

# Metal–metal bonding in pentamethylcyclopentadienylmolybdenum(IV) dinuclear compounds: chloride abstraction from non-bonded $\text{Cp}^*_2\text{Mo}_2\text{Cl}_6$ to afford bonded $[\text{Cp}^*_2\text{Mo}_2\text{Cl}_5]^+$ $\star$

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Received 18 August 1994

## Abstract

Chloride abstraction from  $\text{Cp}^*_2\text{Mo}_2\text{Cl}_6$  ( $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ) is accomplished by interaction with the Lewis acid  $\text{AlCl}_3$  to afford the structurally characterized salt  $[\text{Cp}^*_2\text{Mo}_2\text{Cl}_5]^+[\text{AlCl}_4]^-$ . Crystal data: triclinic, space group  $P\bar{1}$ ,  $a = 8.3903(13)$ ,  $b = 15.797(3)$ ,  $c = 24.036(2)$  Å,  $\alpha = 86.766(11)$ ,  $\beta = 80.916(10)$ ,  $\gamma = 81.616(14)^\circ$ ,  $V = 3110.5(8)$  Å<sup>3</sup>,  $D_c = 1.726$  Mg m<sup>-3</sup>,  $\mu(\text{Mo K}\alpha) = 1.618$  mm<sup>-1</sup>,  $R = 0.0637$ . The structure exhibits two four-legged piano stools joined by three bridging Cl atoms. The Mo–Mo distance of 2.866(2) Å is significantly longer than all other reported bonded Mo(IV)–Mo(IV) distances and longer than the single bond ( $\sigma^2\delta^2\delta^2$ ) distance in the related Mo(III) complexes  $[(\text{ring})\text{MoCl}_2]_2$  (ring = substitute cyclopentadienyl ring). The reasons for this lengthening are analyzed and discussed on the basis of structural data and Fenske–Hall MO calculations.  $[\text{Cp}^*_2\text{Mo}_2\text{Cl}_5]^+$  reacts rapidly with  $\text{Cl}^-$  to afford  $[\text{Cp}^*\text{MoCl}_4]^-$  and exhibits a reversible one-electron oxidation to a neutral  $\text{Cp}^*_2\text{Mo}_2\text{Cl}_5$  species at  $-0.13$  V versus ferrocene/ferricinium. The non-existence of a metal–metal bonded isomeric form of the  $\text{Cp}^*_2\text{Mo}_2\text{Cl}_6$  parent compound is also discussed.

**Keywords:** Crystal structures; Metal–metal bonding; Molybdenum complexes; Pentamethylcyclopentadienyl complexes; Dinuclear complexes

## 1. Introduction

The general question of whether two metals held together in a dinuclear compound by bridging ligands are also able to establish a direct bonding interaction has attracted considerable attention [1]. For complexes of 4d and 5d elements, the formation of a bond is the rule, but there are nevertheless a considerable number of exceptions. For instance, whereas edge-sharing biocahedral  $\text{Re}_2\text{Cl}_4(\mu\text{-Cl})_2(\mu\text{-dppm})_2$  exhibits a metal–metal bond [2], the metals are non-bonded in the similar  $\text{Re}_2\text{Cl}_4(\mu\text{-Cl})_2(\text{dppe})_2$  compound [3] (dppm = bis(diphenylphosphino)methane; dppe = bis(diphenylphosphino)ethane) and the two Ru(III) compounds  $\text{Ru}_2\text{Cl}_4(\mu\text{-Cl})_2(\mu\text{-dmpm})_2$  and  $\text{Ru}_2\text{Cl}_4(\mu\text{-Cl})_2(\text{PBu}_3)_4$  (dmpm = bis(dimethylphosphino)methane) are analogously bonded and non-bonded, respectively [2,4]. An

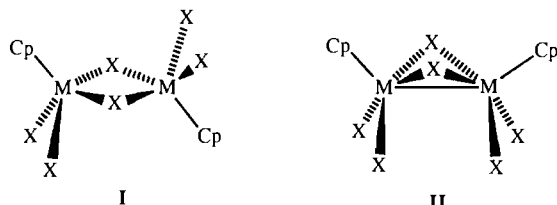
even more striking situation is found in the pair of  $\text{Mo}_2\text{Cl}_4(\mu\text{-Cl})_2\text{L}_4$  ( $\text{L} = \text{PMe}_2\text{Ph}$ ,  $\text{PEt}_3$ ) complexes having not only an identical coordination geometry but also identical stereochemistry, where a metal–metal bond exists in the former but not in the latter [5]. The strength of the metal–metal interaction increases steadily along the series of  $\text{Mo}_2\text{Cl}_4(\mu\text{-Cl})_2(\text{PMe}_x\text{Et}_{3-x})_4$  complexes ( $x = 0, 1, 2, 3$ ) [6]. A metal–metal bond is also *not* formed in the dinuclear  $\text{M}_2\text{Cl}_{10}$  compounds ( $\text{M} = \text{W}$ ,  $d^1\text{-}d^1$  or  $\text{Re}$ ,  $d^2\text{-}d^2$ ), whereas this is present in the corresponding  $\text{M}_2(\text{OMe})_{10}$  compounds [7]. For cyclopentadienyl-substituted complexes, two different forms of  $\text{Cp}^*_2\text{Ru}_2\text{Cl}_2(\mu\text{-Cl})_2$  co-crystallize in a 1:1 ratio, only one of them having an Ru–Ru bond, the geometry of the two forms being otherwise identical [8].

This contribution deals with  $\text{Cp}^*\text{-Mo(IV)}$  systems. Compound  $\text{Cp}^*_2\text{Mo}_2\text{Cl}_6$ , recently reported by us [9], was found to have structure I with no metal–metal bond between the two  $d^2$  Mo(IV) centers. This geometry is identical to that observed for the  $d^1$  Ta(IV) complex  $(\text{C}_5\text{Me}_4\text{Et})_2\text{Ta}_2\text{Br}_6$  (also lacking a metal–metal inter-

$\star$  Dedicated to Professor F.A. Cotton on the occasion of his 65th birthday.

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action) [10], whereas the  $d^3$  Re(IV) compound  $(C_5Me_4Et)_2Re_2Cl_6$  exists in the alternative, metal–metal bonded structure II [11]. We will show here that the metal–metal non-bonded  $Cp^*_2Mo_2Cl_6$  molecule rearranges to a metal–metal bonded structure upon abstraction of a  $Cl^-$  ligand. We also report a theoretical investigation of the  $[Cp^*_2Mo_2Cl_5]^+$  ion and discuss the possible reasons for the weakening of the Mo–Mo bond interaction along the series of Mo(IV) compounds  $[Cp^*_2Mo_2Cl_4]^{2+}$ ,  $[Cp^*_2Mo_2Cl_5]^+$  and  $Cp^*_2Mo_2Cl_6$ .



## 2. Experimental

### 2.1. General

All operations were carried out under an atmosphere of dinitrogen with standard Schlenk-line and glove-box techniques. Solvents were purified by conventional methods and distilled under dinitrogen prior to use. NMR spectra were obtained with a Bruker AF200 spectrometer; the peak positions are reported upfield of TMS as calculated from the residual solvent peaks. Cyclic voltammograms were recorded with an EG&G 362 potentiostat connected to a Macintosh computer through MacLab hardware/software; the electrochemical cell was a locally modified Schlenk tube with a Pt counter electrode sealed through uranium glass/Pyrex glass seals. The cell was fitted with an Ag/AgCl reference electrode and a Pt working electrode. Measurements were carried out with  $n-Bu_4NPF_6$  (~0.1 M) as the supporting electrolyte and potentials are reported versus the  $Cp_2Fe/Cp_2Fe^+$  couple which was introduced into the cell at the end of each measurement.  $Cp^*_2Mo_2Cl_6$  was prepared as previously described [9].  $AlCl_3$  (Aldrich) was sublimed prior to use and  $[Ph_3PNPPPh_3]^+Cl^-$  (Aldrich) was used as received.

