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Crystal and Molecular Structure of [(η^3-Allyl)dicarbonyltris(methyl cyanide)-molybdenum(II)] [bis(η^3-allyl)tetracarbonyl-μ-trichlorodimolybdate(II)] Benzene (1/1)

MICHAEL G. B. DREW
Department of Chemistry, The University, Whiteknights, Reading RG6 2AD, U.K.

BRIAN J. BRISDON and MICHAEL CARTWRIGHT
School of Chemistry, University of Bath, Bath BA2 7AY, U.K.

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The complexes previously reported to be the halogen bridged dimers $[MoX(CO)_2(\eta^3\text{-}C_3H_5)(MeCN)]_2$, *where* X = Cl *or* Br, *have been shown to be* $[Mo(CO)_2(\eta^3\text{-}C_3H_5)(MeCN)_3]^+[Mo_2X_3(CO)_4(\eta^3\text{-}C_3H_5)_2]^-$ *in both the solid and solution states.*

Crystals of the chloro complex grown from benzene contain a solvent molecule and are monoclinic, space group $P2_1/a$ *with cell dimensions* a = *16.352(11),* b = *13.233(10),* c = *16.067(12)* Å, β = *97.5(1)°,* Z = *4. 2265 independent reflections above background have been measured using a twinned crystal on a diffractometer and refined to* R *0.095 using full-matrix least squares. In the cation* $[Mo(CO)_2(\eta^3\text{-}C_3H_5)(MeCN)_3]^+$, *the metal geometry is best considered as an octahedron with the allyl group [Mo–C 2.25(4)–2.36(5)* Å*] occupying one site and together with two carbonyl groups [Mo–C 1.99(4), 1.94(4)* Å*] forming a fac arrangement. The three MeCN groups [Mo–N 2.22(3), 2.19(3), 2.19(3)* Å*] complete the coordination sphere.*

In the anion $[Mo_2Cl_3(\eta^3\text{-}C_3H_5)_2(CO)_4]^-$, *the two independent molybdenum atoms are each bonded to an allyl group [Mo–C 2.23(4)–2.38(4)* Å*] and two carbonyl groups [1.90(4)–1.95(4)* Å*] in a fac-arrangement. The two metal atoms are bridged by three chlorine atoms [Mo–Cl(*trans *to allyl)2.52(1)* Å*; Mo–Cl(*trans *to carbonyl) 2.58(1)–2.62(1)* Å*]. Cations, anions and solvent benzene molecules are separated by the usual van der Waals contacts.*

Introduction

Hydrogen-1 n.m.r. spectroscopy has revealed that $[MoCl(CO)_2(\eta\text{-}C_3H_5)(MeCN)_2]$ undergoes extensive autoionisation in various non-aqueous solvents [1].

$$3[MoCl(CO)_2(\eta\text{-}C_3H_5)(MeCN)_2] \rightleftharpoons [Mo(CO)_2(\eta\text{-}C_3H_5)(MeCN)_3]^+ + [Mo_2Cl_3(CO)_4(\eta\text{-}C_3H_5)_2]^- + 3MeCN \quad (1)$$

The corresponding bromo-complex ionises in a similar but less extensive manner, whereas the iodo-complex does not undergo this reaction at all. There was no evidence in these solution studies of the neutral halogen-bridged dimers $[MoX(CO)_2(\eta\text{-}C_3H_5)(MeCN)]_2$, reported to be formed on recrystallisation of $[MoX(CO)_2(\eta\text{-}C_3H_5)(MeCN)_2]$, where X = Cl or Br but *not* I, from hot benzene [2]. As the empirical formulae of the dimers are the same as those of the known solution complexes $[Mo(CO)_2(\eta\text{-}C_3H_5)(MeCN)_3]$ $[Mo_2X_3(CO)_4(\eta\text{-}C_3H_5)_2]$, where X = Cl or Br [1], we decided to reinvestigate the properties of these two compounds in order to establish their structures unequivocally.

