Novel cyclic hexanuclear complexes containing quadruply bonded units joined by μ_6-carbonate ions

Maw-Cherng Suen,[a] Gwo-Wei Tseng,[a] Jhy-Der Chen,*[a] Tai-Chiun Keng[b] and Ju-Chun Wang[b]

[a] *Department of Chemistry, Chung-Yuan Christian University, Chung-Li, Taiwan, R.O.C.*
[b] *Department of Chemistry, Soochow University, Taipei, Taiwan, R.O.C.*

Received (in Cambridge, UK) 28th April 1999, Accepted 24th May 1999

Three complexes {[*trans*-$Mo_2(O_2CCF_3)_2(\mu$-dppa)]$_3(\mu_6$-$CO_3)(\mu_2$-$X)_3$}F [X = Cl, Br or I; dppa = *N*,*N*-bis(diphenylphosphino)amine], are reported, which are the first cyclic, hexanuclear complexes containing quadruply bonded units joined by carbonate ions.

Complexes containing metal–metal multiple bonds have already been the subject of many studies of their structures and reactivities.[1] Quadruply bonded dinuclear complexes were found to be able to dimerize to form cyclic rectangular clusters. Pairs of dinuclear molecules undergo [2 + 2] cycloaddition by loss of the δ components of the quadruple bonds with the two single bonds formed joining the triply bonded dimers together.[2] Recently tetranuclear complexes of the type [$Mo_2(DArF)_3]_2(\mu$-$H)_2$ (DArF = *N*,*N*′-diarylformamidinate, Ar = *p*-tolyl or *p*-anisyl) containing quadruply bonded dimolybdenum units joined by μ-hydride ions have been prepared by reaction of $Mo_2(DArF)_3Cl_2$ and $NaHBEt_3$.[3] To investigate the bonding mode of the carbonate ion in the dimolybdenum complex, we studied the reaction of [*trans*-$Mo_2(O_2CCF_3)_2(MeCN)_6][BF_4]_2$ with K_2CO_3 and *N*,*N*′-bis(diphenylphosphino)amine (dppa) in CH_2Cl_2. The reaction afforded a novel cyclic, hexanuclear complex containing quadruply bonded units joined by carbonate ions and axially bridged by chloride atoms. The synthesis and structural characterization of this complex and its bromo and iodo analogue form the subject of this report.

The chloro complex, {[*trans*-$Mo_2(O_2CCF_3)_2(\mu$-dppa)]$_3(\mu_6$-$CO_3)(\mu$-$Cl)_3$}F **1** was prepared by reaction of [*trans*-$Mo_2(O_2CCF_3)_2(MeCN)_6][BF_4]_2$ with K_2CO_3 and dppa in CH_2Cl_2.† The chloride atoms in **1** are presumably obtained from the CH_2Cl_2 solvent. The transfer of chloride atoms from the CH_2Cl_2 solvent to quadruply bonded complexes has been observed during the preparation of the complexes $Mo_2Cl_3(O_2CMe)$(etp) {etp = bis[2-(diphenylphosphino)ethyl]phenylphosphine} and $Mo_2Cl_3(O_2CMe)$(tetraphos-2) {tetraphos-2 = tris[2-(diphenylphosphino)ethyl]phosphine}.[4] Reaction of [*trans*-$Mo_2(O_2CCF_3)_2(MeCN)_6][BF_4]_2$ with dppa and K_2CO_3 in MeCN, followed by addition of ZnX_2 (X = Br or I), afforded complexes of the type [*trans*-$Mo_2(O_2CCF_3)_2(\mu$-dppa)]$_3(\mu_6$-$CO_3)(\mu_2$-$X)_3$}F (X = Br, **2**; X = I, **3**).† The appearance of the F ions in **1**–**3** can be ascribed to the dissociation of the BF_4^- ions to give F^- and BF_3, which has been observed during the preparation of a linear trichromium complex [$Cr_3(dpa)_4(F)(FBF_3)](BF_4)$ [dpa$^-$ = anion of bis(2-pyridyl)amine].[5]

