluene. Definitive identification of the compound resulted from the subsequent X-ray structure analysis.

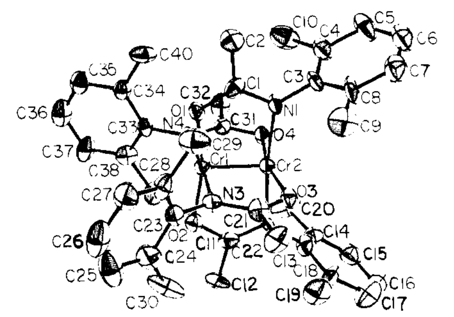

Figure 1. Computer-drawn (ORTEP) picture of $Cr_2[(2,6\text{-xylyl})NC(CH_3)O]_4{\cdot}1.5C_6H_5CH_3$. The atoms are represented by 30% thermal ellipsoids.

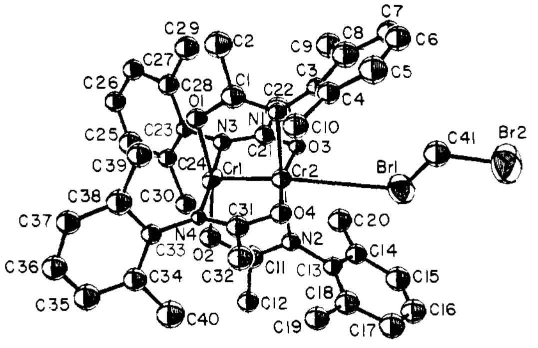

Figure 2. Computer-drawn (ORTEP) picture of the $Cr_2[(2,6\text{-xylyl})NC(CH_3)O]_4$ molecule and the coordinated CH_2Br_2 molecule. The atoms are represented by 30% thermal ellipsoids and the atomic numbering scheme, which applies also to the Mo analogue, is defined.

$Cr_2[(2,6\text{-xylyl})NC(CH_3)O]_4{\cdot}2CH_2Br_2$ (2). The gray-white powder obtained as an intermediate in the synthesis of **1** was stirred with 25 mL of dibromomethane at 70 °C for 1 h. The yellow solution was filtered rapidly while hot. In the filtrate, which was cooled to −5 °C very slowly with stirring over a period of 24 h, yellow crystals were formed. Most of the crystals floated because of the very high density of the solvent and were found to be too small for X-ray crystallographic study, but a few crystals suitable for X-ray work were found adhering to the vessel. Elemental analysis of these crystals corresponded to the composition $Br_4Cr_2O_4N_4C_{42}H_{52}$.

$Mo_2[(2,6\text{-xylyl})NC(CH_3)O)]_4{\cdot}2CH_2Br_2$ (3). This compound was prepared in a manner analogous to **2** starting from dimolybdenum(II) tetracetate. The crystals obtained were golden yellow and had the composition $Br_4Mo_2O_4N_4C_{42}H_{52}$.

Attempted Preparation of $Cr_2[(2,6\text{-xylyl})NC(CH_3)O]_4{\cdot}2CH_2I_2$. The gray-white powder obtained as an intermediate in the synthesis of **1** was stirred with 25 mL of diiodomethane at room temperature for about 2 h in the dark. A small amount of solid was found to dissolve to give a light green solution. The solubility increases at higher temperature, giving a deep green solution; however, no crystalline product could be obtained from these green solutions. It appears to us that chromium(II) is oxidized to chromium(III) by the diiodomethane.

X-ray Crystallography. Suitable crystals of each compound were embedded in epoxy cement within a thin-glass capillary and mounted on an Enraf-Nonius CAD-4F automatic diffractometer. General procedures for both data collection and the solution and refinement of the structures have been discussed previously.[8] Pertinent crys-

