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Q25

A Comparison of CO Bound to Metalloporphyrins and Metal Surfaces

J. PAUL and A. ROSÉN

Department of Physics, Chalmers University of Technology, S-412 96 Gothenburg, Sweden

K. G. PAUL and M. L. SMITH

Department of Physiological Chemistry, University of Umeå, S-901 87 Umeå, Sweden

A thorough understanding of the metal–ligand bond is of great importance in biochemistry as well as in catalysis. Much insight can be gained by an analysis of the various factors that govern the properties of this bond for a model system such as carbon monoxide bound to iron in heme or iron embedded in a metal surface [1]. The delocalized sp-states in a metal show a large dispersion and form an electron gas whereas the Fe 4s electrons in heme reside in the surrounding porphyrin. The porphyrin, basically a poly-pyrrol and thus 'metallic', can transfer long-range effects connecting substituents in the periphery with the Fe–C=O or Fe–O=O complex. Such properties can be simulated by a model in which iron is embedded in an electron gas but with different density for metalloporphyrins compared to metals. To what extent the response of such an electron gas to an external field will influence the matrix elements of photoexcitations is not known. The 3d states of a typical transition metal such as iron are well localized within the Wigner–Seitz cell. It is thus plausible that *e.g.* a CO molecule is bound to a particular surface atom since the bond is believed to be a combined CO5σ–Fe3dσ and Fe3dπ–CO2π bond. The different crystal field separations of 3d states in the reactive pentacoordinated heme compared to the hexacoordinated heme–CO complex is parallelled by the band-narrowing of 3d-states in the surface layer of a metal. Any change of the 3d states either in metalloporphyrins or in metal surfaces will influence the chemical properties since the changes occur close to the Fermi level, *i.e.* the mean energy of the highest occupied and lowest unoccupied molecular orbitals. The stretch frequencies of the metal–carbon (ν_{MC}) and carbon–oxygen (ν_{CO}) bonds are sensitive probes of these changes. The analysis of such vibrational shifts in terms of electronic structure is however not always straightforward. A decreased redox potential (work-function) is followed by a decreased ν_{CO} [2, 3]. This can be interpreted in terms of an enhanced backbonding to the antibonding CO2π level close to the Fermi level. The work-function decrease is provided by preadsorbed potassium on an iron catalyst which means that we cannot completely rule out the possibility of direct CO–K interaction.

In heme models, where the decrease is provided by substitutions in the periphery of the porphyrin, the pyrrols separate the substituents from the CO ligand and direct overlap is negligible. Moreover at high CO coverages of the metal surface we have the possibility of direct CO–CO overlap and formation of CO2π electron bands which will influence the occupation numbers and thus the vibrational frequencies [4, 5]. At intermediate coverages where ordered overlayers occur the ν_{MC} frequency can be influenced by phonon bands. The isolation of the direct Fe–CO electronic effects is however possible for a few model systems. One such system is CO bound to iron adsorbed at dilute coverages onto aluminium, a metal which is inert to CO. Another system is heme solvation as well as steric effects or H-bonds to a protein can be ruled out. A comparison of iron and copper porphyrins is valuable. In a Fe–C=O complex the π states will be heavily mixed whereas in Cu–C=O the effect will be merely a broadened 2π level. This is plausible since a copper surface or a copper porphyrin has a low density of states at the Fermi level compared to iron due to an almost completely filled 3d shell.

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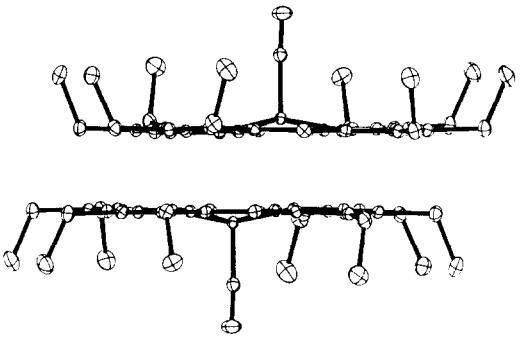

Fig. 2. The $\pi-\pi$ dimer in the solid state.

