Lewis Basicity of a Chlorine Atom Bound to an Aliphatic Carbon Atom as Sensed by a Quadruple Chromium–Chromium Bond. Structures of M$_2$[(2,6-xylyl)NC(CH$_3$)O]$_4$·2CH$_2$Cl$_2$, M = Cr, Mo

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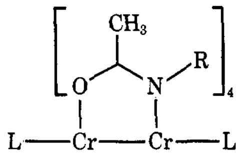
Abstract: Previous studies in this laboratory have shown that the length of the quadruple bond between two chromium atoms is an extremely sensitive function of the amount of σ electron density donated to one or both of the chromium atoms along the outer extensions of the Cr—Cr bond. We report here a compound in which one chlorine atom of a CH$_2$Cl$_2$ molecule approaches one Cr atom of a Cr$_2$[(2,6-xylyl)NC(CH$_3$)O]$_4$ molecule at a distance of 3.354 (3) Å, thereby causing the Cr–Cr distance to become 0.076 (9) Å longer than it is in the absence of this weak axial Cl$\cdots$Cr interaction. The structures of the isomorphous compounds, M$_2$[(2,6-xylyl)NC(O)CH$_3$]$_4$·2CH$_2$Cl$_2$, M = Cr, Mo, are reported. The compounds 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 = 31.037 (7), 31.253 (4) Å, b = 15.836 (4), 15.928 (2) Å, c = 18.288 (3), 18.311 (3) Å, and V = 8989 (5), 9115 (4) Å^3. The Cr–Cr and Mo–Mo distances are 1.949 (2) and 2.083 (3) Å, respectively. The average M–O and M–N distances are 1.973 (6) and 2.096 (6) Å, and 2.08 (1) and 2.17 (2) Å for the Cr and Mo compounds, respectively. There are two CH$_2$Cl$_2$ molecules which occupy positions along the axial extensions of the M–M bond with M–Cl distances of 3.58 (1) and 3.354 (3) Å for the chromium compound and 3.59 (1) and 3.417 Å for the molybdenum compound.

Introduction

Of the many quadruply bonded dimetal compounds that have been prepared, dichromium(II) compounds have exhibited a remarkable and unique variability of the metal–metal bond length, covering a range of more than 0.7 Å. The shortest Cr–Cr bond, 1.828 (2) Å, is found in Cr$_2$[5-methyl-2-methoxyphenyl]$_4$[1] and the longest, 2.541 (1) Å, in Cr$_2$(O$_2$CCF$_3$)$_4$-(Et$_2$O)$_2$.[2] Recent investigations[3] on compounds of the type I,



I

R = 2,6-xylyl,
4-Me$_2$NC$_6$H$_5$
L = THF, NC$_5$H$_5$

designed to investigate the sensitivity of the Cr–Cr bond to axial ligands in these species, prompted us to attempt to prepare the unsolvated compound Cr$_2$[(2,6-xylyl)NC(CH$_3$)O]$_4$ to allow comparison of the Cr–Cr bond length in the solvated and unsolvated species. In our attempts to crystallize this compound from methylene chloride we isolated the disolvate, Cr$_2$[(2,6-xylyl)NC(CH$_3$)O]$_4$·2CH$_2$Cl$_2$. This compound, which we had expected would have the CH$_2$Cl$_2$ molecules in mere van der Waals contact with the ligand atoms, has extended our view concerning the sensitivity of the Cr–Cr bond to interactions along the axial extensions of the Cr–Cr bond. We now report the structure of this compound, Cr$_2$[(2,6-xylyl)NC(CH$_3$)O]$_4$·2CH$_2$Cl$_2$ and, for comparison, that of its isomorphous molybdenum analogue.

Experimental Section

2′,6′-Dimethylacetanilide was prepared by reacting 2,6-xylidine[4] with acetic anhydride. The resulting compound was recrystallized from ethanol/water to form colorless needles having the literature melting point of 176 °C. All manipulations were carried out under an atmosphere of dry argon.

Cr$_2$[(2,6-xylyl)NC(O)CH$_3$]$_4$·3THF. A solution of Li[(2,6-xylyl)-NC(O)CH$_3$] was prepared by dissolving 0.65 g (4 mmol) of 2′,6′-dimethylacetanilide in 25 mL of THF and adding the corresponding amount of n-BuLi in hexane. Excess of n-BuLi is indicated by the appearance of a yellow color in the solution. Anhydrous dichromium tetraacetate (0.34 g, 1 mmol) was added to this solution, and the darkening mixture was stirred for 16 h at room temperature. Subsequent filtration gave an orange-brown solution which was then evaporated to dryness under vacuum to give a brown solid. Crystals of the compound have been shown by X-ray crystallography to be the tritetrahydrofuranate.

Cr$_2$[(2,6-xylyl)NC(O)CH$_3$]$_4$·2CH$_2$Cl$_2$ (1). The tritetrahydrofuranate, obtained by the above procedure, was transferred into an evacuation tube and a vacuum of 10^{-2} Torr was applied. After a short time of evacuation at room temperature, the color of the substance changed from brown to yellow and heating to 90 °C caused a further color change. The now presumably unsolvated material appeared whitish-gray. When CH$_2$Cl$_2$ was added to this almost colorless material, an orange-brown solution formed immediately. Slow evaporation under an argon flow gave yellow-orange crystals, which were suitable for X-ray diffraction.

