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A Tetrakis(amidinato)dichromium Complex with a "Supershort" Chromium–Chromium Quadruple Bond

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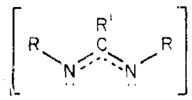
A Cr_2(amidinato)$_4$ compound has for the first time been prepared in the form of crystals suitable for structure determination, and the structure has been solved and refined by X-ray crystallography. The amidinato ligand used is $[MeNCPhNMe]^-$. The complex crystallizes in space group $P\bar{1}$ with $Z = 1$. Unit cell dimensions are $a = 9.770$ (2) Å, $b = 11.717$ (2) Å, $c = 9.620$ (2) Å, $\alpha = 113.93$ (2)°, $\beta = 104.48$ (2)°, $\gamma = 101.30$ (2)°, and $V = 918$ (1) Å^3. The $Cr_2(MeNCPhNMe)_4$ molecule has virtual D_{4h} symmetry and there is no axial coordination, since the four methyl groups on each end screen the axial positions very effectively. The Cr–Cr distance is 1.843 (2) Å, making this one of the shorter of the "supershort" Cr–Cr quadruple bonds. This structure thus provides further evidence that the long Cr–Cr distances found in all $Cr_2(O_2CR)_4$ and $Cr_2(O_2CR)_4L_2$ compounds are primarily the result of axial coordination.

Introduction

Among the many types of bidentate ligand that are sterically adapted to coordinate in a bridging fashion to a multiply bonded dimetal ion are the amidinato ions, **1**. Tetraamidinato complexes of dimolybdenum[1] and dirhenium[2] were prepared and characterized structurally several years ago. The structure of the molybdenum compound, containing the amidinate ions $[PhNCPhNPh]^-$, is basically analogous to that of the acetate and other $Mo_2(O_2CR)_4$ compounds. However, it is important to note that the presence of the eight substituents on the nitrogen atoms completely blocks the axial positions so that both intermolecular association (as occurs in the carboxylates) and coordination of additional ligands, however weak, are made impossible.



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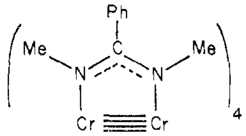
In the same report describing the molybdenum compound, the preparation of a dichromium compound of the analogous formula was also described. It was found, however, that $Cr_2(PhNCPhNPh)_4$ formed only microcrystals and that its insolubility prevented recrystallizing it to obtain single crystals large enough for a structure determination. Many unsuccessful efforts were made in this laboratory by Dr. T. R. Webb and in Durham by Dr. M. Kilner to obtain such crystals. More recently, several formamidino complexes of dichromium, $Cr_2(RNCHNR)_4$, have been reported[3] but again efforts to obtain single crystals, both in our laboratory and in Professor Vrieze's, have been unsuccessful.

As our efforts to understand the enormous variability in the Cr–Cr quadruple bond length in compounds where the ground-state electronic structure should be describable as $\sigma^2\pi^4\delta^2$, to some useful degree of approximation, have continued, the role of axial coordination has come to appear more and more crucial. We have, in fact, been led to consider seriously the possibility that axial coordination may be *uniquely* influential in determining the strength of the Cr–Cr bond.[4] This idea strongly directs attention to the problem of preparing Cr_2L_4 type complexes in which the bidentate ligands, L, are as much like carboxylate ions as possible and yet capable of excluding axial coordination. Since the amidinato type ligand meets these requirements, we recently renewed our efforts to prepare a Cr_2(amidinato)$_4$ type compound that could be obtained in the form of crystals suitable for structure determination. These efforts have been successful, and we report here the preparation and crystal structure determination of the complex **2**.



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Experimental Section

N,*N'*-Dimethylbenzamidine, $CH_3NC(C_6H_5)NHCH_3$, was synthesized in three steps from benzoyl chloride via *N*-methylbenzamide and *N*-methylbenzimide chloride.[5] The identity of the product was confirmed by proton NMR ($CDCl_3/Me_4Si$): δ 2.87 (6 H), 4.35 (1 H), 7.3 (5 H).

