

Acetylacetonato as a Bridging $\kappa(\text{O}),\kappa(\text{O}')$ Ligand. X-ray Structure of $[\{\text{Mn}(\text{CO})_3(\text{dppe})\}_2(\mu\text{-acac})]\text{ClO}_4$

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It is well-known that the strong tendency to form very stable, six-member, chelate rings dominates the chemistry of β -diketonato ligands.² In fact, the various examples of bridges formed by this type of ligands are usually achieved by sharing one or more oxygen atoms of the chelate ring between two or more metals, as in $[\text{Ni}(\text{acac})_2]_3$,³ or by further coordination through the central carbon, as in $[\text{Pt}(\text{CH}_3)_3(\mu\text{-C}_3\text{H}_7\text{COCHCOCH}_3)_2]$.⁴ Other less common coordination modes of acetylacetonato as a bridging ligand have been recently found to involve the coordination through one oxygen and the central carbon to two metals in a cluster edge, as in the complex $[\text{Pt}_4(\mu\text{-CH}_3\text{COO-O,O})_4(\mu\text{-CH}_3\text{COCHCOCH}_3\text{-O,C}^2)_4]$,⁵ or coordination through both oxygen atoms to both metals, as in $[\text{Ba}\{(\text{CH}_3)_3\text{CCOCHCO}(\text{CH}_3)_2(\text{OEt}_2)\}_2]$.⁶ In the latter, the diketonato bridges between the two Ba atoms can be described as having a "side on" coordination, acting as chelate ligands toward both metal atoms simultaneously. Quite surprisingly, there is only one report of a diketonato ligand acting as a bridge in the simplest way, i.e. as $\kappa(\text{O}),\kappa(\text{O}')$ through one oxygen to each metal. Thus, in the erbium complex $[\text{Er}_2\text{O}(\text{OH})_{12}\{(\text{CH}_3)_3\text{CCOCHCO}(\text{CH}_3)_2\}_{10}]$,⁷ two tetramethylheptanedionato ligands act as $\kappa(\text{O}),\kappa(\text{O}')$ bridges between two erbium atoms which also share two hydroxy bridges. Herein we describe the preparation and structural determination of the complex $[(\text{CO})_3(\text{dppe})\text{Mn-OC}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{CO-Mn}(\text{dppe})(\text{CO})_3]\text{-ClO}_4$, which, as far as we know, constitutes the first example in which a $\kappa(\text{O}),\kappa(\text{O}')$ β -diketonato ligand holds together two metals as the only bridge between them.

Experimental Section

Reactions and workup were carried out under a nitrogen atmosphere. Infrared spectra were recorded on a Perkin-Elmer FT 1720-X instrument. NMR spectra were recorded on a Bruker AC-300 spectrometer. Analyses were carried out on a Perkin-Elmer 240B analyzer.

Preparation of $[\{\text{Mn}(\text{CO})_3(\text{dppe})\}_2(\mu\text{-acac})]\text{ClO}_4$. Caution! Perchlorate salts have been reported to produce explosions when in contact with organic substances. Although we have not experienced any explosion handling perchlorate complexes such as those described here, it is advisable to use small amounts of materials, to conduct the reactions behind a protective shield, and to wear safety glasses during all workup, especially when handling the perchlorate salts as dry solids.⁸

To a yellow solution of *fac*- $[\text{Mn}(\text{CO})_3(\text{dppe})(\text{OClO}_3)]^9$ (0.160 g, 0.251 mmol) in CH_2Cl_2 (30 mL) was added 2,4-pentanedione (2 mL of a 0.1