Mo$_2$[(2,6-xylyl)NC(O)CH$_3$]$_4$·2CH$_2$Cl$_2$ (2). This compound was prepared in a manner analogous to that of Cr$_2$[(2,6-xylyl)NC(O)-CH$_3$]$_4$·2CH$_2$Cl$_2$. The tetrahydrofuranate of Mo readily formed large crystals, but these crystals were found to lose solvent very readily.

X-ray Crystallography. Data Collection for Cr$_2$[(2,6-xylyl)-NC(CH$_3$)O]$_4$·2CH$_2$Cl$_2$ (1). Crystals of **1** were transferred under argon to a Petri dish containing degassed mineral oil. The crystals were examined under a microscope and a suitable crystal was chosen and transferred to a slide on which there was a drop of soft epoxy cement. The crystal was then coated with the epoxy cement, secured to the end of a thin glass fiber, and mounted on a Syntex P$\bar{1}$ automatic diffractometer.

Preliminary oscillation photographs indicated that the crystal belonged to the orthorhombic system and examination of selected reflections showed that it was a single crystal of good quality. ω scans showed that several intense reflections had widths at half-height of less than 0.3°. Careful centering of 15 reflections in the range $22 < 2\theta < 32°$, selected to give varied crystal orientations, gave unit cell parameters a = 31.037 (7) Å, b = 15.836 (4) Å, c = 18.288 (3) Å, and V = 8989 (5) Å^3. The procedures preliminary to data collection have

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Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Cr_2[(2,6\text{-xylyl})NC(O)CH_3]_4 \cdot 2CH_2Cl$[a]

atom	x	y	z	$B(1,1)$	$B(2,2)$	$B(3,3)$	$B(1,2)$	$B(1,3)$	$B(2,3)$
Cr(1)	0.37596(6)	0.4963(1)	0.63570(9)	2.25(8)	2.09(7)	1.89(7)	−0.09(7)	−0.08(7)	−0.02(8)
Cr(2)	0.37628(6)	0.4961(1)	0.74229(9)	2.02(7)	2.21(7)	1.88(7)	0.00(7)	−0.02(7)	0.04(8)
Cl(1)	0.1112(1)	0.4922(3)	0.4244(3)	6.4(1)					
Cl(2)	0.1431(2)	0.4860(4)	0.5717(4)	11.1(2)					
Cl(3)	0.3710(3)	0.5237(6)	0.2929(6)	16.0(3)					
Cl(4)	0.3885(3)	0.4787(5)	0.4419(4)	12.7(2)					
O(1)	0.3159(2)	0.5332(5)	0.6221(4)	2.7(4)	2.7(3)	2.4(4)	0.6(3)	−0.3(3)	0.0(3)
O(2)	0.4360(2)	0.4602(5)	0.6217(4)	2.8(4)	2.6(3)	2.2(3)	0.2(3)	0.2(3)	−0.1(3)
O(3)	0.3944(2)	0.6142(4)	0.7544(4)	2.4(3)	1.8(3)	2.4(4)	−0.1(3)	0.2(3)	−0.3(3)
O(4)	0.3577(3)	0.3766(5)	0.7557(4)	3.1(4)	2.3(4)	2.4(4)	−0.5(3)	−0.2(3)	−0.1(3)
N(1)	0.3114(3)	0.5334(6)	0.7456(5)	1.8(4)	3.3(5)	2.0(4)	−0.2(4)	0.4(4)	−0.5(4)
N(2)	0.4411(3)	0.4597(6)	0.7459(5)	2.1(4)	2.1(4)	2.0(4)	−0.0(4)	0.2(4)	0.0(4)
N(3)	0.3956(3)	0.6230(6)	0.6316(5)	2.8(5)	3.0(4)	2.0(4)	0.4(4)	0.5(4)	0.1(4)
N(4)	0.3573(3)	0.3695(5)	0.6327(5)	3.4(5)	1.1(3)	1.7(4)	0.1(4)	0.0(4)	0.1(3)
C(1)	0.2935(4)	0.5455(7)	0.6809(6)	2.6(2)					
C(2)	0.2474(5)	0.5748(8)	0.6700(7)	3.6(3)					
C(3)	0.2848(4)	0.5449(8)	0.8096(7)	2.7(2)					
C(4)	0.2604(4)	0.4781(8)	0.8356(7)	3.5(3)					
C(5)	0.2362(4)	0.4887(8)	0.9012(8)	3.9(3)					
C(6)	0.2388(4)	0.5627(9)	0.9393(8)	4.4(3)					
C(7)	0.2629(4)	0.6324(8)	0.9120(7)	3.1(3)					
C(8)	0.2849(4)	0.6244(7)	0.8458(7)	2.6(2)					
C(9)	0.3089(5)	0.6994(9)	0.8141(8)	4.2(3)					
C(10)	0.2566(5)	0.3962(9)	0.7937(8)	4.7(3)					
C(11)	0.4588(4)	0.4504(7)	0.6807(6)	2.2(2)					
C(12)	0.5065(4)	0.4278(9)	0.6709(8)	3.9(3)					
C(13)	0.4680(4)	0.4457(7)	0.8091(6)	2.3(2)					
C(14)	0.4924(4)	0.5128(8)	0.8374(7)	3.3(3)					
C(15)	0.5180(5)	0.4995(10)	0.8999(9)	4.9(3)					
C(16)	0.5188(5)	0.4194(10)	0.9318(8)	4.8(3)					
C(17)	0.4953(4)	0.3488(9)	0.9008(8)	3.7(3)					
C(18)	0.4701(4)	0.3646(8)	0.8380(7)	3.2(3)					
C(19)	0.4475(5)	0.2903(9)	0.8037(8)	4.0(3)					
C(20)	0.4937(5)	0.5998(10)	0.8032(8)	4.7(3)					
C(21)	0.4011(4)	0.6577(7)	0.6958(6)	2.6(2)					
C(22)	0.4158(5)	0.7501(9)	0.7079(7)	4.0(3)					

