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Electronic Structure of μ-Methylene-Bis-[Dicarbonyl(η^5-Cyclopentadienyl)-Manganese] by UV Photoelectron Spectroscopy

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The results of an investigation on μ-CH_2-$[(\eta^5$-$C_5H_5)Mn(CO)_2]_2$ by means of UV vapour-phase photoelectron spectroscopy and CNDO quantum mechanical calculations are reported and discussed. Three distinct bands are assigned to ionizations from the MOs (27a, 26b, 22a) mainly contributing to the three membered ring bonding. In particular, 27a HOMO and 26b MO mainly represent Mn–Mn and Mn–CH_2–Mn bonding interactions. On the contrary, 22a MO, reminiscent of the Walsh-type totally symmetric MO, is mainly localized on the methylene carbon atom.

Introduction

Polynuclear organometallic molecules form a very interesting class of compounds as reasonable models of catalytic systems [1]; they also represent an intriguing topic from a theoretical point of view, due to the peculiarity of their metal–metal interactions [2]. Vapour-phase photoelectron (p.e.) spectroscopy in connection with quantum mechanical calculations has provided very detailed insight into the electronic structure of carbonyl polynuclear molecules [3–8]. In particular, the nature of the Mn-Mn interaction in $Mn_2(CO)_{10}$ has been discussed [9, 10]. However, the contribution of a direct Mn–Mn interaction to the molecular stability is not fully clarified. For this reason, we have performed a p.e. study on μ-CH_2-$[(\eta^5$-$C_5H_5)Mn(CO)_2]_2$, which has the peculiarity of a Mn–Mn interatomic distance (2.799 Å) [11] that is shorter than in $Mn_2(CO)_{10}$ (2.923 Å) [12], probably due to the presence of the bridging methylene group.

Experimental

The sample used in the spectroscopic investigation was kindly supplied by Prof. W. A. Herrmann [13]

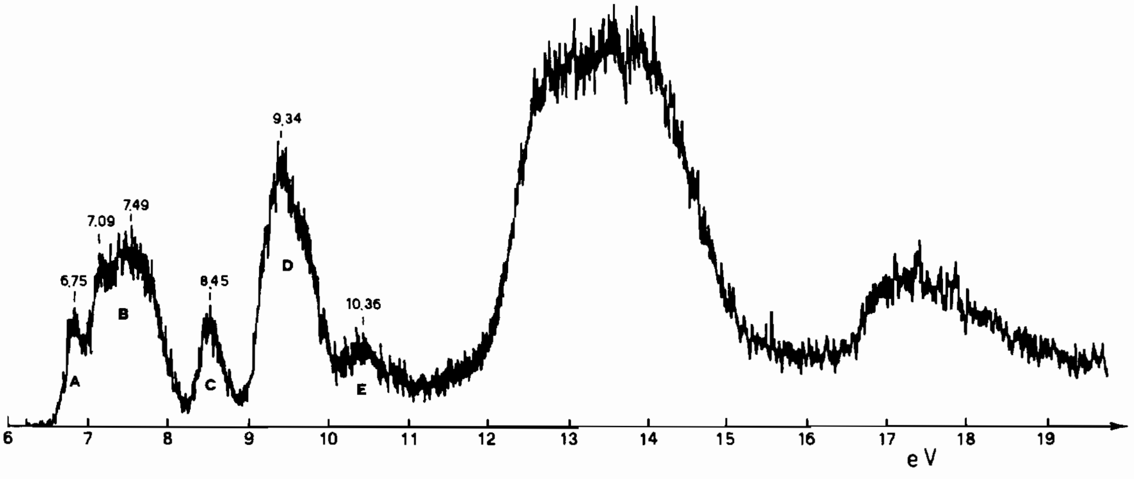

Fig. 1. Full He(I) p.e. spectrum of μ-CH_2-$[(\eta^5$-$C_5H_5)Mn(CO)_2]_2$.

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TABLE I. CNDO Results for μ-CH$_2$-[(η^5-C$_5$H$_5$)Mn(CO)$_2$]$_2$.