### 2.2. Preparation of $[Cp^*_2Mo_2Cl_5][AlCl_4]$

$Cp^*_2Mo_2Cl_6$  (310 mg, 0.46 mmol) and  $AlCl_3$  (122 mg, 0.915 mmol) were introduced in a Schlenk tube equipped with a magnetic stirrer bar. Dichloromethane (30 ml) was added and the resulting mixture was stirred at room temperature. The formation of an orange–brown solution and a small amount of a pale green precipitate was observed. Stirring was continued overnight with no further change, after which time the mixture was filtered

and the mother liquor was layered with heptane (70 ml). Diffusion of the layers at room temperature produced more powdery green precipitate, a small amount of red microcrystals, and well-formed black crystals. The green powder was eliminated by repeatedly washing with heptane and decanting off the turbid green liquid from the heavier crystalline precipitate until clear washings were obtained. The mixture of crystals (the greater portion of them being the larger black ones) were dried under vacuum. Yield 107 mg (28%). A black crystal from this crop was identified as  $[Cp^*_2Mo_2Cl_5][AlCl_4]$  by X-ray crystallography (vide infra).  $^1H$  NMR ( $CD_2Cl_2$ , room temperature,  $\delta$ ): 2.36 (s), 1.35 (br s,  $w_{1/2} = 25$  Hz),  $-4.2$  (br s,  $w_{1/2} = 50$  Hz) (relative integrate intensity: 11:4.6:1). The strongest and sharp resonance at  $\delta$  2.39 is therefore assigned to  $[Cp^*_2Mo_2Cl_5][AlCl_4]$ , whereas the broad resonance at  $\delta$  1.35 is due to  $Cp^*_2Mo_2Cl_5$  and that at  $\delta$   $-4.2$  is due to  $Cp^*_2Mo_2Cl_6$ , following assignments previously made [9]. The  $Cp^*_2Mo_2Cl_6$  material probably forms from  $[Cp^*_2Mo_2Cl_5][AlCl_4]$  by solution equilibria (see Section 3). Consequently, the red microcrystals probably consist of  $Cp^*_2Mo_2Cl_5$  but further studies aimed at characterizing this material were not carried out. This assignment is also consistent with the results of the cyclic voltammetric experiment (see Section 3).

The reaction between  $[Cp^*_2Mo_2Cl_5][AlCl_4]$  and  $Cl^-$  was carried out in an NMR tube. To a  $CD_2Cl_2$  solution of the above crystals (7 mg) was added an excess of  $[Ph_3PNPPPh_3]^+Cl^-$  (~15 mg); the color of the solution changed immediately from orange to yellow. The  $^1H$  NMR at room temperature showed a broad resonance at  $\delta$   $-14.0$  ( $w_{1/2} = 150$  Hz), which corresponds to  $[Cp^*MoCl_4]^-$  [9], as the only  $Cp^*$  resonance.

### 2.3. X-ray crystallography

A black crystal with approximate dimensions  $0.60 \times 0.25 \times 0.25$  mm in a parallelepiped habit was glued on the inside of a thin-walled glass capillary which was then flame-sealed under dinitrogen and placed on the Enraf-Nonius CAD-4 diffractometer. The cell parameters and orientation matrix were determined from 25 reflections in the range  $16.1 < \theta < 24.4^\circ$  and confirmed with axial photographs. Three nearly orthogonal standard reflections were monitored at 1 h intervals of X-ray exposure showing no significant variations in intensity. An absorption correction [12a] based on four  $\psi$ -scan reflections over the  $\theta$  range  $7.3$ – $9.2^\circ$ , each collected twice, was applied (transmission factors varied from 0.752 to 0.998 with an average of 0.900). Data corrections for Lorentz and polarization factors, absorption, and data reduction to observed structure-factor amplitudes were carried out using the program package NRCVax [12b].

The structure was developed in the centrosymmetric triclinic space group  $P\bar{1}$ , which was confirmed by the successful refinement of the structure. All heavy atoms (Mo, Cl, Al) were located by direct methods with the program SHELXS [12c], further indicating that the asymmetric unit is composed of four fragments, two anions and two cations. The carbon atoms were located and refined by successive full-matrix least-squares cycles and difference-Fourier maps. Several cycles of refinement, first isotropically and then anisotropically, converged smoothly and revealed possible rotational disorder in the Cp\* ligand attached to Mo(2). This was evidenced by the large thermal parameters directed in the direction of libration. Further refinement, implementing idealization commands (AFIX) in SHELXL, allowed for the isotropic refinement of two Cp\* rings rotationally offset by 19.1°. These partial occupancy moieties had their thermal parameters constrained to be the same for all atoms allowing for occupancy refinement that converged to 0.524:0.476. At this point the occupancy was fixed and the thermal parameter of each individual partial occupancy carbon atom was freely refined isotropically. Methyl hydrogen atoms were placed in calculated positions and forced to ride on the parent carbon atom during the refinement with  $U_H$  set equal to 1.5 $U$  of the attached C atom. The highest peak in the final difference-Fourier map ( $> 1 e \text{ \AA}^{-3}$ ) are within 0.1 Å from the heavy atoms. Selected crystal data are collected in Table 1, fractional atomic coordinates are in Table 2 and selected bond distances and angles are listed in Table 3. All crystallographic calculations were performed on a Personal computer (PC) with a 486 DX2/66 processor and 16Mb of extended memory.

#### 2.4. MO calculations

The Fenske–Hall MO treatment [13] was carried out on the model compound  $[\text{Cp}_2\text{Mo}_2\text{Cl}_5]^+$ . A minimum basis set was employed and the atomic 1s, 2s, 2p, 3s, 3p, 3d, 4s and 4p orbitals of the Mo atoms, the 1s, 2s and 2p orbitals of the Cl atoms, and the 1s orbital of the C atoms were treated as ‘core’. Atomic parameters for the  $[\text{Cp}^*_2\text{Mo}_2\text{Cl}_5]^+$  ions (two crystallographically independent fragments) were averaged in order to idealize the geometry to  $C_{2v}$  symmetry. The Cp\* ligands were replaced by Cp ligands, which were placed in such a way that the unique carbon atom (sitting on the mirror plane) is eclipsed with the terminal Mo–Cl bond, and the Cp hydrogen atoms were placed in the ring plane radially at a distance of 0.95 Å from the corresponding C atoms. A high-handed coordinate system was chosen, with the z axis parallel to the Mo–Mo vector and the xz plane parallel to the plane identified by the two MO atoms and the unique (axial) bridging Cl atom. The local coordinate system chosen for the

Table 1  
Crystal data and structure refinement for  $[\text{Cp}^*_2\text{Mo}_2\text{Cl}_5][\text{AlCl}_4]$

Empirical formula	$\text{C}_{20}\text{H}_{30}\text{AlCl}_6\text{Mo}_2$
Formula weight	808.35
Temperature (K)	293(2)
Wavelength (Å)	0.71069
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
<i>a</i> (Å)	8.3903(13)
<i>b</i> (Å)	15.797(3)
<i>c</i> (Å)	24.036(2)
$\alpha$ (°)	86.766(11)
$\beta$ (°)	80.916(10)
$\gamma$	81.616(14)
Volume (Å <sup>3</sup> )	3110.5(8)
Z	4
Density (calc.) (Mg m <sup>-3</sup> )	1.726
Absorption coefficient (mm <sup>-1</sup> )	1.618
<i>F</i> (000)	1600
Crystal size (mm)	0.60 × 0.25 × 0.25
$\theta$ Range for data collection (°)	1.54–19.98
Index ranges	$-7 \leq h \leq 8, 0 \leq k \leq 15, -22 \leq l \leq 23$
Reflections collected	5840
Independent reflections	5775
Refinement method	full-matrix least-squares on $F^2$
Observed data ( $I > 2\sigma(I)$ )	3614
Restraints/parameters	0/528
Goodness of fit on $F^2$	1.034
Final <i>R</i> indices	
<i>R</i> 1	0.0637
<i>wR</i> 2	0.1449
<i>R</i> indices (all data)	
<i>R</i> 1	0.1159
<i>wR</i> 2	0.1701
Largest difference peak and hole ( $e \text{ \AA}^{-3}$ )	1.275 and $-0.691$

two Mo atoms has the z axis along the corresponding Mo–CNT vector and the y axis in the plane containing the two Mo atoms, the terminal Cl atoms, and the axial bridging atom; the local coordinate systems for all the Cl atoms coincide with the master coordinate system.