atom	x	y	z	$B(1,1)$
C(23)	0.4009(4)	0.6750(7)	0.5675(6)	2.2(2)
C(24)	0.4391(4)	0.6737(8)	0.5271(7)	3.0(3)
C(25)	0.4440(4)	0.7219(8)	0.4661(7)	3.7(3)
C(26)	0.4099(5)	0.7719(9)	0.4406(8)	4.6(3)
C(27)	0.3718(4)	0.7748(9)	0.4797(8)	4.0(3)
C(28)	0.3661(4)	0.7242(8)	0.5421(7)	3.2(3)
C(29)	0.3244(5)	0.7344(10)	0.5870(9)	5.1(4)
C(30)	0.4780(4)	0.6189(8)	0.5535(7)	3.5(3)
C(31)	0.3519(4)	0.3347(7)	0.6973(6)	2.3(2)
C(32)	0.3376(4)	0.2433(9)	0.7065(7)	3.6(3)
C(33)	0.3522(4)	0.3213(7)	0.5660(6)	2.2(2)
C(34)	0.3867(4)	0.2741(8)	0.5387(7)	3.2(3)
C(35)	0.3834(4)	0.2323(8)	0.4718(7)	3.6(3)
C(36)	0.3451(4)	0.2362(9)	0.4335(8)	4.2(3)
C(37)	0.3072(5)	0.2814(8)	0.4627(8)	3.9(3)
C(38)	0.3120(4)	0.3232(8)	0.5304(7)	2.6(2)
C(39)	0.2732(5)	0.3610(9)	0.5636(8)	4.2(3)
C(40)	0.4278(5)	0.2637(9)	0.5810(8)	4.4(3)
C(41)	0.1591(5)	0.4825(10)	0.4801(9)	5.8(4)
C(42)	0.3749(7)	0.5570(14)	0.3855(12)	8.7(6)

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

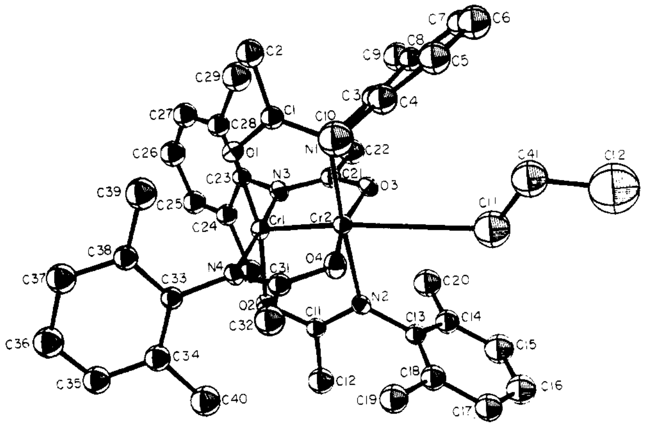

Figure 1. A computer-drawn (ORTEP) picture of the $Cr_2[(2,6\text{-xylyl})NC(CH_3)O]_4$ molecule and the coordinated CH_2Cl_2 molecule. The atoms are represented by their thermal ellipsoids scaled to enclose 50% of the electron density and the atomic numbering scheme, which applies also to the Mo analogue, is defined.

been described previously.[5]

All data were collected using Mo Kα (λ = 0.710 73 Å) radiation monochromatized in the incident beam with a graphite crystal. A total of 4501 independent reflections with $0 < 2\theta \leq 45°$ were collected at 22 ± 4 °C using the θ-2θ scan technique. A variable scan rate from 4 to 24° min^{-1} was used with a scan to background time ratio of 2. The intensities of three standard reflections were measured after every 97 reflections and showed no significant variation during the period of data collection. Lorentz and polarization corrections were applied.[6]

Solution and Refinement of $Cr_2[(2,6\text{-xylyl})NC(CH_3)O]_4 \cdot 2CH_2Cl_2$ (1). The structure was solved[6] in the orthorhombic space group *Pccn*. The positions of the two crystallographically independent chromium atoms were found by the MULTAN direct methods program. Subsequent Fourier and difference syntheses gave the positions of the remaining nonhydrogen atoms. Full-matrix least-squares refinement gave final discrepancy factors of

$$R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.091$$

$$R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.127$$

The function $\sum w(|F_o| - |F_c|)^2$ was minimized with the weighting factor, w, equal to $4F_o^2/\sigma(F_o^2)^2$. All structure-factor calculations and least-squares refinements were executed using only those 2829 reflections for which $F_o^2 > 3\sigma(F_o^2)$. Atomic scattering factors were those of Cromer and Waber.[7] The observed and calculated structure factors are available as supplementary material.