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Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Cr_2[(2,6\text{-xylyl})NC(CH_3)O]_4 \cdot 1.5C_6H_5CH_3$ (1)[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cr(1)	0.2678 (1)	0.6856 (1)	0.20518 (9)	3.24 (7)	3.01 (7)	2.72 (7)	0.06 (9)	−0.01 (6)	−0.36 (9)
Cr(2)	0.2341 (1)	0.6887 (1)	0.30005 (9)	3.17 (7)	3.22 (8)	2.63 (8)	−0.10 (9)	0.34 (6)	−0.45 (8)
O(1)	0.3791 (4)	0.7342 (4)	0.2184 (3)	3.4 (3)	3.2 (3)	2.2 (3)	−0.5 (3)	0.0 (3)	−0.6 (3)
O(2)	0.1644 (4)	0.6356 (5)	0.1690 (4)	3.7 (4)	4.9 (4)	3.1 (4)	−0.5 (3)	−0.1 (3)	0.1 (3)
O(3)	0.1866 (4)	0.8066 (5)	0.2977 (3)	4.2 (4)	3.4 (3)	2.7 (3)	−0.3 (3)	0.2 (3)	−0.7 (3)
O(4)	0.2727 (4)	0.5711 (5)	0.3251 (3)	3.8 (3)	4.1 (4)	2.2 (3)	−0.2 (3)	0.1 (3)	−0.6 (3)
N(1)	0.3484 (5)	0.7398 (6)	0.3328 (4)	2.9 (4)	4.3 (5)	2.1 (4)	−0.9 (4)	0.3 (3)	−0.6 (4)
N(2)	0.1181 (5)	0.6389 (6)	0.2772 (4)	3.3 (4)	4.3 (4)	1.9 (4)	0.4 (4)	−0.4 (3)	−0.1 (4)
N(3)	0.2233 (5)	0.8110 (6)	0.1855 (4)	4.1 (4)	3.5 (4)	3.4 (4)	1.0 (4)	0.2 (4)	0.7 (4)
N(4)	0.3144 (5)	0.5590 (5)	0.2154 (4)	3.9 (4)	2.9 (4)	1.8 (4)	0.7 (4)	0.3 (3)	0.2 (4)
C(1)	0.4004 (6)	0.7518 (7)	0.2812 (6)	2.5 (5)	3.4 (6)	5.1 (6)	−0.5 (5)	0.6 (5)	−0.7 (5)
C(2)	0.4854 (7)	0.7889 (8)	0.2942 (6)	5.3 (7)	4.9 (7)	4.4 (6)	−2.4 (5)	0.7 (5)	0.2 (6)
C(3)	0.3697 (7)	0.7570 (7)	0.4016 (5)	4.1 (5)	4.6 (6)	1.6 (5)	−1.7 (5)	−0.1 (4)	−0.2 (5)
C(4)	0.4128 (7)	0.6961 (9)	0.4392 (6)	4.9 (6)	6.2 (7)	3.4 (6)	−1.9 (6)	0.0 (5)	−1.4 (6)
C(5)	0.4258 (8)	0.7090 (10)	0.5102 (6)	7.6 (8)	9.5 (9)	3.6 (6)	−4.9 (7)	−0.9 (6)	1.8 (7)
C(6)	0.3991 (9)	0.7875 (10)	0.5399 (6)	8.2 (8)	10 (1)	2.7 (6)	−4.3 (7)	0.4 (6)	−2.2 (6)
C(7)	0.3603 (8)	0.8468 (10)	0.5013 (7)	6.3 (7)	8.0 (9)	4.7 (7)	−2.3 (7)	1.0 (6)	−1.8 (7)
C(8)	0.3469 (7)	0.8363 (8)	0.4339 (6)	5.1 (6)	6.6 (8)	2.9 (6)	−0.7 (6)	0.2 (5)	−1.2 (6)
C(9)	0.3103 (8)	0.9072 (9)	0.3943 (8)	5.2 (7)	5.2 (7)	10.5 (9)	−1.3 (6)	0.7 (7)	−4.8 (6)
C(10)	0.4441 (8)	0.6098 (10)	0.4060 (7)	5.0 (7)	8.3 (9)	7.2 (8)	−0.5 (7)	−2.7 (6)	0.7 (8)
C(11)	0.1070 (6)	0.6216 (8)	0.2137 (6)	3.0 (5)	4.0 (6)	4.2 (6)	−0.1 (5)	−0.7 (5)	0.7 (5)
C(12)	0.0295 (8)	0.5815 (10)	0.1819 (7)	4.9 (7)	8.6 (9)	4.8 (7)	−0.5 (7)	−1.2 (6)	−1.6 (7)
C(13)	0.0517 (7)	0.6251 (8)	0.3259 (5)	3.9 (6)	4.6 (6)	2.8 (5)	−0.5 (5)	1.0 (5)	0.6 (5)
C(14)	0.0448 (6)	0.5441 (8)	0.3585 (6)	2.3 (5)	4.7 (6)	4.5 (6)	0.1 (5)	0.3 (5)	−0.7 (5)
C(15)	−0.0182 (8)	0.5316 (9)	0.4054 (7)	5.4 (7)	5.7 (7)	6.6 (8)	−1.5 (6)	−0.2 (6)	0.8 (7)
C(16)	−0.0726 (8)	0.5989 (11)	0.4183 (7)	5.7 (7)	12 (1)	7.5 (9)	−2.6 (8)	3.7 (6)	−3.0 (8)
C(17)	−0.0649 (8)	0.6768 (9)	0.3867 (8)	6.4 (7)	5.4 (8)	8.8 (9)	−0.6 (7)	3.2 (7)	−0.3 (8)
C(18)	−0.0067 (7)	0.6885 (9)	0.3382 (6)	4.1 (6)	5.8 (7)	6.0 (7)	−1.0 (6)	1.7 (5)	−0.8 (7)
C(19)	−0.0045 (8)	0.7732 (10)	0.2987 (7)	5.6 (7)	7.7 (9)	7.2 (9)	2.1 (7)	1.2 (7)	−0.7 (8)
C(20)	0.1000 (8)	0.4698 (8)	0.3422 (8)	6.1 (8)	4.3 (7)	9.9 (9)	−1.6 (6)	−1.1 (7)	3.4 (7)
C(21)	0.1901 (7)	0.8494 (7)	0.2419 (6)	4.9 (6)	2.8 (5)	3.9 (6)	0.3 (5)	−0.0 (5)	−0.5 (5)
C(22)	0.1508 (8)	0.9379 (8)	0.2398 (7)	6.0 (7)	4.5 (7)	6.4 (8)	1.9 (6)	0.4 (6)	−0.7 (6)
C(23)	0.2312 (7)	0.8618 (8)	0.1213 (6)	5.1 (6)	3.9 (6)	3.3 (6)	2.0 (5)	−0.5 (5)	−0.1 (5)
C(24)	0.1750 (8)	0.8491 (8)	0.0687 (7)	6.5 (7)	3.4 (6)	6.6 (8)	1.4 (6)	−1.3 (6)	−0.6 (6)
C(25)	0.1848 (10)	0.8930 (10)	0.0082 (7)	12 (1)	6.2 (8)	4.5 (8)	3.3 (8)	−0.7 (8)	−0.1 (7)
C(26)	0.2470 (10)	0.9502 (9)	0.0012 (7)	14 (1)	7.8 (8)	5.1 (7)	7.2 (7)	3.7 (7)	3.8 (6)
C(27)	0.3035 (8)	0.9662 (9)	0.0558 (7)	7.3 (8)	7.6 (8)	6.0 (7)	2.7 (7)	1.6 (6)	4.1 (6)
C(28)	0.2952 (8)	0.9203 (8)	0.1138 (6)	5.5 (6)	5.0 (7)	3.9 (6)	1.1 (6)	1.2 (5)	0.3 (6)
C(29)	0.3556 (8)	0.9371 (9)	0.1725 (8)	6.1 (8)	5.4 (7)	9.3 (9)	−1.2 (7)	1.9 (7)	2.2 (7)
C(30)	0.1028 (10)	0.7919 (10)	0.0790 (7)	12.7 (9)	6.0 (9)	9.9 (8)	2.7 (8)	−9.3 (6)	−1.5 (7)
C(31)	0.3068 (6)	0.5276 (7)	0.2762 (5)	2.9 (5)	3.3 (5)	2.7 (5)	−0.6 (5)	0.1 (4)	0.5 (5)
C(32)	0.3357 (8)	0.4361 (8)	0.2966 (6)	6.2 (7)	3.5 (6)	4.8 (6)	0.8 (6)	0.7 (6)	−0.2 (6)
C(33)	0.3478 (7)	0.5064 (7)	0.1595 (5)	4.7 (6)	1.9 (5)	2.8 (5)	0.2 (5)	−0.2 (5)	0.5 (4)
C(34)	0.4319 (6)	0.5130 (7)	0.1449 (5)	3.4 (5)	2.8 (5)	3.5 (6)	−0.8 (5)	0.4 (4)	−0.1 (5)
C(35)	0.4614 (7)	0.4659 (8)	0.0882 (6)	5.1 (6)	4.5 (7)	5.0 (7)	1.0 (6)	1.7 (5)	0.8 (6)
C(36)	0.4111 (9)	0.4118 (8)	0.0499 (6)	9.2 (8)	4.7 (7)	4.1 (6)	2.2 (7)	2.5 (6)	−0.5 (6)
C(37)	0.3291 (8)	0.4037 (8)	0.0672 (6)	7.1 (7)	4.6 (7)	4.8 (7)	0.1 (6)	1.5 (6)	−2.3 (6)
C(38)	0.2972 (7)	0.4498 (8)	0.1207 (6)	4.4 (6)	3.7 (6)	5.1 (7)	−0.5 (6)	0.2 (5)	0.1 (6)
C(39)	0.2085 (8)	0.4354 (9)	0.1433 (6)	5.9 (7)	5.8 (7)	5.5 (7)	−1.3 (6)	−0.1 (6)	−3.7 (6)
C(40)	0.4893 (7)	0.5645 (8)	0.1863 (7)	3.6 (6)	4.4 (7)	7.3 (8)	0.3 (6)	0.2 (6)	−0.2 (7)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
C(101)	0.669 (1)	0.724 (1)	0.1227 (9)	9.4 (5)	H(193)	0.0045 (0)	0.8203 (0)	0.3301 (0)	5.0000 (0)
C(102)	0.665 (2)	0.781 (2)	0.0503 (12)	15.8 (8)	H(201)	0.1391 (0)	0.4884 (0)	0.3100 (0)	5.0000 (0)
C(103)	0.752 (2)	0.781 (2)	0.0491 (13)	16.5 (9)	H(202)	0.1281 (0)	0.4504 (0)	0.3834 (0)	5.0000 (0)
C(104)	0.811 (1)	0.757 (2)	0.0880 (12)	14.6 (8)	H(203)	0.0681 (0)	0.4231 (0)	0.3229 (0)	5.0000 (0)
C(105)	0.812 (2)	0.717 (2)	0.1580 (13)	16.5 (9)	H(221)	0.1574 (0)	0.9634 (0)	0.1956 (0)	5.0000 (0)
C(106)	0.718 (2)	0.694 (2)	0.1896 (15)	19.3 (10)	H(222)	0.0937 (0)	0.9325 (0)	0.2481 (0)	5.0000 (0)
C(200)	−0.027 (1)	0.574 (1)	0.9949 (10)	11.0 (6)	H(223)	0.1764 (0)	0.9740 (0)	0.2743 (0)	5.0000 (0)
C(201)	−0.058 (1)	0.434 (2)	1.0296 (12)	14.6 (7)	H(251)	0.1471 (0)	0.8829 (0)	−0.0297 (0)	5.0000 (0)
C(202)	−0.094 (1)	0.523 (2)	1.0244 (11)	13.9 (7)	H(261)	0.2524 (0)	0.9801 (0)	−0.0415 (0)	5.0000 (0)
H(21)	0.4944 (0)	0.7993 (0)	0.3423 (0)	5.0000 (0)	H(271)	0.3463 (0)	1.0081 (0)	0.0519 (0)	5.0000 (0)
H(22)	0.5253 (0)	0.7486 (0)	0.2789 (0)	5.0000 (0)	H(291)	0.3431 (0)	0.9006 (0)	0.2104 (0)	5.0000 (0)
H(23)	0.4902 (0)	0.8424 (0)	0.2697 (0)	5.0000 (0)	H(292)	0.4098 (0)	0.9247 (0)	0.1583 (0)	5.0000 (0)
H(51)	0.4522 (0)	0.6654 (0)	0.5381 (0)	5.0000 (0)	H(293)	0.3524 (0)	0.9966 (0)	0.1861 (0)	5.0000 (0)
H(61)	0.4091 (0)	0.7978 (0)	0.5879 (0)	5.0000 (0)	H(301)	0.1066 (0)	0.7671 (0)	0.1240 (0)	5.0000 (0)
H(71)	0.3414 (0)	0.8987 (0)	0.5225 (0)	5.0000 (0)	H(302)	0.0536 (0)	0.8253 (0)	0.0740 (0)	5.0000 (0)
H(91)	0.3044 (0)	0.8905 (0)	0.3471 (0)	5.0000 (0)	H(303)	0.1018 (0)	0.7464 (0)	0.0455 (0)	5.0000 (0)
H(92)	0.2576 (0)	0.9205 (0)	0.4114 (0)	5.0000 (0)	H(321)	0.3599 (0)	0.4088 (0)	0.2583 (0)	5.0000 (0)
H(93)	0.3448 (0)	0.9573 (0)	0.3983 (0)	5.0000 (0)	H(322)	0.3754 (0)	0.4399 (0)	0.3339 (0)	5.0000 (0)
H(101)	0.4309 (0)	0.6103 (0)	0.3578 (0)	5.0000 (0)	H(323)	0.2899 (0)	0.4025 (0)	0.3105 (0)	5.0000 (0)
H(102)	0.5021 (0)	0.6055 (0)	0.4134 (0)	5.0000 (0)	H(351)	0.5174 (0)	0.4722 (0)	0.0765 (0)	5.0000 (0)
H(103)	0.4182 (0)	0.5611 (0)	0.4266 (0)	5.0000 (0)	H(361)	0.4318 (0)	0.3801 (0)	0.0120 (0)	5.0000 (0)
H(121)	−0.0095 (0)	0.5730 (0)	0.2166 (0)	5.0000 (0)	H(371)	0.2941 (0)	0.3651 (0)	0.0411 (0)	5.0000 (0)
H(122)	0.0069 (0)	0.6194 (0)	0.1472 (0)	5.0000 (0)	H(391)	0.1977 (0)	0.4731 (0)	0.1809 (0)	5.0000 (0)
H(123)	0.0424 (0)	0.5267 (0)	0.1617 (0)	5.0000 (0)	H(392)	0.1710 (0)	0.4480 (0)	0.1057 (0)	5.0000 (0)