### 3. Results and discussion

#### 3.1. Synthesis

We recently reported the formation of  $\text{Cp}^*_2\text{Mo}_2\text{Cl}_6$  by conproportionation of  $\text{Cp}^*_2\text{Mo}_2\text{Cl}_4$  and  $\text{Cp}^*\text{MoCl}_4$  and proposed, on the basis of combined <sup>1</sup>H NMR monitoring and electrochemical studies, that the last step of this process is a chloride transfer from the anion to the cation in the (unobserved)  $[\text{Cp}^*_2\text{Mo}_2\text{Cl}_5]^+[\text{Cp}^*\text{MoCl}_4]^-$  intermediate (Eq. (1) [9]. In order to obtain supporting evidence for the likelihood of the  $[\text{Cp}^*_2\text{Mo}_2\text{Cl}_5]^+$  ion as an intermediate, we have

Table 2

Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $[\text{Cp}^*_2\text{Mo}_2\text{Cl}_5][\text{AlCl}_4]$ 

	x	y	z	$U_{\text{eq}}^a$
Mo(1)	983(2)	1885(1)	4434(1)	46(1)
Mo(2)	1362(2)	2607(1)	5464(1)	47(1)
Mo(3)	-421(2)	3146(1)	9463(1)	48(1)
Mo(4)	-2024(2)	2399(1)	10478(1)	47(1)
Cl(10)	-1349(6)	1258(3)	4822(2)	87(2)
Cl(20)	-882(6)	2064(3)	5991(2)	83(2)
Cl(30)	1326(6)	3796(3)	9938(2)	82(2)
Cl(40)	-437(7)	2958(3)	11062(2)	87(2)
Cl(11)	-497(5)	3222(3)	4819(2)	68(1)
Cl(12)	3081(5)	2753(3)	4555(2)	68(1)
Cl(13)	2349(6)	1144(3)	5179(2)	71(1)
Cl(31)	-2635(6)	2265(3)	9526(2)	76(2)
Cl(32)	-2682(6)	3854(3)	10116(2)	79(2)
Cl(33)	544(5)	1812(3)	9928(2)	60(1)
Al(1)	6308(7)	88(4)	7943(2)	69(2)
Cl(1)	7449(8)	-1189(4)	7824(3)	129(2)
Cl(2)	6089(8)	360(4)	8810(2)	102(2)
Cl(3)	3992(7)	190(4)	7691(3)	109(2)
Cl(4)	7696(11)	951(5)	7471(3)	172(4)
Al(2)	5749(7)	5109(4)	2964(2)	70(2)
Cl(5)	4544(8)	4546(4)	2402(2)	106(2)
Cl(6)	8318(8)	4858(5)	2732(3)	144(3)
Cl(7)	5098(8)	4604(5)	3785(2)	127(2)
Cl(8)	5042(9)	6432(4)	2911(3)	129(2)
C(10)	396(21)	1064(12)	3684(7)	56(5)
C(11)	2009(24)	868(10)	3754(6)	50(5)
C(12)	2794(19)	1611(13)	3620(7)	50(4)
C(13)	1600(28)	2267(13)	3484(6)	68(6)
C(14)	135(22)	1955(12)	3552(7)	60(5)
C(15)	-786(21)	424(12)	3693(8)	89(7)
C(16)	2866(25)	-7(12)	3872(7)	91(7)
C(17)	4573(23)	1645(16)	3548(8)	114(9)
C(18)	1835(27)	3172(11)	3295(8)	99(7)
C(19)	-1541(26)	2446(14)	3457(9)	114(8)
C(20) <sup>b</sup>	2219(16)	3870(9)	5720(6)	27(11)
C(21) <sup>b</sup>	1046(17)	3624(9)	6148(6)	66(12)
C(22) <sup>b</sup>	1703(17)	2867(9)	6398(6)	44(8)
C(23) <sup>b</sup>	3282(16)	2646(8)	6125(5)	45(8)
C(24) <sup>b</sup>	3601(15)	3265(8)	5705(5)	34(9)
C(25) <sup>b</sup>	2031(24)	4639(13)	5345(9)	78(11)
C(26) <sup>b</sup>	-608(25)	4086(13)	6309(9)	89(12)
C(27) <sup>b</sup>	869(25)	2384(13)	6872(8)	134(18)
C(28) <sup>b</sup>	4421(22)	1885(12)	6257(8)	63(10)
C(29) <sup>b</sup>	5138(21)	3278(12)	5313(8)	56(9)
C(20A) <sup>c</sup>	2442(16)	3799(9)	5652(6)	59(18)
C(21A) <sup>c</sup>	995(14)	3829(8)	6051(5)	20(8)
C(22A) <sup>c</sup>	1174(13)	3106(7)	6427(4)	22(7)
C(23A) <sup>c</sup>	2732(15)	2629(7)	6260(5)	48(10)
C(24A) <sup>c</sup>	3516(16)	3057(9)	5781(6)	62(13)
C(25A) <sup>c</sup>	2781(21)	4442(10)	5174(7)	65(11)
C(26A) <sup>c</sup>	-476(16)	4509(9)	6072(5)	75(12)
C(27A) <sup>c</sup>	-74(12)	2884(7)	6918(3)	84(13)
C(28A) <sup>c</sup>	3432(18)	1811(8)	6542(5)	85(13)
C(29A) <sup>c</sup>	5196(19)	2774(12)	5464(7)	106(16)
C(30)	-1031(9)	3339(5)	8555(2)	49(4)
C(31)	276(10)	2676(5)	8557(3)	49(4)
C(32)	1654(10)	3036(7)	8673(3)	49(4)
C(33)	1162(12)	3923(7)	8742(3)	58(5)
C(34)	-500(11)	4109(5)	8682(3)	48(4)

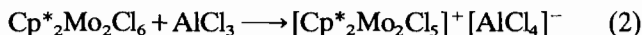
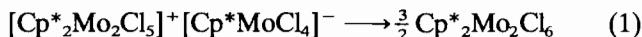
(continued)

Table 2 (continued)

	x	y	z	$U_{\text{eq}}^a$
C(35)	-2604(10)	3298(8)	8379(3)	77(6)
C(36)	265(26)	1763(11)	8420(7)	87(7)
C(37)	3319(21)	2553(14)	8678(9)	106(8)
C(38)	2309(24)	4553(12)	8798(8)	93(7)
C(39)	-1475(24)	4978(11)	8681(8)	92(7)
C(40)	-4349(18)	1716(10)	10675(7)	44(4)
C(41)	-4415(21)	2285(10)	11103(8)	62(5)
C(42)	-3130(24)	1953(12)	11417(6)	57(5)
C(43)	-2163(18)	1266(11)	11110(7)	51(5)
C(44)	-3002(18)	1117(9)	10692(6)	42(4)
C(45)	-5698(20)	1738(11)	10328(7)	69(5)
C(46)	-5750(24)	2993(12)	11275(8)	100(7)
C(47)	-2891(26)	2253(14)	11972(7)	102(7)
C(48)	-718(23)	740(12)	11306(9)	93(7)
C(49)	-2475(22)	371(10)	10295(7)	73(6)

<sup>a</sup>  $U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.<sup>b</sup> Site occupancy factor = 0.524.<sup>c</sup> Site occupancy factor = 0.476.

generated such an ion by interaction of  $\text{Cp}^*_2\text{Mo}_2\text{Cl}_6$  with the strong Lewis acid  $\text{AlCl}_3$  (Eq. (2)). A comparison of Eqs. (1) and (2) shows that  $\text{Cp}^*_2\text{Mo}_2\text{Cl}_6$  is a poorer Lewis acid than  $\text{AlCl}_3$  or, conversely, that  $\text{AlCl}_4^-$  is a poorer  $\text{Cl}^-$  donor than  $\text{Cp}^*\text{MoCl}_4^-$ .



