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Comment on “Observation of alkaline earth complexes $M(\text{CO})_8$ ($M = \text{Ca}, \text{Sr}, \text{or Ba}$) that mimic transition metals”

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Wu *et al.* (Reports, 31 August 2018, p. 912) claim that recently characterized octacarbonyls of Ca, Sr, and Ba mimic the classical Dewar-Chat-Duncanson bonding motif of transition metals. This claim, which contradicts known chemistry and computed electron density distributions, originates in the assumption of a flawed reference state for energy decomposition analyses.

The report by Wu *et al.* (1) concerning the existence and characterization of the unexpected calcium carbonyl, $\text{Ca}(\text{CO})_8$, at low temperatures demonstrates the power of modern spectroscopic methods used in combination with modern electronic structure calculation. There is no doubt that the compound exists, as formulated, under the experimental conditions. However, the description of these complexes as mimicking classic characteristics of transition metal carbonyls, such as backbonding from calcium d orbitals into the π^* orbitals of the carbonyl groups and conformance to the 18-electron rule, conflicts with simple analysis of the computed electron density and the longstanding chemistry of CO in the presence of reducing metals.

Calcium metal is a good reducing agent and its chemistry is dominated by the formation of “saline” compounds with Ca^{2+} ions, even for weakly electronegative counterions (2–8). For more than a century, the chemistry of carbon monoxide in the presence of reducing metals has been understood as reductive in nature; examples include elements from groups 1, 2, and 3 as well as a variety of organometallic complexes. As we demonstrate below, calcium reacts with carbon monoxide by transfer of two valence electrons to form the $[(\text{CO})_8]^{2-}$ dianion that serves as a σ - and π -Lewis base to the resultant Lewis acid, Ca^{2+} . Electron density distributions, bonding patterns, and Ca-CO bonding thermodynamics in $\text{Ca}(\text{CO})_8$ bear little resemblance to the common Dewar-Chat-Duncanson motif of transition metal carbonyls.

The computed electron density distributions of $\text{Ca}(\text{CO})_8$ indicate an ionic formulation, $\text{Ca}^{2+}[(\text{CO})_8]^{2-}$. For example, the QTAIM (quantum theory of atoms in molecules) method (9) results in an effective charge of +1.56 at calcium. This value is consistent over a variety of basis sets, density functional theory (DFT) functionals, and non-DFT methods.

Natural bond orbital (NBO) (10) calculations compute a range of calcium charges (+1.15 to +1.55) that depend on the basis set; basis sets lacking representation of the nd functions give higher charges, whereas the presence of nd functions gives the lower value. Taken at face value, the NBO results may seem to indicate a bonding role for the Ca 3d orbitals, as suggested in the original report. It is easily shown, however, that such a role is specious and that the Ca nd functions serve primarily to augment the diffuse, delocalized charge of the $(\text{CO})_8$ dianion. Similar conclusions, based on basis set extrapolations, have recently appeared (11).

Figure 1 depicts the highest occupied molecular orbital (HOMO) (e_g symmetry) of $\text{Ca}(\text{CO})_8$, the e_g HOMO of the $[(\text{CO})_8]^{2-}$ cluster at the geometry of $\text{Ca}(\text{CO})_8$, and the nominal “Ca d orbital” that shows $\sim 0.4e$ occupation in the default NBO analysis. These orbital depictions include two prominent features: (i) The two electrons of the $[(\text{CO})_8]^{2-}$ cluster are highly delocalized among the π^*_{CO} orbitals and (ii) the nominal d orbital, which extends far from the calcium nucleus with a curious stem-and-bulb shape, consists almost solely of the outermost d Gaussian primitive. This orbital is not a valence “Ca 3d” orbital, because no Ca nucleus is present in this calculation. When d-type functions are absent from the calcium basis set, NBO charges closely agree with AIM charges. The bonding in $\text{Ca}(\text{CO})_8$ evidently arises from a combination of ionic forces and conventional Lewis-base donation of $[(\text{CO})_8]^{2-}$ density into the vacant 4s and 3d orbitals of the Ca^{2+} Lewis acid in the ionic $\text{Ca}^{2+}[(\text{CO})_8]^{2-}$ formulation.

Bond lengths and bonding patterns for the interaction of CO with Ca differ substantially from those with transition metals. The $R_{\text{Ca-C}}$ bond length (2.6 Å) and first Ca-CO bond dissociation energy ($\Delta E_{\text{Ca-CO}} = 9$ kcal/mol) of $\text{Ca}(\text{CO})_8$ are far longer and weaker than those of $\text{Cr}(\text{CO})_6$ ($R_{\text{Cr-C}} = 1.91$ Å,

$\Delta E_{\text{Cr-CO}} = 37$ kcal/mol). The computed enthalpies of successive CO additions to give singlet and triplet calcium carbonyles are shown in Fig. 2. Note that the first three additions of CO to Ca are approximately thermoneutral and each subsequent addition of CO is exothermic by ~ 12 kcal/mol. Apparently, CO binding is enthalpically favorable only when there are enough CO ligands (about four) to stabilize the accumulation of negative charge on the ligands. In contrast, transition metals commonly have large bond enthalpies for only the first few CO additions (12), with subsequent CO additions becoming notably weaker as a result of the change from $2c/2e$ bonding to $3c/4e$ bonding. In keeping with the $\text{Ca}^{2+}[(\text{CO})_8]^{2-}$ formulation, the spin density of the triplet state is $>90\%$ delocalized over the CO ligands.

