

Comment on “Topological Analysis of the Electron Density in the Carbonyl Complexes $M(\text{CO})_8$ ($M = \text{Ca}, \text{Sr}, \text{Ba}$)”



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ABSTRACT: We question the statement of a recent publication (*Organometallics* 2020, 39, 132, DOI: 10.1021/acs.organomet.9b00699) that the $M \rightarrow \text{CO} \pi$ backdonation in the alkaline earth carbonyl complexes $M(\text{CO})_8$ ($M = \text{Ca}, \text{Sr}, \text{Ba}$) is negligible and that the decrease of the CO stretching frequency is rather caused by interligand interactions of the carbonyl groups within the molecules.

In a recent publication, Van der Maelen¹ reports on quantum chemical calculations of the carbonyl complexes $M(\text{CO})_8$ ($M = \text{Ca}, \text{Sr}, \text{Ba}$), whose synthesis and properties had earlier been described by Wu et al.² Using a plethora of real-space partitioning functions, which are mainly based on the electron density $\rho(r)$ rather than the wave function Ψ , the author concludes that there is no significant $M \rightarrow \text{CO} \pi$ backdonation in the alkaline earth octacarbonyls and that the strong redshift of the CO stretching frequency is rather due to intramolecular interactions between neighboring CO groups. We think that the conclusion of the author is not valid, because they were achieved by an erroneous extrapolation of the calculated values.

Real-space partitioning methods like QTAIM³ and IQA⁴ have been developed, and numerous mathematical terms were suggested to characterize a chemical bond by correlating calculated numbers with the proposed nature of the bonding interaction. Partitioning methods like the QTAIM give important information about the electronic structure of molecules, and they are complementary to wave-function-based partitioning methods. However, a correlation is not an explanation, and the interpolation may fail when unusual bonds are considered. The analysis of the electron density provides information *after* the chemical bond has been formed. However, a covalent bond comes from the interference of the wave functions Ψ , and the bond formation cannot be explained using the density ρ . There is an unambiguous relationship $\Psi \rightarrow \rho$ but not in the inverse direction $\Psi \leftarrow \rho$. It has been shown by Heitler and London⁵ that the bond formation is a quantum theoretical phenomenon, which can only be explained in terms of the wave function.⁶ The EDA-NOCV method used by Wu et al.² identifies and uses the interacting fragments for the bonding analysis and investigates the immediate interactions rather than the electronic structure of the final molecule. It is thus a faithful description of the bond formation. The focus of our comment lies on the delocalization index $\delta(A-B)$, which was taken as evidence for the alleged lack of $M \rightarrow \text{CO} \pi$ backdonation in the alkaline earth carbonyl complexes $M(\text{CO})_8$ ($M = \text{Ca}, \text{Sr}, \text{Ba}$).

Table 1 shows the calculated delocalization indices $\delta(M-C)$ and $\delta(M \cdots O)$ of the saturated carbonyl complexes $M(\text{CO})_n$ of

groups 10, 8, 6, 4, and 2 together with the experimental^{7,9} and calculated redshifts of the IR-active stretching mode. The delocalization indices $\delta(M-C)$ and $\delta(M \cdots O)$ of the carbonyl complexes of groups 10, 8, and 6 have rather large values. They become half as large in the adducts of group 4 and are very small in the alkaline earth carbonyl complexes of group 2. Our numbers for the latter complexes slightly deviate from the values reported by Van der Maelen, which may be due to the use of different programs and/or approximations. The differences are not important for the present work. The redshift of the carbonyl ligands continuously increases from the group 10 to group 4 complexes before it becomes a bit smaller for the group 2 complexes. However, the alkaline earth complexes $M(\text{CO})_8$ of $M = \text{Ca}, \text{Sr}, \text{Ba}$ have only two electrons for $M \rightarrow \text{CO} \pi$ backdonation, whereas group 10 complexes have four electrons. Group 8 adducts have eight electrons, and the group 6 species possess six electrons for π backdonation,⁹ which implies that the group 2 metals are even stronger π backdonors than the group 4–10 atoms.