The product of Eq. (2) shows a single sharp  $^1\text{H}$  NMR resonance at  $\delta$  2.36 in  $\text{CD}_2\text{Cl}_2$ , indicating that this compound is diamagnetic. This contrasts with the neutral parent compound, for which a broad and paramagnetically shifted resonance at  $\delta$  -4.23 is observed in the same solvent at room temperature.

### 3.2. Molecular structure

The tetrachloroaluminate salt crystallizes from  $\text{CH}_2\text{Cl}_2$ /heptane in the form of black crystals in the triclinic space group  $P\bar{1}$  with two independent cations and anions in the asymmetric unit. The tetrachloroaluminate ions show the expected regular tetrahedral geometry with an average Al-Cl length of 2.109(14)  $\text{\AA}$  and Cl-Al-Cl angles in the narrow 107.4–111.7° range. Selected metric parameters of the two cations, which are geometrically equivalent, are shown side by side in Table 3 and one of the cations is shown in Fig. 1. Although there is no crystallographically imposed symmetry, the effective molecular symmetry of the cations is  $C_{2v}$ . The parameters are quite similar for the two independent cations and the small differences observed are probably the result of crystal packing effects. For the discussion of bond lengths and angles that follows,

Table 3  
Selected bond distances (Å) and angles (°) for  $[\text{Cp}^*_2\text{Mo}_2\text{Cl}_5][\text{AlCl}_4]^-$ <sup>a</sup>

Distances			
Mo(1)–Mo(2)	2.866(2)	Mo(3)–Mo(4)	2.874(2)
Mo(1)–Cl(10)	2.359(5)	Mo(3)–Cl(30)	2.366(5)
Mo(1)–Cl(11)	2.439(4)	Mo(3)–Cl(31)	2.461(4)
Mo(1)–Cl(12)	2.444(4)	Mo(3)–Cl(32)	2.440(5)
Mo(1)–Cl(13)	2.431(5)	Mo(3)–Cl(33)	2.423(4)
Mo(1)–CNT(1)	2.02(2)	Mo(3)–CNT(3)	2.009(7)
Mo(2)–Cl(11)	2.437(4)	Mo(4)–Cl(31)	2.451(4)
Mo(2)–Cl(12)	2.441(4)	Mo(4)–Cl(32)	2.431(5)
Mo(2)–Cl(13)	2.437(4)	Mo(4)–Cl(33)	2.430(5)
Mo(2)–Cl(20)	2.342(5)	Mo(4)–Cl(40)	2.366(5)
Mo(2)–CNT(2)	2.054(14)	Mo(4)–CNT(4)	2.008(14)
Angles			
Mo(2)–Mo(1)–Cl(10)	95.19(13)	Mo(4)–Mo(3)–Cl(30)	93.94(13)
Mo(2)–Mo(1)–Cl(11)	53.97(11)	Mo(4)–Mo(3)–Cl(31)	54.04(11)
Mo(2)–Mo(1)–Cl(12)	54.03(10)	Mo(4)–Mo(3)–Cl(32)	53.70(12)
Mo(2)–Mo(1)–Cl(13)	54.03(11)	Mo(4)–Mo(3)–Cl(33)	53.80(11)
Mo(2)–Mo(1)–CNT(1)	161.0(5)	Mo(4)–Mo(3)–CNT(3)	161.6(2)
Cl(10)–Mo(1)–Cl(11)	86.3(2)	Cl(30)–Mo(3)–Cl(31)	148.0(2)
Cl(10)–Mo(1)–Cl(12)	149.2(2)	Cl(30)–Mo(3)–Cl(32)	87.1(2)
Cl(10)–Mo(1)–Cl(13)	87.9(2)	Cl(30)–Mo(3)–Cl(33)	87.0(2)
Cl(10)–Mo(1)–CNT(1)	103.8(5)	Cl(30)–Mo(3)–CNT(3)	104.1(3)
Cl(11)–Mo(1)–Cl(12)	74.7(2)	Cl(31)–Mo(3)–Cl(32)	73.9(2)
Cl(11)–Mo(1)–Cl(13)	106.7(2)	Cl(31)–Mo(3)–Cl(33)	74.5(2)
Cl(11)–Mo(1)–CNT(1)	127.0(5)	Cl(31)–Mo(3)–CNT(3)	107.9(3)
Cl(12)–Mo(1)–Cl(13)	75.0(2)	Cl(32)–Mo(3)–Cl(33)	106.5(2)
Cl(12)–Mo(1)–CNT(1)	107.0(5)	Cl(32)–Mo(3)–CNT(3)	129.7(3)
Cl(13)–Mo(1)–CNT(1)	125.2(5)	Cl(33)–Mo(3)–CNT(3)	122.8(2)
Mo(1)–Mo(2)–Cl(11)	54.04(11)	Mo(3)–Mo(4)–Cl(31)	54.36(10)
Mo(1)–Mo(2)–Cl(12)	54.12(10)	Mo(3)–Mo(4)–Cl(32)	53.98(12)
Mo(1)–Mo(2)–Cl(13)	53.83(11)	Mo(3)–Mo(4)–Cl(33)	53.57(11)
Mo(1)–Mo(2)–Cl(20)	94.21(13)	Mo(3)–Mo(4)–Cl(40)	93.60(13)
Mo(1)–Mo(2)–CNT(2)	160.8(3)	Mo(3)–Mo(4)–CNT(4)	161.2(4)
Cl(11)–Mo(2)–Cl(12)	74.8(2)	Cl(31)–Mo(4)–Cl(32)	74.2(2)
Cl(11)–Mo(2)–Cl(13)	106.6(2)	Cl(31)–Mo(4)–Cl(33)	74.6(2)
Cl(11)–Mo(2)–Cl(20)	86.4(2)	Cl(31)–Mo(4)–Cl(40)	148.0(2)
Cl(11)–Mo(2)–CNT(2)	126.0(4)	Cl(31)–Mo(4)–CNT(4)	107.2(5)
Cl(12)–Mo(2)–Cl(20)	148.3(2)	Cl(32)–Mo(4)–Cl(40)	87.2(2)
Cl(12)–Mo(2)–Cl(13)	75.0(2)	Cl(32)–Mo(4)–Cl(33)	106.5(2)
Cl(12)–Mo(2)–CNT(2)	106.7(4)	Cl(32)–Mo(4)–CNT(4)	129.9(5)
Cl(13)–Mo(2)–Cl(20)	86.7(2)	Cl(33)–Mo(4)–Cl(40)	86.5(2)
Cl(13)–Mo(2)–CNT(2)	126.4(4)	Cl(33)–Mo(4)–CNT(4)	122.4(4)
Cl(20)–Mo(2)–CNT(2)	105.0(4)	Cl(40)–Mo(4)–CNT(4)	104.7(5)
Mo(1)–Cl(11)–Mo(2)	71.99(12)	Mo(3)–Cl(31)–Mo(4)	71.60(12)
Mo(1)–Cl(12)–Mo(2)	71.86(12)	Mo(3)–Cl(32)–Mo(4)	72.32(14)
Mo(1)–Cl(13)–Mo(2)	72.14(13)	Mo(3)–Cl(33)–Mo(4)	72.63(13)

<sup>a</sup> CNT(*n*) = centroid of atoms C(10*n*) through C(10*n*+4).

only averages of chemically equivalent parameters over the two cations will be considered.

