Photochemical dynamics of transition metal complexes from time-resolved infrared-to-visible spectroscopies. CO_2-transition-metal binding.

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The utilization of CO_2 as an abundant, renewable carbon source in chemical synthesis represents a compelling strategy that may assist in the future to reduce greenhouse gas emissions. Inspired by biochemical CO_2-fixation such an approach may rest on the activation of the inert gas by a suitable transition metal (TM). In the past, chemists have successfully prepared a number of different CO_2-TM-complexes that can be classified according to the CO_2-binding mode: (i) σ-bonding between TM and the central C-atom, (ii) π-„side-on"-bonding between TM and one of the two C=O bonds, and (iii) σ-"end-on"-bonding between TM and one of the two terminal O-atoms. Whereas in the former two modes the CO_2-ligand is bent, it assumes a linear geometry in the „end-on" motif.

Here, we report on the observation of exceptional "end-on" binding mode, in which the carbonaceous ligand is bent rather than linear [1-3.] To this end, we photolyzed various oxalato complexes of iron, $[L_nFe(C_2O_4)_{(6-n)/2}]^{n-3}$ (L=auxiliary ligand with denticity n) in liquid solution as models for TM-CO_2 binding/unbinding dynamics and ultrafast UV/IR spectroscopy to disclose the primary photochemical events resulting from their impulsive excitation. A single neutral CO_2-molecule is expelled within 500 fs after excitation to generate a penta-coordinated ferrous species bearing a lone CO_2-ligand. In low-spin complexes, the CO_2 was found to bind in a "side-on" fashion, while in high-spin complexes, the "end-on" coordination is favored. In the latter case, the CO_2 is coordinated as a radical anion and as such, it represents the reductively activated form promising carbon-centered chemical reactivity.

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[3] F. H. Pilz, J. Lindner, P. Vöhringer, *Phys. Chem. Chem. Phys.* **2019**, *21*, 23803-23807.