que l'autre (1,310 Å) est en accord avec les valeurs généralement admises pour un radical hydroxyle C—OH.

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The Crystal and Molecular Structure of $\{[(\eta^7\text{-}C_7H_7)Mo(\mu\text{-}OH)]_4\}[(\eta^7\text{-}C_7H_7)Mo(\mu\text{-}Cl)_2(\mu\text{-}OH)Mo(\eta^7\text{-}C_7H_7)]^+.Cl^-.C_6H_5Cl$, a Hydrolysis Product of $[(\eta^7\text{-}C_7H_7)Mo(\mu\text{-}Cl)_3Mo(\eta^7\text{-}C_7H_7)]$, at 173 K

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The title complex crystallizes in the monoclinic space group $P2_1/c$ with $a = 11{\cdot}043$ (3), $b = 16{\cdot}133$ (4), $c = 27{\cdot}934$ (4) Å, $\beta = 110{\cdot}63$ (2)°, $Z = 4$. The structure was refined to $R_w = 0{\cdot}061$ for 6331 reflexions. The tetrameric species $[(\eta^7\text{-}C_7H_7)Mo(\mu\text{-}OH)]_4$ consists of two intersecting tetrahedra of O and Mo atoms, forming a distorted cube. The dimer contains two bridging Cl atoms, a bridging OH group and planar η^7-C_7H_7 rings; the Mo—Mo distance is 3·091 (1) Å, corresponding to a single bond.

Introduction

$[(\eta^7\text{-}C_7H_7)MoX_3Mo(\eta^7\text{-}C_7H_7)]$ (X = halide or alkoxyl) can exist as both neutral and cationic species, and it was hoped to discover the effect of the change in charge on the Mo—Mo interaction by determining the structures of both $[(\eta^7\text{-}C_7H_7)_2Mo_2Cl_3]^+$ and $[(\eta^7\text{-}C_7H_7)_2Mo_2Cl_3]$. Crystals of $[(\eta^7\text{-}C_7H_7)_2Mo_2Cl_3][BF_4]$ were prepared and their structure determined by Alcock (1977). The Mo—Mo distance in this cationic dimeric complex was 3·051 (1) Å, and a single Mo—Mo bond was postulated. The neutral species was prepared by reacting LiCl with $[(\eta^7\text{-}C_7H_7)Mo(\text{toluene})][PF_6]$ in methanol at 65 °C, giving a dark green microcrystalline precipitate (Ashworth, Green, Green, Knight, Pardy & Wainwright, 1977). To obtain crystals suitable for X-ray crystallography, a saturated solution in chlorobenzene was cooled from 90–40 °C over one week. Clearly, partial hydrolysis occurred during the prolonged crystallization as $\{[(\eta^7\text{-}C_7H_7)Mo\ (\mu\text{-}OH)]_4\}[(\eta^7\text{-}C_7H_7)_2Mo_2(\mu\text{-}Cl)_2(\mu\text{-}OH)]Cl.C_6H_5Cl$ was formed instead, and we report the structure of this crystal.

Experimental

Green needles of the title compound were kindly supplied by Dr R. B. A. Pardy and Dr M. L. H. Green. The crystal selected for data collection was mounted in a glass capillary. After survey photography by Weissenberg and precession techniques it was set up on a Syntex $P2_1$ diffractometer and cell dimensions and orientation matrix obtained by a least-squares refinement from the setting angles of 13 reflexions.

Data were collected with graphite-monochromatized Mo $K\alpha$ radiation and an $\omega/2\theta$ scan to a $2\theta_{\max}$ of 55°, at scan rates between 1·3 and 29·3° min^{-1}, depending on the intensity of a 2 s pre-scan. Background counts (0·5 of scan time) were recorded on either side of the peak maximum. The crystal was held at 173 K with the Syntex LT-1 attachment. Three standard reflexions were used and showed no significant change in intensity. After correction for Lorentz and polarization effects, but not for absorption, 6331 reflexions were considered observed $[I/\sigma(I) \geq 3{\cdot}0]$ and used in refinement.

Crystal data

$C_{48}H_{52}Cl_4Mo_6O_5$, M_r = 1426·3. Monoclinic, a = 11·043 (3), b = 16·133 (4), c = 27·934 (4) Å, β = 110·63 (2)°, U = 4657·5 Å^3, D_m = 2·01 (by flotation), D_c = 2·03 g cm^{-3}, Z = 4. Space group $P2_1/c$; systematic extinctions $0k0$, $k = 2n + 1$ and $h0l$, $l = 2n + 1$. Mo $K\alpha$ radiation, λ = 0·71069 Å, μ = 18 cm^{-1}.