Tetrakis(*N*,*N'*-dimethylbenzamidinato)dichromium. A solution of 0.60 g (4 mmol) of *N*,*N'*-dimethylbenzamidine in 25 mL of THF was treated with *n*-butyllithium in hexane until the equivalent amount had been added as shown by the development of a yellow color that persisted. Tetraacetatodichromium (0.34 g, 1 mmol) was added and the mixture was stirred for 24 h. Filtration gave a yellow solution which was slowly evaporated under a slight vacuum to one-third of the original volume. After the solution was allowed to stand overnight, yellow crystals formed which were found suitable for X-ray diffraction.

The mass spectrum (250 °C, 10^{-6} torr) had a peak at m/e 692.251 901; the value calculated for the principal isotopic species of $C_{36}H_{44}N_8Cr_2$ is 692.249 880.

X-ray Crystallography. A crystal of approximate dimensions 0.10 × 0.15 × 0.15 mm was attached to the end of a glass fiber, coated with epoxy glue, and mounted on an Enraf-Nonius CAD-4F automatic diffractometer. Molybdenum Kα radiation (λ 0.710 730 Å), with a graphite-crystal monochromator in the incident beam, was used. The takeoff angle of the X-ray tube was 2.80° and the temperature during data collection was 26 + 1 °C. The standard CAD-4 centering, indexing, and data collection programs were used.

Twenty-five reflections between 12° and 15° in θ were located by a random search procedure and subsequently centered. These reflections were used as the basis for the indexing. The cell constants and the orientation matrix that were obtained were refined by a least-squares fit. The crystals were found to be triclinic with unit cell dimensions $a = 9.770$ (2) Å, $b = 11.717$ (2) Å, $c = 9.620$ (2) Å, $\alpha = 113.93$ (2)°, $\beta = 104.48$ (2)°, $\gamma = 101.30$ (2)° and $V = 918$ (1) Å^3.

The scan width for each reflection was determined as $[0.8 + 0.347 \tan\theta]°$. Reflections were first measured with a scan rate of 20.12°/min. The rate for the final scan was calculated from the preliminary scan results so 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. Scan rates varied from 20.12 to 2.51°/min. All reflections were measured by using an ω–2θ motion. A total of 2391 reflections in the range $0° < 2\theta \leq 45°$, of which 1548 had $I > 3\sigma(I)$, were collected. The width of the adjustable vertical aparture at the detector was given by $(1.5 + \tan\theta)$ mm. The horizontal slit was 4 mm. Of the 96 steps in the scan, the first and last 16 steps were considered to be background.