Table II (*Continued*)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
H(151)	−0.0235 (0)	0.4769 (0)	0.4282 (0)	5.0000 (0)	H(393)	0.2019 (0)	0.3763 (0)	0.1572 (0)	5.0000 (0)
H(161)	−0.1155 (0)	0.5901 (0)	0.4496 (0)	5.0000 (0)	H(401)	0.4611 (0)	0.5923 (0)	0.2224 (0)	5.0000 (0)
H(171)	−0.1000 (0)	0.7238 (0)	0.3982 (0)	5.0000 (0)	H(402)	0.5312 (0)	0.5276 (0)	0.2057 (0)	5.0000 (0)
H(191)	0.0389 (0)	0.7713 (0)	0.2672 (0)	5.0000 (0)	H(403)	0.5136 (0)	0.6076 (0)	0.1582 (0)	5.0000 (0)
H(192)	−0.0556 (0)	0.7814 (0)	0.2739 (0)	5.0000 (0)					

[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 III. Bond Distances (Å) for $Cr_2[(2,6\text{-xylyl})NC(CH_3)O]_4 \cdot 1.5C_6H_5CH_3$ (1)

Cr(1)–Cr(2)	1.937 (2)	C(8)–C(9)	1.44 (1)
Cr(1)–O(1)	1.959 (5)	C(11)–C(12)	1.51 (1)
Cr(1)–O(2)	1.949 (6)	C(13)–C(14)	1.40 (1)
Cr(1)–N(3)	2.079 (7)	C(13)–C(18)	1.38 (1)
Cr(1)–N(4)	2.084 (6)	C(14)–C(15)	1.41 (1)
Cr(2)–O(3)	1.960 (6)	C(14)–C(20)	1.49 (1)
Cr(2)–O(4)	1.960 (6)	C(15)–C(16)	1.38 (2)
Cr(2)–N(1)	2.087 (6)	C(16)–C(17)	1.35 (2)
Cr(2)–N(2)	2.062 (7)	C(17)–C(18)	1.37 (1)
O(1)–C(1)	1.280 (9)	C(18)–C(19)	1.50 (1)
O(2)–C(11)	1.31 (1)	C(21)–C(22)	1.49 (1)
O(3)–C(21)	1.266 (9)	C(23)–C(24)	1.35 (1)
O(4)–C(31)	1.298 (9)	C(23)–C(28)	1.38 (1)
N(1)–C(1)	1.346 (9)	C(24)–C(25)	1.37 (2)
N(1)–C(3)	1.389 (9)	C(24)–C(30)	1.48 (2)
N(2)–C(11)	1.26 (1)	C(25)–C(26)	1.35 (2)
N(2)–C(13)	1.47 (1)	C(26)–C(27)	1.39 (2)
N(3)–C(21)	1.37 (1)	C(27)–C(28)	1.34 (1)
N(3)–C(23)	1.48 (1)	C(28)–C(29)	1.49 (1)
N(4)–C(31)	1.282 (9)	C(31)–C(32)	1.52 (1)
N(4)–C(33)	1.47 (1)	C(33)–C(34)	1.41 (1)
C(1)–C(2)	1.50 (1)	C(33)–C(38)	1.39 (1)
C(3)–C(4)	1.36 (1)	C(34)–C(35)	1.41 (1)
C(3)–C(8)	1.42 (1)	C(38)–C(39)	1.54 (1)
C(4)–C(5)	1.40 (1)	C(101)–C(102)	1.65 (2)
C(4)–C(10)	1.56 (1)	C(101)–C(106)	1.56 (2)
C(5)–C(6)	1.41 (2)	C(102)–C(103)	1.41 (2)
C(6)–C(7)	1.32 (2)	C(103)–C(104)	1.26 (2)
C(34)–C(40)	1.44 (1)	C(104)–C(105)	1.49 (2)
C(35)–C(36)	1.36 (1)	C(105)–C(106)	1.70 (2)
C(36)–C(37)	1.39 (1)	C(200)–C(202)	1.47 (2)
C(37)–C(38)	1.37 (1)	C(200)–C(201)	1.45 (2)
C(7)–C(8)	1.32 (1)	C(201)–C(202)	1.48 (2)

tallographic parameters are summarized in Table I. Corrections for absorption were made on compounds **2** and **3**.

Results

The structure of $Cr_2[(2,6\text{-xylyl})NC(CH_3)O] \cdot 1.5C_6H_5CH_3$ (**1**) is shown in Figure 1, which also defines the atomic labeling scheme for the compound. The atomic positional and thermal parameters are given in Table II, and the bond distances and bond angles are given in Tables III and IV, respectively. Figure 2 shows the structure of the chromium compound of the type $M_2[(2,6\text{-xylyl})NC(CH_3)O]_4 \cdot 2CH_2Br_2$, M = Cr (**2**) and Mo (**3**), and also defines the atomic labeling scheme used for both compounds. The atomic positional and thermal parameters are given in Tables V and VI for the Cr and Mo compounds, respectively. Bond distances and angles for both compounds are given in Tables VII and VIII, respectively.

Compound **1** crystallizes in the monoclinic space group $P2_1/c$. Each molecule occupies a general position within the cell and as a result has no crystallographically imposed symmetry. The four $[(2,6\text{-xylyl})NC(CH_3)O]^-$ ligands are bonded so that the oxygen and nitrogen atoms are trans to each other, thus giving the $Cr_2N_4O_4$ inner set of atoms virtual D_{2d} symmetry. In the absence of any crystallographic symmetry a nonzero mean torsional angle about the Cr–Cr bond is permitted, but the actual value of this, 0.6°, is very small.

Table IV. Bond Angles (Deg) for $Cr_2[(2,6\text{-xylyl})NC(CH_3)O]_4 \cdot 1.5C_6H_5CH_3$ (**1**)