Experimental

The chloro complex was prepared from $[MoCl(CO)_2(\eta\text{-}C_3H_5)(MeCN)_2]$ by literature methods [2]. Analytical and ^1H n.m.r. spectroscopic data indicated that the freshly prepared crystals contained benzene. Specimens suitable for X-ray measurements were kept *in vacuo* at room temperature and contained approximately 9% by weight of benzene, corresponding to one molecule of solvent per three molybdenum atoms (Found: C, 36.9; H, 3.6; N, 4.7. Calc. for $C_{27}H_{30}Cl_3Mo_3N_3O_6$: C, 36.6; H, 3.4; N, 4.7%). Dissolution in CH_2Cl_2 and subsequent removal of the solvent, or prolonged heating of the crystals to 80 °C *in vacuo*, produced the unsolvated complex in the form of a fine yellow powder (Found: C, 32.0; H, 3.0; N, 5.1. Calc. for $C_{21}H_{24}Cl_3Mo_3N_3O_6$: C, 31.2; H, 3.0; N, 5.2%).

The bromo-complex was prepared in an analogous manner and also contained lattice benzene which was lost on prolonged pumping *in vacuo* (Found: C, 26.4; H, 2.9; N, 4.3. Calc. For $Br_3C_{21}H_{24}Mo_3N_3O_6$: C, 26.8; H, 2.6; N, 4.5%).

TABLE I. Atomic Coordinates and Thermal Parameters with Estimated Standard Deviations.

Atomic Coordinates ($\times 10^4$)

Atom	X	Y	Z
Mo(1)	4815(2)	4878(3)	7543(2)
Mo(2)	3288(2)	5539(3)	5871(2)
Cl(1)	4200(6)	3951(7)	6160(7)
Cl(2)	3269(6)	5357(8)	7433(6)
Cl(3)	4708(6)	6307(8)	6496(7)
C(11)	5982(23)	4748(28)	7452(22)
O(11)	6705(16)	4746(20)	7541(16)
C(12)	5225(25)	5790(32)	8439(26)
O(12)	5488(23)	6338(30)	8973(24)
C(13)	5257(24)	3208(30)	7912(25)
C(14)	4520(24)	3453(31)	8187(25)
C(15)	4559(29)	4245(36)	8820(29)
C(21)	2263(28)	4876(34)	5558(27)
C(22)	2502(26)	6633(34)	5931(26)
O(21)	1615(19)	4470(24)	5361(19)
O(22)	2072(21)	7296(27)	6009(20)
C(23)	3196(28)	4997(37)	4491(29)
C(24)	3756(34)	5805(43)	4681(34)
C(25)	3344(30)	6754(38)	4813(30)
Mo(3)	−0101(2)	5222(2)	7552(2)
N(61)	0078(19)	5802(24)	6293(20)
C(61)	0179(23)	6149(30)	5718(25)
C(62)	0315(26)	6560(32)	4855(26)
N(41)	0919(19)	4240(24)	7319(19)
C(41)	1446(23)	3703(29)	7233(23)
C(42)	2092(29)	2983(36)	7158(30)
N(51)	0910(21)	6293(26)	7890(21)
C(51)	1460(25)	6884(31)	7981(25)
C(52)	2100(31)	7688(38)	8017(31)
C(33)	−0605(30)	6213(38)	8592(31)
C(34)	−0875(24)	6588(31)	7737(25)
C(35)	−1417(27)	5925(35)	7179(28)
C(31)	−0075(27)	4475(35)	8629(28)
O(31)	−0061(21)	4033(27)	9224(23)
C(32)	−0912(27)	4193(34)	7173(27)
O(32)	−1393(20)	3552(25)	7004(20)
C(71)	2787(30)	1096(29)	9840(31)
C(72)	3114(30)	2008(29)	9598(31)
C(73)	2633(30)	2882(29)	9547(31)
C(74)	1825(30)	2844(29)	9737(31)
C(75)	1499(30)	1933(29)	9979(31)
C(76)	1979(30)	1059(29)	10030(31)

Anisotropic Thermal Parameters ($\times 10^3$)[a]

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo(1)	40.3(25)	37.7(26)	37.3(25)	−2.3(16)	10.5(20)	−2.9(16)
Mo(2)	45.8(25)	38.4(25)	41.0(24)	1.3(18)	9.8(20)	−3.1(17)
Cl(1)	63(7)	36(6)	62(7)	−11(5)	15(6)	−1(5)
Cl(2)	44(6)	51(7)	54(6)	−6(5)	15(5)	−3(5)
Cl(3)	55(7)	38(6)	68(7)	4(5)	6(6)	−8(5)
Mo(3)	30.1(21)	35.2(23)	46.0(23)	4.3(15)	12.8(18)	2.4(15)

Isotropic Thermal Parameters ($\times 10^3$)[b]