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

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cr	0.4554 (1)	0.4732 (1)	0.5605 (1)	2.80 (3)	4.92 (4)	4.62 (3)	1.57 (3)	1.86 (3)	2.89 (3)
N(1)	0.4919 (5)	0.6948 (5)	0.4983 (6)	3.5 (2)	4.7 (2)	4.8 (2)	1.6 (2)	2.0 (2)	2.7 (1)
N(2)	0.3826 (6)	0.6290 (5)	0.6460 (6)	3.7 (2)	5.1 (2)	5.1 (2)	2.0 (2)	2.5 (1)	3.3 (1)
N(3)	0.2489 (5)	0.3666 (5)	0.3802 (6)	2.6 (2)	5.9 (2)	4.7 (2)	1.3 (2)	1.7 (1)	3.2 (1)
N(4)	0.6411 (6)	0.5685 (5)	0.7710 (6)	3.2 (2)	5.1 (2)	4.7 (2)	1.4 (2)	1.8 (1)	3.0 (1)
C(1)	0.5370 (8)	0.7895 (7)	0.4405 (8)	5.6 (3)	6.3 (3)	6.7 (3)	2.5 (3)	3.3 (2)	4.5 (2)
C(2)	0.4121 (7)	0.7159 (6)	0.5943 (7)	3.3 (3)	4.7 (3)	3.8 (2)	1.2 (2)	0.7 (2)	2.1 (2)
C(3)	0.2881 (8)	0.6422 (7)	0.7454 (9)	6.5 (3)	6.7 (3)	7.1 (3)	3.6 (3)	4.8 (2)	3.8 (2)
C(4)	0.1178 (8)	0.3027 (7)	0.4018 (8)	3.8 (3)	7.1 (3)	6.8 (3)	1.0 (3)	2.7 (2)	3.9 (2)
C(5)	0.2352 (7)	0.3645 (6)	0.2358 (8)	3.2 (2)	4.1 (2)	4.4 (2)	1.5 (2)	1.2 (2)	1.9 (2)
C(6)	0.6417 (8)	0.5703 (7)	0.9228 (8)	5.5 (3)	6.1 (3)	4.5 (2)	2.2 (3)	2.5 (2)	3.0 (2)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
C(7)	0.2423 (10)	1.0418 (8)	0.7127 (10)	7.0 (2)	C(13)	0.0910 (7)	0.2963 (6)	0.0977 (8)	4.1 (1)
C(8)	0.1626 (9)	0.9236 (8)	0.5704 (9)	6.4 (2)	C(14)	−0.0045 (8)	0.3647 (7)	0.0687 (8)	5.0 (2)
C(9)	0.2206 (8)	0.8175 (7)	0.5324 (8)	5.2 (2)	C(15)	−0.1443 (9)	0.2975 (7)	−0.0620 (9)	6.0 (2)
C(10)	0.3544 (7)	0.8300 (6)	0.6356 (7)	4.1 (1)	C(16)	−0.1863 (10)	0.1637 (8)	−0.1654 (10)	6.7 (2)
C(11)	0.4363 (10)	0.9489 (8)	0.7755 (10)	6.4 (2)	C(17)	−0.0921 (11)	0.0939 (8)	−0.1378 (11)	7.5 (2)
C(12)	0.3796 (11)	1.0542 (9)	0.8137 (11)	7.9 (3)	C(18)	0.0499 (9)	0.1620 (7)	−0.0061 (9)	6.0 (2)

[a] The form of the anisotropic thermal parameter is $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

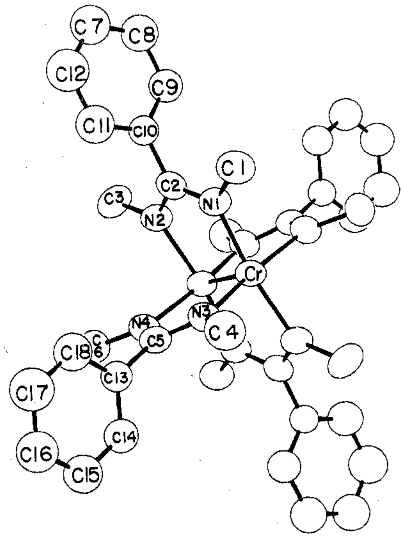


Figure 1. Molecular structure of $Cr_2(MeNCPhNMe)_4$. The numbering scheme used in the tables is defined.

The formulas used to derive the intensity and its standard deviation were

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

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

where P is the gross peak intensity, B_1 and B_2 are the background intensities, and the scan rate is given by $20.12/S$.

During data collection three intensity standards were measured after every hour of X-ray exposure. No decay was observed. In addition, three orientation standards were recentered after every 100 reflections to minimize the effects of crystal movement. If the standard deviation of the h, k, and l values for any orientation reflection exceeded 0.1, a new orientation matrix was calculated on the basis of the recentering of 22 reference reflections.

The data were corrected for Lorentz and polarization effects, but since the linear absorption coefficient is 6.55 cm^{-1}, no absorption correction was applied.

The heavy-atom positions were obtained from a three-dimensional Patterson function. The structure was refined[6] in space group $P\bar{1}$ to convergence by using anisotropic thermal parameters for all the nonhydrogen atoms except the benzene ring carbon atoms. The discrepancy indices $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ had final values of $R_1 = 0.070$ and $R_2 = 0.092$, and the goodness of fit parameter was equal to 1.81. The final difference map showed no peaks of structural significance. A list of observed and calculated structure factors is available as supplementary material.