Cr(2)–Cr(1)–O(1)	99.2 (2)	N(2)–C(11)–C(12)	124.6 (9)
Cr(2)–Cr(1)–O(2)	94.6 (2)	N(2)–C(13)–C(14)	119.3 (8)
Cr(2)–Cr(1)–N(3)	92.4 (2)	N(2)–C(13)–C(18)	122.2 (8)
Cr(2)–Cr(1)–N(4)	92.8 (2)	C(14)–C(13)–C(18)	118.4 (9)
O(1)–Cr(1)–O(2)	166.2 (2)	C(13)–C(14)–C(15)	119.1 (9)
O(1)–Cr(1)–N(3)	89.2 (2)	C(13)–C(14)–C(20)	121.4 (9)
O(1)–Cr(1)–N(4)	90.7 (2)	C(15)–C(14)–C(20)	119 (1)
O(2)–Cr(1)–N(3)	90.4 (2)	C(14)–C(15)–C(16)	120 (1)
O(2)–Cr(1)–N(4)	88.4 (2)	C(15)–C(16)–C(17)	120 (1)
N(3)–Cr(1)–N(4)	174.8 (3)	C(16)–C(17)–C(18)	120 (1)
Cr(1)–Cr(2)–O(3)	97.2 (2)	C(13)–C(18)–C(17)	121 (1)
Cr(1)–Cr(2)–O(4)	96.5 (2)	C(13)–C(18)–C(19)	119.1 (9)
Cr(1)–Cr(2)–N(1)	91.0 (2)	C(17)–C(18)–C(19)	119 (1)
Cr(1)–Cr(2)–N(2)	94.4 (2)	O(3)–C(21)–N(3)	119.4 (8)
O(3)–Cr(2)–O(4)	166.3 (2)	O(3)–C(21)–C(22)	117.3 (9)
O(3)–Cr(2)–N(1)	90.4 (2)	N(3)–C(21)–C(22)	123.1 (9)
O(3)–Cr(2)–N(2)	88.9 (2)	N(3)–C(23)–C(24)	119 (1)
O(4)–Cr(2)–N(1)	89.8 (2)	N(3)–C(23)–C(28)	121.2 (9)
O(4)–Cr(2)–N(2)	89.6 (2)	C(24)–C(23)–C(28)	120 (1)
N(1)–Cr(2)–N(2)	174.6 (3)	C(23)–C(24)–C(25)	118 (1)
Cr(1)–O(1)–C(1)	114.6 (5)	C(23)–C(24)–C(30)	120 (1)
Cr(1)–O(2)–C(11)	116.7 (5)	C(25)–C(24)–C(30)	122 (1)
Cr(2)–O(3)–C(21)	117.7 (6)	C(24)–C(25)–C(26)	121 (1)
Cr(2)–O(4)–C(31)	115.4 (5)	C(25)–C(26)–C(27)	121 (1)
Cr(2)–N(1)–C(1)	113.6 (5)	C(26)–C(27)–C(28)	117 (1)
Cr(2)–N(1)–C(3)	123.2 (6)	C(23)–C(28)–C(27)	122 (1)
C(1)–N(1)–C(3)	123.1 (7)	C(23)–C(28)–C(29)	120 (1)
Cr(2)–N(2)–C(11)	112.3 (6)	C(27)–C(28)–C(29)	118 (1)
Cr(2)–N(2)–C(13)	126.8 (6)	O(4)–C(31)–N(4)	122.5 (8)
C(11)–N(2)–C(13)	120.8 (7)	O(4)–C(31)–C(32)	114.6 (8)
Cr(1)–N(3)–C(21)	113.2 (6)	N(4)–C(31)–C(32)	122.9 (8)
Cr(1)–N(3)–C(23)	126.8 (6)	N(4)–C(33)–C(34)	119.8 (7)
C(21)–N(3)–C(23)	119.7 (7)	N(4)–C(33)–C(38)	120.8 (8)
Cr(1)–N(4)–C(31)	112.8 (6)	C(34)–C(33)–C(38)	119.5 (8)
Cr(1)–N(4)–C(33)	126.6 (5)	C(33)–C(34)–C(35)	118.6 (8)
C(31)–N(4)–C(33)	121.5 (7)	C(33)–C(34)–C(40)	122.6 (8)
O(1)–C(1)–N(1)	121.6 (7)	C(35)–C(34)–C(40)	118.8 (9)
O(1)–C(1)–C(2)	116.8 (8)	C(34)–C(35)–C(36)	121.4 (9)
N(1)–C(1)–C(2)	122.6 (8)	C(35)–C(36)–C(37)	118.8 (9)
N(1)–C(3)–C(4)	119.2 (9)	C(36)–C(37)–C(38)	122 (1)
N(1)–C(3)–C(8)	121.6 (9)	C(33)–C(38)–C(37)	119.7 (9)
C(4)–C(3)–C(8)	119.2 (9)	C(33)–C(38)–C(39)	118.3 (9)
C(3)–C(4)–C(5)	119 (1)	C(37)–C(38)–C(39)	121.8 (9)
C(3)–C(4)–C(10)	121.9 (9)	C(106)–C(101)–C(102)	149 (2)
C(5)–C(4)–C(10)	119 (1)	C(101)–C(102)–C(103)	90 (2)
C(4)–C(5)–C(6)	119 (1)	C(102)–C(103)–C(104)	137 (2)
C(5)–C(6)–C(7)	120 (1)	C(103)–C(104)–C(105)	130 (2)
C(6)–C(7)–C(8)	122 (1)	C(104)–C(105)–C(106)	116 (2)
C(3)–C(8)–C(7)	120 (1)	C(105)–C(106)–C(101)	94 (2)
C(3)–C(8)–C(9)	121 (1)	C(201)–C(200)–C(202)	145 (3)
C(7)–C(8)–C(9)	119 (1)	C(200)–C(201)–C(202)	112 (3)
O(2)–C(11)–N(2)	122.0 (8)	C(200)–C(202)–C(201)	103 (3)
O(2)–C(11)–C(12)	113.5 (9)		

The planes of phenyl rings on each ligand lie essentially perpendicular to the planes of their respective N–C–O bridging atoms (mean dihedral angle = 89.7°) as would be expected in order to minimize the repulsions between the methyl groups at the 2′ and 6′ positions and the bridge. This may be compared with the corresponding mean angle in $Cr_2[PhNC(CH_3)O]_4$, which is 48°. The Cr–Cr bond length, 1.937 (2) Å, in **1** is significantly longer than that in the phenyl analogue,[6] 1.873 (1) Å, and this surprising result is the most important of the findings reported here. The average Cr–O and Cr–N distances in **1** are 1.957 (5) and 2.078 (9) Å, respectively. These distances are almost identical with those observed in

Table V. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Cr_2[(2,6\text{-xylyl})NC(CH_3)O]_4 \cdot 2CH_2Br$ (**2**)[a]

atom	*x*	*y*	*z*	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Br(1)	0.1092 (1)	0.4923 (2)	0.4232 (2)	4.3 (2)	6.6 (2)	4.6 (2)	0.1 (3)	−0.8 (2)	−0.3 (2)
Br(2)	0.1445 (1)	0.4840 (4)	0.5840 (2)	6.2 (2)	19.0 (5)	5.6 (2)	−2.9 (4)	−1.5 (2)	0.5 (3)
Br(3)	0.3702 (2)	0.5253 (4)	0.2820 (3)	11.4 (4)	22.1 (6)	7.7 (3)	−6.4 (4)	−2.8 (3)	2.2 (4)
Br(4)	0.3896 (2)	0.4740 (3)	0.4440 (3)	7.9 (3)	10.2 (3)	8.8 (3)	−0.9 (3)	−0.6 (3)	2.4 (3)
Cr(1)	0.3761 (1)	0.4963 (4)	0.6357 (2)	0.6 (2)	4.1 (2)	2.7 (2)	−0.2 (3)	−0.3 (2)	0.3 (3)
Cr(2)	0.3767 (1)	0.4957 (3)	0.7427 (2)	1.5 (2)	4.1 (2)	2.4 (2)	0.5 (3)	−0.2 (2)	−0.3 (3)