C(11) 38(9), O(11) 54(7), C(12) 52(11), O(12) 99(12), C(13) 47(11), C(14) 52(11), C(15) 70(14), C(21) 61(12), O(21) 70(8),

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TABLE I. *(continued)*

C(22) 55(11), O(22) 82(9), C(23) 68(13), C(24) 88(15), C(25) 72(13), N(61) 45(9), C(61) 45(10), C(62) 57(11), N(41) 45(8), C(41) 42(10), C(43) 71(14), N(51) 57(9), C(51) 48(11), C(52) 75(14), C(33) 76(14), C(34) 51(11), C(35) 65(13), C(31) 61(12), O(31) 89(11), C(32) 61(12), O(32) 77(9), C(71) 139(26), C(72) 93(18), C(73) 113(20), C(74) 121(22), C(75) 129(24) C(76) 163(32).

[a] In the form $\exp(-2\pi^2\Sigma_i\Sigma_jU_{ij}h_ih_jb_ib_j$; i, j = 1, 2, 3) where b_i is the i^{th} reciprocal lattice dimension. [b] In the form $\exp -8\pi^2\sin^2\theta/\lambda^2$.

The complexes $Ph_4As[Mo_2X_3(CO)_4(\eta\text{-}C_3H_5)_2]$, where X = Cl or Br and $[Mo(CO)_2(\eta\text{-}C_3H_5)(MeCN)_3]PF_6$ were prepared by literature methods or extensions of them [1, 3].

Spectroscopic Data

Hydrogen-1 n.m.r. spectra were recorded on a JEOL PS100 spectrometer using $SiMe_4$ as an internal reference. N.m.r. solvents were rigorously dried and deoxygenated before use. Infrared spectra were recorded on Perkin-Elmer 237 and 597 spectrophotometers and calibrated against the absorption of polystyrene at 1601 cm^{-1}. Conductance measurements were made in acetone solution on a Wayne-Kerr Autobalance bridge at 295 K.

Crystal Data

$C_{27}H_{30}N_3Cl_3Mo_3O_6$, M = 886.7, monoclinic, a = 16.352(11), b = 13.233(10), c = 16.067(12) Å, β = 97.5(1)°, U = 3446.7 Å^3, d_m = 1.73, d_c = 1.72, Z = 4, F(000) = 1704, λ = 0.7107 Å, μ = 13.1 cm^{-1}, space group $P2_1/a$ from systematic absences h0l, h = 2n + 1, 0k0, k = 2n + 1.

All crystals were found to be twinned with 0kl common. The crystal chosen for data collection was of approximate size 0.4 × 0.3 × 0.3 mm and had twins in proportion 1:0.6 (this value was later refined). The crystal was set up on a G.E. XRD 5 diffractometer which was used to measure diffraction intensities (by the stationary-crystal–stationary counter method) and cell dimensions (by least-squares refinement of high angle data). The apparatus was equipped with a manual goniostat, scintillation counter and pulse-height discriminator. Zirconium-filtered molybdenum X-radiation was used. 3211 independent reflections were found for the first twin of which 2265 with $I > \sigma(I)$ were used in subsequent calculations. There was not much overlap with the second twin and no general treatment was felt to be necessary (apart from 0kl reflections which were given a separate scale factor in the refinement). However 11 reflections with $F_o \gg F_c$ were subsequently given zero weight in the refinement. Neither an absorption corrections nor an extinction factor were deemed necessary.

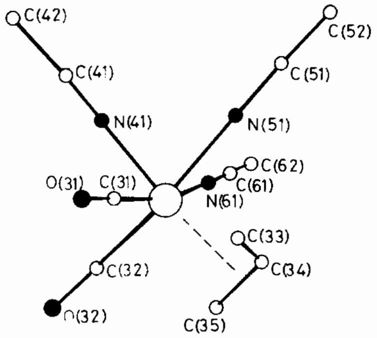

Fig. 1. The cation.

