Inorganic Chemistry

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Correlation between the FeNO Angle and d−p Mixing in $\{FeNO\}^7$ Complexes

Jeanet Conradie[†,‡] and Abhik Ghosh[*,†]

[†]Department of Chemistry and Center for Theoretical and Computational Chemistry, University of Tromsø, N-9037 Tromsø, Norway

[‡]Department of Chemistry, University of the Free State, 9300 Bloemfontein, Republic of South Africa

Supporting Information

ABSTRACT: The great majority of low-spin $\{FeNO\}^7$ complexes exhibit FeNO angles of around 140−145°, whereas a small handful are characterized by linear FeNO units. Conspicuously absent are intermediate FeNO angles of 150−170°. Spurred by the recent observation of such an angle in a square-pyramidal $\{FeNO\}^7$ complex, we carried out a density functional theory survey of 12 additional, largely hypothetical complexes with porphyrin and corrole analogues as equatorial ligands. Our calculations predict several instances of intermediate FeNO angles. The calculations further indicate a strong, positive correlation ($R^2 = 0.9$) between the FeNO angle and metal p character in the Fe d_{z^2}-based highest occupied molecular orbital.

For a given d electron count (more accurately, the Enemark−Feltham count[1]), the MNO angles in metalloporphyrin nitrosyls,[2] as well as those in related low-spin nonporphyrin complexes, are remarkably constant.[3] Thus, the FeNO angle is 140−145° in hundreds of low-spin heme and nonheme $\{FeNO\}^7$ complexes. This constancy is remarkable because high-quality density functional theory (DFT) calculations[4,5] at once accurately reproduce the observed structures and emphasize that they are soft with respect to angular deformation.[6] The question arises as to why the FeNO angles do not vary more, given their flat bending potentials. A small handful of low-spin $\{FeNO\}^7$ complexes such as $[Fe(CN)_4(NO)]^{2-}$ and $[Fe(dtc)_2(NO)]$ (dtc = dithiocarbamate), however, do exhibit linear FeNO moieties.[7] DFT studies[6,7] suggest that the linearity of these complexes is related to enhanced iron pyramidalization relative to hemes, which leads to $d_{z^2}-p_z$ mixing (as shown in Figure 1), which, in turn, minimizes repulsion between the Fe d_{z^2} orbital and the σ lone pair of NO. By varying the degree of pyramidalization and hence the Fe p_z character, one would argue that the FeNO angle might be modulated. This, however, is easier said than done. A major exercise in ligand design and synthesis would be required, which, in the absence of promising applications, might not seem worthwhile.

Harrop and co-workers have recently found a square-pyramidal nonheme $\{FeNO\}^7$ complex with an intermediate FeNO angle of about 160°.[8] The degree of iron pyramidalization in this compound, as well as the amount of Fe p_z character, was found to be higher than that in heme-NO complexes but lower than that in linear $\{FeNO\}^7$ species such as $[Fe(CN)_4(NO)]^{2-}$.[7] Intrigued by this structure, we "thought up"[9] several low-spin, square-pyramidal $\{FeNO\}^7$ complexes (Figure 2) with dianionic porphyrin and corrole analogues as equatorial ligands[10] that we considered likely to engender a range of iron displacements relative to the basal N_4 plane. Gratifyingly, OLYP[11,12]/STO-TZP geometry optimization of these structures (using ADF 2009) yielded several examples of intermediate FeNO angles. Indeed, for two of the equatorial ligands, OxoCor and OxoCz, the FeNO angles are predicted to be near-linear, a unique prediction for porphyrin-type complexes. In addition, the FeNO angles appear to correlate with the amount of metal p character in the molecule's Fe d_{z^2}-based highest occupied molecular orbital (HOMO), as discussed below.

Table 1 presents key optimized metrical parameters of the complexes studied as well as the percentage of Fe d_{z^2} and p_z character in their HOMOs. Figure 3 presents plots of the FeNO angle versus (a) the Fe p_z character and (b) the Fe−N(O) bond distance. The FeNO angle correlates well with both variables. For the former, the correlation is best (as in Figure 3a) when the Fe p_z character is expressed as a percentage of the overall Fe character of the Fe d_{z^2}-based HOMOs.

