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The effect of divergent-bite ligands on metal–metal bond distances in some paddlewheel complexes

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Abstract

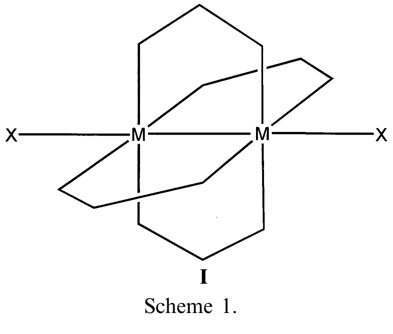
In a paddlewheel type bimetal unit, the most frequent arrangement of the bridging ligands has a conformation such that the two donor orbitals are directed along approximately parallel lines. However, when a ligand has one of the two donor atoms derived from a six-membered ring and the other from a fused five-membered ring, the two donor orbitals will be directed divergently. Such divergent-bite ligands might be expected to elongate the M–M bonds. A Cr–Cr core supported by a set of four divergent-bite ligands, $Cr_2(CHIP)_4$, where CHIP is the anion of 1′,3′-dihydrospiro[cyclohexane-1,2′-[2*H*]imidazo[4,5-*b*]pyridine], has been synthesized and crystallographically characterized. It has a Cr–Cr distance of 2.016(1) Å, which is much longer than those in paddlewheel complexes with non-divergent dinitrogen ligands. This is the first example of a dichromium complex supported by a set of four divergent-bite ligands and no axial coordination. An analogous complex, namely $Mo_2(azin)_4$, where azin represents the anion of 7-azaindole, has also been characterized. Together with $W_2(azin)_4$, which was previously reported, the first series of quadruple bonds wrapped in a sheath of four divergent-bite ligands has been obtained. A comparison of the M–M bond lengths with those in a homologous series having a more flexible ligand, DTolF, which is the anion of di-*p*-tolylformamidine, reveals that the Cr–Cr quadruple bonds are much more sensitive to the effect of the bridging ligand geometry than are Mo–Mo and W–W quadruple bonds; this is very similar to the trend in susceptibility of quadruple bonds towards axial coordination.

Keywords: Crystal structures; Chromium complexes; Metal–metal bonds

1. Introduction

The term paddlewheel complex [1,2] is applied to a complex of the type **I** (see Scheme 1), where only the essential features are shown. A central pair of metal atoms, bonded, sometimes strongly, to each other, is surrounded by four bridging bidentate ligands of the type minimally represented by **IIa** (see Scheme 2), where *X* and *Y* are donor atoms. Most often, but not necessarily, there is a negative charge present. Common and representative examples of **IIa** are **IIb** and **IIc**, a carboxylate ion and an amidate ion, respectively.

In some cases a paddlewheel complex may have a helical twist about the M–M axis. Strictly speaking, the paddlewheel analogy is then compromised. Imagine trying to steer a Mississippi steamboat propelled by a helical paddlewheel! Nevertheless, we also call the twisted ones paddlewheel complexes.



I

Scheme 1.

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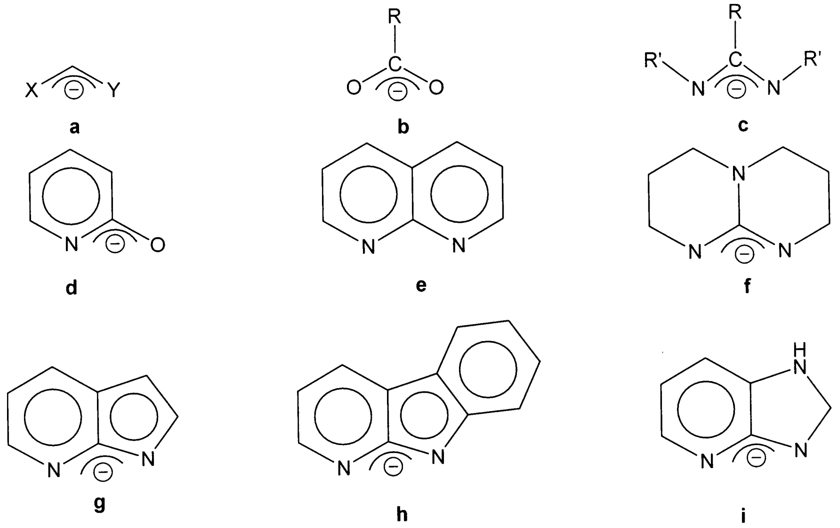


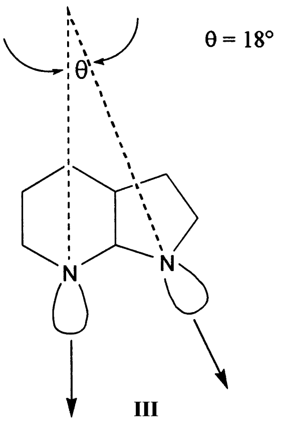
II

Scheme 2.

Of more importance is the fact the ligands making up the paddlewheel blades may be more elaborate than those shown as **IIa**–**IIc**. Typical examples of more elaborate ones are **IId**–**IIh**. Two important features of paddlewheel ligands, especially the more elaborate ones, are (a) the distance between the two donor atoms, and (b) the preferred angle between the directions of their lone pair orbitals. In most cases, the distances do not vary much.