The shapes of molecular $\text{Ca}(\text{CO})_n$ ($n = 2$ to 8) are easily deformed with multiple local minima. Optimization of the geometry using basis sets that lack d orbitals on Ca or optimization after deletion of all Fock matrix elements involving calcium d-type natural atomic orbitals lead to modest changes in geometry (e.g., an increase of the Ca-CO distance of just 0.4 \AA). Such small effects are consistent with nominal calcium-centered d-type basis orbitals acting primarily to augment the basis functions of the $[(\text{CO})_8]^{2-}$ dianion.

Why did the initial energy decomposition analysis (EDA) attribute the bonding in $\text{Ca}(\text{CO})_8$ to strong backbonding from the d^2 electron configuration of Ca? Put simply, the d^2 configuration of Ca is a bad reference point for analyzing the bonding in $\text{Ca}(\text{CO})_8$ as judged by a number of criteria.

Any EDA-type bonding analysis requires a starting reference state from which one can assess the changes in density distributions. The choice of the reference state is critical for meaningful analysis and can usually be chosen sensibly on chemical grounds. For example, the diatomic molecule LiF is well described as ionic at the equilibrium distance; the computed electron density partitions as nearly $+1$ and -1 at Li and F, respectively, and the shape of the quantum mechanical dissociation energy curve closely matches the pure electrostatic curve from near-equilibrium $R_{\text{Li-F}} = 1.6 \text{ \AA}$ out to $\sim 6 \text{ \AA}$. Thus, at Li-F distances around the equilibrium value, the appropriate reference is $\text{Li}^+ \text{F}^-$. However, at very long separations, Li-F dissociates to give Li and F atoms. At distances beyond 7 \AA , the better reference state comprises neutral Li and F atoms. Thus, one should always favor a reference state that approximates the overall charge distribution for the molecular geometry of interest. In EDA analyses, a common (and related) criterion for selecting the best reference is that which minimizes the orbital interaction terms.

One can anticipate the anomalies arising from the choice of a neutral $3d^2$ reference state. The $3d^2$ configuration of Ca lies 150 kcal/mol above the ground state and just 10 kcal/mol below the first ionization limit. In the d^2 state, Ca

is a powerful reductant. From this starting point, the final charge distribution can be accommodated only by strong transfer of d electrons into the overlapping π^*_{CO} orbitals. Thus, the appearance of strong d-orbital “backbonding” is an artifact that wholly results from selection of a high-energy reference state that poorly describes the molecular electron density distribution. As shown in Table 1, alternative EDA analysis using Ca^{2+} and $[(\text{CO})_8]^{2-}$ as the reference fragments is demonstrably superior to the original treatment; the EDA orbital interaction energy is much smaller and the charge distribution better approximates the molecular environment. In this state, the metal acts as a good σ - and π -Lewis acid, as expected for a group 2 metal.

We conclude that the electronic structure of $\text{Ca}(\text{CO})_8$ at the equilibrium geometry does not conform to the Dewar-Chatt-Duncanson model used for transition metal complexes. Although provocative, the interpretation posed by Wu *et al.* (1) contradicts fundamental charge distributions and long-established reactivity of the alkaline earth elements. The numerical evidence that is offered to support the transition metal-like bonding of Ca and CO arises solely from the assumption of a reference state that bears little resemblance to the true molecular electron density distribution. This is not a novel example; problematic interpretations arising from ill-chosen EDA reference states were previously criticized for neutral N-heterocyclic carbene complexes of copper, silver, and gold (13).

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Table 1. Comparison of EDA analyses of $\text{M}(\text{CO})_8$ complexes using different reference states.