M solution in CH_2Cl_2 , 0.2 mmol) and NEt_3 (0.04 mL, 0.288 mmol), and the mixture was stirred for 1 h and then filtered. Evaporation of the solvent produced an oil, which was stirred with hexane (20 mL) to give a pale-yellow solid. Recrystallization from CH_2Cl_2 /hexane gave pale-yellow crystals. Yield: 0.122 g, 76%. Anal. Calcd for $\text{C}_{63}\text{H}_{55}\text{-ClMn}_2\text{O}_{12}\text{P}_4$: C, 59.42; H, 4.35. Found: C, 59.19; H, 4.30. Spectroscopic data: IR (CH_2Cl_2 solution, cm^{-1}) $\nu(\text{CO})$ stretch 2029 vs, 2023 (sh), 1958 s, and 1920 s; $^1\text{H NMR}$ (300.15 MHz, CD_2Cl_2 , TMS as internal reference) δ 7.65–7.32 (m, 40 H, C_6H_5 of dppe), 5.15 (s, 1H, HC of acac), 3.43 (s, 6H, CH_3 of acac), 3.06 (m, 8H, CH_2 of dppe); $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, CD_2Cl_2 , ppm to higher frequencies of external 85% H_3PO_4) δ 73.3 s; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CD_2Cl_2 , TMS as internal reference) δ 219.4 [s (br), MnCO], 197.3 (s, MnOC), 132.8–129.3 (m, C_6H_5 of dppe), 109.1 (s, HC of acac), 28.1 (s, CH_3 of acac), 25.8 [t (virtual), $J(\text{PC}) = 20$ Hz, CH_2 of dppe].

X-ray Crystal Structure of $[\{\text{Mn}(\text{CO})_3(\text{dppe})\}_2(\mu\text{-acac})]\text{ClO}_4$. Relevant crystal data are collected in Table II. A yellow prismatic crystal of dimensions $0.25 \times 0.2 \times 0.2$ mm was mounted on an Enraf-Nonius CAD4 diffractometer. An empirical (ψ -scan based) absorption correction was applied (transmission factors: maximum 1.05, minimum 1.00). Mn atoms were located from a Patterson synthesis, and the remaining non-hydrogen atoms from subsequent difference maps. Atoms of Mn, P, and C and O of carbonyl and acac ligands were refined anisotropically. The remaining carbon atoms were refined isotropically. Least-squares refinement was made in four blocks with CRYSTALS.¹⁰ The oxygen atoms of the perchlorate anion have been found to be statistically disordered. Six peaks were found in difference maps and were refined with a common isotropic temperature factor. The hydrogen atoms were geometrically positioned and were given an overall isotropic temperature factor which was refined. Final $R = 0.071$ ($R_w = 0.075$). After the final cycles of refinement the maximum electron density was $0.54 \text{ e } \text{\AA}^{-3}$ in the proximity of the chlorine atom. Least-squares planes and other calculations were made with PARST.¹¹

Results

Treatment of a dichloromethane solution of *fac*- $[\text{Mn}(\text{CO})_3(\text{dppe})(\text{OClO}_3)]^9$ with 2,4-pentanedione and excess triethylamine produces a pale yellow solution from which the compound $[\{\text{Mn}(\text{CO})_3(\text{dppe})\}_2(\mu\text{-acac})]\text{ClO}_4$ (**1**) can be isolated as a yellow crystalline solid. According to IR monitoring, the same complex is produced when a mixture of *fac*- $[\text{Mn}(\text{CO})_3(\text{dppe})\text{Br}]$, AgBF_4 , 2,4-pentanedione, and excess triethylamine is stirred in CH_2Cl_2 for 2 h. However, in spite of repeated attempts, it was not possible to obtain a pure sample of the tetrafluoroborate salt of **1**. An X-ray structure determination, carried out on a crystal of the perchlorate salt, revealed that the cation (Figure 1) consists of two $\text{Mn}(\text{CO})_3(\text{dppe})$ groups held together by a bridging acetylacetonato ligand which is bonded to each manganese through only one oxygen in a $\kappa(\text{O}),\kappa(\text{O}')$ fashion, this being a very unusual coordination mode for the acac ligand (see Discussion below). The same compound is produced even when the starting complex *fac*- $[\text{Mn}(\text{CO})_3(\text{dppe})(\text{OClO}_3)]$ is made to react with a great excess (up to 1:5) of 1,4-pentanedione and base.