The small $\delta(M-C)$ and $\delta(M \cdots O)$ values were taken by Van der Maelen as evidence that there is no significant π backdonation in the group 2 octacarbonyls. He suggests that the large redshifts of the adducts come from intramolecular interactions between neighbored carbonyl groups, which had previously been proposed as the reason for the redshift in the hexacarbonyls $M^q(\text{CO})_6$ ($M^q = \text{V}^-, \text{Cr}, \text{Mn}^+$).¹⁰ The author found values of $\delta(\text{C}_{\text{CO}} \cdots \text{C}_{\text{CO}})$ between 0.07–0.10 for the alkaline earth complexes $M(\text{CO})_8$, which were suggested to account for the large redshifts. We calculated the fragment $M(\text{CO})_2 (D_{\infty h})$ of $M = \text{Ca}, \text{Sr}, \text{Ba}$ of the octacarbonyls where the two CO groups are at a trans position but with the same $M-\text{CO}$ distance as in $M(\text{CO})_8$. Table 1 shows that the redshift of the CO ligands in $M(\text{CO})_2 (D_{\infty h})$ is even much

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Table 1. Pauling Electronegativities of the Metal Atoms EN(M) and Calculated Delocalization Indices $\delta(M-C)$ and $\delta(M\cdots O)$ of the Carbonyl Complexes^a

M(CO) _n	EN(M)	$\delta(M-C)$	$\delta(M\cdots O)$	$\Delta\nu^c$
Ni(CO) ₄ (T _d)	1.91	0.962	0.154	-86 (-84)
Pd(CO) ₄ (T _d)	2.20	0.830	0.122	-77 (-72)
Pt(CO) ₄ (T _d)	2.20	1.020	0.151	-95 (-95)
Fe(CO) ₅ (D _{3h}) ^b	1.83	0.992/1.046	0.168/0.175	-108/-130 (-101/-122)
Ru(CO) ₅ (D _{3h}) ^b	2.20	1.018/1.058	0.159/0.166	-107/-144 (-108/-133)
Os(CO) ₅ (D _{3h}) ^b	2.20	1.039/1.130	0.157/0.170	-108/-152 (-105/-145)
Cr(CO) ₆ (O _h)	1.66	0.833	0.140	-143 (-134)
Mo(CO) ₆ (O _h)	2.16	0.843	0.132	-139 (-141)
W(CO) ₆ (O _h)	2.36	0.854	0.130	-145 (-148)
Ti(CO) ₈ (O _h)	1.54	0.426	0.075	(-151)
Zr(CO) ₈ (O _h)	1.33	0.432	0.069	-164 (-138)
Hf(CO) ₈ (O _h)	1.30	0.434	0.066	-171 (-143)
Ca(CO) ₈ (O _h)	1.00	0.159	0.020	-156 (-119)
Sr(CO) ₈ (O _h)	0.95	0.139	0.012	-148 (-115)
Ba(CO) ₈ (O _h)	0.89	0.136	0.011	-129 (-107)
Ca(CO) ₂ (D _{∞h})		0.515	0.101	(-232; -227) ^d
Sr(CO) ₂ (D _{∞h})		0.300	0.031	(-238; -237) ^d
Ba(CO) ₂ (D _{∞h})		0.285	0.025	(-217; -226) ^d
Ba(CO) ^{•+} (C _{∞v})		0.300	0.024	-232 (-173)

^aExperimental and calculated (in parentheses) frequency shift of the IR-active stretching mode of CO with regard to free CO. The calculated values are obtained at the M06-D3/def2-TZVPP level using effective core potentials for the period 5 and 6 metal atoms.

^bThe first value is for the axial CO and the second for the equatorial CO ligands. ^cThe experimental values are taken from refs 2, 7, and 8.

^dThe first value is calculated with the frozen bond lengths of M(CO)₈, and the second value with optimized bond lengths.

higher than in the octacarbonyls, although the carbonyl ligands are far away from each other. We are aware of the fact that the frequency calculation of a non-stationary point is questionable, but the higher values are still revealing. We optimized linear M(CO)₂ in the triplet state with enforced D_{∞h} symmetry, which gives structures that are local energy minima on the potential energy surface.¹¹ The M–CO bonds become somewhat shorter, but the redshift of the C–O frequencies remains nearly the same (Table 1). The increase of the stretching frequencies comes from the fact that the two electrons of the metal atoms for M → CO π backdonation act on only two CO ligands in the dicarbonyls.