Crystals of **1**–**3** are isomorphous and conform to the space group *C*2/*c* with four molecules in each unit cell.‡ Fig. 1 shows a representative ORTEP diagram for the cations of **1**–**3**. The molecule resides on a C_2 axis passing through atoms X(1), O(8), C(1) and N(2) and bisecting the Mo(3)–Mo(3a) bond. The core structure is remarkable in that three sets of quadruply bonded $Mo_2(O_2CCF_3)_2(\mu$-dppa) units are joined by a carbonate group (CO_3^{2-}) and axially bridged by three halide atoms. The metal atoms in each $Mo_2(O_2CCF_3)_2(\mu$-dppa) unit are bridged by a dppa ligand and two $CF_3CO_2^-$ groups which are *trans* to each other. Table 1 lists selected bond distances and angles. The Mo–Mo distances for all three complexes are very similar and are normal for Mo–Mo quadruple bonds. The Mo–X distances are relatively long, indicating only weak Mo–X interactions. The Mo–X distances, which show a strong dependence on the nature of the halogen atoms, increase from X = Cl to I. Noticeably, while the angles of Mo–X–Mo decrease from X = Cl to I, the Mo–Mo–X angles become more linear. Each molecule of the three cations can be viewed as three sets of edge-sharing bioctahedra, shown as **I** (Scheme 1), linked by adjacent $CF_3CO_2^-$ groups and dppa ligands, and quadruply bonded by

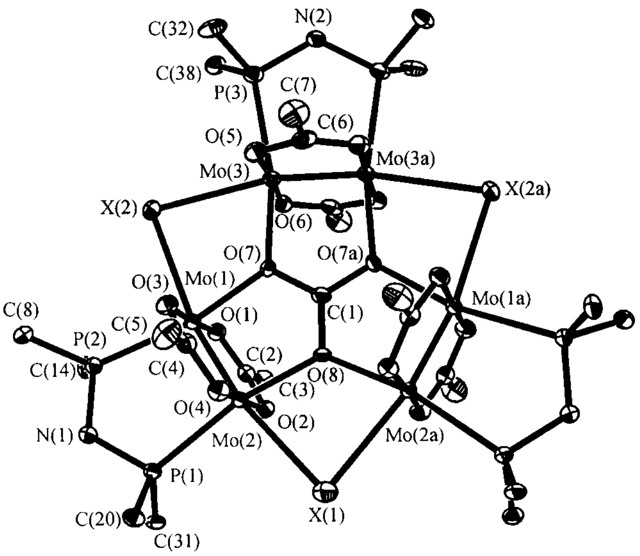
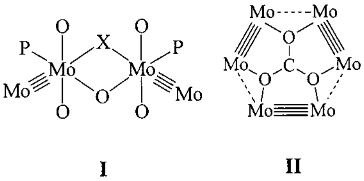


Fig. 1 A representative ORTEP drawing for complexes **1** (X = Cl), **2** (X = Br) and **3** (X = I). The F atoms of the CF_3 groups are removed and the phenyl carbon atoms are designated by their first atoms for clarity.

Table 1 Selected bond distances (Å) and angles (°) for **1** (X = Cl), **2** (X = Br) and **3** (X = I)

	X = Cl	X = Br	X = I
Mo(1)–Mo(2)	2.153(1)	2.152(1)	2.150(1)
Mo(3)–Mo(3a)	2.155(1)	2.148(1)	2.154(2)
Mo(1)–X(2)	2.828(2)	2.958(1)	3.202(1)
Mo(2)–X(1)	2.926(3)	3.029(1)	3.195(1)
Mo(3)–X(2)	2.862(2)	2.994(1)	3.202(1)
Mo(1)–X(2)–Mo(3)	82.9(1)	78.8(1)	72.7(1)
Mo(2)–X(1)–Mo(2a)	81.7(1)	77.8(1)	72.3(1)
Mo(1)–Mo(2)–X(1)	167.9(1)	170.0(1)	173.2(1)
Mo(2)–Mo(1)–X(2)	169.2(1)	171.6(1)	173.1(1)
Mo(3a)–Mo(3)–X(2)	168.2(1)	170.0(1)	173.9(1)



Scheme 1

the adjacent molybdenum atoms. The average separations of the two metal centers in **I** are 3.799, 3.790 and 3.804 Å for **1**, **2** and **3**, respectively, indicating no metal–metal interaction.

The cations of **1–3** show the μ_6-CO_3^{2-} (3L, 6M)[6] anions bridging the six metal centers through the three oxygen atoms of the carbonate group. Such a coordination mode of μ_6-CO_3^{2-} has been seen in the complexes $[(VO)_6(\mu_6\text{-}CO_3)(\mu\text{-}CO_3)(OH)_9]^{5-}$,[7] in which simple μ_6-bridging was seen for the carbonate ion, and in $[Na_2Nd_4L_4(CO_3)L'_4]$ {H_3L = [(*o*-$HOC_6H_4CH{=}NCH_2)_2CH$]H, L′ = tetrahydrofuran or L'_2 = 1,2-dimethoxyethane},[8] where one carbonate oxygen bridges two sodium atoms and each of the others bridges one sodium and two neodymium atoms. The carbonate coordination in **1–3** appears unique in bridging three pairs of multiply bonded metal atoms.