Structure solution and refinement

The six Mo atoms were located from an E map based on the best phase set after weighted, multi-solution

Table 1. *Fractional atomic coordinates, with e.s.d.'s in parentheses*

Table 1 (*cont.*)

	x	*y*	*z*
Mo(1)	0·47772 (8)	0·09659 (5)	0·36276 (3)
Mo(2)	0·77482 (8)	0·09617 (5)	0·36112 (3)
Mo(3)	0·60470 (8)	0·26189 (5)	0·33777 (3)
Mo(4)	0·71001 (9)	0·20029 (5)	0·45343 (3)
O(1)	0·5371 (6)	0·2122 (4)	0·3929 (2)
O(2)	0·5907 (6)	0·1352 (4)	0·3227 (2)
O(3)	0·7701 (6)	0·2121 (4)	0·3920 (2)
O(4)	0·6760 (6)	0·0766 (4)	0·4165 (2)
C(11)	0·308 (1)	0·0978 (7)	0·3902 (5)
C(12)	0·378 (1)	0·0271 (6)	0·4104 (4)
C(13)	0·431 (1)	−0·0298 (6)	0·3849 (4)
C(14)	0·419 (1)	−0·0341 (7)	0·3328 (4)
C(15)	0·354 (1)	0·0229 (7)	0·2936 (4)
C(16)	0·289 (1)	0·0971 (7)	0·2968 (4)
C(17)	0·269 (1)	0·1304 (7)	0·3402 (4)
C(21)	0·777 (1)	−0·0345 (7)	0·3295 (5)
C(22)	0·770 (1)	0·0249 (8)	0·2901 (4)
C(23)	0·847 (1)	0·0987 (7)	0·2950 (5)
C(24)	0·946 (1)	0·1289 (7)	0·3390 (5)
C(25)	0·994 (1)	0·0949 (7)	0·3877 (5)
C(26)	0·958 (1)	0·0235 (7)	0·4074 (4)
C(27)	0·855 (1)	−0·0336 (6)	0·3804 (5)
C(31)	0·428 (1)	0·3122 (7)	0·2729 (4)
C(32)	0·444 (1)	0·3590 (7)	0·3178 (5)
C(33)	0·558 (1)	0·3953 (6)	0·3511 (5)
C(34)	0·681 (1)	0·3935 (7)	0·3479 (5)
C(35)	0·728 (1)	0·3545 (8)	0·3128 (5)
C(36)	0·656 (1)	0·3087 (8)	0·2700 (5)
C(37)	0·520 (2)	0·2855 (7)	0·2534 (4)
C(41)	0·685 (1)	0·3146 (8)	0·4950 (4)
C(42)	0·810 (2)	0·3147 (7)	0·4952 (4)
C(43)	0·901 (1)	0·2485 (9)	0·5081 (5)
C(44)	0·887 (1)	0·1677 (8)	0·5229 (4)
C(45)	0·777 (1)	0·1305 (7)	0·5272 (4)
C(46)	0·658 (1)	0·1678 (8)	0·5236 (4)
C(47)	0·614 (1)	0·248 (1)	0·5085 (4)
Mo(5)	0·33754 (9)	0·15829 (5)	0·08790 (3)
Mo(6)	0·22622 (9)	0·11454 (5)	−0·02717 (3)
Cl(1)	0·1416 (3)	0·0715 (2)	0·0418 (1)
Cl(2)	0·4348 (3)	0·0667 (2)	0·0387 (1)
O(5)	0·273 (1)	0·2207 (4)	0·0179 (3)
C(51)	0·493 (1)	0·2505 (7)	0·1288 (4)
C(52)	0·369 (1)	0·2838 (6)	0·1226 (4)
C(53)	0·264 (1)	0·2477 (7)	0·1338 (4)
C(54)	0·255 (2)	0·1685 (8)	0·1518 (5)
C(55)	0·352 (2)	0·1064 (7)	0·1651 (4)
C(56)	0·477 (2)	0·1067 (7)	0·1632 (5)