Each metal exhibits a four-legged piano stool geometry, the three bridging Cl and the terminal Cl ligand identifying the four legs for each metal. This geometry is ubiquitous to CpMo complexes, and has so far been observed for mononuclear complexes in the II (e.g.  $[\text{Cp}^*\text{Mo}(\text{CO})_3(\text{PPh}_3)]^+$  [14]), III (e.g.  $\text{Cp}^*\text{MoCl}_2(\text{PMe}_3)_2$  [15]), IV (e.g.  $\text{Cp}^*\text{MoCl}_3(\text{PMe}_3)$  [16]) and V ( $\text{Cp}^*\text{MoBr}_4$ ) [17]) oxidation states, and for dinuclear  $\text{Mo}_2(\text{I,I})$  (e.g.  $\text{Cp}^*_2\text{Mo}_2(\text{CO})_6$  [18]),  $\text{Mo}_2(\text{III,III})$  (e.g.  $(\text{C}_5\text{H}_4\text{-i-Pr})_2\text{Mo}_2(\mu\text{-Cl})_4$  [19]),

$\text{Mo}_2(\text{III,IV})$  (e.g.  $[\text{Cp}^*_2\text{Mo}_2(\mu\text{-X})_4]^+$  (X = Br, I) [17]) and  $\text{Mo}_2(\text{IV,IV})$  (e.g.  $\text{Cp}^*_2\text{Mo}_2\text{Cl}_4(\mu\text{-Cl})_2$  [9]) complexes. The structure of  $[\text{Cp}^*_2\text{Mo}_2\text{Cl}_2(\mu\text{-Cl})_3]^+$  is a rare example of two four-legged piano stools sharing *three* legs, another example being the  $\text{Mo}_2(\text{III,III})$  complex  $[\text{Cp}_2\text{Mo}_2(\text{CO})_2(\mu\text{-SMe})_3]^+$  [20].

The presence of a direct metal–metal bond is indicated not only by the Mo–Mo distance of 2.870(4) Å, but also by the diamagnetism as apparent from the <sup>1</sup>H NMR spectrum. The Mo–Mo distance, however, is significantly longer than those of all the other metal–metal bonded Mo(IV) dinuclear compounds that

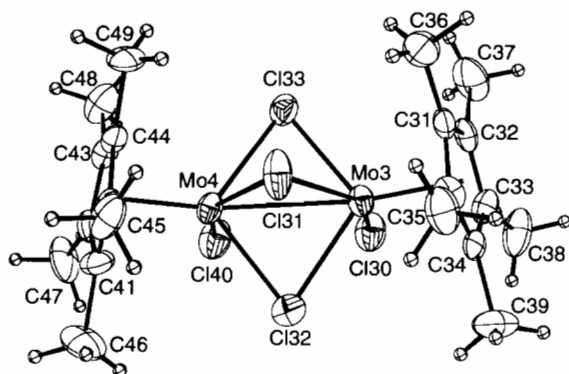
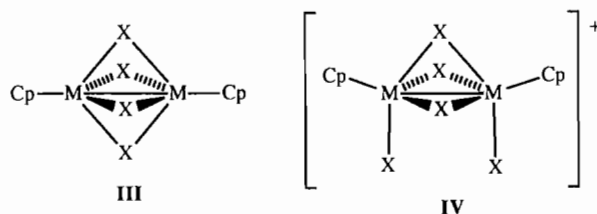


Fig. 1. An ORTEP view of the cation of compound  $[\text{Cp}^*_2\text{Mo}_2\text{Cl}_5]^+[\text{AlCl}_4]^-$  with the numbering scheme employed. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are drawn with arbitrary radii.

we found in the literature (Mo–Mo bond length in parentheses):  $[\text{Mo}(\mu\text{-S})(\text{SCNPr}_2)(\text{S}_2\text{CNP}_2)]_2$  (2.705(2) Å) [21],  $\text{Mo}_2(\text{O-}i\text{-Pr})_8$  (2.523(1) Å) [22],  $[\text{Mo}(\mu\text{-S})(\text{SBU})_2(\text{Me}_2\text{NH})_2]$  (2.730(1) Å) [23],  $[\text{Cl}_3\text{Mo}(\mu\text{-S}_2)(\mu\text{-Cl})_2\text{MoCl}_3]^{2-}$  (2.763(2) Å) [24],  $\text{Cp}^*_2\text{Mo}_2(\mu\text{-S})_2(\mu\text{-S}_2)$  (2.599(2) Å) [25] and a number of  $[(\text{ring})_2\text{Mo}_2(\mu\text{-S})(\mu\text{-SR})(\mu\text{-S}_2\text{CH}_2)]^+$  ions (ring = Cp,  $\text{C}_5\text{H}_4\text{Me}$ ; R = Me,  $\text{CH}=\text{CHPh}$ ,  $\text{C}(\text{Ph})=\text{CH}_2$ ) [26] (in the 2.599–2.610 Å range). Dinuclear non-bonded and paramagnetic Mo(IV) complexes also exist, however, e.g.  $[\text{Mo}_2\text{Cl}_{10}]^{2-}$  [27]. The chemically most related molecule, namely the  $\text{Cp}^*_2\text{Mo}_2\text{Cl}_6$  precursor, has structure I without a metal–metal bond ( $\text{Mo}\cdots\text{Mo}=3.888(1)$  Å) and it is paramagnetic [9]. On the other hand, the title compound is also geometrically related to the Mo(III) dimers  $(\text{ring})_2\text{Mo}_2\text{Cl}_4$  (structure III), where the Mo–Mo distance is 2.607(1) for ring =  $\text{C}_5\text{H}_4\text{-}i\text{-Pr}$  [19] and 2.598(2) Å (av.) for ring =  $\text{C}_5\text{Me}_4\text{Et}$  [28]. The  $\text{Cp}^*_2\text{Mo}_2\text{Cl}_4$  compound was investigated electrochemically and shown to exhibit two successive one-electron oxidations but none of the oxidized products has been isolated [9]. As will be discussed later in relation to the MO calculations, the Mo–Mo bond is expected to be stronger in  $(\text{ring})_2\text{Mo}_2\text{Cl}_4$  than in  $[(\text{ring})_2\text{Mo}_2\text{Cl}_5]^+$ , although the opposite would be predicted on the basis of a simple electron count.

It is useful to continue the comparison between the structure of the title compound (drawn again schematically in IV) and structure III; leaving aside for the moment considerations of oxidation state, structure IV can be ideally imagined as obtained from III by splitting a bridge by addition of an additional X atom. On going from III to IV, the variations of the CNT–Mo–Cl angles indicate the build-up of strain. In a mononuclear structure, these angles are generally around  $110^\circ$  for ligands such as Cl [29], whereas in a series of  $(\text{ring})_2\text{Mo}_2\text{X}_4$  and  $[(\text{ring})_2\text{Mo}_2\text{X}_4]^+$  compounds of structure III (X = Cl, Br, I), these angles are in the  $119\text{--}121^\circ$  range, irrespective of X [17]. On going to the  $[\text{Cp}^*_2\text{Mo}_2\text{Cl}_5]^+$

structure, the two equatorial bridging chloride ligands (we define here the axis of the molecule as coinciding with the  $\text{C}_2$  symmetry operator) increase their CNT–Mo–Cl angle to an average of  $126(3)^\circ$ , this increase being related to the increase in Mo–Mo distance and to the shorter Mo(IV)– $(\mu\text{-Cl})_{\text{eq}}$  distance (2.433(6) Å) with respect to the Mo(III)– $(\mu\text{-Cl})$  distance in III (av. 2.485(6) Å [19] for the  $\text{C}_4\text{H}_4\text{-}i\text{-Pr}$  and 2.488(3) Å [28] for the  $\text{C}_5\text{Me}_4\text{Et}$  compound). This is a stretching strain. On the other hand, the axial bridging Cl ligand shows CNT–Mo–Cl angles that average only  $106.8(13)^\circ$  and the average for the CNT–Mo–Cl angles to the terminal Cl ligands is even smaller,  $104.8(13)^\circ$ . This is a compression strain. The main cause for these effects and for the relatively long Mo–Mo distance is probably the repulsion between the two *syn* terminal Cl ligands, whose separation is only 3.22(4) Å (i.e. smaller than 3.60 Å, that is, twice the Cl van der Waal's radius).



