Preliminary communication

WHY IS THE η^1-C COORDINATION MODE PREFERRED FOR CO_2 IN [Co(N,N'-ETHYLENEBIS(SALICYDENEAMINATO))(CO_2)] $^-$? AN AB-INITIO MO STUDY

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Summary

A theoretical analysis of the possible coordination modes for CO_2 in the [Co(N,N'-ethylenebis(salicydeneaminato))(CO_2)]$^-$ system has been carried out by ab-initio LCAO-MO-SCF methods. Stabilization with respect to dissociation is found only for the η^1-C coordination mode. The results are rationalized in terms of molecular orbital interactions.

Transition metal-CO_2 complexes have recently attracted much interest, since coordination of CO_2 to a transition metal is expected to activate the CO_2 and should therefore promote new reactions involving this otherwise rather stable molecule [1,2]. The stability of CO_2 seems, indeed, to be the main cause for its reluctance to bond to transition metals, and only a limited number of transition metal-CO_2 complexes have been synthesized. The complexes show some variation in the coordination mode of the CO_2 moiety; the η^2-side on mode **1** is found in
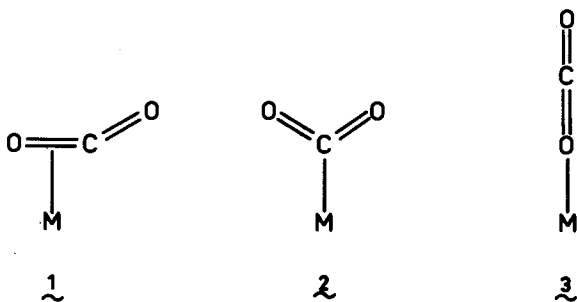
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$Ni(PCy_3)_2(CO_2)$ [3], $Nb(\eta-C_5H_4Me)_2(CH_2SiMe_3)(CO_2)$ [4] and $Mo(PR_3)_4(CO_2)_2$ [5], whereas the η^1-C coordination mode **2** is preferred in $[Co(salen)(CO_2)]^-$ [6] (salen = N,N'-ethylenebis(salicydeneaminato), $RhCl(diars)_2(CO_2)$ [7] (diars = O-phenylenebis(dimethylarsine)) and $W(CO)_5(CO_2)^{2-}$ [8]. There is no example of the η^1-O coordination mode, **3**.

The factors which control the formation and the structure of transition metal-CO_2 complexes are therefore quite complex. There have however, been only two molecular orbital studies [9] devoted to MCO_2 complexes in the last few years. In one of them, the preference for the η^2 side-on coordination mode **1** in the system $Ni(PCy_3)_2(CO_2)$ was rationalized [9a] with the aid of ab-initio LCAO-MO-SCF calculations on the $Ni(PH_3)_2(CO_2)$ model system. We present here preliminary results of an ab-initio MO study of the $[Co(alcn)_2CO_2]^-$ system, (alcn = acetylacetoneiminato, $NHCHCHCHO^-$), which is taken as a model of the $[Co(salen)(CO_2)]^-$ complex, and which can be regarded as a prototype for the η^1-C coordination mode **2**. The relative stabilities of the possible coordination modes **1–3** are investigated and discussed in terms of molecular orbital interactions. The interconversion between **1** and **2** is also considered and discussed.

Computational details

The ab-initio SCF calculations involved the programs ASTERIX [10] and IM-SPACK [11] with two basis sets. For the geometry optimization of the MCO_2 unit a (12,7,5) primitive basis set [12], contracted to [5,3,3], was used for the cobalt atom in conjunction with the usual 4-31G basis set [13] for the hydrogen and first row atoms. A larger basis set (14,9,5) [14] contracted to [6,4,3] for cobalt, (9,5) and (4) contracted to [3,2] and [2] for the first row atoms [15] and hydrogen respectively, was used when necessary, i.e. for energy comparisons between the various coordination modes. A singlet state, arising from the d^8 closed shell configuration for Co^I was assumed for the $[Co(alcn)_2(CO_2)]^-$ system, in view of the diamagnetism of $[Co(salen)(CO_2)]^-$ [6b] and $[Co(salen)]^-$ [6c].

