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XAS Studies of Ni(I), Ni(II), and Ni(III) Complexes

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Abstract: XAS techniques for studying structural and electronic changes taking place during oxidation and reduction reactions of nickel complexes are described and applied to selected models for Factor 430, a nickel containing cofactor catalyzing an important step in the conversion of carbon dioxide to methane by methanogenic bacteria.

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Introduction

Our interest in the chemical and physical properties of organometallic nickel complexes is motivated by the presence of a nickel hydroporphyrin (known as Factor 430 or F430) as a cofactor in a key step in the bacterial reduction of carbon dioxide to methane. [1] We have developed and employed XANES and EXAFS techniques to characterize the changes in structural, electronic, and ligand-binding properties as nickel-containing model complexes are oxidized and reduced through the Ni +1,+2, and +3 oxidation state range. The techniques employed have general applicability to the investigation of organometallic complexes in unstable redox forms.

Techniques

Ni(I) and Ni(III) complexes are unstable towards trace quantities of water or oxygen, and strict anaerobic techniques are required during sample preparation and measurement.[2] An XAS cell based on traditional glass blowing techniques was developed as shown in figure 1.[3] The key advantage of this design is that the synthesis and characterization of the sample(s) takes place within the same sealed vessel, with no external transfers. Drying of solvents, oxidations, reductions, addition of reagents and characterization via EPR, Optical, and XAS spectroscopies are all conveniently handled in specialized "arms".

A modified commercial cryostat, obtained from Cryo Industries of America, Inc. permits thermal control of samples to liquid helium temperatures. The cryostat is of the continuous flow variety in which the sample cell sits immersed in a cold vapor reservoir. A plexiglass collar which mates with the top of the cryostat is attached to the stem of the XAS cell during assembly. An o-ring cinch seal makes a leak-proof connection to the cell and provides mechanical support. The cryostat features an all-fiberglass construction in the sample area, minimizing the possibility of spurious background signal from the cryostat body. The system is equally suitable for LN₂ and LHe cryogens, and can operate from just over the cryogen boiling point to room temperature.

The model complexes used in these studies are cyclam (14-membered ring) derivatives as shown in figure 2.[4] XAS cells as described were charged with a Ni(II)-macrocycle salt and reduced with sodium amalgams to give the Ni(I) form or oxidized with silver perchlorate to give the Ni(III) form. CO and CO₂ adducts were formed via the introduction of circa 1 atmosphere of the appropriate gas. The EXAFS data was quantitatively analyzed with the MacXAFS analysis package [5] using both experimental standards and FEFF [6] simulations.

Results and Discussion

The absorption edge position has proven to be a reliable indicator of the nickel's oxidation state, especially within a series of structurally homologous complexes.[7] The XANES spectra shown in figure 3 confirm that a single oxidation (reduction) step shifts the edge towards higher (lower) energy by approximately 3 eV over the full range of Ni(I) to Ni(III). Square planar nickel complexes also show a characteristic pre-edge peak which has been assigned as a transition to a molecular orbital of largely 4p_z character. Addition of one and two ligands in the axial direction results in the progressive attenuation of this feature, an effect which can be explained as resulting from the raising of the 4p_z orbital energy from the overlap with charge density on the ligand(s). This provides a convenient independent means for determining the coordination numbers for EXAFS analysis.

The combination of the edge position and intensity of the pre-edge peak permit the investigation of ligand-to-metal or metal-to-ligand charge transfers. Figure 3 displays the XANES of a sequence of complexes generated as Ni(II)HTIM is reduced and made to coordinate carbon monoxide and carbon dioxide. The Ni(II) starting complex is five-coordinate, with one molecule of the solvent, acetonitrile, bound. Upon reduction, the fifth ligand is lost and a four-coordinate Ni(I) complex with a significant 4p_z peak results. When CO is added, the complex becomes five coordinate and the edge shifts (reversibly) approximately half-way back to the Ni(II) position. When CO₂ is added, the complex is again five coordinate, but the edge shifts essentially all the way back to the Ni(II) energy.

This is interpreted as resulting from the transfer of approximately 1/2 and 1 electron's charge, respectively, from the metal onto the ligand.