Data Collection for $Mo_2[(2,6\text{-xylyl})NC(CH_3)O]_4 \cdot 2CH_2Cl_2$ (2). A suitable crystal was coated with epoxy cement, secured to the end of a thin glass fiber with epoxy cement, and mounted on an Enraf-Nonius CAD-4F automatic diffractometer. Intensity data were collected using Mo Kα radiation ($\lambda_{\bar{\alpha}}$ = 0.710 73 Å) monochromatized by a graphite crystal in the incident beam. The take-off angle of the X-ray tube was 2.80° and the temperature during data collection was 26 ± 2 °C. Twenty-five reflections were subsequently centered and used as the basis for the indexing, carried out using the standard CAD-4 indexing routine. Indexing yielded the orthorhombic cell a = 31.253 (4) Å, b = 15.928 (2) Å, c = 18.311 (3) Å, and V = 9115 (4) Å^3, which is isomorphous to that of the chromium analogue. The data were collected in the range $0 < 2\theta \leq 45°$ with all reflections measured using

Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Mo_2[(2,6\text{-xylyl})NC(O)CH_3]_4 \cdot 2CH_2Cl_2$[a]

atom	x	y	z	$B(1,1)$	$B(2,2)$	$B(3,3)$	$B(1,2)$	$B(1,3)$	$B(2,3)$
Mo(1)	0.37626(5)	0.4967(1)	0.63119(7)	2.57(6)	2.19(6)	1.95(6)	−0.01(9)	−0.11(8)	−0.1(1)
Mo(2)	0.37635(7)	0.4966(1)	0.74497(7)	2.16(6)	2.51(6)	1.79(5)	0.3(1)	−0.07(6)	−0.1(2)
Cl(1)	0.1099(2)	0.4913(5)	0.4301(4)	7.3(2)					
Cl(2)	0.1433(4)	0.4841(7)	0.5754(6)	13.0(3)					
Cl(3)	0.3687(4)	0.5276(8)	0.2926(8)	15.9(4)					
Cl(4)	0.3895(3)	0.4762(6)	0.4373(7)	12.6(3)					
O(1)	0.3121(4)	0.5357(7)	0.6231(6)	3.2(6)	2.2(5)	1.8(6)	0.5(5)	−0.8(5)	0.7(5)
O(2)	0.4396(4)	0.4589(8)	0.6204(7)	3.6(7)	3.3(6)	1.9(6)	−0.1(5)	0.8(5)	−0.2(6)
O(3)	0.3946(4)	0.6193(7)	0.7540(6)	3.1(6)	1.9(6)	1.6(6)	0.1(5)	0.8(5)	−0.4(5)
O(4)	0.3566(4)	0.3707(8)	0.7537(6)	2.9(6)	2.6(6)	2.0(6)	−1.1(6)	0.5(5)	0.5(5)
N(1)	0.3092(5)	0.5337(12)	0.7463(8)	1.6(8)	5(1)	3.5(9)	−0.9(7)	−0.0(7)	0.4(7)
N(3)	0.3975(5)	0.6280(9)	0.6306(8)	3.1(7)	2.2(7)	1.0(7)	0.1(6)	−0.3(6)	−1.2(6)
N(4)	0.3566(5)	0.3665(9)	0.6316(8)	3.5(7)	2.0(7)	0.9(6)	−0.9(7)	−0.3(6)	−0.8(7)
N(2)	0.4426(5)	0.458(1)	0.7458(8)	1.9(3)					
C(1)	0.2910(6)	0.548(1)	0.684(1)	2.8(4)					
C(2)	0.2449(7)	0.577(1)	0.670(1)	3.9(5)					
C(3)	0.2822(6)	0.545(1)	0.810(1)	2.7(4)					
C(4)	0.2598(6)	0.480(1)	0.837(1)	2.7(5)					
C(5)	0.2361(6)	0.487(1)	0.903(1)	3.5(5)					
C(6)	0.2393(7)	0.564(1)	0.940(1)	4.5(6)					
C(7)	0.2636(6)	0.633(1)	0.913(1)	2.8(5)					
C(8)	0.2840(6)	0.625(1)	0.846(1)	2.9(5)					
C(9)	0.3072(7)	0.701(1)	0.812(1)	4.7(6)					
C(10)	0.2572(7)	0.397(1)	0.795(1)	4.7(6)					
C(11)	0.4610(6)	0.449(1)	0.679(1)	2.6(4)					
C(12)	0.5094(7)	0.426(1)	0.672(1)	4.2(5)					
C(13)	0.4678(6)	0.445(1)	0.810(1)	2.4(4)					
C(14)	0.4928(6)	0.509(1)	0.839(1)	3.7(4)					
C(15)	0.5180(6)	0.497(2)	0.903(1)	4.6(5)					
C(16)	0.5191(7)	0.416(1)	0.931(2)	5.2(6)					
C(17)	0.4961(7)	0.344(1)	0.901(1)	4.2(5)					
C(18)	0.4715(7)	0.365(1)	0.841(1)	3.6(5)					
C(19)	0.4477(7)	0.292(1)	0.803(1)	4.0(5)					
C(20)	0.4947(7)	0.599(2)	0.803(1)	4.9(6)					
C(21)	0.4015(6)	0.661(1)	0.693(1)	2.7(4)					
C(22)	0.4175(7)	0.755(1)	0.705(1)	3.9(5)					