Let us first address why an admixture of metal p_z character in the d_{z^2}-based HOMO leads to linearization of the FeNO unit. As shown in Figure 1, p_z admixture results in a shrinkage of the "top" lobe of the d_{z^2} orbital, which, in turn, leads to reduced repulsion involving the σ lone pair of NO. Figure 4 depicts this effect in Fe(Pz)(NO) (where there is little p_z admixture) and in Fe(OxoCor)(NO) (where p_z admixture is considerable).

Table 1 and Figure 3b also indicate a heretofore little-studied bond-angle−bond-length correlation: the more linear the FeNO units, the shorter the Fe−N(O) distance. This follows straightforwardly from the requirements of $Fe(d_\pi)-NO(\pi^*)$ π bonding. Surprisingly, the FeNO angle correlates poorly with displacement of the iron relative to the basal N_4 plane ($R^2 = 0.31$).[13]

We have documented elsewhere that FeNO bending potentials are soft.[6] Yet, DFT unfailingly reproduces experimentally observed FeNO structures with a high degree of accuracy.[14] We are thus rather confident that our predictions of unusual FeNO angles will be borne out by experiment, *by and large*, should the relevant compounds be synthesized. Although we cannot rule out isolated cases of disagreement between predicted and observed FeNO angles, there is ample precedence for molecular orbital−structural correlations in both organic and inorganic

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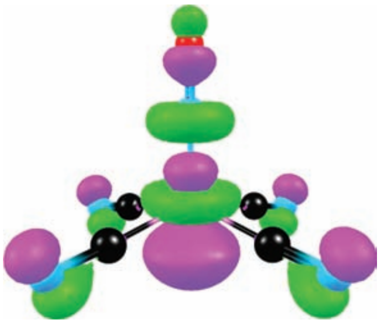

Figure 1. Fe d_{z^2}-based HOMO of C_{4v} $[Fe(CN)_4(NO)]^{2-}$:^{7} note the shrunken top lobe and the swollen bottom lobe of the d_{z^2} orbital, reflecting 11.9% Fe p_z character mixing in with 54.0% Fe d_{z^2} character.