Structure Determination

The positions of the three independent molybdenum atoms were obtained from the Patterson function [with some difficulty as Mo(1) and Mo(3) are close to ½, ½, ¾ and 0, ½, ¾ respectively]. Further Fourier methods gave the positions of all atoms. The structure was refined using SHELX76 [4] with the benzene ring included as a rigid group. The molybdenum and chlorine atoms were given anisotropic, and carbon, nitrogen and oxygen, isotropic thermal parameters. Attempts to refine hydrogen atoms as part of rigid groups were unsuccessful. Scattering factors were taken from reference 5. The final R value was 0.096. The weighting scheme chosen to give average values of $w\Delta^2$ for groups of reflections independent of the value of F_o and $\sin\theta/\lambda$ was $w^{1/2}$ = 1 for $F_o < 80$ and $80/F_o$ for $F_o > 80$. In the final cycle of refinement, no shifts were $> 0.1\ \sigma$. The final difference-Fourier map showed no serious peaks. Final positional and thermal parameters, together with standard deviations are given in Table I. Bond distances and angles are given in Table II. Final observed and calculated structure factors can be obtained from the Editor.

Discussion

Solid-state Structure

The X-ray structure determination reveals that the solvated chloro-complex does not possess a molecular bis-μ-halo bridged structure. The three independent molybdenum atoms are contained within the two ionic entities $[Mo(CO)_2(\eta\text{-}C_3H_5)(MeCN)_3]^+$ and $[Mo_2Cl_3(CO)_4(\eta\text{-}C_3H_5)_2]^-$. This is fully consistent with the formation of the complex from the bis-MeCN compound, which reversibly loses MeCN and ionises in solution according to equation (1). In the

TABLE II. Molecular Dimensions (distances, A and angles °).

Cation

Mo(3)–N(61)	2.22(3)	N(61)–Mo(3)–N(41)	81.6(11)
Mo(3)–N(41)	2.19(3)	N(61)–Mo(3)–N(51)	79.5(12)
Mo(3)–N(51)	2.19(3)	N(61)–Mo(3)–C(31)	167.2(16)
Mo(3)–C(31)	1.99(5)	N(61)–Mo(3)–C(32)	97.0(15)
Mo(3)–C(32)	1.94(4)	N(61)–Mo(3)–C(33)	123.7(15)
Mo(3)–C(33)	2.36(5)	N(61)–Mo(3)–C(34)	89.2(13)
Mo(3)–C(34)	2.25(4)	N(61)–Mo(3)–C(35)	81.7(14)
Mo(3)–C(35)	2.35(4)	N(41)–Mo(3)–N(51)	81.9(12)
		N(41)–Mo(3)–C(31)	85.6(16)
N(61)–C(61)	1.06(5)	N(41)–Mo(3)–C(32)	92.0(16)
N(41)–C(41)	1.14(5)	N(41)–Mo(3)–C(33)	143.0(13)
N(51)–C(51)	1.19(5)	N(41)–Mo(3)–C(34)	163.0(13)
C(61)–C(62)	1.53(6)	N(41)–Mo(3)–C(35)	152.4(13)
C(41)–C(42)	1.44(6)	N(51)–Mo(3)–C(31)	100.2(15)
C(51)–C(52)	1.49(6)	N(51)–Mo(3)–C(32)	173.3(17)
Mo(3)–N(61)–C(61)	174(3)	N(51)–Mo(3)–C(33)	77.7(15)
Mo(3)–N(41)–C(41)	177(3)	N(51)–Mo(3)–C(34)	82.3(13)
Mo(3)–N(51)–C(51)	173(3)	N(51)–Mo(3)–C(35)	116.3(14)
N(61)–C(61)–C(62)	175(4)	C(31)–Mo(3)–C(32)	82.0(18)
N(41)–C(41)–C(42)	177(4)	C(31)–Mo(3)–C(33)	68.2(18)
N(51)–C(51)–C(52)	174(4)	C(31)–Mo(3)–C(34)	103.5(17)
C(31)–O(31)	1.18(6)	C(31)–Mo(3)–C(35)	109.5(17)
C(32)–O(32)	1.16(5)	C(32)–Mo(3)–C(33)	108.9(14)
Mo(3)–C(31)–O(31)	178(4)	C(32)–Mo(3)–C(34)	103.4(17)
Mo(3)–C(32)–O(32)	175(4)	C(32)–Mo(3)–C(35)	68.4(17)
C(33)–C(34)	1.47(6)	C(33)–Mo(3)–C(34)	37.2(15)
C(34)–C(35)	1.47(6)	C(33)–Mo(3)–C(35)	64.3(16)
C(33)–C(34)–C(35)	117(4)	C(34)–Mo(3)–C(35)	37.1(15)