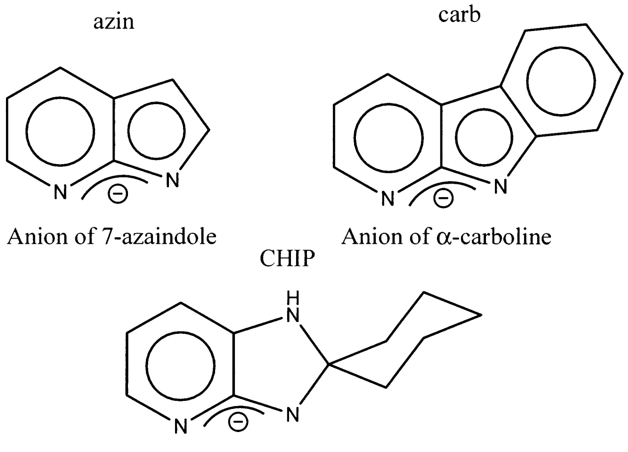
With regard to the second point, there are obviously three possibilities. Convergent, parallel, and divergent. Moreover, depending on its structure and rigidity, a ligand may be constrained to only one of these categories or it may be compliant, that is, able to adjust, within limits, to the distance preferred by the dimetal unit. An example of a ligand constrained to be parallel is **IIe**. In the case of **IIf**, there is a tendency to be convergent, though this is not rigidly required because of flexibility in the conformations of the saturated rings. In a ligand where a rigid six-membered ring is fused to a five-membered ring, such as **IIg**, **IIh** and **IIi**, divergence is constrained, as shown more explicitly in Scheme 3. In **IIi**, where divergence is favored, there may be a little more flexibility than for **IIg** and **IIh.**

The question we set out to address in this work was the following one: What effect does the fact that a ligand is constrained (**IIg**, **IIh**) or at least predisposed (**IIi**) to divergence have on the M–M bond length? We have employed three specific examples of type **IIg**, **IIh** and **IIi** ligands, namely those shown in Scheme 4. This is the first time that the α-carboline anion [3][3],



III

Scheme 3.



azin

carb

Anion of 7-azaindole

Anion of α-carboline

CHIP

Anion of 1',3'-dihydrospiro[cyclohexane-1,2'-[2*H*]imidazo[4,5-*b*]pyridine]

IV

Scheme 4.

represented by carb, and the ligand designated as CHIP have been reported in the literature to form paddle-wheel complexes. The anion of 7-azaindole, azin, has been employed previously [4,5]; the instances most relevant to the present work are $W_2(azin)_4$ [5a] and $Cr_2(azin)_4(DMF)_2$ [5c] (DMF is dimethyl formamide). Other complexes with divergent-bite ligands such as oxindolate [6] and saccharinate [7] are also known.

2. Experimental

2.1. General considerations

All syntheses and sample manipulations were carried out under an atmosphere of nitrogen with standard Schlenk and glove box techniques. The compound α-carboline (Hcarb) was prepared according to a literature method [8]. The compounds 7-azaindole (Hazin) and 1′,3′-dihydrospiro[cyclohexane-1,2′-[2*H*]imidazo-[4,5-*b*]pyridine] (H(CHIP)) were purchased from Aldrich and sublimed prior to use. Tetrakis(trifluoroacetato)dimolybdenum was prepared following a known procedure [9]. Anhydrous $CrCl_2$ was purchased from Strem Chemicals, and stored in a dry box under argon. Methyllithium (1.0 M solution in THF–cumene) and butyllithium (1.6 M in hexanes) were purchased from Aldrich. NMR spectra were obtained on a Varian VXR-300 spectrometer. Infrared spectra were recorded from KBr pellets on a Perkin–Elmer 16 PC FTIR spectrometer.

2.1.1. Preparation of $Li(acetone)_4[Cr_2(carb)_4Cl]\cdot 2CH_3COCH_3$ (**1**)

The compound Hcarb (0.47 g, 2.8 mmol) was dissolved in THF (20 ml), and deprotonated at −78°C by adding 3.0 ml (3.0 mmol) of 1.0 M MeLi in THF–cumene; a pale yellow solution of Li(carb) [10] was obtained. Anhydrous $CrCl_2$ (0.30 g, 2.4 mmol) was added through a solids addition tube. After stirring at room temperature for 24 h, an orange solid was collected by filtration, washed with 3 × 30 ml of benzene, and extracted with acetone (10 ml). The dark-red solution obtained was then layered with hexanes; red crystals of **1** were obtained after 3 days. Yield: 0.24 g (29%). IR (KBr pellet, cm^{-1}): 1623.9 (m), 1594.1 (m), 1550.7 (m), 1496.8 (w), 1469.1 (m), 1446.0 (s), 1418.3 (vs), 1362.6 (m), 1328.6 (w), 1276.7 (vs), 1229.6 (s), 1198.8 (m), 1150.9 (w), 1121.6 (m), 1106.3 (m), 1008.2 (m), 924.8 (w) 878.3 (w), 801.2 (m), 768.4 (vs), 738.5 (m), 689.1 (w), 631.4 (w), 585.5 (w), 542.4 (m), 469.9 (w), 445.9 (w).

2.1.2. Preparation of $Li(acetone)_3$-(μ-Cl)$Cr_2(carb)_4\cdot$acetone (**2**)

This was prepared in a similar way to **1**. The orange solid collected by filtration was extracted with CH_2Cl_2 (20 ml); the dark-red solution obtained was then taken to dryness under vacuum and the solid was redissolved in acetone. The dark-red solution was then layered with hexanes; long red prisms of **2** were obtained in a week. Yield: 0.18 g (25%). IR (KBr pellet, cm^{-1}): 1624.7 (m), 1596.0 (s), 1560.1 (m), 1497.2 (w), 1444.8 (s), 1413.3 (vs), 1363.2 (w), 1318.1 (w), 1275.0 (s), 1226.2 (s), 1220.6 (m), 1152.6 (w), 1108.2 (m), 1010.0 (m), 958.9 (w), 927.3 (m), 855.9 (w), 802.2 (m), 768.1 (s), 739.2 (m), 689.9 (w), 583.3 (w), 542.3 (m), 447.6 (w).