Quantitative results from non-linear least-squares fits of the isolated first shell EXAFS oscillations are presented in table 1. Reduction to Ni(I), which adds an electron to the unoccupied $d_{x^2-y^2}$ orbital, results in a dramatic distortion away from four-fold symmetry in the Ni-N bondlengths in NiTDI, as well as a general expansion of the macrocycle core. This effect is easily seen in the transforms shown in figure 4 as an amplitude reduction due to increased disorder. The HTIM and TMC ligands used here, however, have true four-fold symmetry in that all nitrogens are chemically identical, and as shown in the transform magnitude plots and quantitative results, they also remain symmetric when the metal is reduced. Hence we conclude that the previously observed asymmetric expansions are not a general property of Ni(I), but reflect specific structural properties of the macrocycles. The Ni(III)-N bondlengths are similar to those of Ni(II); the electron is removed from the d_{z^2} orbital which is orthogonal to the macrocycle plane. The Ni-CO bond is very short, but the CO₂ complex has a normal high-spin Ni(II) type length for the Ni-C bond.

Conclusion

The combination of strict anaerobic techniques with flexible sample handling permits the investigation of many systems of biological and bioinorganic significance with XAS methods. The sensitivity of the nickel edge to oxidation state and axial ligation make it unusually amenable to interpretation.

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References

- [1] W.L. Ellefson, W.B. Whitman and R.S. Wolfe, Proc. Natl. Acad. Sci. USA 79 (1982) 3707. Albracht, S.P.J.; Ankel-Fuchs, D.; Van der Zwaan, J.W.; Fontjin, R.D.; Thauer, R.K. Biochim. Biophys. Acta 1986, 870, 50. And references therein.
- [2] G. Jaun and A. Pfaltz, J. Chem. Soc., Chem. Commun. (1986), 1327
- [3] L.R. Furenlid, M.W. Renner and J. Fajer, Rev. Sci. Instrum. 61 (1990), 1326.
- [4] E. Fujita, to be published.
- [5] See contribution in these proceedings.
- [6] J.J. Rehr, J. Mustre de Leon, S.I. Zabinsky and R.C. Albers, J. Am. Chem. Soc. 113 (1991) 5135.
- [7] M.K. Eidsness, R.J. Sullivan, J.R. Schwartz, P.L. Hartzell, R.S. Wolfe, A. Flank, S.P. Cramer and R.A. Scott, J. Am. Chem. Soc. 108 (1986) 3120.
- [8] L.R. Furenlid, M.W. Renner, D.J. Szalda and E. Fujita, J. Am. Chem. Soc. 113 (1991) 883.

Table 1

Quantitative results of EXAFS analysis of Ni TMC, HTIM, and TDI complexes

Compound	N	R	$\Delta\sigma^2$	χ^2_{gof}	Standard	k range	T
Ni(2)TMC	4 N	1.97	.005	.043	Feff	3.1 - 12.5	RT
Ni(2)TMC + Pyridine	5 N	2.11	.006	.1	Feff	2.9 - 12.3	150° K
Ni(3)TMC Cl ₂	4 N	1.97	.000	.016	NiOEP NiCl ₂	3.6 - 11.9	RT
	2 Cl	2.48	.000				
Ni(2)HTIM•CH ₃ CN	6 N	2.08	.004	.018	Feff	3.0 - 11.2	150° K
Ni(1)HTIM	4 N	2.05	.005	.021	Feff	3.0 - 12.0	150° K
Ni(1)HTIM + CO	4 N	2.11	.004	.018	Feff	3.0 - 12.0	150° K
	1 C	1.86	.007				
Ni(1)HTIM + CO ₂	4 N	2.08	0.003	.069	Feff	3.0 - 12.0	150° K
	1 C	2.10	0.006				
Ni(2)TDI	4 N	1.93	.000	.012	Ni Cyclam	3.5 - 10.5	RT
Ni(1)TDI	2 N	1.97	.004	.020	Ni Cyclam		RT
	2 N	2.06	.003				

Figure Captions

Figure 1. Glass sample cell and associated cryostat for XAS investigations of redox reactions.

Figure 2. Structures of Ni macrocycle complexes. (HTIM = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradecane), (TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane), (TDI = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)

Figure 3. XANES spectra of Ni(II)HTIM, Ni(I)HTIM, Ni(I)HTIM+CO, Ni(I)HTIM+CO₂, and Ni(III)TMC.

Figure 4. Transform magnitudes of Ni(II) (solid) and Ni(I) (dashed) HTIM as contrasted with Ni(II) (solid) and Ni(I) (dashed) TDI.

Ni HTIM

Ni TMC

Ni TDI