Anion

	n = 1	*n = 2*
Mo–Cl(1)	2.62(1)	2.58(1)
Mo–Cl(2)	2.59(1)	2.52(1)
Mo–Cl(3)	2.52(1)	2.61(1)
Mo–C(n1)	1.94(4)	1.90(4)
Mo–C(n2)	1.93(4)	1.95(4)
Mo–C(n3)	2.38(4)	2.32(5)
Mo–C(n4)	2.23(4)	2.18(6)
Mo–C(n5)	2.30(5)	2.35(5)
Cl(1)–Mo–Cl(2)	78.1(3)	80.0(4)
Cl(1)–Mo–Cl(3)	78.5(3)	77.5(4)
Cl(1)–Mo–C(n1)	99.6(11)	98.0(14)
Cl(1)–Mo–C(n2)	169.2(13)	164.8(13)
Cl(1)–Mo–C(n3)	81.2(9)	83.3(12)
Cl(1)–Mo–C(n4)	85.1(10)	91.6(15)
Cl(1)–Mo–C(n5)	119.4(11)	127.6(13)
Cl(2)–Mo–Cl(3)	77.8(3)	77.3(3)
Cl(2)–Mo–C(n1)	167.8(14)	95.4(14)
Cl(2)–Mo–C(n2)	98.0(13)	85.9(14)
Cl(2)–Mo–C(n3)	120.5(10)	156.1(12)
Cl(2)–Mo–C(n4)	88.3(10)	159.8(14)
Cl(2)–Mo–C(n5)	82.0(12)	142.2(12)
Cl(3)–Mo–C(n1)	90.0(11)	172.0(13)
Cl(3)–Mo–C(n2)	90.9(13)	104.5(13)
Cl(3)–Mo–C(n3)	148.9(10)	115.6(12)
Cl(3)–Mo–C(n4)	160.3(10)	83.0(14)
Cl(3)–Mo–C(n5)	149.5(12)	84.0(12)

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TABLE II. *(continued)*

C(n1)–Mo–C(n2)	82.1(16)		78.0(19)
C(n1)–Mo–C(n3)	70.5(15)		70.1(18)
C(n1)–Mo–C(n4)	103.5(15)		104.0(19)
C(n1)–Mo–C(n5)	109.3(16)		103.9(17)
C(n2)–Mo–C(n3)	109.3(16)		108.5(17)
C(n2)–Mo–C(n4)	104.9(16)		103.5(20)
C(n2)–Mo–C(n5)	69.5(17)		67.4(18)
C(n3)–Mo–C(n4)	34.5(14)		36.5(19)
C(n3)–Mo–C(n5)	61.6(16)		61.5(17)
C(n4)–Mo–C(n5)	37.4(16)		37.2(19)
Mo–C(n1)–O(n1)	167(3)		179(4)
C(n1)–O(n1)	1.17(5)		1.19(5)
Mo–C(n2)–O(n2)	179(4)		176(4)
C(n2)–O(n2)	1.16(6)		1.14(6)
C(n3)–C(n4)	1.38(6)		1.41(7)
C(n4)–C(n5)	1.46(6)		1.45(8)
C(n3)–C(n4)–C(n5)	118(4)		113(5)
Mo(1)–Cl(1)–Mo(2)		85.4(3)	
Mo(1)–Cl(2)–Mo(2)		87.3(3)	
Mo(1)–Cl(3)–Mo(2)		86.9(3)	

[a] Geometry of the benzene ring was fixed during refinement.

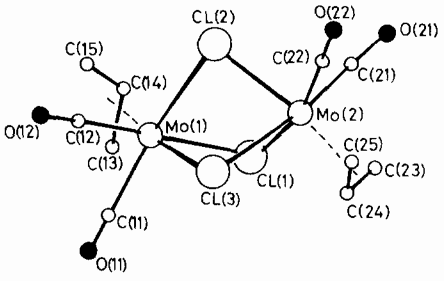

Fig. 2. The anion.

presence of a large excess of a non-coordinating solvent such as benzene, the ionic product preferentially crystallises out. Recrystallisation of [MoCl(CO)$_2$(η-C$_3$H$_5$)(MeCN)$_2$] from other non-coordinating solvents such as CHCl$_3$ and CH$_2$Cl$_2$ yields the non-solvated product as a fine powder, but crystals suitable for an X-ray diffraction study were obtained only from benzene.