2.1.3. Preparation of $Cr_2(CHIP)_4$ (**3**), and $\mathbf{3}\cdot 5C_6H_6$

The compound H(CHIP) (0.76 g, 4.0 mmol) was dispersed in THF (20 ml), and deprotonated at −78°C by addition of 2.5 ml (4.0 mmol) of 1.6 M butyllithium in hexanes. Anhydrous $CrCl_2$ (0.30 g, 2.4 mmol) was then added via a solids addition tube. The dark-red suspension was then stirred for 12 h, and taken to dryness under vacuum. The orange–red solid obtained was then extracted with hot benzene (2 × 35 ml). The volume of the solution was reduced to ca. 30 ml; a clear red solution was obtained by filtration through Celite into a Schlenk tube, and layered with diethyl ether. Red block-shaped crystals of **3** grew in the upper part of the tube; red needle-shaped crystals of $\mathbf{3}\cdot 5C_6H_6$ were obtained at the bottom of the Schlenk tube. Yield: block-shaped crystals, 0.186 g (22%); needle-like crystals, 0.072 g (7.7%). IR (KBr, cm^{-1}) for $\mathbf{3}\cdot 5C_6H_6$: 1637.6 (w), 1627.1 (w), 1598.7 (w), 1563.3 (w), 1545.3 (w), 1524.6 (s), 1511.0 (s), 1499.1 (s), 1480.3 (m), 1461.4 (m), 1447.5 (m), 1410.5 (m), 1376.2 (m), 1343.4 (m), 1261.7 (vs), 1218.3 (w), 1094.7 (vs), 1023.2 (vs), 905.3 (w), 801.4 (vs), 689.2 (w), 659.4 (w), 562.0 (w), 477.5 (w), 449.3 (w).

2.1.4. Preparation of $Mo_2(azin)_4$ (**4**) as $\mathbf{4}\cdot 2CH_3COCH_3$ and $\mathbf{4}\cdot 2$THF

The compound Hazin (0.50 g, 4.2 mmol) was dissolved in THF (20 ml), and deprotonated at −78°C by adding 4.2 ml (4.2 mmol) of 1.0 M MeLi in THF–cumene, then a solution of $Mo_2(OOCCF_3)_4$ (0.70 g, 1.1 mmol) in THF (20 ml) was added to the Li(azin) solution, at low temperature. The resulting dark suspension was then stirred at room temperature for 12 h. A yellow solid was collected by filtration, and extracted with acetone (20 ml). The acetone extract was then filtered through a column of Celite, and layered with hexanes; dark-green crystals of $\mathbf{4}\cdot 2CH_3COCH_3$ were obtained in a week. Yield: 0.22 g (27%). Compound

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[3] The crystal structures of α-carboline and the structure of $Ni_2(carb)_4$ were described in Ref. [3]. The molecule of α-carboline is, as expected, perfectly flat, and the Ni–Ni distance in $Ni_2(carb)_4$ is 2.581 Å.

Table 1
Crystal and structure refinement data

Complex	**1**	**2**	**3**	**3**·5C_6H_6	**4**·2CH_3COCH_3	**4**·2THF
Empirical formula	$C_{62}H_{64}N_8O_6Cr_2ClLi$	$C_{56}H_{52}N_8O_4Cr_2ClLi$	$C_{44}H_{56}N_{12}Cr_2Cl_2$	$C_{74}H_{86}N_{12}Cr_2$	$C_{34}H_{32}N_8O_2Mo_2$	$C_{36}H_{36}N_8O_2Mo_2$
Formula weight	1163.60	1047.45	857.01	1247.55	776.55	804.61
Space group	$P2_1/c$	$P\bar{1}$	$I4_1/a$	$C2/c$	$P2_1/c$	$P2_1/c$
Unit cell dimensions						
a (Å)	20.899(2)	12.918(3)	19.332(1)	23.943(5)	9.125(5)	9.1507(6)
b (Å)	14.803(2)	13.192(3)	19.332(1)	15.625(3)	12.453(3)	13.213(2)
c (Å)	19.192(3)	15.274(3)	10.972(1)	18.048(4)	14.845(6)	14.176(2)
α (°)	90	88.89(3)	90	90	90	90
β (°)	91.90(3)	86.06(3)	90	99.04(3)	105.73(4)	105.083(7)
γ (°)	90	86.96(3)	90	90	90	90
V (Å^3)	5934(1)	2592.6(9)	4100.5(6)	6668(2)	1624(1)	1655.0(3)
Z	4	2	4	4	2	2
T (K)	213(2)	213(2)	213(2)	213(2)	213(2)	213(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
D_{calc} (g cm^{-3})	1.302	1.342	1.388	1.243	1.564	1.615
μ (Mo Kα) (cm^{-1})	4.68	5.25	5.79	3.78	8.16	8.05
R_1 [a,c]/R_1 [d]	0.061/0.083	0.044/0.050	0.039/0.042	0.057/0.079	0.049/0.053	0.051/0.060
wR_2 [b,c]/wR_2 [d]	0.137/0.166	0.109/0.117	0.105/0.115	0.112/0.136	0.117/0.121	0.117/0.127

[a] $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$

[b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [\max(F_o^2 \text{ or } 0) + 2(F_c^2)]/3$.

[c] Denotes value of the residual considering only the reflections with $I > 2\sigma(I)$.

[d] Denotes the value of the residual considering all the reflections.