As may be expected, the terminal Mo–Cl bonds (average 2.358(11) Å) are shorter than the bridging ones. Among the latter, the bonds located equatorially (2.433(6) Å) are marginally shorter than those located axially (2.449(9) Å). No large difference in the Mo–Cl–Mo angles of equatorial versus axial ligands is observed, and the average value for the combined group ( $72.1(6)^\circ$ ) is substantially larger than the corresponding averages in compounds  $(\text{ring})_2\text{Mo}_2\text{Cl}_4$  (ring =  $\text{C}_5\text{H}_4\text{-}i\text{-Pr}$ ,  $\text{C}_5\text{Me}_4\text{Et}$ ) of type III ( $63.25(10)$  and  $62.91(12)^\circ$ , respectively) [19,28], this being another structural consequence of the larger Mo–Mo separation and shorter Mo–Cl bonds in the title compound. For the metal–metal non-bonded precursor  $\text{Cp}^*_2\text{Mo}_2\text{Cl}_6$ , these angles increase to  $103.34(6)^\circ$  [9]. The average Mo–CNT distance (2.02(2) Å) compares with that found in the  $\text{Cp}^*_2\text{Mo}_2\text{Cl}_6$  precursor (2.028(7) Å) and the Cp\* rings are slightly distorted from the  $\eta^5$  configuration, the difference between shortest and longest Mo–C distances being 0.13(2), 0.12(2), 0.10(1) and 0.13(2) Å in the four rings, respectively.

### 3.3. Electronic structure

On the basis of simple electron counting rules, each metal in the  $[\text{Cp}^*_2\text{Mo}_2\text{Cl}_5]^+$  ion has a 16-electron configuration if the metal–metal interaction is not considered. Given the NMR evidence for the diamagnetism of the complex, the formation of a metal–metal double bond could be predicted. However, the Mo–Mo bond

is found to be significantly longer in the title compound than in the quadruply-bridged systems (ring)<sub>2</sub>Mo<sub>2</sub>Cl<sub>4</sub> (type III), although in the latter one the metal–metal bond order is one. The Mo–Mo bond in [Cp\*<sub>2</sub>Mo<sub>2</sub>Cl<sub>5</sub>]<sup>+</sup> is also longer relative to any of the dinuclear Mo(IV) compounds that do contain a bond [21–26]. These observations stimulated a more detailed MO analysis on the [Cp<sub>2</sub>Mo<sub>2</sub>Cl<sub>5</sub>]<sup>+</sup> model complex, which we report here (see Fig. 2 for a summary of the salient results). Calculations on similar piano stool dimers, e.g. Cp<sub>2</sub>Mo<sub>2</sub>(μ-S)<sub>2</sub>(μ-S<sub>2</sub>) and Cp<sub>2</sub>Mo<sub>2</sub>(μ-Cl)<sub>4</sub>, both of type III, have been reported before [30].

Qualitative considerations are very helpful to understand the nature of the electronic structure in this compound. The formation of the dinuclear core, electronically speaking, can be conveniently thought of as deriving from the combination of two mononuclear four-legged piano stool fragments, whose electronic structure is well known [31] and features two mostly metal-based orbitals in the frontier region, namely d<sub>z<sup>2</sup></sub> and d<sub>xy</sub>, the former one being at slightly higher energy (see Fig. 2, left-hand side). Upon combination of the two halves of the molecule in C<sub>2v</sub> symmetry, the two d<sub>z<sup>2</sup></sub> orbitals give rise to bonding and antibonding combinations of type a<sub>1</sub> and b<sub>2</sub>, respectively, whereas the two d<sub>xy</sub> orbitals give rise to combinations of type a<sub>2</sub> and b<sub>1</sub>. If the two Mo–CNT vectors were perfectly co-linear such as in system III, these interactions could be ideally described as σ and δ and the diagram reported for Cp<sub>2</sub>Mo<sub>2</sub>Cl<sub>4</sub>, which is qualitatively analogous to that obtained here, would result [30b]. On the other hand, these vectors form angles of ~161° with the Mo–Mo vector and we feel justified to keep using the σ and

δ labels for convenience. The σ and σ\* combinations are expected to differ substantially in energy because the two d<sub>z<sup>2</sup></sub> orbitals have significant overlap, whereas the d<sub>xy</sub> orbitals have a much poorer overlap giving rise to a much smaller separation between δ and δ\*. On the basis of d<sub>xy</sub>–d<sub>xy</sub> overlap only, the δ orbital (b<sub>1</sub>) would be expected to be lower in energy than the δ\* orbital (a<sub>2</sub>). However, the influence of the bridging Cl lone pairs can modify the picture in a way similar to what has been described before for other classes of compounds, e.g. the edge-sharing bioctahedral M<sub>2</sub>(μ-X)<sub>2</sub>L<sub>8</sub> system [32] and system III [30b]. In both cases, the energy of the δ orbital is raised above that of the δ\* by the out-of-phase combination with the proper symmetry-adapted linear combination of the bridging ligands' lone pairs (in our case here, the p<sub>x</sub> orbitals of the two equatorial ligands and the p<sub>y</sub> orbital of the axial ligand). On the other hand, the δ\* orbital has no counterpart in the ligand orbitals with which to interact.

The results of the Fenske–Hall calculations are in perfect accord with all the above expectations (see Fig. 2, right-hand side). (For a listing of orbital energies for the relevant molecular orbitals and percent contributions of different types of atomic orbitals, see Section 5.) The b<sub>1</sub> orbital (LUMO, –12.30 eV) is raised in energy above the a<sub>2</sub> orbital (HOMO, –13.28 eV) by the antibonding interaction with the lone pairs of the bridging Cl atoms; the three bridging Cl atoms contribute about equally to this interaction (7.12% contribution from p<sub>x</sub> orbitals of the two equatorial Cl atoms; 4.51% contribution from the p<sub>y</sub> orbital of the axial Cl atom). An antibonding interaction exists, however, also with the two terminal Cl atoms' p<sub>y</sub> orbitals (14.78%). The a<sub>2</sub> orbital has no contribution from the bridging Cl lone pairs and it has a greater contribution from the terminal Cl p<sub>y</sub> orbitals with respect to the b<sub>1</sub> orbital (33.6%), but this is evidently not sufficient to keep the energy order as expected on the basis of the sole d<sub>xy</sub>–d<sub>xy</sub> overlap. The metal–metal σ-bonding orbital (a<sub>1</sub>) is found at –15.16 eV, while the corresponding antibonding combination (b<sub>2</sub>) is at –8.52 eV. The b<sub>2</sub> orbital has a significant contribution from the equatorial bridging Cl atoms' p<sub>z</sub> lone pairs as illustrated in Fig. 2 (18.34%) whereas this contribution is absent (symmetry forbidden) in the a<sub>1</sub> orbital. There are, however, various other contributions of Cl lone pair combinations of proper symmetry type in the orbital a<sub>1</sub>. The total contributions of metal atomic orbitals to the molecular orbitals illustrated in Fig. 2 are: 75.78% to a<sub>1</sub>, 62.78% to a<sub>2</sub>, 69.84% to b<sub>1</sub> and 74.04% to b<sub>2</sub>.

The four available metal electrons occupy the MOs given in Fig. 2 to give rise to a (a<sub>1</sub>)<sup>2</sup>(a<sub>2</sub>)<sup>2</sup>, or σ<sup>2</sup>δ\*<sup>2</sup> configuration; while the first orbital contributes sub-

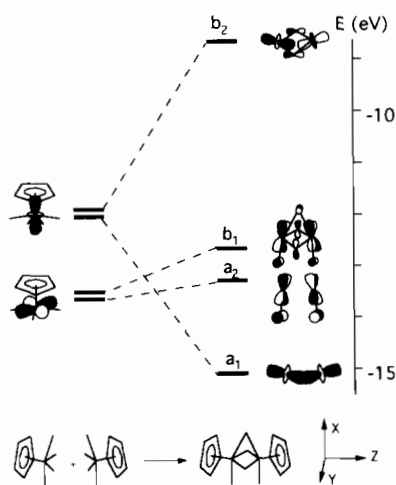


Fig. 2. An MO interaction diagram for the [Cp<sub>2</sub>Mo<sub>2</sub>Cl<sub>5</sub>]<sup>+</sup> ion. The right hand side shows the energy and qualitative constitution of the MOs as they are calculated by the Fenske–Hall program. The master coordinate system used in the calculation is shown in the lower right hand side corner. The left hand side shows the energy and shape of the orbitals of the two ideal separated halves of the ion and are placed arbitrarily on the energy scale.