C(57)	0·537 (1)	0·1705 (9)	0·1460 (5)
C(61)	0·239 (1)	0·0102 (6)	−0·0802 (4)
C(62)	0·316 (1)	0·0780 (7)	−0·0849 (4)
C(63)	0·281 (1)	0·1634 (7)	−0·0924 (4)
C(64)	0·163 (1)	0·1995 (7)	−0·0938 (4)
C(65)	0·049 (1)	0·1634 (7)	−0·0905 (4)
C(66)	0·032 (1)	0·0794 (7)	−0·0831 (4)
C(67)	0·113 (1)	0·0098 (7)	−0·0797 (4)
Cl(3)	0·2583 (3)	0·0838 (2)	0·5143 (1)
Cl(4)	0·909 (1)	0·1669 (7)	0·1603 (5)
C(71)	0·935 (2)	0·264 (1)	0·1891 (7)
C(72)	0·893 (2)	0·338 (2)	0·1646 (7)
C(73)	0·923 (2)	0·411 (2)	0·194 (1)
C(74)	0·995 (2)	0·407 (2)	0·243 (1)
C(75)	1·035 (2)	0·333 (2)	0·2633 (6)
C(76)	1·011 (2)	0·265 (1)	0·2404 (7)
H(1)	0·4687	0·2415	0·4022
H(2)	0·5576	0·1161	0·2864
H(3)	0·8546	0·2420	0·4010
H(4)	0·6961	0·0263	0·4388
H(5)	0·2659	0·2810	0·0091
H(11)	0·2809	0·1311	0·4149
H(12)	0·3923	0·0149	0·4471
H(13)	0·4869	−0·0739	0·4072
H(14)	0·4601	−0·0829	0·3225
H(15)	0·3551	0·0090	0·2588
H(16)	0·2518	0·1296	0·2644
H(17)	0·2207	0·1842	0·3348
H(21)	0·7172	−0·0831	0·3185
H(22)	0·7036	0·0138	0·2556
H(23)	0·8292	0·1325	0·2632
H(24)	0·9860	0·1824	0·3345
H(25)	1·0663	0·1269	0·4127
H(26)	1·0089	0·0101	0·4439
H(27)	0·8376	−0·0786	0·4019
H(31)	0·3367	0·2964	0·2523
H(32)	0·3642	0·3669	0·3268
H(33)	0·5497	0·4264	0·3808
H(34)	0·7481	0·4255	0·3754
H(35)	0·8227	0·3603	0·3193
H(36)	0·7035	0·2892	0·2476
H(37)	0·4897	0·2452	0·2244
H(41)	0·6369	0·3678	0·4841
H(42)	0·8408	0·3679	0·4850
H(43)	0·9876	0·2619	0·5061
H(44)	0·9658	0·1319	0·5316
H(45)	0·7834	0·0694	0·5335
H(46)	0·5971	0·1314	0·5333
H(47)	0·5239	0·2614	0·5068
H(51)	0·5539	0·2877	0·1199
H(52)	0·3527	0·3412	0·1082
H(53)	0·1869	0·2840	0·1279
H(54)	0·1716	0·1538	0·1559
H(55)	0·3273	0·0536	0·1780
H(56)	0·5288	0·0553	0·1756
H(57)	0·6255	0·1571	0·1461
H(61)	0·2816	−0·0454	−0·0769
H(62)	0·4061	0·0642	−0·0826
H(63)	0·3472	0·2018	−0·0972
H(64)	0·1589	0·2612	−0·0979
H(65)	−0·0254	0·2012	−0·0938
H(66)	−0·0526	0·0656	−0·0796
H(67)	0·0763	−0·0457	−0·0764
H(72)	0·8417	0·3406	0·1273
H(73)	0·8907	0·4663	0·1781
H(74)	1·0195	0·4581	0·2653
H(75)	1·0889	0·3305	0·3006
H(76)	1·0465	0·2123	0·2588