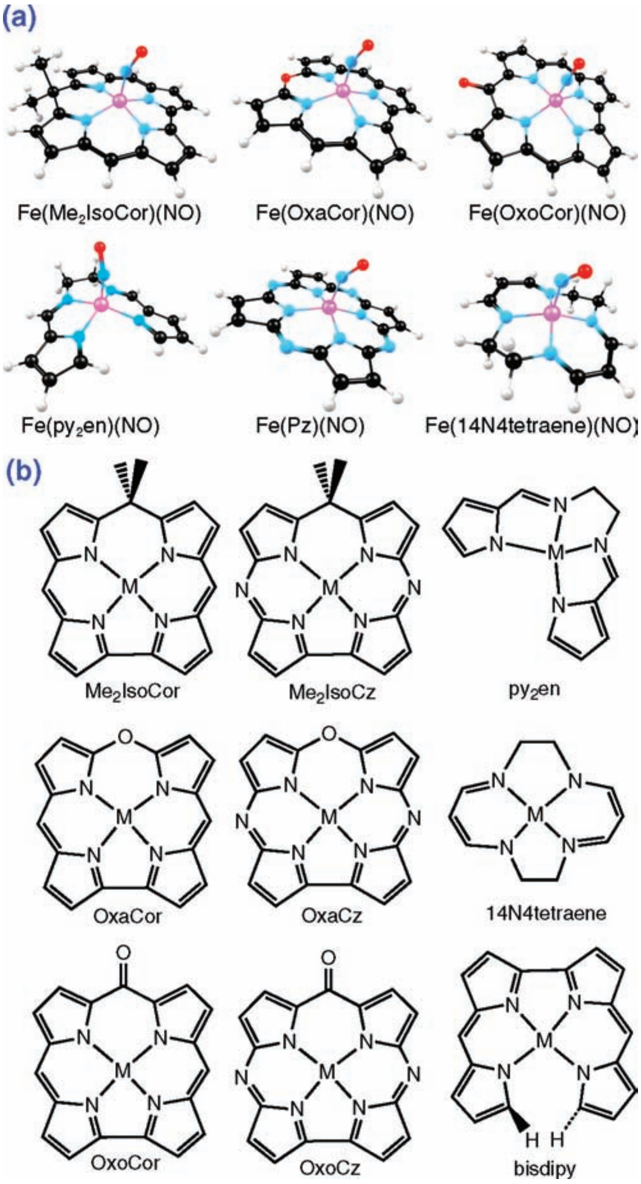

Figure 2. Complexes studied in this work: (a) ball-and-stick representations of selected optimized structures and (b) structural formulas of selected FeN_4-based complexes.

Table 1. Selected Results from OLYP/TZP Optimizations: FeNO Angle (deg), Iron Displacement from the N_4 Plane, $d(Fe-N_4)$ (Å), Fe−N(O) Distance (Å), % Fe d and % Fe p Character of the HOMO, and Fe p Character as a Percentage of the Overall Fe Character (Last Column)

	FeNO	$d(Fe-N_4)$	$d(Fe-NO)$	% d	% p	p/(p + d) × 100%
Fe(14N4tetra-ene)(NO)	138.8	0.371	1.732	42.0	1.5	3.5
Fe(Pz)(NO)	146.2	0.325	1.712	49.1	2.6	4.9
Fe(P)(NO)	146.4	0.238	1.707	36.8	1.6	4.2
Fe(T^{t}BuP)(NO)	147.5	0.341	1.693	35.1	1.6	4.2
Fe(py_2en)(NO)	153.1	0.488	1.670	40.6	3.6	8.2
Fe(OxaCor)(NO)	154.3	0.439	1.678	45.5	4.2	8.5
Fe(bisdipy)(NO)	155.0	0.386	1.678	27.8	2.5	8.1
Fe(Me_2IsoCor)(NO)	156.4	0.410	1.671	46.9	5.0	9.7
Fe(OxaCz)(NO)	157.3	0.495	1.672	45.0	4.5	9.0
Fe(Me_2IsoCz)(NO)	163.3	0.462	1.657	41.7	5.1	10.9
Fe(OxoCor)(NO)	173.1	0.422	1.646	38.7	5.6	12.7
Fe(OxoCz)(NO)	177.8	0.457	1.631	27.6	4.2	13.2

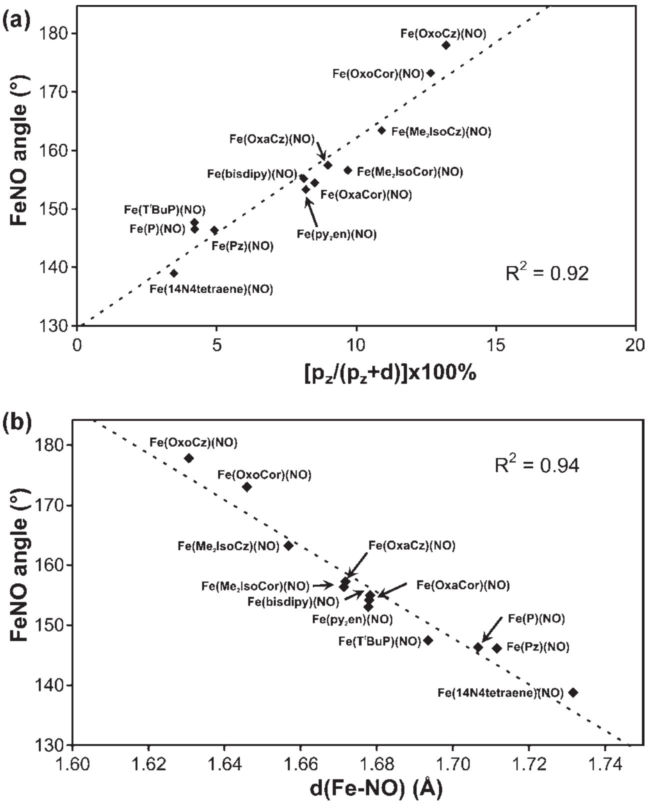

Figure 3. Variation of the FeNO angle (deg) as a function of (a) the Fe p_z character [defined as p/(p + d) × 100% for the Fe d_{z^2}-based HOMO] and (b) the Fe−N(O) distance.