4 has also been crystallized from THF–hexanes as dark-green block-shaped crystals of **4**·2THF. NMR (CD_2Cl_2, δ, ppm): 8.126 (doublet, 1H), 7.874 (doublet, 1H), 7.572 (1H), 6.916 (triplet, 1H), 6.550 (1H). IR (KBr pellet, cm^{-1}): 1637.2 (m), 1618.7 (m), 1595.3 (m), 1581.9 (m), 1561.0 (m), 1544.0 (m), 1523.2 (m), 1508.4 (m), 1497.5 (m), 1477.0 (m), 1459.3 (m), 1447.8 (w), 1438.0 (w), 1421.0 (m), 1410.1 (m), 1387.5 (w), 1376.1 (w), 1363.9 (w), 1341.1 (m), 1278.6 (m), 1261.9 (m), 1199.5 (w), 1182.9 (w), 1148.3 (s), 1097.6 (vs), 1055.6 (s), 1036.6 (s), 930.3 (w), 883.2 (w), 862.3 (w), 800.4 (vs), 768.2 (s), 730.5 (s), 671.1 (w), 657.8 (w), 622.5 (w), 591.8 (w), 562.0 (w), 534.0 (w), 502.6 (w), 474.0 (w), 461.2 (w), 445.0 (w), 424.1 (w).

2.2. X-ray crystallography

Data collection for all crystals was carried out on a Nonius FAST area detector diffractometer with each crystal mounted on the tip of a glass fiber under a stream of nitrogen at −60°C. Cell parameters were obtained by least-squares refinement of 250 reflections ranging in 2θ from 18.1 to 41.6°. Laue groups and centering conditions were confirmed by axial images. Data were collected using 0.2° intervals in φ over the range $0 \leq \varphi \leq 220°$ and 0.2° intervals in ω for two different regions in the range $0 \leq \omega \leq 72°$; in this way, nearly a full sphere of data was collected. The highly redundant data sets were corrected for Lorentz and polarization effects, and for absorption.

The positions of the metal atoms and sometimes the atoms of the first coordination sphere were located from a direct-methods E-map; other non-hydrogen atoms were found in alternating difference-Fourier syntheses and least-squares refinement cycles and, during the final cycles, refined anisotropically. Hydrogen atoms were placed in idealized positions for **1**, **2**, **4**·2CH_3COCH_3 and **4**·2THF; the displacement parameter for each H atom was fixed to 1.2 (aromatic) or 1.5 (methyl) times the isotropic equivalent displacement of the attached C atom. In compound **3** and **3**·5C_6H_6, hydrogen atoms were found from difference maps and refined isotropically.

In compound **4**, all the atoms of the azin ligands were found to be disordered; they were modeled as having two opposite orientations with the occupancy of each one close to 50%.

Crystallographic data for **1**, **2**, **3**, **3**·5C_6H_6, **4**·2CH_3COCH_3, and **4**·2THF are given in Table 1; selected bond distances and angles for **1** and **2**, **3** and **3**·5C_6H_6 are listed in Tables 2 and 3, respectively.

3. Results and discussion

3.1. Synthetic considerations

The azin ligand has been used with only limited success for the preparation of quadruply bonded paddlewheel complexes [5]. One of the reasons has been the difficulty in crystallizing the compounds formed and then the serious crystallographic disorder problem that may occur. This problem arises because the five- and six-membered rings are similar enough in size that molecular packing in the crystal allows each of the ligands to be oriented in either direction. Thus we have modified the azin ligand by fusing a phenyl ring to the five-membered ring; the ligand so obtained is the anion, carb, of α-carboline (Hcarb). This produced crystals without a disorder problem as is evidenced by the crystal structures of **1** and **2**. However, the asymmetric nature of the carb ligand may well lead to a mixture of four regio isomers. Simple geometry optimizations using the MM2 [4] method revealed that the energy differences between any two of the four isomers are quite small. This implies that none of the four isomers will dominate in the final product, and thus, it is not surprising that attempts to crystallize $Cr_2(carb)_4$ from a CH_2Cl_2 solution of $Cr_2(carb)_4$ complexes might be unsuccessful. We believe that because the C_{4v} isomer is uniquely capable of having a Cl^- ion coordinated at one end, it alone is isolated in an ionic form. Actually there were two ionic forms, **1** and **2**. All attempts to eliminate the LiCl and thus to isolate the simple C_{4v} molecule have failed.

Table 2
Selected bond lengths (Å) and angles(°) for compound **1** and compound **2**