tangent refinement (Germain, Main & Woolfson, 1971), with three origin-defining phases (0,3,16, 425, 72$\bar{7}$) and two multi-solution phases (4,10,0, 346); 417 phases with $E > 1\cdot5$ were used in this refinement. Subsequent difference syntheses revealed all other non-hydrogen atoms. Refinement was by least squares with a large-block approximation to the normal matrix: a 2 × 2 block was calculated from the derivatives of the scale and dummy overall temperature factor, three blocks from those of the positional parameters of the tetramer, dimer, and Cl$^-$ ion and chlorobenzene solvate, respectively, and a further three from those of the corresponding temperature factors. All non-hydrogen atoms had anisotropic temperature factors. The H atoms were located in their expected positions from a difference synthesis but were positioned geo-

Table 2. *Interatomic distances* (Å) *and bond angles* (°)

Tetramer

Mo(1)–Mo(2)	3·297 (1)	Mo(2)–Mo(3)	3·200 (1)
Mo(1)–Mo(3)	3·202 (1)	Mo(2)–Mo(4)	3·359 (1)
Mo(1)–Mo(4)	3·349 (1)	Mo(3)–Mo(4)	3·183 (1)
Mo(1)–O(1)	2·056 (6)	Mo(2)–O(2)	2·036 (6)
Mo(1)–O(2)	2·044 (6)	Mo(2)–O(3)	2·068 (6)
Mo(1)–O(4)	2·199 (6)	Mo(2)–O(4)	2·208 (6)
Mo(3)–O(1)	2·092 (6)	Mo(4)–O(1)	2·066 (7)
Mo(3)–O(2)	2·081 (6)	Mo(4)–O(3)	2·056 (6)
Mo(3)–O(3)	2·080 (6)	Mo(4)–O(4)	2·217 (6)
Mo(1)–C(11)	2·261 (11)	Mo(3)–C(31)	2·295 (10)
Mo(1)–C(12)	2·297 (10)	Mo(3)–C(32)	2·288 (10)
Mo(1)–C(13)	2·241 (9)	Mo(3)–C(33)	2·276 (11)
Mo(1)–C(14)	2·277 (10)	Mo(3)–C(34)	2·267 (10)
Mo(1)–C(15)	2·269 (11)	Mo(3)–C(35)	2·291 (10)
Mo(1)–C(16)	2·247 (11)	Mo(3)–C(36)	2·286 (10)
Mo(1)–C(17)	2·235 (10)	Mo(3)–C(37)	2·240 (11)
Mo(2)–C(21)	2·288 (10)	Mo(4)–C(41)	2·247 (12)
Mo(2)–C(22)	2·276 (10)	Mo(4)–C(42)	2·255 (10)
Mo(2)–C(23)	2·257 (10)	Mo(4)–C(43)	2·262 (12)
Mo(2)–C(24)	2·244 (11)	Mo(4)–C(44)	2·279 (10)
Mo(2)–C(25)	2·267 (11)	Mo(4)–C(45)	2·232 (11)
Mo(2)–C(26)	2·302 (10)	Mo(4)–C(46)	2·290 (10)
Mo(2)–C(27)	2·262 (10)	Mo(4)–C(47)	2·290 (12)
O(1)–O(2)	2·559 (9)	O(2)–O(3)	2·551 (9)
O(1)–O(3)	2·582 (9)	O(2)–O(4)	2·627 (9)
O(1)–O(4)	2·619 (9)	O(3)–O(4)	2·614 (8)
C(11)–C(12)	1·38 (2)	C(31)–C(32)	1·42 (2)
C(12)–C(13)	1·41 (2)	C(32)–C(33)	1·40 (2)
C(13)–C(14)	1·42 (2)	C(33)–C(34)	1·40 (2)
C(14)–C(15)	1·42 (2)	C(34)–C(35)	1·41 (2)
C(15)–C(16)	1·42 (2)	C(35)–C(36)	1·39 (2)
C(16)–C(17)	1·41 (2)	C(36)–C(37)	1·45 (2)
C(17)–C(11)	1·41 (2)	C(37)–C(31)	1·38 (2)
C(21)–C(22)	1·44 (2)	C(41)–C(42)	1·38 (2)
C(22)–C(23)	1·45 (2)	C(42)–C(43)	1·42 (2)
C(23)–C(24)	1·41 (2)	C(43)–C(44)	1·39 (2)
C(24)–C(25)	1·39 (2)	C(44)–C(45)	1·40 (2)
C(25)–C(26)	1·39 (2)	C(45)–C(46)	1·42 (2)
C(26)–C(27)	1·46 (2)	C(46)–C(47)	1·40 (2)
C(27)–C(21)	1·38 (2)	C(47)–C(41)	1·46 (2)

O(1)–Mo(1)–O(2)	77·2 (3)	O(1)–Mo(3)–O(2)	75·6 (2)
O(1)–Mo(1)–O(4)	75·9 (2)	O(1)–Mo(3)–O(3)	76·5 (2)
O(2)–Mo(1)–O(4)	76·4 (2)	O(2)–Mo(3)–O(3)	75·6 (2)
O(2)–Mo(2)–O(3)	76·9 (2)	O(1)–Mo(4)–O(3)	77·6 (3)

Table 2 (*cont.*)

O(2)–Mo(2)–O(4)	76·4 (2)	O(1)–Mo(4)–O(4)	75·3 (2)
O(3)–Mo(2)–O(4)	75·3 (2)	O(3)–Mo(4)–O(4)	75·3 (2)
Mo(1)–O(1)–Mo(3)	101·1 (3)	Mo(2)–O(3)–Mo(3)	101·0 (3)
Mo(1)–O(1)–Mo(4)	108·7 (3)	Mo(2)–O(3)–Mo(4)	109·1 (3)
Mo(3)–O(1)–Mo(4)	99·9 (3)	Mo(3)–O(3)–Mo(4)	100·6 (3)
Mo(1)–O(2)–Mo(2)	107·8 (3)	Mo(1)–O(4)–Mo(2)	96·9 (2)
Mo(1)–O(2)–Mo(3)	101·8 (3)	Mo(1)–O(4)–Mo(4)	98·7 (3)
Mo(2)–O(2)–Mo(3)	102·0 (3)	Mo(2)–O(4)–Mo(4)	98·8 (2)
C(17)–C(11)–C(12)	130 (1)	C(37)–C(31)–C(32)	129 (1)
C(11)–C(12)–C(13)	127 (1)	C(31)–C(32)–C(33)	127 (1)
C(12)–C(13)–C(14)	130 (1)	C(32)–C(33)–C(34)	128 (1)
C(13)–C(14)–C(15)	127 (1)	C(33)–C(34)–C(35)	131 (1)
C(14)–C(15)–C(16)	129 (1)	C(34)–C(35)–C(36)	126 (1)
C(15)–C(16)–C(17)	128 (1)	C(35)–C(36)–C(37)	129 (1)
C(16)–C(17)–C(11)	128 (1)	C(36)–C(37)–C(31)	128 (1)
C(27)–C(21)–C(22)	129 (1)	C(47)–C(41)–C(42)	129 (1)
C(21)–C(22)–C(23)	127 (1)	C(41)–C(42)–C(43)	128 (1)
C(22)–C(23)–C(24)	128 (1)	C(42)–C(43)–C(44)	130 (1)
C(23)–C(24)–C(25)	129 (1)	C(43)–C(44)–C(45)	128 (1)
C(24)–C(25)–C(26)	131 (1)	C(44)–C(45)–C(46)	129 (1)
C(25)–C(26)–C(27)	127 (1)	C(45)–C(46)–C(47)	129 (1)
C(26)–C(27)–C(21)	129 (1)	C(46)–C(47)–C(41)	127 (1)