chemistry, of which the Bürgi−Dunitz trajectory for nucleophilic addition to carbonyl groups may be the best-known example.[15]

To conclude, unusual, intermediate FeNO angles should be accessible in square-pyramidal $\{FeNO\}^7$ complexes with

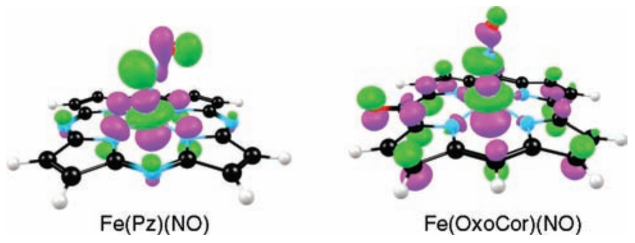

Figure 4. Plots of the d$_{z^2}$-based HOMOs of Fe(Pz)(NO) and Fe(OxoCor)(NO). Contour = 0.04 e/Å^3.

porphyrin- and corrole-inspired equatorial ligands. Admittedly, the complexes investigated here are largely hypothetical;[9] a number of the ligands, however, are not. Thus, isocorrole (Me$_2$IsoCor),[16,17] oxacorrole (OxaCor),[18] and oxocorrole (OxoCor)[19] are all known ligands, although their *meso*-aza analogues are not.[20] We therefore believe that synthetic inorganic chemists should be able to synthesize, with reasonable effort, additional examples of low-spin {FeNO}^{7} complexes with FeNO angles of 150−170°.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Optimized Cartesian coordinates of the various molecules studied. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: abhik.ghosh@uit.no.

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(9) In a recent essay titled "Why think up new molecules?" (Hoffmann, R. *Am. Sci.* **2008**, *96*, 373–374), Prof. Roald Hoffmann writes: "I love explaining. But as a theoretician, I also want to take part in the work of creation. I can do so by thinking up interesting molecules not yet made."

(10) Abbreviations: P = porphyrin; Pz = porphyrazine; T^{t}BuP = *meso*-tetrakis(*tert*-butyl)porphyrin, a highly ruffled porphyrin; Me$_2$IsoCor = 10-dimethylisocorrole, a dianionic corrole analogue with interrupted conjugation; OxaCor = 10-oxacorrole, a dianionic corrole analogue; OxoCor = 10-oxocorrole, a dianionic corrole analogue; OxaCz = 5,15-diaza-10-oxacorrole, a dianionic corrolazine analogue; OxoCz = 5,15-diaza-10-oxocorrole, a dianionic corrolazine analogue; bisdipy = an α−α′-linked bisdipyrrin; py$_2$en = an open-chain porphyrin-salen hybrid ligand; 14N4tetraene = a dianionic tetraazamacrocyclic ligand.

(11) (a) The OPTX exchange functional: Handy, N. C.; Cohen, A. J. *Mol. Phys.* **2001**, *99*, 403–412. (b) The LYP correlation functional: Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789.

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(13) This result also means that the p$_z$ character content of the HOMO does not correlate well with displacement of the iron from the equatorial N4 plane. In other words, although sterically constrained ligands such as those shown in Figure 2b remain a fertile field for the creation of {FeNO}^{7} complexes with unusual, intermediate FeNO angles, explicit computations are likely to be helpful in placing one's hunches on firmer footing.

(14) Because of the softness of the FeNO bending potentials, care was exercised in evaluating the true minimum of the FeNO angle. This involved exceptionally fine grids and exceptionally tight criteria for both self-consistent-field and geometry optimizations. Furthermore, a potential energy curve was constructed wherein the energy (from a series of constrained optimizations) was plotted against the FeNO angle, while all other internal coordinates were fully optimized.

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