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Cis- and *Trans*-Arrangements of Bis-μ-Acetato Groups in Molybdenum(II) Dimers: Crystal Structures of $Mo_2(O_2CMe)_2(MeCOCHCOMe)_2$ and $(Ph_4As)_2[Mo_2(O_2CMe)_2Cl_4]\cdot 2MeOH$

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The potential versatility in the co-ordination chemistry for a pair of metal atoms held together by a strong metal–metal bond is gradually being realised in the progression of synthetic and structural studies reported for such systems [1, 2]. In particular, complexes of Mo_2^{4+} are currently receiving much attention. $Mo_2(O_2CMe)_4$ was the first such compound to be prepared [3] and characterised [4] and studies on this and related tetra-μ-carboxylato-complexes have been important in the understanding of the strength [5] and structure [6] of metal–metal quadruple bonds. In order to pursue certain of these studies in more detail we have prepared a number of complexes containing carboxylate and other ligands co-ordinated to Mo_2^{4+}. Here we report the isolation and X-ray crystallographic characterisation of $[Ph_4As]_2[Mo_2(O_2CMe)_2Cl_4]\cdot 2MeOH$ (I) and $Mo_2(O_2CMe)_2(pd)_2$ (II) (pd = 2,4-pentanedionate).

Preparation

All manipulations were carried out under an atmosphere of purified dinitrogen. I was prepared by reacting $Mo_2(O_2CMe)_4$ with an excess of Ph_4AsCl in dilute hydrochliric acid. Crystals suitable for X-ray crystallographic studies were obtained by recrystallisation from Analar MeOH. II was prepared by the reaction of $Mo_2(O_2CMe)_4$ with Na(pd) in thf under reflux. The subsequent concentration and cooling of this mixture resulted in the precipitation of a pale-brown powder. Sublimation of this material afforded yellow crystals of $Mo_2(O_2CMe)_4$ and a small quantity of brown crystals which were separated and used for X-ray crystallographic measurements. II was also prepared by the reaction of I with Na(pd) in EtOH.

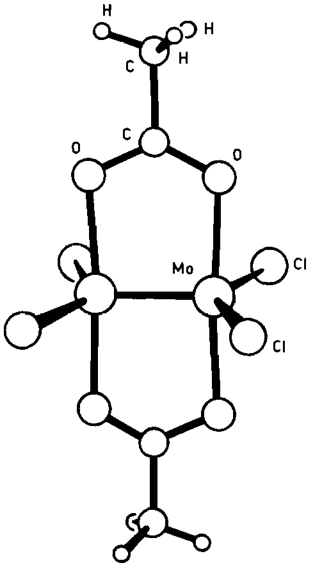

Figure 1. Atomic arrangement of the anion in $[Ph_4As]_2[Mo_2(OAc)_2Cl_4]\cdot 2MeOH$.

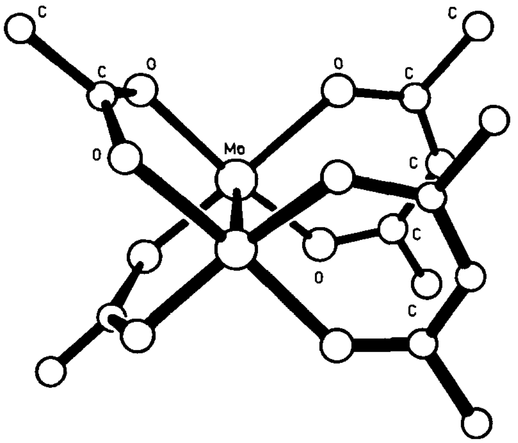

Figure 2. Molecular structure of $Mo_2(OAc)_2(pd)_2$ (hydrogen atoms omitted for clarity).

Crystal Data

$C_{54}H_{54}O_6As_2Mo_2$ (I), triclinic, a = 10.571, b = 11.330, c = 13.397 Å; α = 75.16, β = 67.19, γ = 64.24°. Space group $P\bar{1}$, Z = 1, R = 0.0575 (0.0726 weighted) for 2165 independent reflections.

$C_{15}H_{20}O_8Mo_2$ (II), monoclinic, a = 8.041, b = 12.373, c = 18.851; β = 102.02°. Space group $P2_{1/c}$, Z = 4, R = 0.0335 (0.0434 weighted) for 1806 independent reflections.

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The atomic arrangements about the Mo_2^{4+} centre in the compounds I and II are illustrated in Figures 1 and 2, respectively. The $[Mo_2(O_2CMe)_2Cl_4]^{2-}$ anion has the *trans* configuration required since the moiety is located on a crystallographic centre of symmetry. The framework of this complex closely corresponds to D_{2h} point symmetry with dimensions, Mo–Mo = 2.086(2), $\overline{\text{Mo–O}}$ = 2.120(12), $\overline{\text{Mo–Cl}}$ = 2.434(4) Å, and Cl–Mo–Cl = 141.8(1)°. The methanol molecules of the compound I are not co-ordinated to the molybdenum atoms. The constituent molecules of II have a *cis* configuration of the two μ-acetato-groups and two bidentate pentanedionato-groups. The molecular framework closely approximates to C_{2v} point symmetry with dimensions Mo–Mo = 2.129(1), $\overline{\text{Mo–O}}$(OAc) = 2.10(2), $\overline{\text{Mo–O}}$(pd) = 2.09(1) Å, and O(pd)–Mo–O(pd) = 86.0(4)°. There are O(OAc)....Mo intermolecular contacts, approximately co-linear with the metal–metal axis, of length 2.709 Å. The dimensions of the bridging acetato-groups of I and II and the pentanedionato-groups of II are typical of the corresponding dimensions reported for other structure determinations [1, 2, 7].

Discussion

The intermetallic distances in these complexes are typical of those observed for other Mo^{II}–Mo^{II} quadruple bonds [1]; the slightly longer bond in II *versus* I probably being associated [2] with the Mo....O(OAc) intermolecular contacts of II whereas there is no comparable axial binding for I. Although *cis* and *trans* arrangements of a pair of μ-acetato-groups have been characterised for a number of complexes with a dimetal centre, the ready synthesis of II from I illustrates the flexible co-ordination chemistry of such centres. The characterisation of II is of particular interest since it is the first time that a 2,4-pentanedionatogroup has been characterised in studies of Mo_2^{4+} and related complexes.

Acknowledgment

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