Dimer

Mo(5)–Mo(6)	3·091 (1)		
Mo(5)–Cl(1)	2·517 (3)	Mo(6)–Cl(1)	2·518 (3)
Mo(5)–Cl(2)	2·503 (3)	Mo(6)–Cl(2)	2·509 (3)
Mo(5)–O(5)	2·088 (8)	Mo(6)–O(5)	2·080 (7)
Mo(5)–C(51)	2·251 (12)	Mo(6)–C(61)	2·281 (10)
Mo(5)–C(52)	2·218 (10)	Mo(6)–C(62)	2·248 (10)
Mo(5)–C(53)	2·260 (11)	Mo(6)–C(63)	2·257 (11)
Mo(5)–C(54)	2·276 (12)	Mo(6)–C(64)	2·218 (10)
Mo(5)–C(55)	2·266 (12)	Mo(6)–C(65)	2·269 (11)
Mo(5)–C(56)	2·280 (12)	Mo(6)–C(66)	2·236 (10)
Mo(5)–C(57)	2·239 (13)	Mo(6)–C(67)	2·297 (10)
C(51)–C(52)	1·42 (2)	C(61)–C(62)	1·42 (2)
C(52)–C(53)	1·42 (2)	C(62)–C(63)	1·43 (2)
C(53)–C(54)	1·39 (2)	C(63)–C(64)	1·42 (2)
C(54)–C(55)	1·42 (2)	C(64)–C(65)	1·42 (2)
C(55)–C(56)	1·39 (2)	C(65)–C(66)	1·39 (2)
C(56)–C(57)	1·40 (2)	C(66)–C(67)	1·42 (2)
C(57)–C(51)	1·41 (2)	C(67)–C(61)	1·40 (2)

Cl(1)–Mo(5)–Cl(2)	81·3 (1)	Cl(1)–Mo(6)–Cl(2)	81·2 (1)
Cl(1)–Mo(5)–O(5)	80·8 (3)	Cl(1)–Mo(6)–O(5)	80·9 (3)
Cl(2)–Mo(5)–O(5)	80·9 (2)	Cl(2)–Mo(6)–O(5)	81·0 (3)
Cl(1)–Mo(5)–Mo(6)	52·14 (7)	Cl(1)–Mo(6)–Mo(5)	52·11 (7)
Cl(2)–Mo(5)–Mo(6)	52·01 (7)	Cl(2)–Mo(6)–Mo(5)	51·84 (7)
O(5)–Mo(5)–Mo(6)	42·0 (2)	O(5)–Mo(6)–Mo(5)	42·2 (2)
Mo(5)–Cl(1)–Mo(6)	75·75 (9)	Mo(5)–O(5)–Mo(6)	95·8 (3)
Mo(5)–Cl(2)–Mo(6)	76·15 (8)		
C(57)–C(51)–C(52)	126 (1)	C(67)–C(61)–C(62)	129 (1)
C(51)–C(52)–C(53)	130 (1)	C(61)–C(62)–C(63)	128 (1)
C(52)–C(53)–C(54)	128 (1)	C(62)–C(63)–C(64)	127 (1)
C(53)–C(54)–C(55)	127 (1)	C(63)–C(64)–C(65)	131 (1)
C(54)–C(55)–C(56)	131 (1)	C(64)–C(65)–C(66)	125 (1)
C(55)–C(56)–C(57)	128 (1)	C(65)–C(66)–C(67)	132 (1)
C(56)–C(57)–C(51)	130 (1)	C(66)–C(67)–C(61)	127 (1)

Chlorobenzene solvate

Cl(4)–C(71)	1·73 (2)		
C(71)–C(72)	1·38 (3)	C(74)–C(75)	1·33 (3)
C(72)–C(73)	1·41 (3)	C(75)–C(76)	1·25 (3)
C(73)–C(74)	1·34 (3)	C(76)–C(71)	1·38 (2)

Cl(4)–C(71)–C(72)	125 (2)	C(72)–C(73)–C(74)	119 (2)
Cl(4)–C(71)–C(76)	116 (2)	C(73)–C(74)–C(75)	118 (2)
C(76)–C(71)–C(72)	118 (2)	C(74)–C(75)–C(76)	127 (2)
C(71)–C(72)–C(73)	118 (2)	C(75)–C(76)–C(71)	119 (2)

metrically (C—H = 1·0 Å, $U_{\rm iso} = 0{\cdot}05$ Å^2) and included in the structure factor calculations. Their location was readjusted after each cycle. In the final stages of refinement, each reflexion was assigned a weight according to $w^{-1} = 1 + [(|F_o| - 55)/45]^2$, chosen to minimize the variation of $w(|F_o| - |F_c|)^2$ with $|F_o|$ and the final weighted R_w was 0·061 for 6331 reflexions.

All calculations were performed with the Oxford *CRYSTALS* package (Carruthers, 1975) on the Oxford University ICL 1906A computer and the University of London CDC 7600 computer. Complex neutral-atom scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

Results and discussion

The final atomic positional parameters are given in Table 1.* Table 2 lists interatomic distances and bond angles for the non-hydrogen atoms, with e.s.d.'s calculated from the variance–covariance matrix; equations of important molecular planes are given in Table 3. Fig. 1 shows the tetrameric and Fig. 2 the dimeric species.