Discussion

The acetylacetonato ligand in the cation of **1** shows a quite unusual geometry. The relevant bond lengths and angles within the acac ligand are summarized in the schemes of Figure 2, together with those of the bridging heptanedionato found in the erbium complex mentioned above.⁷ Due to the limited accuracy of the values of distances and angles in both structures, the comparisons can only be carried up to a limited extent. The main differences between them concern the conformation of the O–C–C–O sequence. In the erbium complex, the diketonato ligand displays a planar *all-cis* configuration which resembles that commonly found in chelate complexes, whereas in the diman-

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Table I. Crystallographic Data for $[\{\text{Mn}(\text{CO})_3(\text{dppe})\}_2(\mu\text{-acac})]\text{ClO}_4$

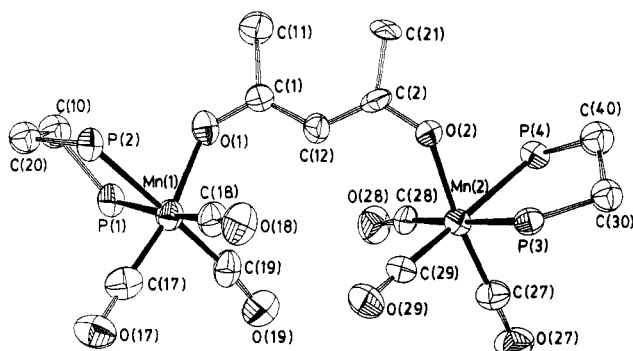
formula	$\text{C}_{63}\text{H}_{55}\text{ClMn}_2\text{O}_{12}\text{P}_4$
fw	1273.34
cryst system,	monoclinic
space group	$P2_1/n$ (No. 14)
a , Å	17.518(2)
b , Å	11.302(3)
c , Å	31.823(5)
β , deg	102.75(1)
V , Å ³	6145(6)
Z	4
T , K	293
ρ_{calc} , g cm ⁻³	1.38
$\lambda(\text{Mo K}\alpha)$, Å	0.710 69
μ , cm ⁻¹	5.98
residuals R , R_w^a	0.071, 0.075

$$^a R = \sum(|F_o| - |F_c|) / \sum|F_o|; R_w = [\sum(w(|F_o| - |F_c|)^2) / \sum w|F_o|^2]^{1/2}.$$

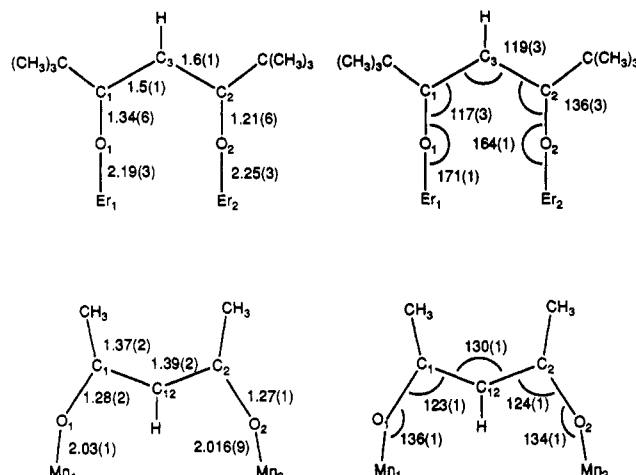
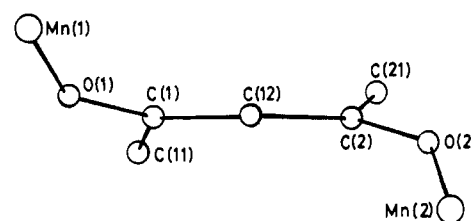
Table II. Refined Atomic Coordinates for the Significant Atoms in $[\{\text{Mn}(\text{CO})_3(\text{dppe})\}_2(\mu\text{-acac})]\text{ClO}_4$ (Esd's in Parentheses)