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
O(1)	0.3158 (6)	0.532 (1)	0.6230 (9)	2.6 (5)	C(18)	0.4688 (10)	0.358 (2)	0.836 (2)	3.7 (8)
O(2)	0.4358 (6)	0.460 (1)	0.6216 (10)	2.9 (5)	C(19)	0.4466 (10)	0.287 (2)	0.799 (2)	3.5 (8)
O(3)	0.1036 (6)	0.612 (1)	0.2544 (9)	1.8 (4)	C(20)	0.4930 (10)	0.599 (2)	0.806 (2)	3.9 (8)
O(4)	0.3565 (6)	0.376 (1)	0.7554 (9)	2.6 (5)	C(21)	0.4027 (9)	0.655 (2)	0.698 (2)	2.6 (7)
N(1)	0.3111 (7)	0.534 (1)	0.747 (1)	2.2 (5)	C(22)	0.4173 (9)	0.750 (2)	0.709 (2)	4.4 (8)
N(2)	0.4425 (7)	0.459 (1)	0.747 (1)	2.3 (6)	C(23)	0.4020 (9)	0.673 (2)	0.567 (1)	1.9 (7)
N(3)	0.3957 (7)	0.625 (1)	0.634 (1)	2.1 (5)	C(24)	0.4406 (9)	0.671 (2)	0.529 (2)	2.5 (7)
N(4)	0.3570 (7)	0.369 (1)	0.632 (1)	1.3 (5)	C(25)	0.4459 (10)	0.723 (2)	0.460 (2)	4.1 (9)
C(1)	0.2967 (9)	0.548 (2)	0.682 (2)	3.6 (8)	C(26)	0.4120 (9)	0.771 (2)	0.439 (2)	3.1 (8)
C(2)	0.2467 (12)	0.577 (2)	0.669 (2)	4.4 (8)	C(27)	0.3715 (9)	0.775 (2)	0.481 (1)	3.0 (8)
C(3)	0.2867 (8)	0.547 (2)	0.809 (2)	2.1 (7)	C(28)	0.3687 (9)	0.726 (2)	0.544 (2)	3.0 (8)
C(4)	0.2607 (8)	0.480 (2)	0.836 (1)	2.9 (7)	C(29)	0.3252 (10)	0.734 (2)	0.585 (2)	4.0 (8)
C(5)	0.2366 (9)	0.485 (2)	0.904 (2)	4.6 (9)	C(30)	0.4775 (9)	0.618 (2)	0.556 (2)	2.9 (8)
C(6)	0.2372 (9)	0.561 (2)	0.935 (2)	3.7 (8)	C(31)	0.3506 (9)	0.336 (2)	0.696 (2)	2.9 (7)
C(7)	0.2629 (9)	0.631 (2)	0.916 (2)	3.3 (8)	C(32)	0.3360 (9)	0.240 (2)	0.711 (2)	3.6 (8)
C(8)	0.2858 (10)	0.625 (2)	0.847 (2)	4.3 (9)	C(33)	0.3508 (9)	0.322 (2)	0.567 (2)	2.4 (7)
C(9)	0.3092 (10)	0.699 (2)	0.814 (2)	4.0 (8)	C(34)	0.3840 (9)	0.274 (2)	0.539 (2)	3.2 (8)
C(10)	0.2572 (10)	0.396 (2)	0.795 (2)	3.6 (8)	C(35)	0.3836 (10)	0.235 (2)	0.470 (2)	4.1 (8)
C(11)	0.4572 (10)	0.448 (2)	0.683 (2)	3.7 (8)	C(36)	0.3441 (9)	0.236 (2)	0.434 (2)	3.7 (8)
C(12)	0.5069 (9)	0.425 (2)	0.669 (2)	3.0 (8)	C(37)	0.3106 (9)	0.281 (2)	0.460 (2)	3.3 (8)
C(13)	0.4672 (8)	0.442 (2)	0.809 (2)	2.3 (7)	C(38)	0.3102 (10)	0.324 (2)	0.530 (2)	3.9 (8)
C(14)	0.4921 (9)	0.513 (2)	0.838 (1)	2.9 (7)	C(39)	0.2733 (9)	0.365 (2)	0.567 (2)	3.4 (8)
C(15)	0.5188 (9)	0.497 (2)	0.901 (2)	4.1 (8)	C(40)	0.4281 (10)	0.267 (2)	0.581 (2)	4.8 (9)
C(16)	0.5190 (10)	0.419 (2)	0.929 (2)	4.2 (9)	C(41)	0.1610 (10)	0.479 (2)	0.483 (2)	4.1 (8)
C(17)	0.4953 (10)	0.348 (2)	0.902 (2)	4.0 (9)	C(42)	0.3744 (12)	0.564 (2)	0.383 (2)	7.2 (11)

[a] The form of the anisotropic thermal parameter is $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2Bhka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Table VI. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Mo_2[(2,6\text{-xylyl})NC(CH_3)O]_4 \cdot 2CH_2Br_2$ (3)

atom	*x*	*y*	*z*	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo(1)	0.37603 (7)	0.4964 (2)	0.6316 (1)	2.5 (1)	2.09 (9)	1.78 (8)	−0.3 (1)	0.1 (1)	0.4 (1)
Mo(2)	0.37672 (7)	0.4968 (2)	0.7450 (1)	2.37 (9)	2.40 (8)	1.81 (8)	0.2 (2)	0.1 (1)	−0.2 (2)
Br(1)	0.1080 (1)	0.4922 (2)	0.4276 (2)	6.5 (2)	5.7 (2)	4.0 (2)	0.6 (2)	−0.7 (1)	−0.1 (2)
Br(2)	0.1449 (1)	0.4838 (4)	0.5866 (2)	9.1 (3)	18.6 (5)	5.4 (2)	−3.5 (4)	−2.2 (2)	1.5 (3)
Br(3)	0.3685 (2)	0.5303 (4)	0.2830 (3)	13.2 (4)	21.1 (5)	7.3 (2)	−5.7 (4)	−3.2 (3)	3.7 (3)
Br(4)	0.3894 (1)	0.4724 (3)	0.4412 (2)	11.0 (3)	8.3 (3)	6.7 (2)	−0.6 (3)	−0.0 (3)	2.2 (2)
O(1)	0.3123 (5)	0.5365 (10)	0.6233 (8)	1.7 (9)	2.5 (9)	1.9 (8)	0.4 (7)	−0.3 (7)	0.3 (8)
O(2)	0.4389 (5)	0.4582 (10)	0.6222 (9)	3 (1)	2.0 (9)	2.6 (9)	−0.3 (8)	0.2 (8)	1.1 (8)
O(3)	0.3967 (5)	0.6193 (10)	0.7545 (9)	1.8 (8)	3.1 (9)	2.2 (8)	−0.2 (8)	0.0 (8)	0.7 (8)
O(4)	0.3568 (5)	0.3729 (9)	0.7546 (9)	3.9 (9)	1.3 (8)	1.9 (8)	0.1 (8)	0.0 (9)	1.0 (8)

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
N(1)	0.3105 (6)	0.540 (1)	0.745 (1)	2.8 (5)	C(20)	0.4958 (8)	0.599 (2)	0.805 (2)	3.3 (7)
N(2)	0.4444 (6)	0.458 (1)	0.746 (1)	2.1 (5)	C(21)	0.4044 (8)	0.660 (1)	0.695 (1)	2.4 (6)
N(3)	0.3978 (7)	0.629 (1)	0.631 (1)	2.2 (5)	C(22)	0.4189 (8)	0.757 (2)	0.708 (2)	4.1 (8)
N(4)	0.3550 (7)	0.366 (1)	0.631 (1)	2.3 (5)	C(23)	0.4031 (9)	0.678 (2)	0.566 (2)	3.1 (7)
C(1)	0.2929 (8)	0.549 (2)	0.683 (2)	3.4 (7)	C(24)	0.4424 (8)	0.674 (2)	0.529 (1)	2.9 (7)
C(2)	0.2465 (10)	0.582 (2)	0.673 (2)	4.0 (7)	C(25)	0.4474 (9)	0.725 (2)	0.464 (2)	3.7 (8)
C(3)	0.2853 (7)	0.548 (1)	0.810 (1)	2.0 (6)	C(26)	0.4134 (8)	0.770 (2)	0.439 (2)	3.8 (8)
C(4)	0.2588 (8)	0.483 (2)	0.837 (1)	3.4 (7)	C(27)	0.3738 (9)	0.774 (2)	0.479 (1)	3.7 (8)
C(5)	0.2365 (8)	0.490 (2)	0.902 (1)	4.2 (7)	C(28)	0.3686 (8)	0.729 (2)	0.543 (2)	3.1 (7)
C(6)	0.2389 (9)	0.567 (2)	0.938 (2)	4.3 (8)	C(29)	0.3260 (9)	0.735 (2)	0.587 (2)	4.4 (8)
C(7)	0.2629 (8)	0.633 (2)	0.914 (1)	2.6 (7)	C(30)	0.4790 (8)	0.621 (2)	0.556 (2)	2.9 (7)
C(8)	0.2871 (8)	0.626 (2)	0.847 (1)	2.4 (7)	C(31)	0.3508 (8)	0.331 (2)	0.696 (2)	2.8 (6)
C(9)	0.3094 (9)	0.701 (2)	0.814 (2)	4.0 (7)	C(32)	0.3351 (8)	0.238 (2)	0.707 (1)	3.2 (7)
C(10)	0.2568 (9)	0.399 (2)	0.794 (2)	3.7 (7)	C(33)	0.3507 (8)	0.319 (1)	0.566 (1)	1.4 (6)
C(11)	0.4616 (7)	0.447 (1)	0.679 (1)	1.7 (6)	C(34)	0.3837 (7)	0.275 (1)	0.538 (1)	1.7 (6)
C(12)	0.5101 (9)	0.425 (2)	0.670 (2)	3.8 (8)	C(35)	0.3818 (8)	0.236 (2)	0.466 (1)	2.5 (6)
C(13)	0.4688 (7)	0.443 (1)	0.809 (1)	2.0 (6)	C(36)	0.3427 (8)	0.242 (2)	0.433 (2)	2.9 (6)
C(14)	0.4944 (8)	0.509 (2)	0.839 (1)	3.7 (7)	C(37)	0.3079 (8)	0.282 (2)	0.459 (2)	3.3 (7)
C(15)	0.5180 (8)	0.494 (2)	0.903 (1)	4.1 (7)	C(38)	0.3104 (9)	0.321 (2)	0.530 (1)	3.2 (7)
C(16)	0.5176 (9)	0.415 (2)	0.929 (2)	4.0 (8)	C(39)	0.2734 (9)	0.363 (2)	0.566 (2)	3.8 (8)
C(17)	0.4936 (9)	0.344 (2)	0.903 (2)	3.3 (7)	C(40)	0.4269 (8)	0.266 (2)	0.576 (1)	2.9 (7)
C(18)	0.4692 (9)	0.361 (2)	0.837 (2)	3.5 (7)	C(41)	0.1616 (10)	0.482 (2)	0.486 (2)	6.9 (10)
C(19)	0.4466 (9)	0.292 (2)	0.802 (2)	3.7 (7)	C(42)	0.3751 (10)	0.560 (2)	0.390 (2)	6.2 (10)