The asymmetric unit of the adduct contains a cation [Mo(CO)$_2$(η-C$_3$H$_5$)(MeCN)$_3$]$^+$, an anion [Mo$_2$Cl$_3$(η-C$_3$H$_5$)$_2$(CO)$_4$]$^-$ and a solvent benzene molecule. These three moieties are separated by the normal van der Waals contacts. Figs. 1 and 2 show the geometries of the cation and anion. Around each molybdenum Mo(n), carbonyl groups are numbered C(n1), O(n1) and C(n2), O(n2), and the allyl group C(n3), C(n4), C(n5). In both cation and anion the η^3-allyl group is best considered as occupying one site of an octahedron, and all three molybdenum atoms are bonded to two carbonyl groups and an allyl ligand in a *fac*-arrangement. The *fac*-Mo(CO)$_2$ allyl moiety seems quite stable [6] and seven structures (listed in reference 6) have been determined containing it. The low accuracy of the present determination precludes detailed discussion of the geometry of this unit, but there appears to be no feature inconsistent with the data obtained from other structure determinations. In particular we note that for all three allyl groups Mo–C(n4) is shorter than Mo–C(n3) and Mo–C(n5), and that the angles between *cis*-carbonyls [82.0(18), 82.1(16) and 78.0(19)[b]] are similar to those found in other structures [6].

The detailed geometry of the Mo(CO)$_2$ allyl unit has been described [6] in terms of two angles; those between the planes C(n1), C(n2), C(n3), C(n5) and planes C(n3), C(n4), C(n5) and C(n1), C(n2), O(n1), O(n2). These angles at 46.7 and 56.5° (n = 1), 50.3 and 54.2° (n = 2) and 43.3 and 54.1° (n = 3) are comparable to those found in related molecules e.g. 45 and 54° in [Mo(CO)$_2$(η-C$_3$H$_5$)(pd)py], where pd = pentane-2,4-dionate and py = pyridine [6].

In the cation, the octahedron is completed by three methyl cyanide groups (also *fac*). Dimensions of these ligands are as expected and similar to those in other complexes [7–9]. In the anion the coordination spheres are completed by three chlorine atoms which bridge the two molybdenum atoms. Here, unlike the methyl cyanides, some systematic variations in bond lengths are observable. Two of the Mo–Cl bonds, *viz.* Mo(1)–Cl(3) and Mo(2)–Cl(2), are at 2.52(1) Å much shorter than the other four [2.58(1)–2.62(1) Å]. These shorter bonds are *trans* to the allyl group while the other four are all *trans* to a carbonyl ligand. As shown in Fig. 3 (a projection of

TABLE III. Conductance, Selected Infrared and ^{1}H N.m.r. Data on Allyl Complexes.

Complex	Λ^a (S cm^2 mol^{-1})	I.r. Data (nujol)		^{1}H N.m.r. Data in $(CD_3)_2CO$ (p.p.m. rel. to TMS) and Assignments^b	
		ν(CO)	ν(CN)		
$[Mo(CO)_2(\eta\text{-}C_3H_5)(MeCN)_3][Mo_2Cl_3(CO)_4(\eta\text{-}C_3H_5)_2]$	135	1817	2290	0.84 (4, d)	anion
		1840		1.50 (2, d)	cation
		1872		3.36 (4, d)	anion
		1920		3.62 (2, d)	cation
		1935		3.69 (2, m)	anion
		1957		4.05 (1, m)	cation
$[Mo(CO)_2(\eta\text{-}C_3H_5)(MeCN)_3][Mo_2Br_3(CO)_4(\eta\text{-}C_3H_5)_2$	130	1820	2285	0.86 (4, d)	anion
		1845		1.20 (d)	neutral
		1870		1.50 (2, d)	cation
		1922		3.30 (d)	neutral
		1935		3.54 (4, d)	anion
		1958		3.66 (2, d)	cation
				~3.9 (m)	anion + neutral
				4.05 (1, m)	cation
$[Mo(CO)_2(\eta\text{-}C_3H_5)(MeCN)_3]PF_6$		1865	2290	1.44 (2, d)	
		1955		3.50 (2, d)	
				4.06 (1, tt)	
$Ph_4As[Mo_2Cl_3(CO)_4(\eta\text{-}C_3H_5)_2]$		1802		0.82 (4, d)	
		1830		3.36 (4, d)	
		1910		3.68 (2, tt)	
		1928			
$Ph_4As[Mo_2Br_3(CO)_4(\eta\text{-}C_3H_5)_2]$		1820		0.92 (4, d)	
		1845		3.50 (4, d)	
		1920		3.90 (2, tt)	
		1936			

$^a10^{-4}$ mol dm^{-3} in acetone. ^{b}Allyl signals only, with intensity and multiplicity in parentheses (s = singlet, d = doublet, m = multiplet and tt = triplet of triplets).