MO	Eigenvalue (eV)	Population (%)				Dominant character
		Mn (2 atoms)	CH$_2$	C$_5$H$_5$ (2 groups)	CO (4 groups)	
27a	−6.90	78	2	10	10	Mn–Mn bonding interaction
28b	−7.77	74	3	14	9	3d metal-like MOs (non-bonding)
26a	−7.89	80	0	11	9	
25a	−8.10	71	4	9	16	
27b	−8.18	79	9	6	6	
26b	−8.59	51	14	20	15	Mn–CH$_2$ bonding interaction
25b	−9.23	23	3	70	4	πC$_5$H$_5$ MOs + some metal contribution
24a	−9.45	20	1	76	3	
23a	−9.56	20	0	75	5	
24b	−9.58	25	2	69	4	
22a	−12.16	20	48	21	11	CH$_2$ σ 'lone pair' toward the center of the ring
23b	−12.72	4	4	70	22	C$_5$H$_5$ σ MOs
21a	−12.78	3	0	90	7	
22b	−12.93	2	0	96	2	
20a	−13.06	5	5	88	2	

and was sublimed *in vacuo* prior to use. P.e. spectra were measured on a Perkin-Elmer PS-18 spectrometer modified for He(II) measurements by inclusion of a hollow cathode discharge lamp giving a high photon flux at He(II) wavelengths (Helectros Developments). They were calibrated by reference to peaks due to admixed inert gases and to the He 1s^{-1} self ionization.

CNDO type calculations were performed with a modified version [14] which proved suitable for transition metal complexes. The geometrical data used in the calculations refer to the most recent low temperature X-ray determination [11] (C$_2$ point group). The calculated eigenvalues were related to the measured ionization energies (IEs) by Koopmans' approximation [15].

Results and Discussion

The full He(I) excited p.e. spectrum of μ-CH$_2$-[(η^5-C$_5$H$_5$)Mn(CO)$_2$]$_2$ is shown in Fig. 1, together with the pertinent IEs. The low IE region of the spectrum (up to 11 eV) contains five well resolved bands, labelled A, B, C, D, E. The profile of band B reveals the presence of at least two components. Significant variations in relative band intensities are observed on switching from He(I) to He(II) excitation source (Figs. 2a and 2b).

The title compound is diamagnetic and, assuming the methylene group as neutral, the 18-electron rule is obeyed if we have two manganese atoms in the formal (d^6) oxidation state 1+. Therefore 12 electrons should ionize from MOs characterized by their high contribution from manganese 3d AOs. Furthermore, on a qualitative basis four of these electrons should be involved, together with two electrons from the methylene group, in the triatomic ring bonding. In order to discuss the electronic structure of this three-membered ring, a comparison with the previous results [3] on the *triangulo* cluster Ru$_3$(CO)$_{12}$ (D$_{3h}$) is convenient. In this latter molecule the outmost e$'$ and a$'_1$ MOs, which mainly contribute to the Ru$_3$ ring bonding, involve both 5sp and 4d AOs of ruthenium atoms and they are quasi-degenerate. In the title compound the lower symmetry completely removes any degeneracy so that the three MOs involved in the ring bonding should have different energies. The results of CNDO calculations (Table I) finely match this qualitative picture and allow a complete assignment of the spectrum with confidence (Fig. 3). In particular, bands A, C and E are to be assigned respectively to ionizations from 27a, 26b and 22a MOs mainly contributing to the three-membered ring bonding. The broad band B is assigned to 3d metal-like MOs (28b, 26a, 25a, 27b), having essentially non-bonding character. Band D corresponds to 25b, 24a, 23a, 24b π MOs of the C$_5$H$_5$ ligands, which correlate with the e$''_1$ MO of the free anion ligand in D$_{5h}$ symmetry. The He(I) relative intensities are also in qualitative agreement with the theoretical count of electrons. Furthermore He(II) intensity changes give support to these assignment. The marked decrease in relative intensity of band D strongly indicates a low contribution of 3d manganese AOs to the corresponding MOs,

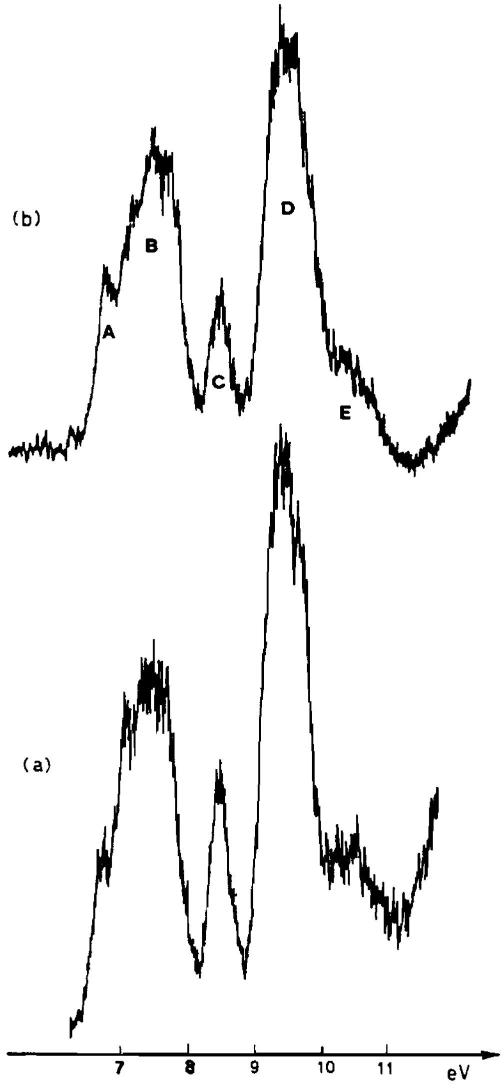

Fig. 2. Low IE region of the p.e. spectrum of μ-CH_2-$[(\eta^5$-$C_5H_5)Mn(CO)_2]_2$. (a) He(I) p.e. spectrum. (b) He(II) p.e. spectrum.