Energy term	Assignment	Reference states [using published coordinates; see (<i>J</i>)]					
		$\text{M}(s^0d^2e_g \text{ triplet}) + (\text{CO})_8$			$\text{M}^{2+}(\text{singlet}) + [(\text{CO})_8]^{2-}(e_g \text{ triplet})$		
		Ca	Sr	Ba	Ca	Sr	Ba
ΔE_{int}		-243.4	-224.6	-144.7	-584.4	-550.1	-523.8
ΔE_{hybrid}		42.0	46.9	37.6	11.4	7.2	-1.02
ΔE_{Pauli}		19.2	30.3	30.0	69.1	73.7	68.7
ΔE_{estat}		-65.7	-61.7	-78.4	-483.6	-472.7	-451.6
ΔE_{orb}		-239.0	-240.0	-133.9	-181.3	-158.4	-140.9
$\Delta E_{\text{orb}(1) e_g}$	$\text{M}(d) \rightarrow (\text{CO})_8$ π^* -backdonation	-205.8	-206.7	-93.4	-40.2*	-36.1*	-38.1*
					$\text{M}(d) \leftarrow \text{CO}$ π^* -donation	$\text{M}(d) \leftarrow \text{CO}$ π^* -donation	$\text{M}(d) \leftarrow \text{CO}$ π^* -donation
$\Delta E_{\text{orb}(2) t_{2g}}$	$\text{M}(d) \leftarrow (\text{CO})_8$ σ -donation	-21.4	-20.5	-23.1	-52.3	-46.1	-38.1
$\Delta E_{\text{orb}(3) a_{1g}}$	$\text{M}(s) \leftarrow (\text{CO})_8$ σ -donation	-2.4	-2.9	-2.7	-10.3	-8.4	-6.0
$\Delta E_{\text{orb}(4) t_{1u}}$	$\text{M}(p) \leftarrow (\text{CO})_8$ σ -donation	-1.1	-0.8	-2.1	-21.4	-16.1	-12.1
$\Delta E_{\text{orb}(5)}$	$(\text{CO})_8$ polarization	-0.5	-0.5	-2.2	-42.5	-41.8	-42.2
$\Delta E_{\text{orb}(\text{rest})}$		-7.6	-7.7	-7.0	-3.2	-2.7	-3.3

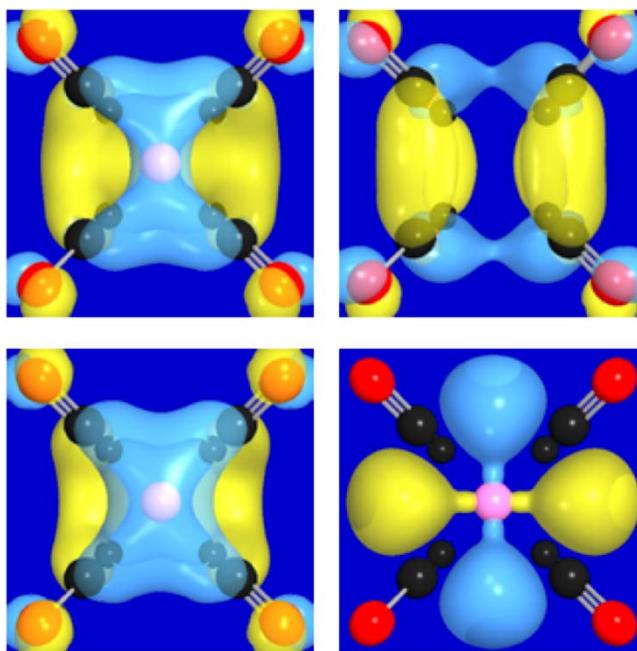


Fig. 1. Components of the highest occupied molecular orbitals in $\text{Ca}(\text{CO})_8$. Top left: One of the doubly degenerate highest occupied Kohn-Sham (HOMO) orbitals of triplet $\text{Ca}(\text{CO})_8$. Top right: A HOMO of triplet $[(\text{CO})_8]^{2-}$ at the geometry of $\text{Ca}(\text{CO})_8$. Bottom left: The HOMO of triplet $[(\text{CO})_8]^{2-}$ computed with Ca ghost basis functions, but no Ca nucleus, added to the basis set. Bottom right: One of two nominal calcium d natural atomic orbitals that act to augment the basis functions of the triplet $[(\text{CO})_8]^{2-}$. The view is perpendicular to one face of the cubic coordination geometry; carbon atoms are black, oxygen atoms red, and calcium atoms lavender. All density distributions were computed by DFT methods (M062X/Def2TZVPP) at the optimized coordinates of Wu *et al.* (1).

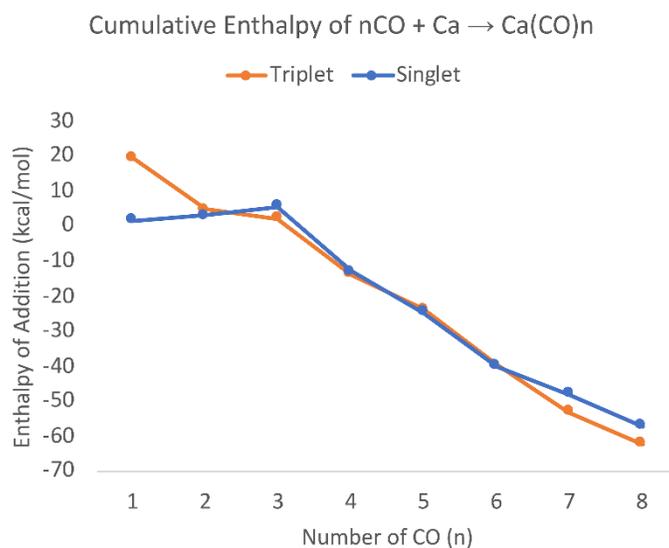


Fig. 2. Enthalpies of addition of ground-state CO to ground-state Ca to give singlet and triplet products as calculated by DFT methods (M062X/Def2TZVPP with GD3 empirical dispersion correction).

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