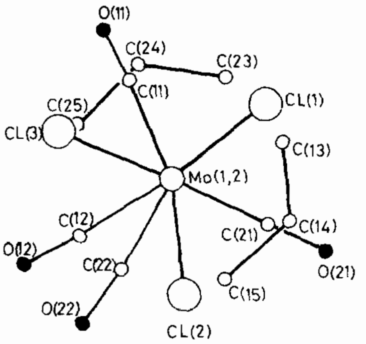

Fig. 3. The dimeric anion projected onto the bridging chlorine plane.

the dimeric anion onto the Cl_3 plane), this dimeric unit has approximate C_2 symmetry, the axis running through Cl(1) and the midpoint of the Mo(1), Mo(2) vector.

It is noticeable that while there is only one intermolecular contact less than 3.5 Å concerning a benzene ring atom, there are many more between atoms in the ions, but none less than van der Waals radii. Clearly as indicated by its high thermal parameters, this solvent molecule is very loosely packed.

Spectroscopic Properties

The solid state infrared data, conductivities and ^{1}H n.m.r. data on the chloro- and bromo-complexes are given in Table III and apart from arene absorptions, no significant differences were noted between corresponding solvated and unsolvated complexes. In the carbonyl stretching region of the infrared spectrum of the chloro-complex, six strong bands were observed. Those centred at 1872 and 1957 cm^{-1} may be assigned to the A_1 and B_1 carbonyl modes of the cation by comparison with the data for $[Mo(CO)_2(\eta\text{-}C_3H_5)(MeCN)_3]PF_6$. The four remaining bands may be assigned to the carbonyl stretching frequencies of the anion in close correspondence with the four CO stretches observed for $Ph_4As[Mo_2Cl_3(CO)_4(\eta\text{-}C_3H_5)_2]$ (Table III). In solution in acetone the complex has a molar conductivity typical of a 1:1 electrolyte [10] while the ^{1}H n.m.r. spectrum clearly shows that two allyl containing species are present in solution with chemical shifts and relative intensities appropriate for $[Mo(CO)_2(\eta\text{-}C_3H_5)(MeCN)_3]^+$ $[Mo_2Cl_3(CO)_4(\eta\text{-}C_3H_5)_2]^-$. The intensity of the coordinated MeCN signal at 2.57 p.p.m. is somewhat lower than expected from the stoichiometry of the cation, indicating that replacement by acetone of up to one third of the MeCN groups is occurring. Signals from the displaced MeCN are partially masked by signals from the incompletely deuterated acetone in the solvent.

The solid-state infrared spectrum of the bromo-complex is very similar to that of the chloride and almost a superimposition of $[Mo(CO)_2(\eta\text{-}C_3H_5)(MeCN)_3]PF_6$ and $Ph_4As[Mo_2Br_3(CO)_4(\eta\text{-}C_3H_5)_2]$ in the carbonyl stretching region, implying an ionic formulation analogous to that of the chloride. In acetone the complex behaves as a 1:1 electrolyte, but the ^{1}H n.m.r. spectrum in this solvent reveals signals due to the neutral species $[MoBr(CO)_2(\eta\text{-}C_3H_5)(MeCN)_2]$ as well as the anion and cation (Table III). The neutral complex no doubt arises from the interaction of free MeCN (from partial replacement of MeCN by acetone in the cation) with the ionic complex, so forming some of the bis-MeCN product by a reversible reaction analogous to equation (1). This equilibrium process lies far to the right for the chloro-complex, but far to the left for the bromide [1]. In non-coordinating solvents such as $CHCl_3$, only two sets of allyl signals (due to the anion and the cation) are observed, whereas in CD_3CN, mainly the neutral species with only traces of the anions and cations are present, and the bis-MeCN complex may be crystallised out on partial evaporation of the nitrile solution. Thus the solid state and solution spectroscopic data indicate that both the bromo- and chloro-complexes of stoichiometry $[MoX(CO)_2(\eta\text{-}C_3H_5)(MeCN)]$ should be reformulated as $[Mo(CO)_2(\eta\text{-}C_3H_5)(MeCN)_3]^+[Mo_2X_3(CO)_4(\eta\text{-}C_3H_5)_2]^-$

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