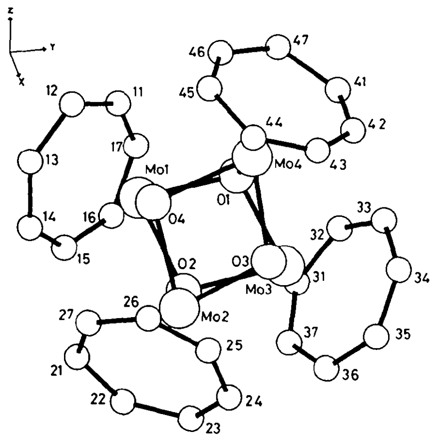

Fig. 1. Projection of $[(\eta^7\text{-}C_7H_7)Mo(\mu\text{-}OH)]_4$ on to the plane defined by Mo(2)O(3)O(4)Mo(4). For clarity, the C atoms are labelled by their serial number only.

Table 3. *Some least-squares best planes*

In the equations, x, y and z represent fractional coordinates with respect to the crystallographic axes. The table gives the displacement (Å) of the specified atom from the plane.

Plane 1: ring C(11) to C(17)

Equation of plane: $-9{\cdot}051x - 8{\cdot}493y + 2{\cdot}159z = -2{\cdot}788$

C(11)	0·012	C(15)	0·021
C(12)	0·022	C(16)	−0·008
C(13)	−0·034	C(17)	−0·018
C(14)	0·005	Mo(1)*	−1·573

Normal to Mo(1) meets plane 0·02 Å from centroid.

Plane 2: ring C(21) to C(27)

Equation of plane: $-8{\cdot}951x + 8{\cdot}580y + 14{\cdot}393z = -2{\cdot}493$

C(21)	−0·013	C(25)	−0·009
C(22)	−0·007	C(26)	−0·018
C(23)	0·001	C(27)	0·030
C(24)	0·015	Mo(2)*	1·580

Normal to Mo(2) meets plane 0·02 Å from centroid.

Plane 3: ring C(31) to C(37)

Equation of plane: $-0{\cdot}041x + 13{\cdot}332y - 14{\cdot}684z = 0{\cdot}105$

C(31)	0·034	C(35)	−0·001
C(32)	−0·004	C(36)	0·020
C(33)	−0·013	C(37)	−0·041
C(34)	0·005	Mo(3)*	−1·598

Normal to Mo(3) meets plane 0·01 Å from centroid

Plane 4: ring C(41) to C(47)

Equation of plane: $-0{\cdot}045x - 4{\cdot}552y - 25{\cdot}040z = -13{\cdot}878$

C(41)	0·019	C(45)	0·048
C(42)	0·009	C(46)	−0·028
C(43)	−0·016	C(47)	−0·013
C(44)	−0·019	Mo(4)*	1·580

Normal to Mo(4) meets plane 0·01 Å from centroid.

Plane 5: ring C(51) to C(57)

Equation of plane: $0{\cdot}444x + 5{\cdot}690y + 24{\cdot}044z = 4{\cdot}733$

C(51)	0·008	C(55)	−0·000
C(52)	−0·006	C(56)	0·011
C(53)	0·010	C(57)	−0·013
C(54)	−0·010	Mo(5)*	−1·569

Normal to Mo(5) meets plane 0·04 Å from centroid.

Plane 6: ring C(61) to C(67)

Equation of plane: $-0{\cdot}176x - 1{\cdot}960y - 25{\cdot}789z = 2{\cdot}001$

C(61)	0·006	C(65)	0·005
C(62)	−0·020	C(66)	−0·018
C(63)	0·013	C(67)	0·014
C(64)	−0·001	Mo(6)*	−1·565

Normal to Mo(6) meets plane 0·04 Å from centroid.

Plane 7: chlorobenzene molecule

Equation of plane: $-10{\cdot}712x - 1{\cdot}486y + 15{\cdot}422z = -7{\cdot}513$

Cl(4)	−0·003	C(74)	0·001
C(71)	0·017	C(75)	−0·003
C(72)	−0·013	C(76)	−0·004
C(73)	0·005		

* Atom not included in the plane calculation.