Geometry optimization was limited to the parameters of importance for the specific problem: for instance, the Co–C distance and the CO_2 geometry were optimized in the η^1-C coordination mode, see Fig. 1a. In the η^2 geometry (Fig. 1b) the length of the coordinated C–O bond and the corresponding O–C–O angle were optimized for two Co to C–O distances d (d 2.0 and 2.5 Å). The other C–O bond length was not optimized, but kept at 1.16 Å (experimental value in CO_2 [17]). Finally, it was found sufficient in the case of the η^1-O coordination mode (Fig. 1c) to consider only the variation of the Co–O distance, since this mode is highly destabilized relative to the other two. The geometry of the $Co(alcn)_2$ moiety was based on the known geometry of $[Co(salen)(CO_2)]^-$ [3] for the CoN_2O_2 core and that of $[Co(alcn)_2]$ [16] for the remaining part of the alcn ligand.

Results and discussion

We first note that there is good agreement for the η^1-C coordination mode between the optimized and the experimental structures, (see Fig. 1a). The computed binding energy for the larger basis set is 6.2 kcal/mol. This must be corrected, however, for the so-called basis set superposition error [18]. This correction is unlikely to be more than a few kcal/mol [19], and a small binding energy can therefore be expected for the η^1-C coordination mode.
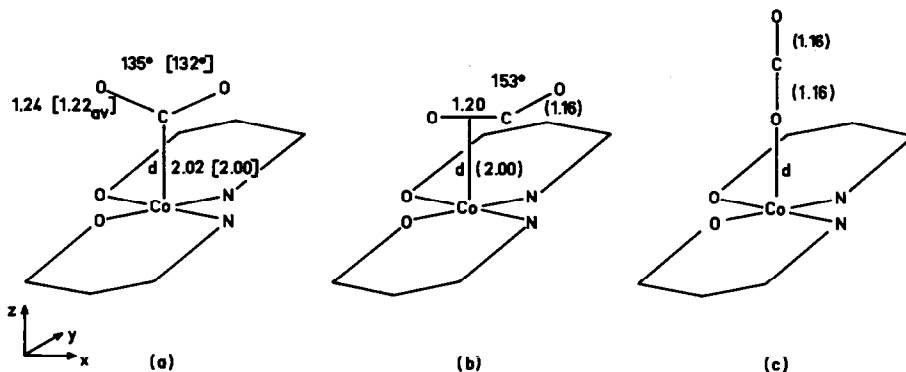
Fig. 1. Geometry of the $[Co(alcn)_2CO_2]^-$ molecule: (a) with the η^1-C coordination mode; (b) with the η^2 coordination mode; (c) with the η^1-O coordination mode. [ ], experimental values; ( ), assumed values; the other values are the optimized ones. For the η^2 geometry with d 2.5 Å, the C–O bond length and the O–C–O bond angle are optimized at 1.16 Å and 166°, respectively.

On the other hand, the η^2- and η^1-O coordination modes appear to be less stable than the η^1-C mode. The destabilization (computed with the smaller basis set) amounts to 31.5 kcal/mol for the η^2 coordination mode and is even greater for the η^1-O mode. Moreover, neither of these two coordination modes appear to give binding, the potential energy curves computed with the small basis set as a function of the Co to CO_2 distance always being repulsive. Use of the larger basis set cannot be expected to give the opposite result since it is known to give smaller binding energies [19].

We also find no energy minimum on the interconversion path between the η^2- and the η^1-C coordination modes. On this path, modelled by a linear transit between the two limit structures, the energy continuously decreases on going from η^2- to η^1-C, again pointing to the greater stabilization of the η^1 structure. It may therefore be concluded that even if the η^2 coordination mode prevailed in the early stages of the $CoCO_2$ complex formation the system would rearrange to yield the η^1-C coordination mode as the final form.

The schematic orbital diagrams depicted in the Fig. 2 provide a rationalization of the above features. The CO_2 ligand is characterized by three in-plane valence orbitals, namely π, $n\pi$, and π^*, of which only two (π and $n\pi$) are occupied. In the η^1-C mode (Fig. 2a), the predominant interaction is a two electron stabilizing one