[a] The form of the anisotropic thermal parameter is $\exp[-0.25(h^2a^2B_{11} + k^2b^2B_{22} + l^2c^2B_{33} + 2hkaB_{12} + 2hlacB_{13} + 2klbcB_{23})]$, where *a*, *b*, and *c* are reciprocal lattice constants.

Table VII. Bond Distances (Å) for the Compounds $M_2[(2,6\text{-xylyl})NC(CH_3)O]_4 \cdot 2CH_2Br_2$, M = Cr (**2**), Mo (**3**)

	M = Cr	M = Mo
M(1)-M(2)	1.961 (4)	2.085 (2)
M(1)-Br(4)	3.544 (5)	3.544 (4)
M(1)-O(1)	1.97 (1)	2.10 (1)
M(1)-O(2)	1.96 (1)	2.07 (1)
M(1)-N(3)	2.13 (2)	2.22 (2)
M(1)-N(4)	2.10 (2)	2.18 (2)
M(2)-Br(1)	3.335 (4)	3.390 (3)
M(2)-O(3)	1.95 (1)	2.06 (1)
M(2)-O(4)	2.01 (1)	2.08 (1)
M(2)-N(1)	2.13 (2)	2.18 (2)
M(2)-N(2)	2.13 (2)	2.21 (2)
Br(1)-C(41)	1.96 (2)	2.00 (3)
Br(2)-C(41)	1.92 (2)	1.93 (3)
Br(3)-C(42)	1.96 (2)	2.03 (3)
Br(4)-C(42)	1.87 (3)	1.75 (3)
O(1)-C(1)	1.26 (2)	1.26 (3)
O(2)-C(11)	1.32 (2)	1.28 (2)
O(3)-C(21)	1.26 (2)	1.29 (2)
O(4)-C(31)	1.28 (2)	1.28 (2)
N(1)-C(1)	1.29 (2)	1.29 (3)
N(1)-C(3)	1.38 (2)	1.44 (2)
N(2)-C(11)	1.28 (2)	1.35 (2)
N(2)-C(13)	1.39 (2)	1.41 (2)
C(5)-C(6)	1.34 (3)	1.40 (3)
C(6)-C(7)	1.41 (2)	1.36 (3)
C(7)-C(8)	1.45 (3)	1.45 (3)
C(8)-C(9)	1.52 (3)	1.50 (3)
C(11)-C(12)	1.61 (3)	1.57 (3)
C(13)-C(14)	1.47 (2)	1.44 (3)
C(13)-C(18)	1.42 (3)	1.40 (3)
C(14)-C(15)	1.45 (3)	1.41 (3)
C(14)-C(20)	1.48 (3)	1.56 (3)
C(15)-C(16)	1.33 (3)	1.34 (3)
C(16)-C(17)	1.44 (3)	1.45 (3)
C(17)-C(18)	1.47 (3)	1.46 (3)
C(18)-C(19)	1.49 (3)	1.46 (3)
C(21)-C(22)	1.59 (3)	1.62 (3)
C(23)-C(24)	1.39 (2)	1.41 (3)
C(23)-C(28)	1.41 (2)	1.41 (3)
C(24)-C(25)	1.52 (3)	1.45 (3)
C(24)-C(30)	1.51 (2)	1.51 (3)
C(25)-C(26)	1.36 (3)	1.36 (3)
C(26)-C(27)	1.48 (3)	1.45 (3)
C(27)-C(28)	1.40 (3)	1.38 (3)
C(28)-C(29)	1.55 (3)	1.56 (3)
C(31)-C(32)	1.61 (3)	1.58 (3)
C(33)-C(34)	1.39 (3)	1.35 (3)
C(33)-C(38)	1.44 (3)	1.43 (3)
C(34)-C(35)	1.40 (3)	1.46 (3)
C(34)-C(40)	1.58 (3)	1.53 (3)
C(35)-C(36)	1.39 (3)	1.37 (3)
C(36)-C(37)	1.35 (2)	1.35 (3)
C(37)-C(38)	1.47 (3)	1.45 (3)
C(38)-C(39)	1.47 (3)	1.49 (3)

$Cr_2[(Ph)NC(CH_3)O]_4$,[6] i.e., 1.97 (1) and 2.06 (1) Å, respectively.

Compounds **2** and **3** are isomorphous, both to each other and to the corresponding dichloromethane analogues.[2] The compounds crystallize in the orthorhombic space group *Pccn* with eight molecules per unit cell. The molecules occupy general positions within the cell and therefore have no crystallographically imposed symmetry.

The basic structural features of **2** and **3** are very similar to those found in **1**. However, each molecule now has two CH_2Br_2 molecules that occupy positions along the axial extension of the metal–metal bonds, with M–Br distances of 3.335 (4) and 3.554 (5) Å for the chromium compound, **2**, and 3.390 (3) and 3.544 (4) Å for the molybdenum compound, **3**. The chromium–chromium distance in **2** is 1.961 (4) Å and is significantly longer than 1.937 (2) Å observed in **1** and the 1.949 (2) Å found in the analogous dichloromethane adduct. The distance is also substantially longer than the 1.873 (1) Å distance found in $Cr_2[PhNC(CH_3)O]_4$.[6] The molybdenum–molybdenum distance of 2.085 (2) Å is essentially identical with that found in the dichloromethane analogue, 2.083 (2) Å. The average Cr–O and Cr–N distances in **2** are 1.97 (1) and 2.12 (1) Å and are in good agreement with those found in **1** and the dichloromethane analogue. The average Mo–O and Mo–N distances are 2.08 (1) and 2.20 (2) Å, respectively, and are identical with these found in the dichloromethane analogue.

Discussion

Recent studies in this laboratory have established the fact that the length of the chromium–chromium quadruple bond is highly sensitive to the presence of electron donors in the axial position.[1] In a series of $Cr_2[(2,6\text{-xylyl})NC(CH_3)O]_4L_2$ compounds, where L is pyridine or a substituted pyridine, it has been found that the Cr–Cr bond length varies almost linearly with the pK_a (in aqueous solution) of the axial donor,[9] showing that the donation of σ electrons in the axial position is a crucial factor determining the Cr–Cr separation. Such donation competes with the metal–metal σ bond for the d_{z^2} orbitals on each chromium atom and therefore weakens the Cr–Cr bond.

Table IX presents a summary of relevant structural parameters in the compounds $M_2[(2,6\text{-xylyl})NC(CH_3)O]_4 \cdot L_2$ where M = Cr, Mo, and L = $C_6H_5CH_3$, CH_2Cl_2,[2] and CH_2Br_2. The chromium CH_2Cl_2 and CH_2Br_2 adducts each have one short metal–halogen distance, 3.354 (3) and 3.335 (4) Å, respectively, and one long metal–halogen distance, 3.58 (1) and 3.554 (5) Å, respectively. It is probably safe to assume that the longer metal–halogen distances are too long for there to be any significant donor interaction between the halogen atom and the metal atom. However, the interpretation of the shorter metal–halogen distances is not as clear cut, since it does not necessarily seem safe to assume that these distances are equal to or greater than would be expected for nonbonded or van der Waals contacts. No values are available for the van der Waals radius of the chromium atom. If we make the rough assumption that, as for main-group atoms, the van der Waals radius should be at least 0.50 Å greater than the single-bond covalent radius[10] (which is ca. 1.2 Å for Cr[10]) we have at least 1.70 Å as an estimated van der Waals radius for the Cr atom. Since the van der Waals radii of Cl and Br are 1.80 and 1.95 Å, respectively, van der Waals contacts should be ≥3.50 Å and ≥3.65 Å for Cl···Cr and Br···Cr, respectively. Thus, the shorter of the observed Cr···Cl and Cr···Br distances would be shorter than the estimated packing contacts. However, the reliability of the estimated van der Waals radius of Cr is quite uncertain. The conclusion that *none* of the halogen atoms is engaged in significant bonding to the chromium atoms is entirely consistent with, but not necessarily required by, the interatomic distances.