atom	x	y	z	$U_{\text{eq}}, \text{Å}^2$
Mn(1)	0.0823(1)	0.0568(2)	0.76038(7)	0.0596
Mn(2)	0.2410(1)	0.1765(2)	0.93925(7)	0.0553
P(1)	-0.0025(3)	-0.1054(4)	0.7515(1)	0.0595
P(2)	-0.0129(3)	0.1435(4)	0.7053(1)	0.0594
P(3)	0.3146(2)	0.3472(4)	0.9590(1)	0.0572
P(4)	0.1996(2)	0.2057(4)	1.0034(1)	0.0541
O(1)	0.0049(6)	0.1074(9)	0.7958(3)	0.0616
O(2)	0.1517(5)	0.2899(9)	0.9188(3)	0.0557
O(17)	0.1690(7)	-0.039(1)	0.6995(4)	0.1005
O(18)	0.1787(7)	0.273(1)	0.7690(4)	0.0942
O(19)	0.2013(7)	-0.066(1)	0.8252(4)	0.0986
O(27)	0.3712(7)	0.022(1)	0.9794(4)	0.0943
O(28)	0.1519(7)	-0.044(1)	0.9191(4)	0.0887
O(29)	0.2969(7)	0.169(1)	0.8587(4)	0.0970
C(1)	0.0075(8)	0.169(1)	0.8297(5)	0.0591
C(2)	0.0894(8)	0.286(1)	0.8897(5)	0.0564
C(11)	-0.0724(9)	0.193(2)	0.8386(5)	0.0813
C(12)	0.0765(9)	0.204(1)	0.8563(5)	0.0597
C(21)	0.0328(9)	0.382(2)	0.8953(5)	0.0733
C(17)	0.1315(9)	0.002(1)	0.7232(6)	0.0676
C(18)	0.1398(9)	0.189(2)	0.7662(5)	0.0741
C(19)	0.1518(9)	-0.015(2)	0.8018(5)	0.0696
C(27)	0.320(1)	0.087(1)	0.9635(5)	0.0717
C(28)	0.1830(9)	0.047(2)	0.9262(5)	0.0634
C(29)	0.2737(9)	0.172(2)	0.8902(5)	0.0694

$$^a U_{\text{eq}} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j.$$

**Figure 1.** ORTEP¹⁴ drawing of the cation in $[\{\text{Mn}(\text{CO})_3(\text{dppe})\}_2(\mu\text{-acac})]\text{ClO}_4$ (**1**), showing the atom numbering. The phenyl rings of the dppe ligands have been omitted for clarity.

ganese complex **1** the disposition of the ligand can be described as W-shaped. This configuration allows for a greater separation between the oxygen atoms and permits the accommodation of the two bulky $\text{Mn}(\text{CO})_3(\text{dppe})$ fragments. This factor could account also for the nonplanarity of the diketonato ligand, which can be noticed in the view of Figure 3. Thus, the group of atoms O(1), C(1), C(12), and C(11) displays a planar arrangement, with the atom Mn(1) at 0.216(2) Å from that plane. Likewise, Mn(2) lies at 0.371(2) Å from the plane defined by O(2), C(2),

**Figure 2.** Schematic views of the geometry of the diketonato ligands in the cation of **1** and in $[\text{Er}_2\text{O}(\text{OH})_{12}\{(\text{CH}_3)_3\text{COCHCO}(\text{CH}_3)_3\}_{10}]$. Data for the erbium complex were taken from ref 7.**Figure 3.** Perspective view of the acac ligand in **1** along the line bisecting the C(1)-C(12)-C(2) angle. Plane 1 is defined by O(1), C(1), C(11), and C(12). Plane 2 is defined by O(2), C(2), C(21), and C(12). The dihedral angle between the two planes = 30.3(7)°.**Table III.** Selected Distances (Å) and Angles (deg) for $[\{\text{Mn}(\text{CO})_3(\text{dppe})\}_2(\mu\text{-acac})]\text{ClO}_4$