π $n\pi$ π^*
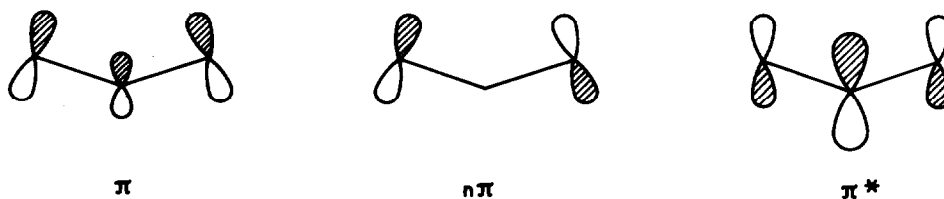
between d_{z^2} and π^* (although it is somewhat reduced by an additional but weaker interaction with π). This strong interaction populates the CO_2 π^* orbital and there is a significant charge transfer from Co to CO_2: the Co d_{z^2} orbital population is decreased by ca. 0.63e upon CO_2 coordination, and the CO_2 electron population is
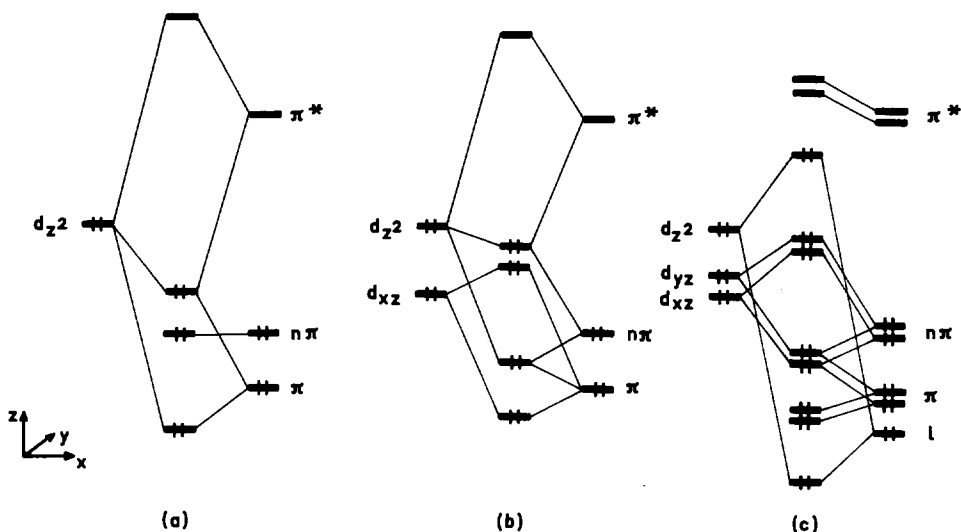
Fig. 2. Schematic orbital interaction diagram between $[Co(alcn)_2]^-$ and CO_2 to form $[Co(alcn)_2(CO_2)]^-$ for various coordination modes of CO_2: (a) η^1-C coordination mode; (b) η^2 coordination mode; (c) η^1-O coordination mode. In the η^1-C and η^2 cases, the out-of-plane components are omitted for simplicity since they do not contribute significantly to the interaction pattern.

increased by ca. 0.71e. The electron transfer from Co d_{z^2} to CO_2 π^* is consistent with the C–O bond elongation found experimentally and theoretically.

Change from the η^1-C to the η^2 coordination mode (Fig. 2b) reduces the bonding interaction between the Co d_{z^2} orbital and the CO_2 π^* orbital since the overlap is appreciably reduced. The lobes on the C and O atoms of the π^* orbital are of opposite signs and their contributions to the overlap with d_{z^2} therefore almost cancel. In addition two sets of four electron destabilizing interaction become operative: one between $n\pi$ and d_{z^2} and another one between d_{xz} and π. This latter interaction is somewhat reduced through the in-phase mixing with the π^* orbital. In the HOMO, which is a rather intricate mixing of the d_{z^2}, d_{xz}, π, $n\pi$ and π^* orbitals, the repulsive interactions dominate, however, leading to its destabilization (-2.99 eV vs. -3.79 eV in the η^1-C mode), and consequently to the destabilization of the η^2 structure. The reduced interaction between the Co d_{z^2} orbital and the CO_2 π^* orbital also leads to a substantial decrease in the Co to CO_2 charge transfer, the Co d_{z^2} orbital population being decreased by 0.07e only upon CO_2 coordination in the η^2 mode [20].

The orbital interaction pattern (Fig. 2c) for the η^1-O mode is easier to visualize. The strong destabilization of this isomer can be traced to a strong four electron destabilizing interaction between d_{z^2} and the lone pair of the oxygen atom pointing toward Co, and to another four electron destabilizing interaction (in both planes) between the $d\pi$ orbitals (d_{xz} and d_{yz}) of the cobalt atom and the $n\pi$ orbitals of the CO_2 ligand. (The π and π^* orbitals interact with the $d\pi$ orbital to a much smaller extent because of a greater energy gap and a smaller overlap, respectively). The absence of any noticeable stabilizing interaction accounts for the highly repulsive potential energy curve as CO_2 approaches the $[Co(alcn)_2]^-$ system through an oxygen end.

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