Hexametallic complexes exhibit a fascinating variety of structural patterns.[9] Aggregates are known with the six metal centers as a planar edge-bridged square, a puckered hexagon, an edge-linked bitetrahedron, an edge-bridged tetrahedron, a face-capped tetrahedron and less regular arrays.[9] No complexes of these types containing multiply bonded metal centers have been reported. The cations of complexes **1–3** therefore represent a unique structural type for cyclic transition-metal M_6 complexes. The six metal atoms are shifted from their mean planes in pseudo-hexagonal, planar rearrangements, shown as **II** (Scheme 1), by only 0.059, 0.049 and 0.023 Å for **1**, **2** and **3**, respectively. Complexes **1–3** are in marked contrast to the cyclic complex $[Mo_6O_8(OEt)_6Cl_8]$[10] which exhibits a chair configuration of metal atoms incorporating three Mo–Mo single bonds. The only trimer of quadruply bonded dimers that has been reported is the linear complex $[Mo_6(O_2CCHF_2)_{12}(bpy)$ (bpy = 2,2′-bipyridine), which comprises a central, quadruply bonded $Mo_2(O_2CCHF_2)_4$ unit whose axial ligands are two $[Mo_2(O_2CCHF_2)_2(bpy)_2](O_2CCHF_2)_2$ units.[11]

We thank the National Science Council of the Republic of China for support.

Notes and references

† $[Mo_2(O_2CCF_3)_2(MeCN)_6](BF_4)_2$ (0.25 g, 0.30 mmol), K_2CO_3 (0.014 g, 0.10 mmol) and dppa (0.12 g, 0.30 mmol) were placed in a flask containing 10 mL CH_2Cl_2. The mixture was stirred at room temp. for 3 h to yield a red solution. The volume of the solvent was reduced and *n*-hexane added to induce precipitation. The red solid was then filtered off and washed with diethyl ether and then redissolved in CH_2Cl_2. Layering of the red solution with diethyl ether gave well formed red crystals. The crystals were collected and dried *in vacuo*. Yield: 0.11 g (43%). [Calc. for $C_{85}H_{63}Cl_3F_{19}Mo_6N_3O_{15}P_6$ (*M* = 2595.29): C, 39.34; H, 2.54; N, 1.62. Found: C, 38.94; H, 2.85; N, 1.50%. IR (KBr disk): 3427 br, 3053 br, 1577 m, 1434 m, 1191 m, 1165 m, 1097 m, 927 m, 799 s, 737 m, 694 m, 526 m. UV–VIS: λ = 513 nm (MeCN). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 11.7. Complexes **2** and **3** were prepared by reactions of $[Mo_2(O_2CCF_3)_2(MeCN)_6](BF_4)_2$ (0.25 g, 0.30 mmol), K_2CO_3 (0.014 g, 0.10 mmol) and dppa (0.12 g, 0.30 mmol) with $ZnBr_2$ (0.067 g, 0.3 mmol) and ZnI_2 (0.096 g, 0.3 mmol), respectively, in MeCN. The other procedures were similar to those for **1**. Yield for **2**: 0.12 g (43 %) [Calc. for $C_{85}H_{63}Br_3F_{19}Mo_6N_3O_{15}P_6$ (*M* = 2728.61): C, 37.42; H, 2.33; N, 1.54. Found: C, 37.58; H, 2.43 ; N, 1.54%]. IR (KBr disk): 3452 br, 3058 br, 1590 m, 1435 m, 1275 m, 1203 m, 1152 m, 1100 m, 730 s, 691 m, 529 m. UV–VIS: λ = 508 nm (MeCN). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 11.4. Yield for **3**: 0.081 g (30 %) [Calc. for $C_{85}H_{63}I_3F_{19}Mo_6N_3O_{15}P_6$ (*M* = 2869.61): C, 35.58; H, 2.21; N, 1.46. Found: C, 35.32; H, 2.11 ; N, 1.50%]. IR (KBr disk): 3566 br, 3057 br, 1618 m, 1436 m, 1190 m, 1165 m, 1099 m, 741 s, 696 m, 528 m. UV–VIS: λ = 503 nm (MeCN). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 10.6 in $CDCl_3$.

‡ *Crystal data*: for **1**, $C_{97}H_{91}Cl_{11}F_{19}Mo_6N_3O_{17}P_6$, *M* = 3083.1, monoclinic, space group *C*2/*c*, *a* = 27.783(2), *b* = 17.091(1), *c* = 27.085(1) Å, β = 107.147(1)°, V = 12289(2) Å^3, *Z* = 4, D_c = 1.67 g cm^{-3}, μ = 0.999 mm^{-1}, 17303 reflections measured, no. of unique reflections = 8674 (R_{int} = 0.0401), no of parameters = 749, *R* = 0.0620 and R_w = 0.0722[$F > 4\sigma(F)$].