atom	x	y	z	$B(1,1)$
C(23)	0.4012(7)	0.678(1)	0.563(1)	2.9(4)
C(24)	0.4411(6)	0.675(1)	0.528(1)	2.9(5)
C(25)	0.4441(7)	0.723(1)	0 464(1)	3.4(5)
C(26)	0.4091(7)	0.772(1)	0.436(1)	4.2(6)
C(27)	0.3733(7)	0.775(1)	0.476(1)	3.9(5)
C(28)	0.3672(7)	0.729(1)	0.541(1)	3.5(5)
C(29)	0.3240(7)	0.735(1)	0.584(1)	3.8(5)
C(30)	0.4765(7)	0.622(1)	0.550(1)	3.9(5)
C(31)	0.3517(6)	0.330(1)	0.695(1)	2.7(4)
C(32)	0.3375(6)	0.238(1)	0.704(1)	3.4(5)
C(33)	0.3513(6)	0.317(1)	0.565(1)	2.0(4)
C(34)	0.3863(6)	0.271(1)	0.536(1)	3.1(5)
C(35)	0.3811(7)	0.232(1)	0.468(1)	3.9(5)
C(36)	0.3431(7)	0.238(1)	0.434(1)	4.4(5)
C(37)	0.3082(7)	0.280(1)	0.458(1)	4.2(6)
C(38)	0.3111(6)	0.321(1)	0.528(1)	2.8(4)
C(39)	0.2740(7)	0.358(1)	0.564(1)	3.5(5)
C(40)	0.4262(7)	0.263(1)	0.580(1)	3.8(5)
C(41)	0.1592(9)	0.487(2)	0.478(2)	9.1(9)
C(42)	0.3755(9)	0.563(2)	0.387(2)	8.1(8)

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

an ω-2θ motion. The scan width for each reflection was determined as 0.8 + 0.347(tan θ) and each reflection was measured with a preliminary scan rate of 20.12°/min. The scan rate for the final scan was calculated from the preliminary scan such that the ratio $I/\sigma(I)$ would be at least 20 and the maximum scan time would not exceed 30 s. If in the preliminary scan $I/\sigma(I) \geq 20$, this measurement was used as the datum. The scan rates used varied from 20.12 to 2.51°/min. The width of the adjustable verticle aperture at the detecter was given by (1.5 + tan θ) mm. The horizontal slit was 4 mm of the 96 steps in the profile scan; the first and last 16 steps were considered to be background. Intensities and standard deviations on the intensities were assigned as

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

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

where P is the gross peak intensity, B_1 and B_2 are the background intensities, and S is the scan rate. During data collection, three orientation standards as well as three intensity standards were measured every 100 reflections. The intensity standards showed no significant decrease in intensity throughout data collection so no decay correction was applied. Lorentz and polarization corrections were applied.[6]

Solution and Refinement on $Mo_2[(2,6\text{-xylyl})NC(CH_3)O]_4 \cdot 2CH_2Cl_2$ (2). Since the compound was seen to be isomorphous with **1** refinement was begun immediately using the coordinates obtained for **1.** Subsequent full-matrix least-squares refinement yielded final discrepancy factors of $R_1 = 0.062$ and $R_2 = 0.078$.

Results

The structure of the Cr compound is shown in Figure 1, which also defines the atomic numbering scheme used for both compounds. The atomic positional and thermal parameters are given in Tables I and II for the Cr and Mo compounds, respectively. Bond distances and angles for both compounds are given in Tables III and IV and a summary of the crystallographic parameters is given in Table V.

The compounds $Cr_2[(2,6\text{-xylyl})NC(O)CH_3]_4 \cdot 2CH_2Cl_2$ (**1**) and $Mo_2[(2,6\text{-xylyl})NC(O)CH_3]_4 \cdot 2CH_2Cl_2$ (**2**) are isomorphous and crystallize in the space group *Pccn*. Each molecule occupies a general position in the cell and as a result has no crystallographically imposed symmetry. The $[(2,6\text{-xylyl})NC(O)CH_3]^-$ ligands are bonded so that the oxygen and nitrogen atoms are trans to each other and each metal atom is coordinated to two oxygen and two nitrogen atoms. The idealized symmetry of the arrangement is D_{2d}. The phenyl groups on each ligand are rotated approximately perpendicular to the O-M_2-N planes; the average dihedral angles are 93.3 and 93.6° for **1** and **2**, respectively. Each molecule has two CH_2Cl_2 molecules that occupy positions along the axial extension of the metal-metal bonds. The Cl(1)-C(41)-Cl(2) and Cl(3)-C(42)-Cl(4) planes intersect the O(1)-M_2-N(1) planes at angles of 11 and 119 and 15 and 116° for compounds **1** and **2**, respectively.