Results

The crystals of $Cr_2(MeNCPhNMe)_4$ are formed by the packing of discrete molecules which make only van der Waals contacts with one another. The mass spectrum shows that these molecules survive intact in the vapor. The crystals belong to the space group $P\bar{1}$ and there is only one molecule per unit cell, residing on an inversion center at the origin. The asymmetric unit is half of the molecule and the coordinates of all the nonhydrogen atoms in this unit are given in Table I. The carbon atoms of the phenyl rings were refined isotropically, while all other atoms were refined anisotropically. The structure of the molecule is shown in Figure 1, and the atomic numbering scheme is defined.

While the molecule is required by crystallographic constraints to have only inversion symmetry, it actually has D_{4h} symmetry within experimental error. The planes of the phenyl rings are essentially perpendicular to the Cr_2N_2C ring planes; the two independent dihedral angles between phenyl rings and their associated Me–N–C–N–Me units are 86.2° and 91.3°. The four Cr–N distances range from 2.024 to 2.043 Å with each individual one having an esd of 0.005. They are therefore equal within the uncertainties (3σ criterion) and have an average value of 2.032 ± 0.007 Å (Table II).

The average of the four N⋯C distances in the amidino groups is 1.335 ± 0.010 Å and the average of the four N–CH$_3$ bond lengths is 1.463 ± 0.009 Å. These are in agreement with the lengths expected for C–N bonds of orders 1.5 and 1.0 between sp^2 hybridized N atoms and C atoms that are sp^2 and sp^3 hybridized, respectively. The Cr–Cr–N angles are effectively identical, with an average value of 96.0 ± 0.2°, while each individual one has an esd of 0.1°. The N–Cr–N angles, each with an esd of 0.2°, have an average value of 89.4 ± 0.2°. The two N–C–N angles within the amidine groups are identical within the errors at 116.3 (5)°.

Discussion

The Cr–Cr bond length in this compound, 1.843 (2) Å, is the third shortest M–M distance known in a chemical compound. The only two shorter Cr–Cr distances are 1.828 (2) Å in Cr_2(5-methyl-2-methoxyphenyl)$_4$[7] and 1.830 (4) Å in $Li_6[Cr(o\text{-}C_6H_4O)_4]Br_2 \cdot 6Et_2O$.[8]

The complete absence of any axial interaction with the chromium atoms in this structure is assured by the eight methyl groups in two ways. First, they make it impossible for

Table II. Bond Distances and Bond Angles in $Cr_2(CH_3NCPhNCH_3)_4$

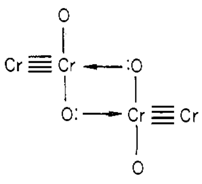
Distances (Å)

Cr-Cr′	1.843 (2)	Cr-N(3)	2.036 (4)
N(1)	2.025 (5)	N(4)	2.043 (5)
N(2)	2.024 (5)		
N(1)-C(1)	1.471 (7)	N(3)-C(4)	1.458 (7)
C(2)	1.332 (7)	C(5)	1.351 (7)
N(2)-C(3)	1.472 (7)	N(4)-C(6)	1.450 (7)
C(2)	1.318 (7)	C(5)	1.339 (7)
C(2)-C(10)	1.496 (8)	C(5)-C(13)	1.467 (8)
C(10)-C(9)	1.369 (8)	C(13)-C(14)	1.390 (8)
C(11)	1.377 (9)	C(18)	1.383 (8)
C(9)-C(8)	1.418 (9)	C(18)-C(17)	1.426 (9)
C(8)-C(7)	1.380 (9)	C(17)-C(16)	1.39 (1)
C(7)-C(12)	1.387 (9)	C(16)-C(15)	1.377 (9)
C(12)-C(11)	1.402 (9)	C(15)-C(14)	1.408 (9)

Angles (deg)