For **2**, $C_{97}H_{91}Br_3Cl_8F_{19}Mo_6N_3O_{17}P_6$, *M* = 3216.5, monoclinic, space group *C*2/*c*, *a* = 27.573(2), *b* = 17.203(1), *c* = 27.301(2) Å, β = 106.462(1)°, *V* = 12419(2) Å^3, *Z* = 4, D_c = 1.72 g cm^{-3}, μ = 1.889 mm^{-1}, 28959 reflections measured, no. of unique reflections = 8952 (R_{int} = 0.0459), no of parameters = 696, *R* = 0.0555 and R_w = 0.0754 [$F > 4\sigma(F)$].

For **3**: $C_{93}H_{75}I_3F_{19}Mo_6N_7O_{15}P_6$, *M* = 2985.7, monoclinic, space group *C*2/*c*, *a* = 29.983(2), *b* = 17.336(1), *c* = 23.514(1) Å, β = 114.462(1)°, *V* = 11125(1) Å^3, *Z* = 4, D_c = 1.78 g cm^{-3}, μ = 1.666 mm^{-1}, 15724 reflections measured , no. of unique reflections = 7418 (R_{int} = 0.0363), no of parameters = 661, *R* = 0.0561 and R_w = 0.0683 [$F > 4\sigma(F)$].

The diffraction data of **1–3** were collected on a Siemens CCD diffractometer, which was equipped with graphite-monochromated Mo-Kα (λ = 0.71073 Å) radiation. Structure solution was carried out using SHELXTL PLUS. During structural refinement, it was found that the three F atoms of one of the three trifluoroacetate groups of complex **1** and all the F atoms of the trifluoroacetate groups of complex **3** were disordered. The occupancies of the disordered F atoms were set to be 0.5 and refined as the other normal atoms.

CCDC 182/1267. See: http://www.rsc.org/suppdata/1999/1185/ for crystallographic files in .cif format.

1 F. A. Cotton and R. A. Walton, *Multiple Bonds between Metal Atoms*, Oxford University Press, London, 2nd edn., 1993; R. H. Cayton, M. H. Chisholm, J. C. Huffman and E. B. Lobkovsky, *J. Am Chem. Soc.*, 1991, **113**, 8709; K. Mashima, M. Tanaka and K. Tani, *J. Am Chem. Soc.*, 1997, **119**, 4307, and references cited therein.

2 T. R. Ryan and R. E. McCarley, *Inorg. Chem.*, 1982, **21**, 2072; F. A. Cotton and G. L. Powell, *Inorg. Chem.*, 1983, **22**, 871; F. A. Cotton and M. Shang, *J. Cluster Sci.*, 1991, **2**, 121; R. T. Carlin and R. E. McCarley, *Inorg. Chem.*, 1989, **28**, 3432; J.-D. Chen and F. A. Cotton, *J. Am. Chem. Soc.*, 1991, **113**, 5857; F. A. Cotton, B. Hong and M. Shang, *Inorg. Chem.*, 1993, **32**, 4876.

3 F. A. Cotton, L. M. Daniels, G. T. Jordan IV, C. Lin and C. A. Murillo, *J. Am. Chem. Soc.*, 1998, **120**, 3398.

4 C.-T. Lee, S.-F.Chiang, C.-T. Chen, J.-D. Chen and C.-D. Hsiao, *Inorg. Chem.*, 1996, **35**, 2930.

5 F. A. Cotton, L. M. Daniels, C. A. Murillo and I. Pascual, *J. Am. Chem. Soc.*, 1997, **119**, 10 223

6 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, John Wiley & Sons, New York, 5th edn., 1988, pp. 481–483.

7 T. C. W. Mak, P.-J. Li, C.-M. Zheng and K.-Y. Huang, *J. Chem. Soc., Chem. Commun.*, 1986, 1597.

8 G. B. Deacon, T. Feng, D. C. R. Hockless, P. C. Junk, B. W. Skelton, and A. H. White, *Chem. Commun.*, 1997, 342.

9 I. G. Dance, in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, New York, 1987, vol. 1, pp. 135–177.

10 C. Limberg, S. Parsons and A. J. Downs, *J. Chem. Soc., Chem. Commun.*, 1994, 497.

11 E. F. Day, E. J. C. Huffman, K. Folting and G. Christou, *J. Chem. Soc., Dalton Trans.*, 1997, 2837.

Communication 9/03410B