The Mo-Mo bond distance, 2.083 (2) Å, is within 3σ of the 2.088 (1) Å Mo-Mo distance observed in $Mo_2(O_2CCMe_3)_4$[8] and is among the shorter Mo-Mo bonds known;[9] the very short, 2.037 (3) Å, distance in $Mo_2[(C_5NH_4)NC(O)CH_3]_4$[10] is a special case and, therefore, cannot be directly compared. The short Mo-Mo bond in **2** is consistent with the observation that the ligand, $[PhNC(CH_3)O]^-$, forms a compound, $Cr_2[PhNC(CH_3)O]_4$, having an extremely short Cr-Cr bond,

Table III. Bond Distances for the Compounds $M_2[(2,6\text{-xylyl})NC(CH_3)O]_4 \cdot 2CH_2Cl_2$, M = Cr, Mo

atoms	distance, Å	
	M = Cr	M = Mo
M(1)-M(2)	1.949(2)	2.083(2)
-Cl(4)	3.58(1)	3.59(1)
-O(1)	1.970(5)	2.11(1)
-O(2)	1.964(5)	2.08(1)
-N(3)	2.097(6)	2.18(1)
-N(4)	2.091(6)	2.16(1)
M(2)-Cl(1)	3.354(3)	3.417(6)
-O(3)	1.965(5)	2.04(1)
-O(4)	1.993(5)	2.10(1)
-N(1)	2.100(6)	2.18(2)
-N(2)	2.095(6)	2.16(1)
Cl(1)-C(41)	1.81(1)	1.78(2)
Cl(2)-C(41)	1.75(1)	1.84(2)
CL(3)-C(42)	1.78(2)	1.82(3)
Cl(4)-C(42)	1.67(2)	1.72(2)
O(1)-C(1)	1.295(9)	1.30(2)
O(2)-C(11)	1.299(8)	1.28(2)
O(3)-C(21)	1.291(9)	1.31(2)
O(4)-C(31)	1.272(9)	1.27(2)
N(1)-C(1)	1.321(9)	1.30(2)
-C(3)	1.443(9)	1.45(2)
N(2)-C(11)	1.321(9)	1.38(2)
-C(13)	1.443(9)	1.43(2)
N(3)-C(21)	1.307(9)	1.27(2)
-C(23)	1.442(9)	1.48(3)
N(4)-C(31)	1.315(9)	1.30(2)
-C(33)	1.447(9)	1.47(2)
C(1)-C(2)	1.52(1)	1.53(2)
C(3)-C(4)	1.38(1)	1.34(2)
-C(8)	1.42(1)	1.44(2)
C(4)-C(5)	1.43(1)	1.41(2)
-C(10)	1.51(1)	1.53(2)
C(5)-C(6)	1.36(1)	1.41(2)
C(6)-C(7)	1.42(1)	1.42(2)
C(7)-C(8)	1.40(1)	1.40(2)
C(8)-C(9)	1.52(1)	1.54(2)
C(11)-C(12)	1.54(1)	1.56(2)
C(13)-C(14)	1.40(1)	1.40(2)
-C(18)	1.39(1)	1.41(2)
C(14)-C(15)	1.41(1)	1.41(2)
-C(20)	1.51(1)	1.58(2)
C(15)-C(16)	1.40(1)	1.39(2)
C(16)-C(17)	1.45(1)	1.46(2)
C(17)-C(18)	1.41(1)	1.38(2)
C(18)-C(19)	1.51(1)	1.54(2)
C(21)-C(22)	1.55(1)	1.60(2)
C(23)-C(24)	1.40(1)	1.40(2)
-C(28)	1.41(1)	1.39(2)
C(24)-C(25)	1.36(1)	1.40(2)
-C(30)	1.56(1)	1.45(2)
C(25)-C(26)	1.40(1)	1.40(2)
C(26)-C(27)	1.38(1)	1.44(2)
C(27)-C(28)	1.41(1)	1.42(2)
C(28)-C(29)	1.54(1)	1.56(3)
C(31)-C(32)	1.52(1)	1.54(2)
C(33)-C(34)	1.40(1)	1.42(2)
-C(38)	1.41(1)	1.43(2)
C(34)-C(35)	1.40(1)	1.40(2)
-C(40)	1.50(1)	1.49(2)
C(35)-C(36)	1.38(1)	1.35(2)
C(36)-C(37)	1.48(1)	1.36(2)
C(37)-C(38)	1.41(1)	1.44(2)
C(38)-C(39)	1.47(1)	1.46(2)

1.873 (3) Å. The average Mo-O and Mo-N distances are 2.08 (1) and 2.17 (2) Å, and the Mo-Cl distances are 3.59 (1) and 3.417 (6) Å, respectively. The remaining distances and associated angles show no unusual features and therefore need no further discussion.

The Cr-Cr bond length, 1.949 (2) Å, in **1** is comparable only to the 1.955 (2) Å distance observed in $Cr_2(chp)_4$,[11] chp = 6-chloro-2-hydroxypyridine anion. It is substantially longer than the Cr-Cr distance, 1.873 (1) Å, found in $Cr_2[PhNC(O)CH_3]_4$. The implications of these observations will be discussed below. The average Cr-O and Cr-N distances are 1.973 (6) and 2.096 (6) Å and the Cr-Cl distances are 3.58 (1) and 3.354 (3) Å. The remaining distances show no unusual features and will therefore not be discussed.

Discussion

It has been well established in earlier studies of the Cr-Cr quadruple bond that (1) it has a marked tendency to attract donors to the axial positions and (2) the length of the Cr-Cr bond is a highly sensitive function of the extent of σ donation in these axial positions. This is most clearly evident in the behavior of a series of compounds[3] of type I, where the Cr-Cr distance is ~1.87 Å when there are no axial ligands, ~2.01 Å when one axial THF is present, ~2.23 Å when two axial THF ligands are coordinated, and ~2.35 Å when two pyridine ligands are present.