Compound **1**		Compound **2**	
Bond lengths			
Cr(1)–Cr(2)	2.530(1)	Cr(2)–Cr(1)	2.5172(8)
Cr(1)–Cl(1)	2.509(2)	Cr(2)–Cl(1)	2.603(1)
		Cl(1)–Li	2.325(5)
Cr(1)–N(1)	2.119(4)	Cr(2)–N(2)	2.114(2)
Cr(1)–N(3)	2.116(4)	Cr(2)–N(4)	2.107(2)
Cr(1)–N(5)	2.120(4)	Cr(2)–N(6)	2.112(2)
Cr(1)–N(7)	2.118(4)	Cr(2)–N(8)	2.118(2)
Cr(2)–N(2)	2.064(4)	Cr(1)–N(1)	2.057(2)
Cr(2)–N(4)	2.050(4)	Cr(1)–N(3)	2.028(2)
Cr(2)–N(6)	2.054(4)	Cr(1)–N(5)	2.040(2)
Cr(2)–N(8)	2.048(4)	Cr(1)–N(7)	2.031(2)
Bond angles			
Cl(1)–Cr(1)–Cr(2)	179.33(5)	Cr(1)–Cr(2)–Cl(1)	178.90(3)
N(1)–Cr(1)–Cr(2)	90.0(1)	N(2)–Cr(2)–Cr(1)	87.49(7)
N(3)–Cr(1)–Cr(2)	87.6(1)	N(4)–Cr(2)–Cr(1)	85.97(7)
N(5)–Cr(1)–Cr(2)	86.7(1)	N(6)–Cr(2)–Cr(1)	86.62(7)
N(7)–Cr(1)–Cr(2)	86.0(1)	N(8)–Cr(2)–Cr(1)	86.04(7)
N(2)–Cr(2)–Cr(1)	87.9(1)	N(1)–Cr(1)–Cr(2)	88.24(7)
N(4)–Cr(2)–Cr(1)	88.3(1)	N(3)–Cr(1)–Cr(2)	89.82(7)
N(6)–Cr(2)–Cr(1)	89.2(1)	N(5)–Cr(1)–Cr(2)	89.02(7)
N(8)–Cr(2)–Cr(1)	90.0(1)	N(7)–Cr(1)–Cr(2)	89.27(8)
N(1)–C(5)–N(2)	124.2(4)	N(1)–C(11)–N(2)	123.2(3)
N(3)–C(16)–N(4)	122.8(4)	N(3)–C(22)–N(4)	122.9(3)
N(5)–C(27)–N(6)	123.8(4)	N(5)–C(33)–N(6)	123.5(3)
N(7)–C(38)–N(8)	122.8(4)	N(7)–C(44)–N(8)	122.7(3)

Table 3
Selected bond lengths (Å) and angles (°) for compound **3** and compound **3**$\cdot 5C_6H_6$

Compound **3**		Compound **3**$\cdot 5C_6H_6$	
Bond lengths			
Cr–CrA	2.016(1)	Cr(1)–Cr(1A)	2.125(2)
Cr–N(1)	2.061(2)	Cr(1)–N(1A)	2.042(3)
Cr–N(2A)	2.041(2)	Cr(1)–N(2)	2.064(3)
		Cr(1)–N(4A)	2.039(3)
		Cr(1)–N(5)	2.066(3)
Bond angles			
CrA–Cr–N(1)	94.62(6)	N(1A)–Cr(1)–Cr(1A)	94.4(1)
CrA–Cr–N(2A)	94.51(6)	N(2)–Cr(1)–Cr(1A)	90.3(1)
N(2)–C(11)–N(1)	123.6(2)	N(4A)–Cr(1)–Cr(1A)	94.9(1)
		N(5)–Cr(1)–Cr(1A)	89.90(9)
		N(1)–C(11)–N(2)	123.2(4)
		N(4)–C(22)–N(5)	124.1(4)

To increase the possibility of isolating a particular isomer and to increase the solubility of the final complex, a further modification of the ligand was desirable. The ligand CHIP served well for these purposes. The bulkiness of the cyclohexyl ring both favors the D_{2d} isomer and makes for greater solubility. A possible complication owing to the presence of two amine protons did not arise because the N atom bound to a carbon atom at an *ortho* position of the pyridyl N atom is more acidic, and thus by carefully controlling the temperature at −78°C, H(CHIP) was selectively deprotonated at the desired position.

The synthesis of $Mo_2(azin)_4$ was quite straightforward; crystallization from THF and acetone resulted in two different crystal forms, which have different strengths of axial coordination and thus different Mo–Mo distances (see below).

3.2. Structural considerations

Compound **1** crystallized in the space group $P2_1/c$; all atoms are in general positions. The structure of the anion $[Cr_2(carb)_4)(Cl)]^-$ is depicted in Fig. 1. The dichromium unit is surrounded by four carb ligands; all phenyl rings are oriented toward one end, with a chloride ion axially coordinated to the opposite end. For each ligand, all atoms are coplanar, the chloride ion and the two chromium atoms are aligned, and thus the anion has idealized C_{4v} symmetry. The Cr–Cl bond length is 2.509(2) Å, and the Cr–Cr distance is 2.531(1) Å, which can be compared with those distances in a 7-azaindole complex $Cr_2(azin)_4(DMF)_2$ [5c], where two DMF molecules are axially coordinated to a dichromium unit with a Cr–O distance of 2.274(5) Å, and a longer Cr–Cr separation of 2.604(2) Å.

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[4] The program CACHE was used to perform these geometry optimizations. (Cache Scientific Inc., 1993, release 3.5.)