The asymmetric unit contains a tetramer, a dimer, a Cl⁻ ion and a molecule of chlorobenzene solvate, with the Cl⁻ ion hydrogen bonded to the O atom of the bridging hydroxyl group in the dimeric species, Cl(3)···O(5) 3·159 (8) Å, Cl(3)···H(5)—O(5) 162·6 (4)°, and to one of the O atoms in the tetrameric species, Cl(3)···O(4) 3·159 (6) Å, Cl(3)···H(4)—O(4) 178·6 (4)°. The O···Cl distances lie within the range 3·09–3·18 Å, established by neutron diffraction studies (Hamilton & Ibers, 1968), and the O—H···Cl angles lie on the outskirts of the literature range (153–

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* Lists of structure factors and anisotropic thermal parameters for the non-hydrogen atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33513 (58 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

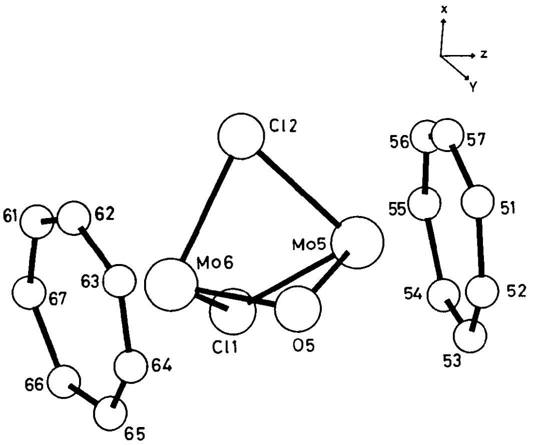

Fig. 2. The $[(\eta^7\text{-}C_7H_7)Mo(\mu\text{-}Cl)_2(\mu\text{-}OH)Mo(\eta^7\text{-}C_7H_7)]^+$ cation. For clarity, the C atoms are labelled by their serial number only.

166°). The chlorobenzene molecule is planar (plane 7 in Table 3) and interatomic distances and angles are normal, albeit with somewhat high e.s.d.'s, probably a consequence of its high thermal motion.

The presence of a Cl^- ion indicates that either the dimer or the tetramer is charged. The tetrameric unit must be neutral if the eighteen-electron rule is to be satisfied for all the Mo atoms without metal–metal bonding. A positive charge would require Mo–Mo bonding leading to a distortion and a shortening of Mo–Mo distances. However, no significant distortions are observed. Consequently the tetramer is thought to be neutral with Mo atoms of formal valency 2.

If $\eta^7\text{-}C_7H_7$ is a seven-electron donor, then the $[Mo_2(\eta^7\text{-}C_7H_7)_2Cl_2OH]^+$ cation with a Mo–Mo bond gives each Mo 18 electrons, the complex is diamagnetic, and the Mo atoms have a formal valency of 4. In the neutral species, $[Mo_2(\eta^7\text{-}C_7H_7)_2Cl_3]$, either one Mo has formal valency 3 and the other 4, or, if as proposed (Ashworth, Green, Green, Knight, Pardy & Wainwright, 1977), the Mo atoms are equivalent in chemical terms, then both have formal valence $3\frac{1}{2}$. The Mo–Mo distance, 3·091 (1) Å, is similar to those observed in related dimeric cations, $[Mo_2(\eta^7\text{-}C_7H_7)_2Cl_3]^+$, 3·051 (1) (Alcock, 1977) and 3·060 (2) (Bowerbank, Green, Kirsch, Mortreux, Smart & Stone, 1977), and $[Mo_2(\eta^7\text{-}C_7H_7)_2Br(OH)_2]^+$, 2·882 (2) Å (Welch, 1977); a metal–metal bond is required to explain the diamagnetism of the species. A better criterion for assessing metal–metal bonding in multibridged systems than the $M\cdots M$ separation is the bridging angle which is normally obtuse in complexes with non-bonding metal–metal systems (Dahl, de Gil & Feltham, 1969). In $[Mo_2(\eta^7\text{-}C_7H_7)_2Cl_3]^+$ and $[Mo_2(\eta^7\text{-}C_7H_7)_2Br(OH)_2]^+$ the bridging angles are all acute [74·4 (5)–79·7 (8)° and 66·26 (8)–88·4 (6)°, respectively] in agreement with this criterion. However, in $[Mo_2(\eta^7\text{-}C_7H_7)_2Cl_2(OH)]^+$, while the Mo–Cl–Mo angles are similar to those found in $[Mo_2(\eta^7\text{-}C_7H_7)_2Cl_3]^+$ [75·75 (9) and 76·15 (8)°], the Mo–O–Mo bridging angle is 95·8 (3)°. This wider bridging angle is necessary to accommodate the shorter Mo–O bonds [2·088 (8) and 2·080 (7) Å] compared with the Mo–Cl bonds [2·503 (3)–2·518 (3), mean 2·512 (7) Å] across the bridge. The Mo–O and Mo–Cl distances agree with those found in related complexes, Mo–O 2·064 (13)–2·086 (13) in $[Mo_2(\eta^7\text{-}C_7H_7)_2Br(OH)_2]^+$, and Mo–Cl 2·38 (2)–2·55 (2) Å in $[Mo_2(\eta^7\text{-}C_7H_7)_2Cl_3]^+$.

Assuming that the η^7-cycloheptatrienyl ring acts as the seven-electron donor, C_7H_7, and interacts with three vacant metal orbitals, the cation may formally be described as a seven-coordinate Mo^{IV} complex with each metal atom providing the cap of the other's distorted capped octahedral geometry. In the rings the C–C bonds are in the range 1·39 (2)–1·43 (2) [mean 1·41 (1) Å], while the C–C–C angles vary from 125 (1) to 132 (1) [mean 129 (2)°], with no systematic variation. The rings are planar (planes 5 and 6 in Table 3), and can be described as essentially regular heptagons. In the dimer, the Mo–C distances are in the range 2·22 (1)–2·30 (1) [mean 2·26 (2) Å], the perpendiculars to the rings are 1·569 for Mo(5) and 1·565 Å for Mo(6), and the perpendiculars to the η^7-cycloheptatrienyl rings at the Mo atoms meet the rings close (0·04 Å) to their centroids.