Van der Maelen points out that the QTAIM properties of the earth alkaline bonds significantly deviate from typical dative bonds and that the calculated indices suggest large electrostatic character of the M–CO bonds in M(CO)₈ (M = Ca, Sr, Ba). We agree with this finding, and the EDA-NOCV

analysis comes to the same conclusion irrespective of the choice of the interacting fragments.^{2,12} However, we dispute the conclusion that this indicates the irrelevance of the π backdonation. Figure 1 shows the shape of the degenerate

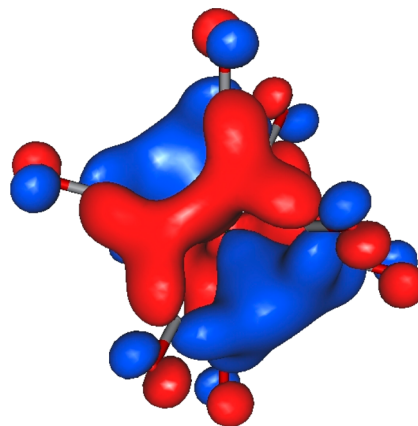


Figure 1. Shape of one of the degenerate SOMO of Ca(CO)₈ (isosurface value of 0.032 au).

SOMO of Ca(CO)₈, which reveals a significant contribution of the calcium *d*(π) AO as well as the delocalized nature of the orbital, which explains the rather large value for the delocalization index of $\delta(C_{CO}\cdots C_{CO}) = 0.10$ for the neighboring CO groups.¹ However, the value of $\delta(C_{CO}\cdots C_{CO})$ for the fragment Ca(CO)₂ (D_{∞h}) calculated by us is even higher (0.29), although the CO groups are now farther away from each other without direct overlap of the orbitals. This underscores the relevance of the metal *d*(π) AOs and the importance of the π backdonation for the redshift of the CO stretching frequencies. Since the $\delta(C_{CO}\cdots C_{CO})$ data in Ca(CO)₂ in spite of the longer distance are higher than those in Ca(CO)₈, we conclude that the values come from the indirect interactions via the metal atom rather than from direct interligand interactions. The metal atom in M(CO)₈ acts on eight CO, but in M(CO)₂ it acts on only two CO. Therefore, the delocalization index and the redshift are larger in the dicarbonyls although they are rather farther away from each other than the neighbored CO in the octacarbonyl.

Table 1 also shows the observed and calculated redshifts of Ba(CO)^{•+}, which likewise exhibits a large redshift of the CO ligand.¹³ The calculated values $\delta(M-C)$ and $\delta(M\cdots O)$ of Ba(CO)^{•+} are similarly small as in Ba(CO)₂ (D_{∞h}). Van der Maelen also calculated Ba(CO)^{•+}, which has obviously no interligand interaction. He concluded that “...in this particular case there is indeed significant π backdonation, consistent with the DCD model for the Ba–CO bond.” However, he does not give an explanation of why positively charged Ba^{•+} is capable of strong π backdonation, whereas neutral Ba is not.

A straightforward explanation of the trend of the calculated and experimental values presented in Table 1, supporting a strong π backdonation in the alkaline earth complexes M(CO)₈, is given if the electronegativities (EN) of the metal atoms M in the carbonyl complexes are considered. With the exception of tungsten, there is a continuous decline in EN(M) from group 10 to group 6 and in particular to group 4 and 2 metals. The decrease of the electronegativity of M means that the M–CO π bonds become strongly polarized toward the carbonyl end, most notably in the group 2 complexes, inducing small values for $\delta(M-C)$ and $\delta(M\cdots O)$. This does not mean,

however, that π backdonation is no longer important for the redshift of the stretching frequencies. On the contrary, the large polarization leads to a shift of the electronic charge toward the carbonyl ligands, which is experimentally observed in the IR spectra. The $M \rightarrow CO$ π backdonation in the alkaline earth complexes $M(CO)_8$ is not negligible, rather it is very strong and even stronger than that in the other carbonyl complexes shown in Table 1 if the number of electrons involved in the π orbital interactions is considered.

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■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.organomet.0c00419>.

Computational details and calculated vibrational frequencies of linear $M(CO)_2$ (PDF)
Cartesian coordinates (XYZ)

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Complete contact information is available at:

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Notes

The authors declare no competing financial interest.

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