It is clear from these and other results on compounds containing Cr-Cr quadruple bonds that the extreme sensitivity of the length of this bond to axial σ donation should allow it to serve as a probe for detecting even very weak Lewis basicity. In compound **1** we have a remarkable example of this phenomenon. The two CH_2Cl_2 molecules in **1** lie in the axial positions of the central $Cr_2[(2,6\text{-xylyl})NC(CH_3)O]_4$ molecule and are oriented in such way that for each one of them one chlorine atom is close to the axial line. The distances, Cr(1)···Cl = 3.58 (1) Å and Cr(2)···Cl = 3.354 (3) Å, are long and would ordinarily be dismissed as mere nonbonded, "packing" contacts. This may well be a correct description of the longer one, but it cannot be said of both because of the behavior of the Cr-Cr bond. The observed Cr-Cr distance, 1.949 (2) Å, is 0.076 Å longer than that in $Cr_2[PhNC(CH_3)O]_4$,[12] in which the axial positions are devoid of even "packing" contacts. The 0.076 Å increase is roughly half of that produced by the coordination of one THF molecule.[3]

So far as we know, there is no previous evidence that a chlorine atom covalently bonded to a carbon atom can use a lone pair to function as a Lewis base. The present situation provides such evidence because of two unusual properties. First, the Lewis acid concerned, the quadruple Cr-Cr bond, is an unusually good electron pair acceptor. Second, it has within itself the ability to show in a simple, structural way that electron donation has occurred, even when the usual structural criterion (normally the only one available), namely, closeness of approach of donor to acceptor, is inconclusive.

In the analogous, isostructural molybdenum compound, for example, the corresponding Mo···Cl distances, 3.59 (1) and 3.417 (6) Å, are very similar, although the difference between 3.354 and 3.417 Å may be important. In any event, however, there is no significant structural response on the part of the Mo_2 unit to show whether (or not) any significant Cl → Mo electron donation is occurring. The Mo-Mo distance, 2.083 (2) Å, is within the narrow range 2.065-2.095 Å expected for a compound of this type. It is, of course, well known that Mo-Mo quadruple bonds are not very receptive to axial donors. Thus, compound **2** shows that CH_2Cl_2 molecules may approach very closely without there being any definite evidence of actual electron donation. The significance of the chromium compound in revealing the occurrence of a donor-acceptor interaction is thereby emphasized.

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Table IV. Bond Angles for the Compounds $M_2[(2,6\text{-xylyl})NC(CH_3)O]_4\cdot 2CH_2Cl_2$, M = Cr, Mo