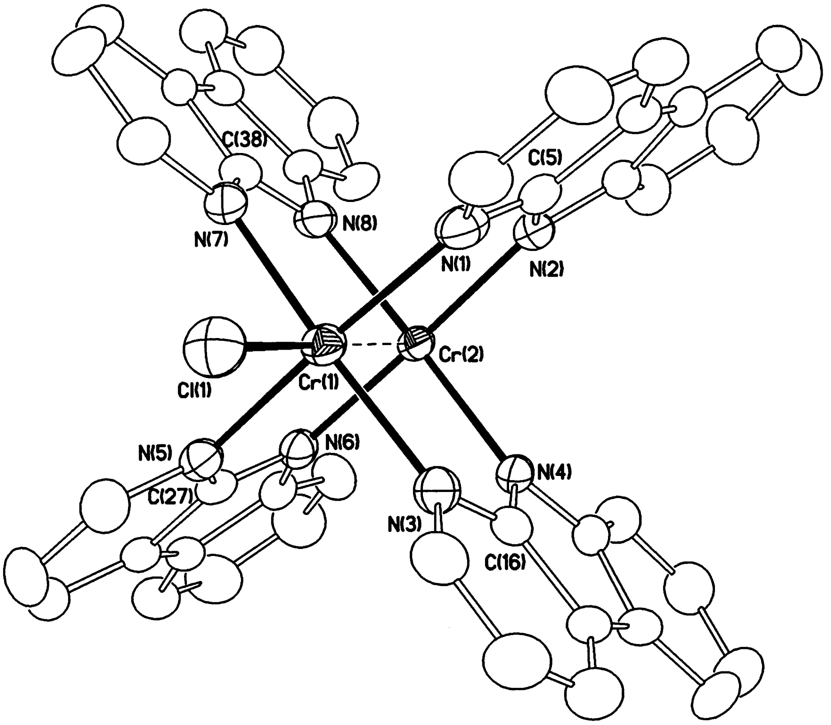

Fig. 1. A drawing of the molecular structure of $[Cr_2(carb)_4(Cl)]^-$ in **1**. Ellipsoids are shown at the 50% probability level; hydrogen atoms have been omitted for clarity.

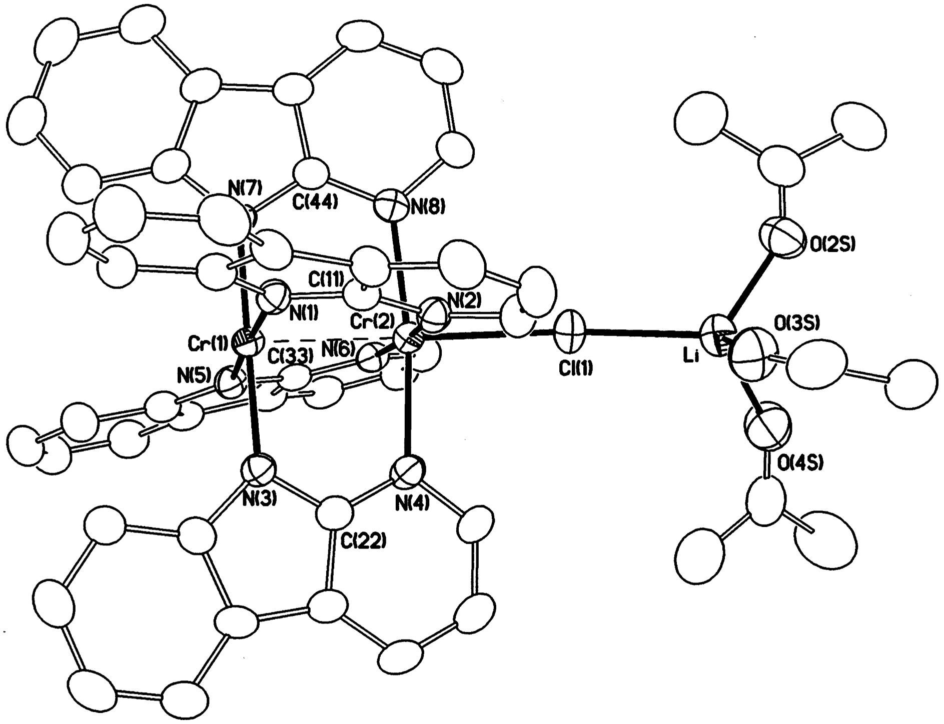

Fig. 2. A drawing of the molecular structure of $[Cr_2(carb)_4(\mu\text{-}Cl)Li(acetone)_3]$ in **2**. Ellipsoids are drawn at 50% probability level, and hydrogen atoms are omitted for clarity.

Attempts to remove the Cl^- anion by refluxing a suspension of **1** in toluene failed. Compound **2**, a coordination isomer of **1**, in which the four carb ligands are arranged in a way similar to that in **1**, but with the Cl^- anion now shared by a Cr atom and a Li atom, has also been obtained and characterized by X-ray crystallography. A drawing of the molecular structure of **2** is shown in Fig. 2. The Cr–Cl distance of 2.603(1) Å is

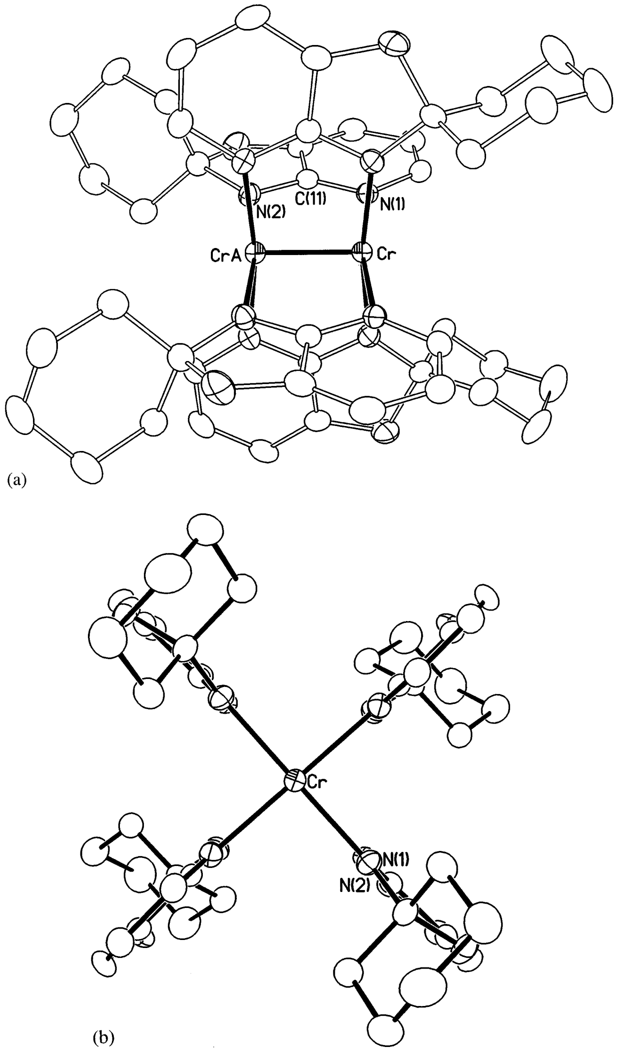

Fig. 3. A top view and a side view of the molecular structure of **3**. Ellipsoids are shown at the 50% probability level; hydrogen atoms are omitted for clarity.