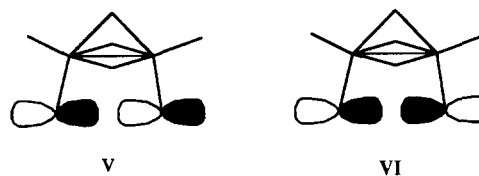


stantially to the metal–metal attractive interaction ( $d_{z^2} - d_{z^2}$  overlap population = 0.125), the latter provides a small destabilizing contribution ( $d_{xy} - d_{xy}$  overlap population = -0.050). The calculated HOMO–LUMO separation of 0.98 eV, although quantitatively not reliable, is qualitatively in accord with the diamagnetism of the ion (insignificant population of the excited  $^3B_2$  state corresponding to the  $(a_1)^2(a_2)^1(b_1)^1$  configuration).

We can address at this point the question: why is this Mo–Mo bond longer than the single bond in the Mo(III) dimers of type III (with X = Cl) or with respect to other Mo(IV)–Mo(IV) bonding distances? The MO diagram for system III [30b] is similar to the one derived here for system IV, with the additional pair of electrons occupying the  $\delta$  orbital to give rise to a  $\sigma^2\delta^{*2}\delta^2$  configuration. Literature data indicate that the Mo–Mo distance is substantially insensitive to the occupation of the  $\delta$  orbital. For instance, the  $[\text{Cp}^*_2\text{Mo}_2(\mu\text{-Br})_4]^{n+}$  ( $n=0,1$ ) pair [17] shows identical Mo–Mo separations within experimental error and the distance in the Mo(IV) dimer  $\text{Cp}^*_2\text{Mo}_2(\mu\text{-S})_2(\mu\text{-S}_2)$ , 2.599(2) Å [25] and in other Mo(IV) dimers of type III, e.g.  $[(\text{ring})_2\text{Mo}_2(\mu\text{-S})(\mu\text{-SR})(\mu\text{-S}_2\text{CH}_2)]^+$  (ring =  $\eta^5\text{-C}_5\text{H}_5$ ,  $\eta^5\text{-C}_5\text{H}_4\text{Me}$ ; 2.599–2.610 Å) [26] is not significantly different from those in tetrathiolato-bridged Mo(III) dimers,  $(\text{ring})_2\text{Mo}_2(\mu\text{-SR})_4$  (2.596–2.603 Å) [33], and in the tetrachloro-bridged Mo(III) dimers mentioned above (Cl and S have approximately the same dimension). Only the size of the bridging donor atoms seems to affect the metal–metal separation: Mo–Mo distances for the series of tetrahalide compounds  $(\text{ring})_2\text{Mo}_2\text{X}_4$  are: 2.598(2) Å (X = Cl, ring =  $\text{C}_5\text{Me}_4\text{Et}$ ) [28]; 2.643(4) Å (X = Br, ring =  $\text{Cp}^*$ ) [17]; 2.708(3) Å (X = I, ring =  $\text{Cp}^*$ ) [34]. For systems of type III, therefore, we can conclude that the Mo–Mo distance is substantially insensitive to the occupation of the  $\delta$  orbital and depends mostly on the size of the bridging atoms. In short, the rigidity of the  $\text{M}_2(\mu\text{-X})_4$  moiety is restraining the metal–metal bond. The Mo(IV)  $[\text{Cp}^*_2\text{Mo}_2\text{Cl}_4]^{2+}$  species is accessible electrochemically but it is too reactive to be isolated and structurally characterized. Theoretical predictions [30b] assign to it a  $\sigma^2\delta^{*2}$  electronic configuration (namely identical to that of  $[\text{Cp}_2\text{Mo}_2\text{Cl}_5]^+$ ) and, on the basis of the above arguments, its metal–metal separation should be close to that observed for the neutral Mo(III) compounds.

On going from III to structure IV, the structure partially opens up and the metal–metal bond gains flexibility. We can therefore argue that the destabilizing effect of the  $\delta^*$  electrons can play a more important role here. In dinuclear systems containing multiple metal–metal bonds and no bridging ligands [1a], the occupation of  $\delta$  orbitals has in general a limited effect which never amounts to as much as the difference of Mo–Mo separation between  $[\text{Cp}_2\text{Mo}_2\text{Cl}_5]^+$  and  $(\text{ring})_2\text{Mo}_2\text{Cl}_4$  (ring =  $\text{C}_5\text{H}_4\text{-i-Pr}$ ,  $\text{C}_5\text{Me}_4\text{Et}$ ) systems, that

is 0.27 Å. However, the metal–metal bonding in those systems is dominated by the stronger  $\sigma$  and  $\pi$  contributions, the  $\delta$  bond being only a very small component of the overall metal–metal bonding, whereas in the  $\text{Cp}^*\text{Mo(IV)}$  systems analyzed here, the bonding contribution is only provided by a ‘bent’  $\sigma$  bond. The smaller  $\sigma$  bond overlap in IV with respect to III due to the bending of the bond can by itself be responsible for the weaker Mo–Mo interaction in the latter system. In addition, the higher Mo effective nuclear charge in the dinuclear Mo(IV) cation with respect to the dinuclear Mo(III) neutral complex is expected to contract the metal orbitals, resulting in a less effective overlap in the more oxidized complex. Finally, perhaps the most important factor could be the unfavorable *syn*-Cl–Cl interaction examined above within the context of the structural results. The calculations indeed confirm that this is a destabilizing interaction: the separation between in-phase and out-of-phase combinations of the terminal Cl  $p_z$  orbitals (V and VI, respectively) is large (1.94 eV, versus 1.19 and 0.09 eV between in- and out-of-phase combinations of the terminal Cl  $p_y$  and  $p_x$  orbitals, respectively), and the p–p orbital overlap populations reflect the repulsive interaction (-0.027, -0.010 and -0.001 for  $p_z$ ,  $p_y$  and  $p_x$  orbitals, respectively). The molecular orbital corresponding to interaction V is in fact the highest energy lone-pair based MO and is located slightly above the Mo–Mo  $\sigma$  bonding orbital, at -15.03 eV.



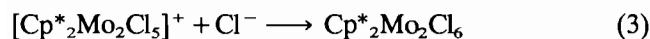
Other previously reported Mo(IV) dimers have different molecular and electronic structures (e.g. based on five-coordination geometries) that allow all the metal electrons to effectively participate in Mo–Mo bonding (e.g. compound  $[\text{Mo}(\mu\text{-S})(\text{SBu})_2(\text{Me}_2\text{NH})]_2$  has a double ( $\sigma^2\pi^2$ ) metal–metal bond [23]) and/or smaller bridging donor atoms (e.g. oxygen in  $\text{Mo}_2(\text{O-i-Pr})_2$  [22]) and/or weaker interligand repulsions. Presumably for one or more of these reasons, the Mo–Mo bond distance in  $[\text{Cp}^*_2\text{Mo}_2\text{Cl}_5]^+$  is longer than for any of these previously reported compounds.