Cr′-Cr-N(1)	95.7 (1)	N(1)-Cr-N(3)	89.8 (2)
N(2)′	96.0 (1)	N(4)′	89.4 (2)
N(3)	96.4 (1)	N(2)′-Cr-N(3)	88.8 (2)
N(4)′	95.9 (1)	N(4)′	89.5 (2)
N(1)-Cr-N(2)′	168.3 (2)	N(3)-Cr-N(4)′	167.6 (2)
Cr-N(1)-C(1)	123.4 (4)	Cr-N(3)-C(4)	124.4 (4)
C(2)	115.7 (4)	C(5)	115.5 (3)
Cr′-N(2)-C(2)	115.9 (4)	Cr′-N(4)-C(5)	115.9 (4)
C(3)	119.5 (5)	C(6)	123.6 (4)
C(1)-N(1)-C(2)	120.8 (5)	C(4)-N(3)-C(5)	119.9 (5)
C(2)-N(2)-C(3)	119.5 (5)	C(5)-N(4)-C(6)	120.5 (5)
N(1)-C(2)-N(2)	116.6 (5)	N(3)-C(5)-N(4)	116.1 (5)
C(10)	121.3 (5)	C(13)	121.3 (5)
N(2)-C(2)-C(10)	122.0 (5)	N(4)-C(5)-C(13)	122.5 (5)
C(2)-C(10)-C(9)	120.0 (5)	C(5)-C(13)-C(14)	121.1 (5)
C(11)	120.5 (5)	C(18)	119.4 (5)
C(9)-C(10)-C(11)	119.4 (6)	C(14)-C(13)-C(18)	119.5 (6)
C(10)-C(11)-C(12)	119.8 (7)	C(13)-C(18)-C(17)	119.9 (6)
C(11)-C(12)-C(7)	121.4 (8)	C(18)-C(17)-C(16)	119.9 (7)
C(12)-C(7)-C(8)	118.5 (8)	C(17)-C(16)-C(15)	119.8 (7)
C(7)-C(8)-C(9)	119.8 (7)	C(16)-C(15)-C(14)	120.2 (6)
C(8)-C(9)-C(10)	121.6 (7)	C(15)-C(14)-C(13)	120.5 (6)

intermolecular association of the type found in the unsolvated $Cr_2(O_2CR)_4$ compounds to occur. They are bonded to the nitrogen atoms through the very lone pairs used to form the axial bonds in the carboxylato case, as shown in **3**. Second, they make it impossible for any additional ligand to approach closely to chromium atoms. The four methyl groups on each end form square arrays such that for a ligand L to approach along the molecular axis to a Cr–L distance of 2.8 Å it would approach to within 3.0 Å of the methyl groups as shown in **4**. The van der Waals radius of a methyl group is approximately 2.0 Å[9] and thus the radius of any ligand approaching the chromium atom along the molecular axis would have to be no more than about 1.0 Å. Since even first-row atoms such as C, N, and O have van der Waals radii of 1.4–1.5 Å, it is clearly impossible for any ligand to gain access to the chromium atoms in this direction.



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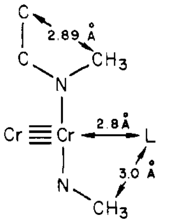

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There is also no possibility of increasing the size of the "aperture" by bending the methyl groups back away from the axis, since to do this they would have to approach more closely to the phenyl groups. As indicated in **4**, the distances from the methyl carbon atoms to the nearest phenyl carbon atoms are already only ca. 2.89 Å; this short distance cannot be further shortened without overcoming enormous repulsive forces.

The full implications of the existence of such a short Cr–Cr bond in this amidinato complex will be discussed fully in a later paper where a number of other results bearing on the role of axial ligands upon the Cr–Cr bond strength will be presented. It is interesting to note here, however, that had it been possible to obtain the first amidine complex of dichromium in crystalline form at the same time as its molybdenum analogue,[1] the existence of "supershort" Cr–Cr quadruple bonds would presumably have been discovered several years sooner than it actually was.[10]

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Registry No. $Cr_2(MeNCPhNMe)_4$, 71616-30-3; *N,N′*-dimethylbenzamidine, 29019-38-3; tetraacetatodichromium, 15020-15-2.

Supplementary Material Available: A table of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

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