(a) Distances			
Mn(1)-P(1)	2.336(5)	Mn(1)-P(2)	2.349(5)
Mn(1)-O(1)	2.03(1)	Mn(1)-C(17)	1.73(2)
Mn(1)-C(18)	1.79(2)	Mn(1)-C(19)	1.78(2)
Mn(2)-P(3)	2.328(5)	Mn(2)-P(4)	2.337(4)
Mn(2)-O(2)	2.016(9)	Mn(2)-C(27)	1.75(2)
Mn(2)-C(28)	1.79(2)	Mn(2)-C(29)	1.78(2)
O(1)-C(1)	1.28(2)	C(1)-C(11)	1.51(2)
C(1)-C(12)	1.37(2)	C(12)-C(2)	1.39(2)
O(2)-C(2)	1.27(1)	C(2)-C(21)	1.51(2)
C(17)-O(17)	1.19(2)	C(18)-O(18)	1.15(2)
C(19)-O(19)	1.16(2)	C(27)-O(27)	1.18(2)
C(28)-O(28)	1.16(2)	C(29)-O(29)	1.16(2)

(b) Angles			
C(17)-Mn(1)-O(1)	168.2(6)	C(27)-Mn(2)-O(2)	172.5(6)
C(18)-Mn(1)-O(1)	97.8(6)	C(28)-Mn(2)-O(2)	94.9(6)
C(19)-Mn(1)-O(1)	98.6(6)	C(29)-Mn(2)-O(2)	96.3(6)
P(1)-Mn(1)-O(1)	78.6(3)	P(3)-Mn(2)-O(2)	84.5(3)
P(2)-Mn(1)-O(1)	81.1(3)	P(4)-Mn(2)-O(2)	79.9(3)
C(1)-O(1)-Mn(1)	136.0(10)	C(2)-O(2)-Mn(2)	134.0(10)
C(11)-C(1)-O(1)	113.0(13)	C(21)-C(2)-O(2)	111.6(14)
C(12)-C(1)-O(1)	122.7(14)	C(21)-C(2)-O(2)	111.6(14)
C(12)-C(1)-C(11)	124.1(14)	C(21)-C(2)-C(12)	124.7(14)
C(2)-C(12)-C(1)	129.5(15)		

C(12), and C(21). The two planes form an angle of 30.4(7)°, the central carbon C(12) of the acac ligand serving as pivot. Other significant difference concerns the angles M-O-C, which display values around 135° in complex **1**, while, in the erbium complex, they are close to linearity (see Figure 2). The coordination around manganese atoms can be described as octahedral, with some distortion induced by the different requirements of the ligands. The interbond angles around the manganese atoms range from 78.6(3) to 98.6(6)° (*cis* positions) and from 168.2(6) to 177.2(5)° (*trans* positions). Each metal atom, the two phosphorus atoms of the dppe ligand, and the two carbon atoms of the carbonyl groups form a nearly planar

arrangement. The greatest deviations are observed with C(18) [at 0.084(17) Å from the plane around Mn(1)] and with C(29) [at 0.094(18) Å from the plane around Mn(2)].

The formation of the $\kappa(\text{O}),\kappa(\text{O}')$ bridge instead of a chelate ring in the complex cation **1** may be rationalized by considering a balance between several factors: The oxygen-donor acac anion behaves as a hard ligand, and therefore, its affinity for the low-valent, softer $\text{Mn}(\text{CO})_3(\text{dppe})$ fragment is not big enough to displace one carbonyl or one P atom of the diphosphine at room temperature. When more forcing conditions, such as heating in boiling toluene, are used to promote the dissociation of CO, extensive decomposition is noticed by IR monitoring. In such conditions, the only observed product is the dicarbonyl *trans*- $[\text{Mn}(\text{CO})_2(\text{dppe})_2]^+$,¹² the usual end point in the decomposition

of tricarbonyl complexes containing dppe.^{9,13} This also confirms the greater affinity of the manganese atom for the softer dppe ligand.

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Supplementary Material Available: Tables of atom coordinates, anisotropic thermal parameters, hydrogen atom locations, bond lengths, bond angles, torsion angles, and least-squares planes (13 pages). Ordering information is given on any current masthead page.

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