The η^7-cycloheptatrienyl rings, although individually planar, are bent symmetrically away from the plane of the three bridging atoms to subtend a mutual dihedral angle of *ca* 14°. Both the rings are tipped towards the hydroxyl bridge, the one at Mo(5) by 7·3°, and the one at Mo(6) by 6·5°. This effect has been explained by Welch (1977) to be primarily the result of the inequivalence of the metal-to-bridge atom distances.

The tetramer contains interpenetrating tetrahedra of the Mo and O atoms, analogous to $\{[(\eta^6\text{-}C_6H_6)Ru(OH)]_4\}.(SO_4)_2.12H_2O$ (Gould, Jones, Robertson & Stephenson, 1977) and $[(CH_3)_3Pt(OH)]_4$ (Preston, Mills & Kennard, 1968; Spiro, Templeton & Zalkin, 1968). Each Mo atom has bonds to three hydroxyl groups, the Mo–O distances being in the range 2·036 (6)–2·217 (6) Å, and the O–Mo–O and Mo–O–Mo angles in the ranges 75·3 (2)–77·6 (3) [mean 76·2 (8)°] and 96·9 (2)–109·1 (3)°, respectively. The arrangement of the Mo and O atoms may thus be described as a substantially distorted cube in which the Mo···Mo and O···O face diagonals are in the ranges 3·183 (1)–3·359 (1) and 2·551 (9)–2·627 (9) Å, respectively (Fig. 1). The Mo–O and O···O distances involving O(4) are significantly longer and the Mo–O(4)–Mo angles are smaller than the other analogous distances and angles involving O(1)–O(3), perhaps a reflexion of the presence of the O(4)···Cl(3) hydrogen bond in the structure.

The seven-electron donor, C_7H_7, formally occupies three adjacent coordination sites, completing the octahedral coordination about each Mo. In the η^7-cycloheptatrienyl rings the C—C bonds are in the range 1·38 (2)–1·46 (2) [mean 1·41 (2) Å], while the C—C—C angles vary from 126 (1) to 131 (1) [mean 128 (1)°], with no systematic variation. They can be described as essentially regular heptagons and are planar within experimental error (planes 1 to 4 in Table 3). The Mo—C distances are in the range 2·23 (1)–2·30 (1) [mean 2·27 (2) Å]; the perpendicular distances from the Mo atoms to the rings vary from 1·573–1·598 [mean 1·583 (11) Å], and the perpendiculars to the η^7-cycloheptatrienyl rings at the Mo atoms meet the rings close (0·02 Å mean) to their centroids. The difference in formal valences of the Mo atoms in the tetramer, Mo^{II}, and the dimer, Mo^{IV}, is reflected in these ring-normal distances, those in the tetramer [1·583 (11) Å, mean] being significantly longer than those in the dimer (1·567 Å, mean).

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The Crystal and Molecular Structures of Dichloro(triphenylphosphine)(η^5-tetramethylethylcyclopentadienyl)cobalt Toluene Solvate and Tri-μ-chloro-bis(η^5-tetramethylethylcyclopentadienyl)dicobalt Tetrachloroferrate

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The crystal structures of dichloro(triphenylphosphine)(η^5-tetramethylethylcyclopentadienyl)cobalt toluene solvate, $C_{36}H_{40}Cl_2CoP$, compound I, monoclinic, $a = 8{\cdot}560$ (6), $b = 17{\cdot}791$ (5), $c = 21{\cdot}065$ (5) Å, $\beta = 98{\cdot}87$ (6)°, $Z = 4$, space group $P2_1/n$, 2679 reflexions, $R = 0{\cdot}061$ and tri-μ-chloro-bis(η^5-tetramethylethylcyclopentadienyl)dicobalt tetrachloroferrate, $C_{22}H_{34}Cl_7Co_2Fe$, compound II, orthorhombic, $a = 15{\cdot}940$ (4), $b = 25{\cdot}819$ (3), $c = 15{\cdot}067$ (1) Å, $Z = 8$, space group $Pbca$, 2108 reflexions, $R = 0{\cdot}086$ have been determined from diffractometer data. The coordination around the Co atoms in both compounds may be described as distorted octahedral; in compound II the two Co octahedra share one face, with a Co···Co distance of 2·887 (2) Å.

Introduction

The chemistry of pentaalkylcyclopentadienyl transition metal complexes has been comparatively unexplored. The work of Maitlis and coworkers (Lee, Moseley, White & Maitlis, 1975) has shown that certain η^5-pentamethylcyclopentadienyl complexes of rhodium and iridium possess properties markedly different from their unsubstituted analogues. Therefore, in the development of the chemistry of η^5-tetra-