

A Dimeric Quadruply Metal–Metal Bonded Molybdenum(II)–Schiff's Base Complex: Bis[*N,N'*-ethylenebis(acetylacetonimine)molybdenum(II)]

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Reduction of dichloro-*N,N'*-ethylenebis(acetylacetonimine)molybdenum(IV), [Mo(acacen)Cl₂], with sodium in the presence of diphenylacetylene afforded the diamagnetic dimer [Mo(acacen)]₂ containing an Mo–Mo quadruple bond [Mo–Mo, 2.1678(4) Å], as shown by an X-ray crystal structure determination.

Schiff's base complexes are becoming an important class of compound for studying chemical reactivity of the metal centre rather than structural and spectroscopic properties only. Among the most studied reactions, reduction was used for producing metal-centred nucleophiles or ligand-centred radical anions.¹ Reduction using alkali metals led to either bifunctional complexes² or polynuclear compounds via the reductive coupling of the imino groups of the ligand.³ Formation of metal–metal bonds from the reduction of Schiff's base complexes is quite a rare event, observed only once in the presence of an unusual bridging ligand.⁴

We report here the formation of a dimeric Schiff's base complex containing an Mo–Mo quadruple bond which is not supported by any bridging ligand. Such metal–metal bonded [ML₄]₂ dimers are rather numerous in metal–porphyrin chemistry;⁵ apart from porphyrin complexes, only two well defined complexes, which contain a tetra-aza-annulene ligand, have been reported.^{6,7}

Dichloro-*N,N'*-ethylenebis(acetylacetonimine)molybdenum(IV), [Mo(acacen)Cl₂], (1) was obtained by a published procedure.⁸ Complex (1) has a pseudo-octahedral structure,⁹ with the acacen in the equatorial plane and the two chlorines *trans* to each other. Reduction of (1) by sodium sand (2 equiv.) in the presence of a stoichiometric amount of Ph₂C₂ led to a deep red solution from which (2) crystallized as a red solid.

Complex (2) crystallized from a solution in tetrahydrofuran (thf) in rather low yield. The addition of *n*-hexane led to recovery of a significant amount of the red solid (2) (ca. 50%).[†] Reduction of (1) with sodium sand or sodium-naphthalene in the absence of Ph₂C₂ gave different results which are under investigation. Although the role of Ph₂C₂ is not yet clear, it probably stabilizes the monomeric [Mo(acacen)] unit forming a complex which is relatively labile

towards dimerisation forming (2). A related process is the thermal decomposition of [Mo(tpp)Ph₂C₂] leading to the dimer [Mo(tpp)]₂ (tpp = tetraphenylporphyrin).¹⁰ The stabilization by Ph₂C₂ prevents the further reduction of either the monomeric Mo^{II} complex, [Mo(acacen)], or the Mo–Mo unit in [Mo(acacen)]₂. Complex (2), which is diamagnetic, is very air-sensitive in solution and is moderately stable to air in the solid state.[†] The structure of (2) was determined by a single crystal X-ray analysis.[‡] Figure 1 shows a view of the centrosymmetric (C_i) dimer, with a selection of bond distances and angles. Analogous structures have been reported recently for [Mo(tpp)]₂¹¹ and [Mo(tmtaa)]₂⁺ (tmtaa = dibenzotetra-

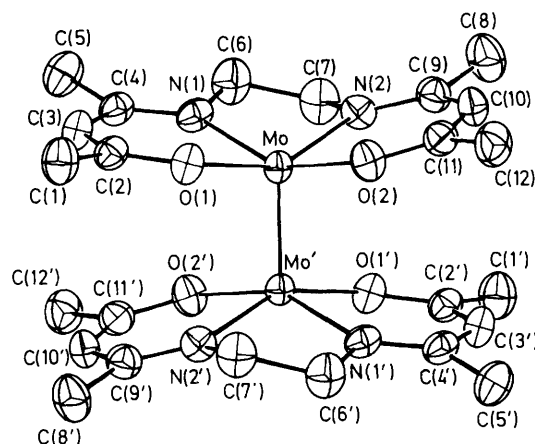
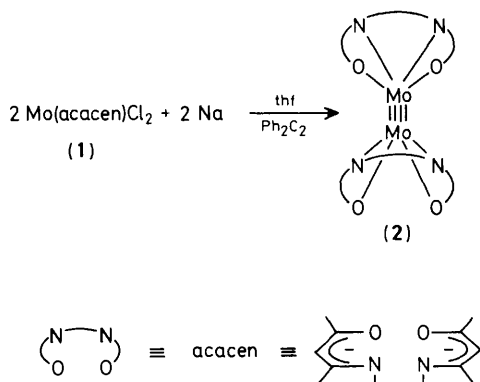