We previously[2] interpreted the Cr–Cr distance of 1.949 (2) Å in $Cr_2[(2,6\text{-xylyl})NC(CH_3)O]_4 \cdot 2CH_2Cl_2$ as evidence for Cl→Cr bonding by comparing it with the Cr–Cr distance of 1.873 (3) Å in $Cr_2[PhNC(CH_3)O]_4$. As noted in the Introduction, the Cr–Cr distance in the $Cr_2[(2,6\text{-xylyl})NC(CH_3)O]_4$ molecule itself was not available despite a number of attempts to obtain the necessary crystallographic data. We have now found that the Cr–Cr distance in the $Cr_2[(2,6\text{-xylyl})NC(CH_3)O]_4$ molecule, in an environment that does not afford even the weakest degree of axial interaction, 1.937 (2) Å, is appreciably greater than that, 1.873 (3) Å, in the phenyl analogue and, in fact, is nearly as long as that in $Cr_2[(2,6\text{-xylyl})NC(CH_3)O]_4 \cdot 2CH_2Cl_2$, 1.949 (2) Å. This calls into

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(9) Baral, S.; Cotton, F. A.; Ilsley, W. H., manuscript in preparation.

(10) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960; pp 246–260.

Table VIII. Bond Angles (Deg) for the Compounds $M_2[(2,6\text{-xylyl})NC(CH_3)O]_4 \cdot 2CH_2Br_2$, M = Cr (**2**), Mo (**3**)

	M = Cr	M = Mo		M = Cr	M = Mo
M(2)-M(1)-Br(4)	170.5 (2)	170.5 (2)	C(3)-C(8)-C(7)	120 (2)	117 (2)
M(2)-M(1)-O(1)	97.4 (4)	94.7 (4)	C(3)-C(8)-C(9)	117 (2)	121 (2)
M(2)-M(1)-O(2)	96.9 (5)	94.3 (4)	C(7)-C(8)-C(9)	123 (2)	122 (2)
M(2)-M(1)-N(3)	91.0 (5)	90.0 (5)	O(2)-C(11)-N(2)	126 (2)	120 (2)
M(2)-M(1)-N(4)	91.7 (5)	90.5 (5)	O(2)-C(11)-C(12)	113 (2)	119 (2)
O(1)-M(1)-O(2)	165.7 (6)	171.0 (5)	N(2)-C(11)-C(12)	121 (2)	121 (2)
O(1)-M(1)-N(3)	89.6 (6)	90.1 (6)	N(2)-C(13)-C(14)	116 (2)	119 (2)
O(1)-M(1)-N(4)	90.3 (6)	90.1 (6)	N(2)-C(13)-C(18)	119 (2)	118 (2)
O(2)-M(1)-N(3)	90.3 (6)	89.2 (6)	C(14)-C(13)-C(18)	125 (2)	123 (2)
O(1)-M(1)-N(4)	89.2 (6)	90.5 (6)	C(13)-C(14)-C(15)	117 (2)	119 (2)
N(3)-M(1)-N(4)	177.3 (6)	179.5 (7)	C(13)-C(14)-C(20)	125 (2)	122 (2)
M(1)-M(2)-Br(1)	173.0 (2)	172.3 (2)	C(15)-C(14)-C(20)	118 (2)	118 (2)
M(1)-M(2)-O(3)	96.3 (4)	95.2 (4)	C(14)-C(15)-C(16)	118 (2)	117 (3)
M(1)-M(2)-O(4)	96.7 (4)	94.5 (4)	C(15)-C(16)-C(17)	127 (2)	128 (2)
M(1)-M(2)-N(1)	91.4 (5)	89.7 (5)	C(16)-C(17)-C(18)	118 (2)	114 (2)
M(1)-M(2)-N(2)	92.9 (5)	91.0 (5)	C(13)-C(18)-C(17)	114 (2)	119 (2)
O(3)-M(2)-O(4)	167 (1)	170.3 (6)	C(13)-C(18)-C(19)	122 (2)	122 (2)
O(3)-M(2)-N(1)	91 (1)	89.4 (6)	C(17)-C(18)-C(19)	123 (2)	119 (2)
O(3)-M(2)-N(2)	87 (1)	88.4 (6)	O(3)-C(21)-N(3)	122 (2)	123 (2)
O(4)-M(2)-N(1)	88.1 (6)	90.8 (7)	O(3)-C(21)-C(22)	117 (2)	114 (2)
O(4)-M(2)-N(2)	92.3 (6)	91.3 (6)	N(3)-C(21)-C(22)	121 (2)	123 (2)
N(1)-M(2)-N(2)	175.7 (7)	177.8 (8)	N(3)-C(23)-C(24)	122 (2)	118 (2)
M(1)-O(1)-C(1)	114 (1)	116 (1)	N(3)-C(23)-C(28)	118 (2)	118 (2)
M(1)-O(2)-C(11)	114 (1)	120 (1)	C(24)-C(23)-C(28)	120 (2)	123 (2)
M(2)-O(3)-C(21)	118 (1)	117 (1)	C(23)-C(24)-C(25)	120 (2)	118 (2)
M(2)-O(4)-C(31)	114 (1)	118 (1)	C(23)-C(24)-C(30)	120 (2)	122 (2)
M(2)-N(1)-C(1)	110 (1)	116 (1)	C(25)-C(24)-C(30)	119 (2)	120 (2)
M(2)-N(1)-C(3)	127 (1)	124 (1)	C(24)-C(25)-C(26)	118 (2)	119 (2)
C(1)-N(1)-C(3)	123 (2)	120 (2)	C(25)-C(26)-C(27)	122 (2)	121 (3)
M(2)-N(2)-C(11)	110 (1)	114 (1)	C(26)-C(27)-C(28)	118 (2)	121 (2)
M(2)-N(2)-C(13)	128 (1)	125 (1)	C(23)-C(28)-C(27)	123 (2)	117 (3)
C(11)-N(2)-C(13)	122 (2)	121 (2)	C(23)-C(28)-C(29)	123 (2)	122 (2)
M(1)-N(3)-C(21)	113 (1)	114 (2)	C(27)-C(28)-C(29)	115 (2)	120 (3)
M(1)-N(3)-C(23)	124 (1)	124 (1)	O(4)-C(31)-N(4)	123 (2)	121 (2)
C(21)-N(3)-C(23)	124 (2)	122 (2)	O(4)-C(31)-C(32)	111 (2)	116 (2)
M(1)-N(4)-C(31)	114 (1)	116 (2)	N(4)-C(31)-C(32)	126 (2)	123 (2)
M(1)-N(4)-C(33)	125 (1)	122 (1)	N(4)-C(33)-C(34)	121 (2)	122 (2)
C(31)-N(4)-C(33)	121 (2)	121 (2)	N(4)-C(33)-C(38)	120 (2)	118 (2)
O(1)-C(1)-N(1)	127 (2)	124 (2)	C(34)-C(33)-C(38)	119 (2)	121 (2)
O(1)-C(1)-C(2)	112 (2)	114 (2)	C(33)-C(34)-C(35)	125 (2)	122 (2)
N(1)-C(1)-C(2)	121 (2)	123 (2)	C(33)-C(34)-C(40)	120 (2)	124 (2)
N(1)-C(3)-C(4)	120 (2)	122 (2)	C(35)-C(34)-C(40)	115 (2)	114 (2)
N(1)-C(3)-C(8)	123 (2)	117 (2)	C(34)-C(35)-C(36)	115 (3)	114 (2)
C(4)-C(3)-C(8)	117 (2)	120 (2)	C(35)-C(36)-C(37)	121 (3)	126 (3)
C(3)-C(4)-C(5)	124 (2)	122 (2)	C(36)-C(37)-C(38)	124 (2)	118 (2)
C(3)-C(4)-C(10)	121 (2)	119 (2)	C(33)-C(38)-C(37)	113 (2)	117 (2)
C(5)-C(4)-C(10)	115 (2)	119 (2)	C(33)-C(38)-C(39)	119 (2)	119 (2)
C(4)-C(5)-C(6)	114 (2)	116 (2)	C(37)-C(38)-C(39)	128 (2)	123 (2)
C(5)-C(6)-C(7)	127 (2)	124 (2)	Br(1)-C(41)-Br(2)	108 (1)	106 (1)
C(6)-C(7)-C(8)	117 (2)	120 (2)	Br(3)-C(42)-Br(4)	110 (1)	111 (1)

