

METAL IDENTITY AND PRODUCT BINDING TUNE STRUCTURE AND CHARGE DISTRIBUTION: INFRARED SPECTRA OF CATALYTICALLY RELEVANT METAL BIPYRIDINE COMPLEXES

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Electrocatalytic reduction of CO₂ into feedstock for chemical fuels is a promising approach to achieving a carbon neutral fuel cycle.^a While this has been an active field of study for decades, relatively little is known about the key reaction intermediates and molecular-level processes of proposed catalytic mechanisms, necessitating a deeper understanding to inform the design of future catalysts.

We present cryogenic gas-phase infrared spectra of catalytically relevant model systems consisting of a transition metal center (Co, Ni, or Cu) coordinated to two bipyridine-based ligands, either bare or with a formate adduct.^b Bipyridine derivatives are frequently ligands for molecular catalysts where a transition metal ion is coordinated to four N atoms. This family of metal-4N catalysts has been studied extensively due to their exceptional performance and ease of synthesis. Formate is one of many possible CO₂ reduction products.^{c,d} Density functional theory was used to assign spectral features and calculate charge distributions.

The vibrational spectra inform us of the structure of and intermolecular forces in each complex, revealing the binding motif of the formate adduct to the metal center and the dependence of this arrangement on the identity of the metal. The calculated charge distributions demonstrate the role of the organic ligands to act as charge reservoirs, where they show remarkable electronic flexibility in response to the addition of a formate adduct and the nature of the coordinated metal center. This work showcases the influence of transition metal identity on the formate-metal binding motif and the significant role of the organic ligand framework in adjusting the redox properties of these complexes.

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