Figure 1. An ORTEP drawing of the [Mo(acacen)]₂ dimer (48% probability ellipsoids). Bond distances (Å): Mo–Mo', 2.1678(4); Mo–N(1), 2.115(4); Mo–N(2), 2.117(4); Mo–O(1), 2.088(3); Mo–O(2), 2.089(2). Bond angles (°): Mo'–Mo–O(1), 105.7(1); Mo'–Mo–O(2), 105.9(1); Mo'–Mo–N(1), 99.4(1); Mo'–Mo–N(2), 99.9(1); O(1)–Mo–O(2), 91.3; O(1)–Mo–N(1), 88.5(1); O(1)–Mo–N(2) 153.3(1); O(2)–Mo–N(1), 153.7(1); O(2)–Mo–N(2), 89.0(1); N(1)–Mo–N(2), 79.8(1). Prime indicates the transformation $-x, -y, -z$.



[‡] Crystal data: C₂₄H₃₆Mo₂N₄O₄, *M* = 636.5, triclinic, space group *P* $\bar{1}$, *a* = 8.869(1), *b* = 10.762(1), *c* = 7.844(12) Å, α = 94.94(1), β = 113.55(1), γ = 104.67(1)°, *U* = 649.0(2) Å³, *Z* = 1, *D*_c = 1.629 g cm⁻³, Mo-*K*_α radiation (λ = 0.7107 Å), μ (Mo-*K*_α) = 9.78 cm⁻¹; crystal dimensions 0.18 × 0.32 × 0.48 mm. The structure was solved by the heavy atom method (Patterson and Fourier synthesis) and refined by full-matrix least-squares. For 2146 unique observed structure amplitudes [*I* > 3σ(*I*), no correction for absorption] collected at room temperature on a Philips PW 1100 diffractometer in the range 6 < 2θ < 52° the *R* value is 0.028 (*R*_w = 0.031). All the hydrogen atoms were located in a difference Fourier map and introduced as fixed contributors in the final stage of refinement. All calculations were carried out using SHELX 76. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

[†] Satisfactory analytical data have been obtained.

methyltetra-aza[14]annulene dianion).⁷ The two acacen ligands are in an eclipsed conformation. The oxygen atoms of one acacen unit eclipse the nitrogen atoms of the other at a separation of 3.109(4) [O(1) ··· N(2')] and 3.099(4) Å [N(1) ··· O(2')]. The N₂O₂ sets of donor atoms are planar, with molybdenum out of the plane by 0.469(1) Å; cf. 0.458 Å in [Mo(tpp)]₂¹¹ and 0.57 Å in [Mo(tmtaa)]₂⁺.⁷ The two [Mo(acacen)] units are bent away from the Mo–Mo fragment, adopting an 'umbrella' conformation. The Mo–Mo distance of 2.1678(4) Å is consistent with a metal–metal quadruple bond¹² and is significantly shorter than the analogous distance in [Mo(tpp)]₂, 2.239(1) Å.¹¹

The molybdenum–donor atom distances are significantly longer in (2) [Mo–O_{av}, 2.089(2); Mo–N_{av}, 2.116(4) Å] than in the corresponding molybdenum(IV) complexes [Mo(acacen)Cl₂] (1)⁹ [Mo–O_{av}, 1.988(5), Mo–N_{av}, 2.074(6) Å] and [{Mo(acacen)Cl}₂(μ-O)]⁹ [Mo–O_{av}, 2.026(5); Mo–N_{av}, 2.089(6) Å]. The reduction of molybdenum(IV) chelate complexes provides a promising synthetic methodology for a variety of metal–metal bonded [Mo(chelate)]₂ dimers. Moreover, the easy accessibility of a large number of Schiff's base ligands should allow both the electronic properties of the M₂ unit and the metal–metal bond order to be controlled.

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