Table IX. Some Bond Distances (Å) in the Compounds $Cr_2L_4 \cdot 1.5C_6H_5CH_3$, $M_2L_4 \cdot 2CH_2Cl_2$, and $M_2L_4 \cdot 2CH_2Br_2$ (M = Cr, Mo and L = (2,6-xylyl)NC(CH_3)O^- anion)

compds	M-M	M-X[a]	(M-N)$_{av}$	(M-O)$_{av}$
$Cr_2L_4 \cdot 1.5C_6H_5CH_3$	1.937 (2)		2.078 (9)	1.957 (5)
$Cr_2L_4 \cdot 2CH_2Cl_2$[b]	1.949 (2)	3.354 (3), 3.58 (1)	2.096 (6)	2.12 (1)
$Cr_2L_4 \cdot 2CH_2Br_2$	1.961 (4)	3.335 (4), 3.554 (5)	2.12 (1)	1.97 (1)
$Mo_2L_4 \cdot 2CH_2Cl_2$[b]	2.083 (3)	3.417 (6), 3.59 (1)	2.17 (2)	2.08 (1)
$Mo_2L_4 \cdot 2CH_2Br_2$	2.085 (2)	3.390 (3), 3.544 (4)	2.20 (2)	2.08 (1)

[a] X = halogen. [b] Data from ref 2.

question our earlier interpretation and also raises the question of why **1** has a considerably greater Cr–Cr bond length than its phenyl analogue. We shall address these two points in that order.

The full set of results now available no longer presents such unequivocal evidence for axial Cl→Cr interaction as previously appeared to be the case. However, there are still the following indications that at least a slight interaction of this nature does occur. First, the chromium–halogen bond length decreases as we go from dichloromethane to dibromomethane. Innocent van der Waals contacts would be expected to show the reverse trend. This observation suggests that the bromine atom in dibromomethane is interacting more strongly with the Cr–Cr bond than the chlorine atom in dichloromethane. Second, there is the increase in the chromium–chromium distance from 1.937 (2) Å in the absence of axial ligands to 1.961 (4) Å in the CH_2Br_2 adduct. Although the change in bond length, 0.024 Å, is small, as seen in Figure 3, there is a definite trend toward increasing bond length in the following order of axial ligand atoms: none < Cl < Br. Similar behavior is also shown by the two molybdenum adducts $Mo_2[(2,6\text{-xylyl})NC(CH_3)O]_4 \cdot 2L$, L = CH_2Cl_2, CH_2Br_2. The Mo–L distances again decrease in going from the CH_2Cl_2 to the CH_2Br_2 adduct, showing that even here the Br atom acts as a stronger donor toward Mo than does Cl. The Mo–Mo bond lengths are essentially identical, but this is not unexpected, since the molybdenum–molybdenum bond is known to be rather insensitive toward axial interactions.

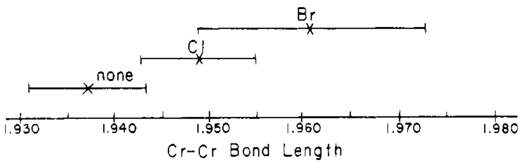

Figure 3. Plot of the Cr–Cr bond length showing the 3σ error limit, in the compounds $Cr_2[(2,6\text{-xylyl})NC(CH_3)O]_4 \cdot 1.5C_6H_5CH_3$ and $Cr_2[(2,6\text{-xylyl})NC(CH_3)O]_4 \cdot 2CH_2X_2$, X = Cl, Br.

The question of why the Cr–Cr bond is ca. 0.07 Å longer in $Cr_2[(2,6\text{-xylyl})NC(CH_3)O]_4$ than in $Cr_2[PhNC(CH_3)O]_4$, which we shall henceforth refer to simply as the xylyl and the phenyl compounds, is one we cannot unequivocally answer. This appreciable difference was not, as already emphasized, an expected result. Since our attempt to explain the observation will be rather speculative, it will, in accord with the "First Law of Well-Regulated Discourse"[11] be kept brief.

We do not believe that the simple inductive effect of replacing hydrogen atoms at the 2- and 6-positions can account for the results. We turn instead to the indirect effect of these methyl groups, namely, their influence on the dihedral angle between the phenyl or xylyl group and the plane of the bridging amido group. As we have reported above, in the phenyl compound this angle is 48° (cos 48° = 0.67) while in the xylyl compound steric factors require it to be essentially 90° (cos 90° = 0). This means that in the phenyl compound conjugation of the phenyl π system with the amide π system is about two-thirds the maximum possible value while in the xylyl compound conjugation is shut off completely. Our tentative explanation of the change in Cr–Cr bond length would then be as follows. Delocalization of phenyl π-electron density toward the Cr_2^{4+} unit reduces its positive charge thus allowing slight expansion of the 3d orbitals and increasing their overlap in the σ, π, and/or δ components of the quadruple bond. This bond, is, therefore, stronger and shorter in the phenyl compound, where considerable conjugation is possible than in the xylyl compound where no conjugation can occur.

A test of this proposal would require the synthesis of Cr_2L_4 compounds containing ligands, L, which permit even smaller dihedral angles; in such compounds, the Cr–Cr distance should be even shorter than in the acetanilido compound. Efforts to prepare and structurally characterize one or more such compounds will be made.

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Registry No. **1**, 77611-46-2; **2**, 77611-47-3; **3**, 77611-48-4; $Cr_2(O_2CCH_3)_4$, 15020-15-2; $Mo_2(O_2CCH_3)_4$, 14221-06-8.

Supplementary Material Available: Listings of observed and calculated structure factors for all three structures (25 pages). Ordering information is given on any current mashead page.

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[11] Cotton, F. A.; Hunter, D. L. *J. Am. Chem. Soc.* **1976**, *98*, 1413. See ref 13 therein.

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Crystal and Molecular Structure of Tetrakis(trifluoroacetato)bis(dimethyl sulfone)dirhodium(II). A Compound with Axially Coordinated Sulfone Ligands

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Dark green crystals of the title compound are deposited upon slow evaporaton of a benzene–chloroform solution of $Rh_2(O_2CCF_3)_4$ containing excess dimethyl sulfone. The crystals belong to the triclinic space group $P\bar{1}$ with two molecules in a unit cell of dimensions a = 10.482 (1) Å, b = 14.004 (2) Å, c = 9.533 (2) Å, α = 108.17 (2)°, β = 101.64 (2)°, γ = 82.27 (1)°, and V = 1298.3 (8) Å^3. The structure was solved with use of a combination of Patterson and direct methods to locate the two independent Rh atoms followed by full-matrix least-squares refinement and difference Fourier techniques. A total of 3682 independent reflections (Mo K$\bar{\alpha}$) with $I > 3\sigma(I)$ were used to refine the 40 nonhydrogen atoms to final discrepancy indices of R_1 = 0.048 and R_2 = 0.068. Two crystallographically unique $Rh_2(O_2CCF_3)_4(Me_2SO_2)_2$ molecules (A and B) are found in the unit cell on centers of inversion with Rh–Rh bond lengths of 2.401 (1) and 2.399 (1) Å for molecules A and B, respectively. The four trifluoroacetate groups bridge the Rh–Rh bonds with the axial positions occupied by dimethyl sulfone molecules which coordinate to the Rh atoms through one of their two oxygen atoms at distances of 2.291 (3) and 2.284 (3) Å. Bond distances and angles within the two independent molecules in the crystallographic asymmetric unit are essentially identical. The coordinated dimethyl sulfone molecules exhibit a distorted tetrahedral geometry about the sulfur atoms with average S–O bond lengths which are essentially the same for both the coordinated (1.455 (3) Å) and uncoordinated (1.450 (4) Å) sulfone oxygen atoms.

Introduction

Much current work on metal–metal bonded compounds is concerned with understanding the interaction of axial ligands with the dimetal unit and the resulting effect upon the metal–metal bond length. Quadruply bonded dichromium(II) compounds display an unusual sensitivity in the Cr–Cr bond length toward coordination by ligands along the Cr–Cr bond axis.[1,2] A considerable number of axial ligands have been used although they have been largely limited to relatively weak σ-donor ligands having nitrogen, oxygen, or halogen donor atoms.[1-4] Such a variety of adducts is not currently known

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(2) Cotton, F. A.; Ilsley, W. H.; Kaim, W. *J. Am. Chem. Soc.* **1980**, *102*, 3464 and references therein.

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