#### 3.4. Reaction with $\text{Cl}^-$ . Structure I versus II for $\text{Cp}^*_2\text{Mo}_2\text{Cl}_6$

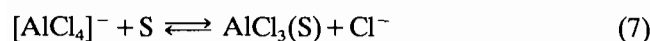
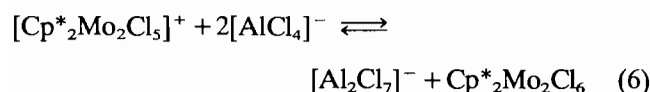
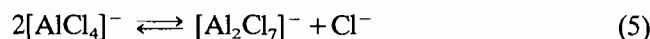
$[\text{Cp}^*_2\text{Mo}_2\text{Cl}_5]^+[\text{AlCl}_4]^-$  reacts instantaneously with an excess of  $\text{Cl}^-$  in  $\text{CH}_2\text{Cl}_2$  at room temperature to give the  $[\text{Cp}^*\text{MoCl}_4]^-$  ion. This reaction presumably occurs in two stages, the first one being the addition of a  $\text{Cl}^-$  ion to afford the neutral hexachloro parent



dimer (Eq. (3)). Then, the latter compound reacts with additional  $\text{Cl}^-$  to form the anion (Eq. (4)), as has been reported before [9].



The dinuclear intermediate is not observed spectroscopically when an excess of  $\text{Cl}^-$  is added. However, when  $\text{CD}_2\text{Cl}_2$  solutions of the tetrachloroaluminate salt *without* any added chloride salt are investigated by  $^1\text{H}$  NMR, a minor amount of  $\text{Cp}^*_2\text{Mo}_2\text{Cl}_6$  is always observed. This material may already be present as an impurity in the salt, but it could also be formed again from the dinuclear cation because of the release of  $\text{Cl}^-$  from the anion by the establishment of equilibria with oligonuclear aluminate ions (e.g., Eq. (5)). In other words, the  $[\text{Cp}^*_2\text{Mo}_2\text{Cl}_5]^+$  ion may be sufficiently Lewis acidic to compete with  $\text{AlCl}_3$  for  $\text{Cl}^-$  (Eq. (6)). Equilibrium (5) has been investigated in melts [35], and the structural characterization of several  $[\text{Al}_2\text{Cl}_7]^-$  salts obtained by solution methods has been reported, for instance  $[(\text{C}_6\text{Me}_6)_3\text{Zr}_3\text{Cl}_6][\text{Al}_2\text{Cl}_7]_2$  [36]. Yet another possibility is that  $\text{Cl}^-$  is released from  $[\text{AlCl}_4]^-$  by the interaction with adventitious donors S, e.g. water, see Eq. (7).

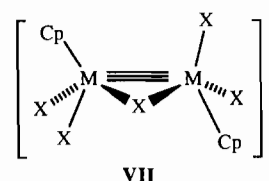


Whatever the source of the neutral dimer, one consideration that comes immediately to mind is that attack of the cation by  $\text{Cl}^-$  should lead naturally to the *syn* structure **II** rather than to the observed structure **I** for the dinuclear product of Eq. (3). A  $\text{Cp}^*_2\text{Mo}_2\text{Cl}_6$  isomer with structure **II** could be metal–metal bonded and diamagnetic (the MO scheme is expected to be similar to that presented here for the  $[\text{Cp}_2\text{Mo}_2\text{Cl}_5]^+$  cation). On the other hand, no new product forms upon dissolution of the tetrachloroaluminate salt, only the paramagnetic isomer with structure **I** does. The important implication of this observation is that a hypothetical  $\text{Cp}^*_2\text{Mo}_2\text{Cl}_6$  dimer of type **II**, if formed, isomerizes quickly to the alternative, paramagnetic structure **I**. On the basis of the results of the calculations illustrated above, we have learned that the opening of one bridge from structure **III** to structure **IV** weakens substantially the Mo–Mo interaction for a number of reasons, one of them being the introduction of ligand–ligand repulsions. Therefore, we extrapolate that the opening of one additional bridge on going from structure **IV** of  $[\text{Cp}^*_2\text{Mo}_2\text{Cl}_5]^+$  to a hypothetical structure **II** for  $\text{Cp}^*_2\text{Mo}_2\text{Cl}_6$  will weaken further the Mo–Mo interaction

to the point of inducing the conversion to the isomeric structure **I**.

### 3.5. Electrochemical behavior

We had implicated before a neutral  $\text{Cp}^*_2\text{Mo}_2\text{Cl}_5$  species in the mechanism of formation of  $\text{Cp}^*_2\text{Mo}_2\text{Cl}_6$  [9] and had proposed for it a structure identical with the one that we have now found for the  $[\text{Cp}^*_2\text{Mo}_2\text{Cl}_5]^+$  cation. Therefore, we were expecting to observe a reversible reduction process for the title compound. Indeed, the compound shows a reversible reduction at  $E_{1/2} = -0.13$  V in  $\text{CH}_2\text{Cl}_2$  solution. This wave comes suspiciously close to the reversible wave that we reported for the  $[\text{Cp}^*\text{MoCl}_4]^-/\text{Cp}^*\text{MoCl}_4$  couple ( $E_{1/2} = -0.16$  V) [9], but the absence of such species from solution is firmly established by the  $^1\text{H}$  NMR study and by the observation that the cyclic voltammogram remains unaltered after the addition of a large excess of  $\text{AlCl}_3$ . The observation of a diffusion limited anodic current while holding the potential at  $E > -0.13$  V is consistent with the presence of  $\text{Cp}^*_2\text{Mo}_2\text{Cl}_5$  impurities in the sample, in agreement with the spectroscopic characterization of the material (see Section 2). At  $E < -0.13$  V, a diffusion limited cathodic current is observed. Past the first reduction process, other ill-defined reductive processes are observed, but no indication of reversibility is evident at scan rates up to  $500$   $\text{mV s}^{-1}$ . Thus, after reduction to  $[\text{Cp}^*_2\text{Mo}_2\text{Cl}_5]^-$ , a rearrangement to a different structural type or further chemical reactivity must rapidly take place. We would like to point out that the reducing electrons occupy the  $b_1$  orbital in Fig. 2, which has a significant Mo–( $\mu\text{-Cl}$ )  $\pi^*$  component, therefore the reduction process is expected to weaken the Mo–( $\mu\text{-Cl}$ ) bonds and perhaps cause an opening of the bridge system. In this respect, it is relevant to note that the related complex  $[\text{Cp}_2\text{Mo}_2\text{Cl}_5]^-$ , i.e. the Cp analogue of the product of two-electron reduction of the title compound, has a completely different structure with a single Cl bridge and an Mo–Mo triple bond, see **VII** [37].



## 4. Conclusions

The  $[\text{Cp}^*_2\text{Mo}_2\text{Cl}_5]^+$  ion has a novel structural type for  $\text{Cp}^*\text{Mo}(\text{IV})$  halide complexes. We have reported here its molecular and electronic structure, and examined in detail the metal–metal bonding interaction. A greater number of bridging chloride ligands (or more

specifically a smaller number of terminal Cl ligands) favors a short contact between the two metal centers, whereas the addition of terminal Cl<sup>-</sup> ligands weakens the Mo–Mo interaction. In this respect, [Cp\*<sub>2</sub>Mo<sub>2</sub>Cl<sub>5</sub>]<sup>+</sup> finds its proper place between [Cp\*<sub>2</sub>Mo<sub>2</sub>Cl<sub>4</sub>]<sup>n+</sup> (n = 0, 1, 2) and the non-bonded Cp\*<sub>2</sub>Mo<sub>2</sub>Cl<sub>6</sub>.

## 5. Supplementary material

Full tables of crystal data, bond distances and angles, anisotropic displacement parameters and hydrogen atom coordinates (20 pages), and a listing of molecular orbitals and % contribution from atomic orbital for the model system [Cp<sub>2</sub>Mo<sub>2</sub>Cl<sub>5</sub>]<sup>+</sup> (1 page) are available from the authors on request. The crystallographic tables have also been deposited with the Cambridge Crystallographic Data Centre.

## Acknowledgements

We are grateful to the DOE-OER for support of this work under contract DE-FG05-92ER 14230. Additional support from the NSF and the Alfred P. Sloan Foundation through awards to R.P. is also gratefully acknowledged.

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