TABLE II. Gross Atomic Charges and Relevant Overlap Populations for μ-CH_2-$[(\eta^5$-$C_5H_5)Mn(CO)_2]_2$.[a,b]

Gross Atomic Charges		Overlap Populations	
Mn	+1.018	Mn–Mn	−0.002
C′	+0.257	Mn–C′	+0.265
O	−0.416	C′–O	+0.950
C″	−0.255	Mn–C″	+0.113
H″	+0.132	C″–C″	+1.052
C‴	−0.325	C″–H″	+0.806
H‴	+0.078	Mn–C‴	+0.318
		C‴–H‴	+0.717

[a]Averaged values. [b]C′ refers to the carbonyl groups; C″, H″ refer to the cyclopentadienyl rings; C‴, H‴ refer to the methylene group.

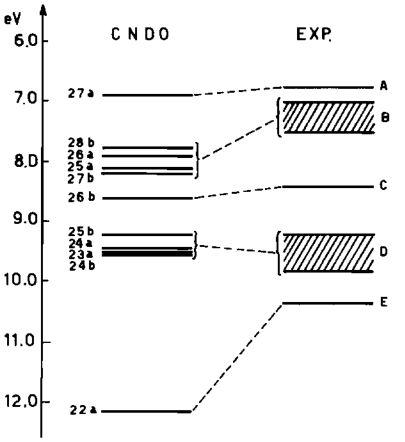

Fig. 3. Comparison between the computed and experimental ionization energies of μ-CH_2-$[(\eta^5$-$C_5H_5)Mn(CO)_2]_2$.

in agreement with the theoretical results, because of the expected decrease in the cross-section ratio [16] $\sigma(C_{2p})/\sigma(Mn_{3d})$ on passing from He(I) to He(II) source.

The detailed analysis of the 27a, 26b and 22a eigenvectors provides interesting information about the interactions within the three-membered ring. The 27a MO represents a bonding Mn–Mn interaction, mainly σ in nature, whereas no significant contribution from the methylene carbon AOs is present. On the contrary, 26b MO involves all the ring atoms and represents bonding Mn–CH_2–Mn σ interactions, with a significant bending from the internuclear axes between the methylene carbon and the manganese atoms. However, the same MO has a marked antibonding character as regards the direct Mn–Mn interaction. Finally 22a MO is strongly reminiscent of the Walsh-type totally symmetric MO peculiar to both cyclopropane [17] and $Ru_3(CO)_{12}$ [3]. Nevertheless in the title compound this MO is mainly localized on the methylene carbon atom and looks like a lone pair pointing towards the center of the three membered ring. The high localization of this MO could somewhat explain the large difference between the calculated and experimental IE values (Fig. 3), being quite accepted that the relaxation energy contribution to the ionization process strongly depends on the localization degree of the MO from which the ionization occurs [18]. Also the He(I)/He(II) relative intensity changes of the bands A, C and E are in tune with the proposed assignment, since band A, which is assigned to the MO having the largest Mn 3d character, is strongly increased in intensity with respect to the other two bands.

The spectral region beyond 11 eV consists of very broad and ill resolved structures. These bands are due to ionizations from the Mn–CO σ bonding levels, the CO π levels and from σ and inner π MOs of the C_5H_5 rings.

Finally we want to briefly discuss the gross atomic charges and the overlap populations obtained by Mulliken's population analysis [19] of the deorthogonalized [20] eigenvectors (Table II). The actual charge on Mn atoms is +1.018, in agreement with the formal (d^6) oxidation state derived by qualitative arguments. The overlap population between Mn and methylene carbon atom indicates a strong bond, comparable with the Mn–CO bond. On the contrary, the Mn–Mn overlap population is nearly zero.

Conclusions

The proposed picture of the electronic structure of the title compound, in particular as regards the three-membered ring, indicates the HOMO character of the direct Mn–Mn interaction. Even if we attach scarce significance to the value of the overlap population itself, it seems reasonable that the Mn–Mn direct contribution to the overall stability of the triatomic ring is rather small, since significant Mn–Mn antibonding character is present in the 26b MO.

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