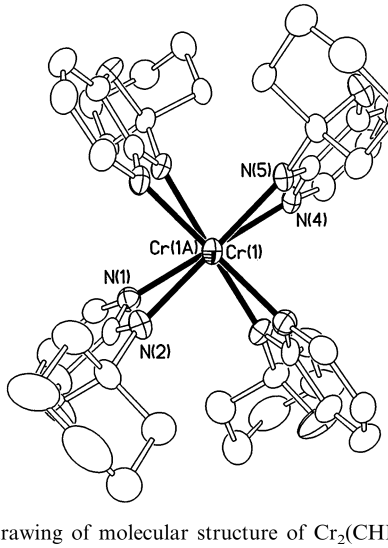

Fig. 4. A drawing of molecular structure of $Cr_2(CHIP)_4$ in **3**·$5C_6H_6$ showing the twisting of the ligand frame.

0.094(2) Å longer than that in **1**. As expected, the Cr–Cr distance of 2.5172(8) Å is slightly shorter than the Cr–Cr distance of 2.531(1) Å in **1**. However, we have still not achieved our goal of characterizing a simple $Cr_2(carb)_4$ molecule.

With the CHIP ligand we obtained the first example of a dichromium unit in a sheath of divergent ligands without axial coordination. This compound, $Cr_2(CHIP)_4$ (**3**) crystallizes in space group $I4_1/a$ with the Cr–Cr vector along a crystallographic $\bar{4}$ axis. Thus, the molecule has S_4 ($\bar{4}$) symmetry crystallographically, but, as can be seen in Fig. 3, it has effectively the higher symmetry D_{2d}. The Cr–Cr distance is 2.016(1) Å, which may be compared with distances of 1.851(7) Å in $Cr_2(hpp)_4$ [11] (hpp is **IIf**) and 1.858(1) Å in $Cr_2(PhN_3Ph)_4$ [12]. The increased Cr–Cr distance (by approximately 0.16 Å) for $Cr_2(CHIP)_4$ clearly shows the importance of the divergent nature of the CHIP ligand. However, it is evident in Fig. 3(a) that although the CHIP ligand is divergent, the Cr–N bonds in $Cr_2(CHIP)_4$ actually converge (by about 9.1°). Evidently, the CHIP ligand is compliant enough that a balance is struck between its divergent tendency and the preference of the Cr_2^{4+} unit to have a bond length of <1.9 Å.

The much longer Cr–Cr distances in $Cr_2(azin)_4(DMF)_2$ and $[Cr_2(carb)_4Cl]^-$ cases can be attributed to a combination of two factors: (a) the azin and carb ligands are not compliant; and (b) the presence of axial ligands. Indeed, there may be synergic interplay between these two properties.

Compound **3**·$5C_6H_6$ crystallizes in space group $C2/c$ with a twofold axis going through the middle of the Cr–Cr bond. A diagram of the molecular structure of $Cr_2(CHIP)_4$ in **3**·$5C_6H_6$ is given in Fig. 4. The average N–Cr–Cr–N torsional angle is 14.5°, and the average convergent angle is reduced by 4.3(1) to 4.8(1)°[5] to release the strain caused by the convergence of the two Cr–N bonds in each ligand; the Cr–Cr bond is now elongated by 0.109(2) Å, to 2.125(2) Å. Since in the Cr_2(carboxylate)$_4$ case, benzene can be a significant axial donor to the dichromium unit [13], the positions of the five benzene molecules in **3**·$5C_6H_6$ have been carefully checked; none of them is so placed as to be an axial ligand. Thus, the elongation of the Cr–Cr separation in **3**·C_6H_6 can mainly be attributed to the release of the strain caused by the convergence of the two Cr–N bonds in each divergent-bite ligand due to the Cr–Cr bonding.

The successful syntheses of $W_2(azin)_4$ [5a] and $Cr_2(CHIP)_4$ encouraged us to obtain a homologous series

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[5] Since in this case the N–Cr–Cr–N torsional angle is not equal to zero, the convergent angle can be obtained by the extrapolation of the M–N bond projections on the torsional angle dividing plane.