Q26

Preparation and Structural Characterization of Nitrosyl Complexes of Ferric Porphyrinates

W. ROBERT SCHEIDT, YOUNG JA LEE

Department of Chemistry, University of Notre Dame, Notre Dame, Ind. 46556, U.S.A.

and KEIICHIRO HATANO

Department of Pharmaceutical Science, Nagoya City University, Nagoya, Japan 467

Nitrosyl complexes of ferric porphyrinates have been prepared by reaction of perchloratoporphinatoiron(III) complexes with nitric oxide. Two species have been structurally characterized: aquonitrosyl(*meso*-tetraphenylporphinato)iron(III) perchlorate, $[Fe(TPP)(NO)(H_2O)]ClO_4$, and nitrosyl(octaethylporphinato)iron(III) perchlorate, $[Fe(OEP)(NO)]ClO_4$.

Crystal data: $[Fe(TPP)(NO)(H_2O)]ClO_4$, monoclinic, $a = 10.303(2)$ Å, $b = 8.124(2)$ Å, $c = 21.364(8)$ Å, and $\beta = 97.76(2)°$, $Z = 2$, space group $P2_1/n$, 3999 observed data, $R_1 = 0.057$, $R_2 = 0.079$, all measurements at 96 K. $[Fe(OEP)(NO)]ClO_4$, monoclinic, $a = 12.890(2)$ Å, $b = 20.363(3)$ Å, $c = 14.969(2)$ Å, and $\beta = 95.48(2)°$, $Z = 4$, space group $P2_1/n$, 5956 observed data, $R_1 = 0.058$, $R_2 = 0.063$, all measurements at 292 K.

All complexes are low-spin $\{FeNO\}^6$ species. $[Fe(OEP)(NO)]ClO_4$ is the first five-coordinate low-spin ferric porphyrinate to be structurally characterized. The Fe–N–O moiety is essentially linear in both species. For $[Fe(TPP)(NO)(H_2O)]ClO_4$, $Fe-N_p$ =

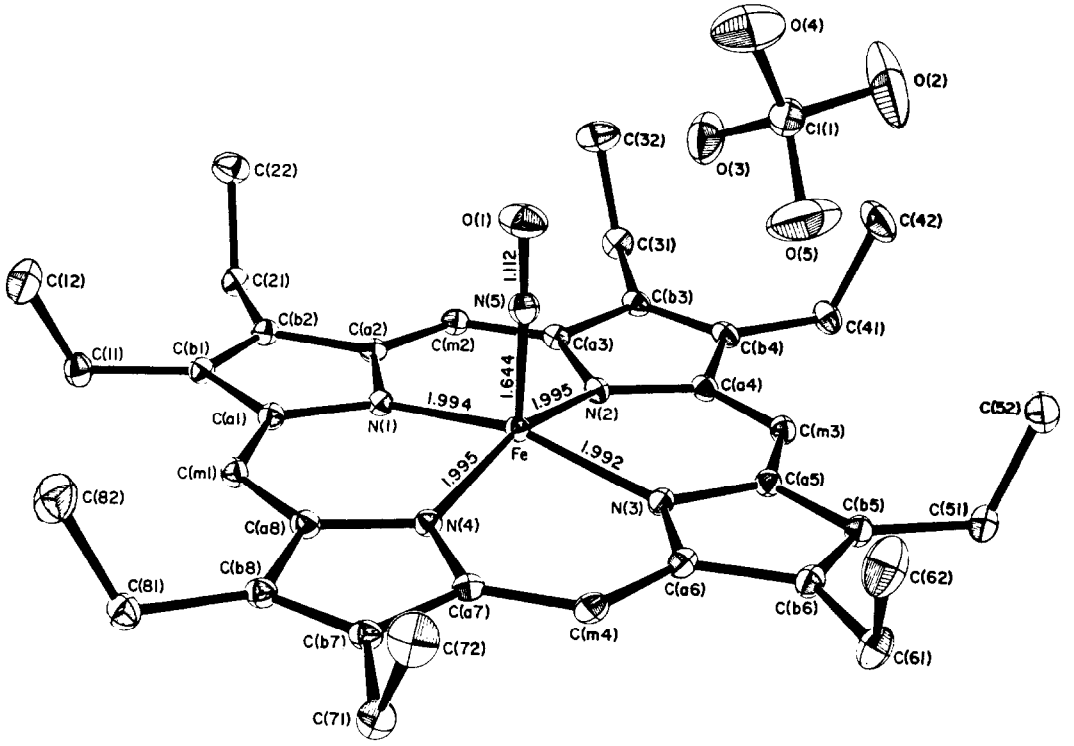

Fig. 1. Structure of $[Fe(OEP)(NO)]ClO_4$.