atoms	angles, deg		atoms	angles, deg	
	M = Cr	M = Mo		M = Cr	M = Mo
M(2)-M(1)-Cl(4)	172.0(2)	171.5(2)	C(3)-C(8)-C(7)	118.8(7)	118.0(1.6)
-O(1)	97.6(2)	94.1(3)	-C(9)	121.2(8)	122.3(1.6)
-O(2)	97.2(2)	95.4(3)	C(7)-C(8)-C(9)	120.0(7)	119.7(1.6)
-N(3)	92.1(2)	90.3(4)	O(2)-C(11)-N(2)	120.7(7)	121.5(1.3)
-N(4)	91.5(2)	89.8(3)	-C(12)	117.2(7)	117.7(1.6)
O(1)-M(1)-O(2)	165.3(2)	170.5(4)	N(2)-C(11)-C(12)	122.1(7)	120.8(1.6)
-N(3)	89.2(2)	89.0(4)	N(2)-C(13)-C(14)	119.4(7)	121.3(1.5)
-N(4)	91.1(2)	90.7(4)	-C(18)	118.5(7)	120.7(1.6)
O(2)-M(1)-N(3)	89.9(2)	90.7(4)	N(2)-C(13)-C(18)	122.3(8)	117.7(1.6)
-N(4)	88.8(2)	89.6(5)	C(13)-C(14)-C(15)	119.3(8)	122.0(1.8)
N(3)-M(1)-N(4)	176.4(2)	179.6(5)	-C(20)	123.4(8)	121.5(1.5)
M(1)-M(2)-Cl(1)	173.58(9)	172.7(1)	C(15)-C(14)-C(20)	117.3(8)	116.5(1.7)
-O(3)	96.5(2)	94.6(3)	C(14)-C(15)-C(16)	119.0(9)	117(2)
-(4)	97.1(2)	94.4(3)	C(15)-C(16)-C(17)	121.9(9)	125(2)
-N(1)	91.3(2)	90.6(4)	C(16)-C(17)-C(18)	117.4(8)	113(2)
-N(2)	92.1(2)	90.5(3)	C(13)-C(18)-C(17)	119.9(8)	125.5(1.8)
O(3)-M(2)-O(4)	166.4(2)	171.0(4)	-C(19)	122.8(8)	117.3(1.6)
-N(1)	90.2(2)	90.5(6)	C(17)-C(18)-C(19)	117.2(8)	117.1(1.6)
-N(2)	89.1(2)	90.2(5)	O(3)-C(21)-N(3)	120.0(7)	122.5(1.5)
O(4)-M(2)-N(1)	89.2(2)	88.5(5)	-C(22)	115.6(7)	114.3(1.6)
-N(2)	90.7(2)	90.6(5)	N(3)-C(21)-C(22)	124.4(7)	123.2(1.6)
N(1)-M(2)-N(2)	176.5(2)	178.7(5)	N(3)-C(23)-C(24)	121.3(7)	117.8(1.6)
M(1)-O(1)-C(1)	116.7(5)	118(1)	-C(28)	119.7(7)	117.4(1.6)
M(1)-O(2)-C(11)	116.4(5)	117(1)	C(24)-C(23)-C(28)	118.9(8)	125(2)
M(2)-O(3)-C(21)	117.4(5)	117(1)	C(23)-C(24)-C(25)	121.4(8)	115.0(1.6)
M(2)-O(4)-C(31)	115.7(5)	117(1)	-C(30)	120.0(7)	124.6(1.7)
M(2)-N(1)-C(1)	114.8(5)	117.3(1.2)	C(25)-C(24)-C(30)	118.6(8)	120.4(1.6)
-C(3)	127.4(5)	127(1)	C(24)-C(25)-C(26)	120.4(9)	123.5(1.7)
C(1)-N(1)-C(3)	117.8(6)	115.7(1.6)	C(25)-C(26)-C(27)	119.5(9)	116.5(2.0)
M(2)-N(2)-C(11)	113.6(5)	116(1)	C(26)-C(27)-C(28)	120.5(9)	124(2)
-C(13)	128.6(5)	125(1)	C(23)-C(28)-C(27)	119.1(9)	116(2)
C(11)-N(2)-C(13)	117.8(6)	119.3(1.4)	-C(29)	121.7(8)	124(2)
M(1)-N(3)-C(21)	114.1(5)	115.3(1.1)	C(27)-C(28)-C(29)	118.5(8)	120.0(1.7)
-C(23)	127.5(5)	123.5(1.0)	O(4)-C(31)-N(4)	121.2(7)	120.8(1.5)
C(21)-N(3)-C(23)	118.3(7)	121.2(1.3)	-C(32)	116.4(7)	114.9(1.6)
M(1)-N(4)-C(31)	114.5(5)	118(1)	N(4)-C(31)-C(32)	122.4(9)	124.2(1.7)
-C(33)	124.0(4)	123(1)	N(4)-C(33)-C(34)	120.0(7)	120.1(1.4)
C(31)-N(4)-C(33)	121.5(6)	118.9(1.3)	-C(38)	118.4(7)	117.9(1.5)
O(1)-C(1)-N(1)	119.7(7)	120.2(1.4)	C(34)-C(33)-C(38)	121.7(8)	121.9(1.7)
-C(2)	116.4(7)	112.3(1.7)	C(33)-C(34)-C(35)	120.8(9)	117.7(2.0)
N(1)-C(1)-C(2)	124.0(7)	127.5(1.8)	-C(40)	121.7(8)	119.0(1.7)
N(1)-C(3)-C(4)	119.6(7)	120.8(1.6)	C(35)-C(34)-C(40)	117.5(8)	123.3(1.9)
-C(8)	119.1(7)	116.7(1.6)	C(34)-C(35)-C(36)	119.0(9)	119.6(2.1)
C(4)-C(3)-C(8)	121.2(7)	122.2(1.6)	C(35)-C(36)-C(37)	121.6(9)	125.8(2.3)
C(3)-C(4)-C(5)	119.1(8)	122.0(1.6)	C(36)-C(37)-C(38)	117.5(8)	117.8(1.7)
-C(10)	121.6(8)	120.3(1.5)	C(33)-C(38)-C(37)	118.2(8)	117.1(1.7)
C(5)-C(4)-C(10)	119.2(8)	117.6(1.5)	-C(39)	122.7(8)	120.3(1.6)
C(4)-C(5)-C(6)	120.0(8)	116.1(1.6)	C(37)-C(38)-C(39)	117.8(8)	122.3(1.6)
C(5)-C(6)-C(7)	121.2(9)	123.4(1.7)	Cl(1)-C(41)-Cl(2)	107.6(6)	104.3(1.2)
C(6)-C(7)-C(8)	119.4(8)	118.0(1.6)	Cl(3)-C(42)-Cl(4)	112.7(9)	107.2(1.3)

Table V. Crystallographic Data

parameter	**1**	**2**
formula	$Cr_2Cl_4N_4O_4C_{42}H_{52}$	$Mo_2Cl_4H_4O_4C_{42}H_{52}$
space group	*Pccn*	*Pccn*
a, Å	31.037(7)	31.253(4)
b, Å	15.836(4)	15.928(2)
c, Å	18.288(3)	18.311(3)
$\alpha = \beta = \gamma$, deg	90.0	90.0
V, A^3	8989(5)	9115(4)
d_x, g/cm³	1.364	1.473
Z	8	8
formula wt	922.71	1010.60
crystal size, mm	0.5 × 0.5 × 0.4	0.4 × 0.4 × 0.3
μ, cm^{-1}	7.856	8.186
range of 2θ, deg	0–45	0–45
no. of data, $F_o^2 > 3\sigma(F_o^2)$	2829	1799
no. of variables	275	270
R_1	0.091	0.062
R_2	0.127	0.078
esd	2.530	1.865

Supplementary Material Available: Table of structure factors for both compounds (20 pages). Ordering information is given on any current masthead page.

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