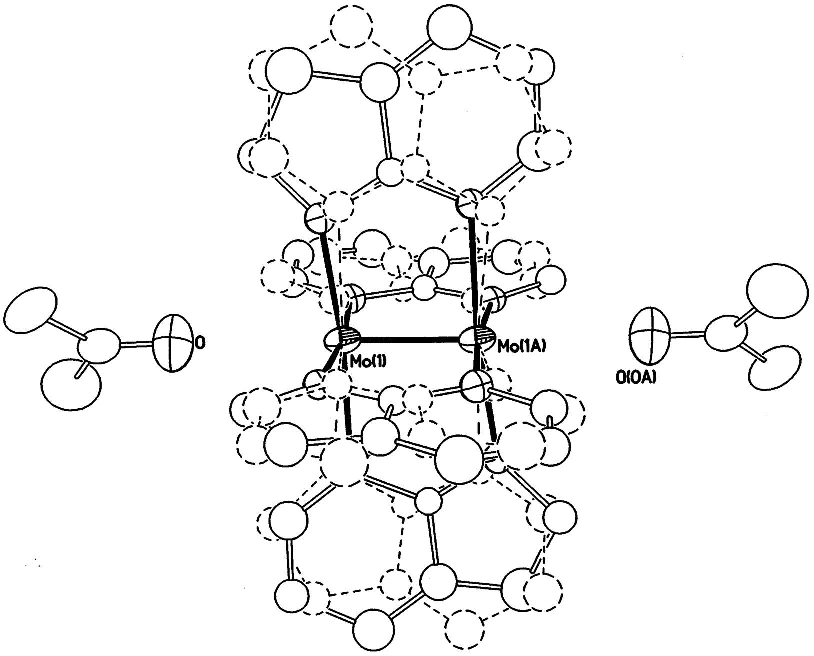

Fig. 5. A drawing of the molecular structure of $\mathbf{4}\cdot 2CH_3COCH_3$. Also shown are the two disordered orientation of the ligands, and axial coordination from the two acetone molecules.

of compounds with metal atoms from the first, second and third transition series, embraced by a set of divergent-bite ligands.

Compound $\mathbf{4}\cdot 2THF$ and compound $\mathbf{4}\cdot 2CH_3COCH_3$ are isotypic with $W_2(azin)_4\cdot 2THF$ [5a]. The orientational disorder was modeled successfully as mentioned previously in the crystallographic section of this paper. A notable observation in the two $Mo_2(azin)_4$ complex is the lengthening of the Mo–Mo bond by axial coordination. In $\mathbf{4}\cdot 2CH_3COCH_3$, the two oxygen donors of the acetone molecules point directly to the dimolybdenum unit at a distance of 2.710(2) Å (Fig. 5). The Mo–Mo distance is 2.135(1) Å. Normally the axial coordination of an oxygen donor, which is 2.710(2) Å away from a dimolybdenum unit, is negligible. However, in $\mathbf{4}\cdot 2THF$, the Mo–Mo distance of 2.1239(9) Å is 0.011(1) Å shorter than in $\mathbf{4}\cdot 2CH_3COCH_3$, and now the oxygen donors (from THF) are 3.069(2) Å away. This reminds us of the complex $Mo_2(OOCCF_3)_4(py)_2$ [14], where the axial nitrogen donors are 2.548(8) Å away, but the Mo–Mo distance is lengthened from 2.090(4) Å in $Mo_2(OOCCF_3)_4$ [9] by 0.039(6) to 2.129(2) Å in $Mo_2(OOCCF_3)_4(py)_2$. In the latter case, the nitrogen donors are stronger and closer than the axial O donors in $\mathbf{4}\cdot 2CH_3COCH_3$. A possible explanation for the above observation is that the five-membered-ring geometry in $Mo_2(azin)_4$ and the weak basicity of the bridging ligands in $Mo_2(OOCCF_3)_4$ make them more susceptible to axial coordination.

A list of bond lengths of quadruple bonds supported by a non-divergent-bite ligand DTolF (DTolF represents the anion of di-*p*-tolylformamidine [15]) and divergent-bite ligands are given in Table 4. Also in Table 4 are the FSRs, formal shortness ratio [1], defined for a bond A–B as:

$$FSR_{AB} = D_{A-B}/(R_1^A + R_1^B)$$

where R_1^A and R_1^B are Pauling's atomic radii of A and B, respectively; D_{A-B} represents the bond distance of an A–B bond. From the FSR differences and bond length differences in Table 4, it can be concluded that the Cr–Cr bond is the most sensitive one to the geometry change of the bridging ligands. This reminds us of the trend of sensitivity to axial coordination [16], the Cr–Cr bond being the most sensitive one. To what extent these

Table 4
Comparison of homologous series of Cr, Mo, W complexes supported by non-divergent-bite ligands and divergent-bite ligands

Non-divergent-bite cases			Divergent-bite cases			Differences	
Complexes	M–M (Å)	FSR	Complexes	M–M (Å)	FSR	(M–M) (Å)	FSR
$Cr_2(DTolF)_4$	1.930(2)	0.814	$Cr_2(CHIP)_4$	2.016(1)	0.850	0.086(2)	0.036
$Mo_2(DTolF)_4$	2.085(4)	0.804	$Mo_2(azin)_4\cdot 2THF$	2.1239(9)	0.819	0.039(4)	0.015
$W_2(DTolF)_4$	2.187(1)	0.838	$W_2(azin)_4\cdot 2THF$	2.227(2)	0.854	0.040(2)	0.016

trends reflect the M–M bond strengths needs to be explored further.

3.3. Concluding remarks

A non-axially coordinated Cr–Cr quadruply bonded complex in a sheath of four divergent-bite ligands and its Mo analogue have, for the first time, been isolated and crystallographically characterized. In the dichromium complex, the FSR is found to be 0.85 (bond length 2.016(1) Å) when axial coordination is absent. When axial coordination coexists with divergent-bite geometry, the Cr–Cr bond is significantly elongated, by as much as 0.515(1) Å for an axially coordinated Cl^- anion. The divergent-bite geometry also increases the Mo–Mo separation, but the Mo_2^{4+} unit is not as sensitive. By the comparison of a homologous series of quadruply bonded group six metal complexes supported by non-divergent bite ligands with that of those complexes supported by divergent-bite ligands, it has been found that the trend of sensitivity to the effect of the bridging ligand geometry is Cr–Cr $>$ W–W $\approx$ Mo–Mo.

4. Supplementary material

Full listings of atomic coordinates, bond distances, bond angles, anisotropic displacement parameters, hydrogen atom coordinates (26 pages) are available from author F.A. Cotton.

Acknowledgements

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