1. Scalar coupling relaxation contributes primarily to transverse relaxation and line width and not to longitudinal relaxation. In most instances, an independently measured R_1 significantly slower than R_2 confirms the presence of scalar coupling relaxation.

2. Because it enters the ^{13}C relaxation equation as a squared term, a large coupling constant can broaden a resonance beyond recognition, removing much of the mystery from missing peaks whose absence is otherwise unexplainable.

3. Tris(diamine) complexes of metals such as chromium with few magnetically active nuclei or of rhodium that is not quadrupole relaxed will *not* contain a scalar coupling contribution to ^{13}C relaxation, and this convenient criterion for identifying *lel* ring conformations will not be available for analyzing the stereochemistry of complexes containing these materials.

Registry No. Tris((±)-2,3-butanediamine)cobalt(3+), 30768-19-5.

Contribution from the Departments of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221, and Purdue University, West Lafayette, Indiana 47907

Thin-Layer Spectroelectrochemical Studies of Copper and Nickel Unsymmetrical Schiff Base Complexes

R. C. Elder,*† Elmo A. Blubaugh, Jr.,†‡ William R. Heineman,† Philip J. Burke,§‖ and David R. McMillin§

Received November 24, 1982

The metal binding sites in proteins are highly developed for the purpose of efficiently performing very specific function(s). At least for copper- and zinc-binding proteins, the metal ion is often found in a site of low symmetry comprised of a mixed set of donor atoms (Table I). Moreover, the three-dimensional arrangement of the ligands in the resting state may be somewhat strained so as to facilitate the formation of some kinetically important state in a reaction sequence.[1] Of the variety of ligands utilized, the imidazole moiety of histidine is frequently involved thanks in part to the fact that its pK value occurs in the physiologically important range.[2]

Chelates derived from Schiff base condensation reactions form a convenient vehicle for preparing related small molecules, including, ultimately, synthetic representations of important protein centers. Ligands can be designed to incorporate mixed donor sets[3,4] as well as relevant geometrical constraints,[4-6] and their characteristic imine nitrogens can be viewed as analogues of histidine nitrogen. The ease with which these ligands form complexes with a variety of metals is also an advantage since the metal replacement technique has been so useful in the characterization of the protein systems.[7-9] Here we show that electrochemical methods can be a useful probe in systematic studies of low-symmetry complexes of this type.

Experimental Section

Materials and Nomenclature. Ligand abbreviations are based on the starting materials for the 1:1:1 condensations; sl, py, and pl denote the terminal ligands salicylaldehyde, pyridine-2-carbaldehyde, and pyrrole-2-carbaldehyde, respectively, and e, p, and t, in order, denote the bridging diamines ethylenediamine, propylenediamine, and 2,5-diamino-2,5-dimethylhexane. Thus plppl denotes the symmetrical Schiff base adduct of propylenediamine with 2 equiv of pyrrole-2-carbaldehyde. The syntheses of all complexes except [Ni(slppy)]BF_4 have been described.[3] The BF_4^- salt, synthesized in a fashion analogous to the preparation of the previously reported NO_3^- salt, was characterized by UV–vis and IR absorption spectroscopy. Except for the absence of bands at 1340 and 825 cm^{-1} attributable to NO_3^- and the presence of bands at 1070, 770, and 520 cm^{-1} attributable to BF_4^-,[10] the complex gave the same IR spectrum as [Ni(slppy)]NO_3.

Table I. Properties of the Binding Sites of Selected Copper- and Zinc-Containing Proteins

protein	metal	ligating atoms	no. of histidine ligands	approximate symmetry	ref
superoxide dismutase	Cu	N_4O	4	distorted square pyramidal	*a*
laccase[b]	Cu	N_3O_2?	3?	distorted square pyramidal	*c*
plastocyanin	Cu	N_2SS^*	2	distorted tetrahedral	*d*
alcohol dehydrogenase	Zn	NS_2O	1	distorted tetrahedral	*e*
carbonic anhydrase	Zn	N_3O	3	distorted tetrahedral	*f*

[a] Tainer, J. A.; Getzoff, E. D.; Beem, K. M. Richardson, J. S.; Richardson, D. C. *J. Mol. Biol.* **1982**, *160*, 181. [b] Type 2 copper site. [c] Goldberg, M.; Vuk-Pavlovic, S.; Pecht, I. *Biochemistry* **1980**, *19*, 5181. [d] Freeman, H. C. In "Coordination Chemistry"; Laurent, J. P., Ed.; Pergamon Press: New York, 1981; Vol. 21, p 29. [e] Branden, C.-I.; Jornvall, H.; Eklund, H.; Furugren, B. *Enzymes, 3rd Ed.* **1975**, *11*, Chapter 3. [f] Kannan, K. K.; Nostrand, B.; Fridborg, K.; Lovgren, S.; Ohlsson, A.; Petef, M. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 51.

Instrumentation. UV–visible spectra were recorded with a Harrick Rapid Scanning spectrophotometer (RSS-B) with data acquisition and display controlled by a microprocessor-based computer system.[11] The sample compartment contained an optically transparent thin-layer electrode (OTTLE) and Lucite cell holder, both of which were maintained in an argon atmosphere with an enclosed Lucite box. Two opposing 1-in.-diameter holes were drilled into the box and two quartz plates inserted to provide a gas-tight container with a quartz optical path. Electrochemistry was performed with a 173 potentiostat/galvanostat (Princeton Applied Research Corp.) driven either by a 175 Universal Programmer for cyclic voltammetry or by the microprocessor system for spectropotentiostatic experiments. The OTTLE was constructed from 500 lines/in. gold minigrid and quartz plates as described elsewhere.[12] The OTTLE was immersed in a sample cup containing a coiled-platinum-wire auxiliary electrode and an aqueous saturated sodium chloride calomel electrode (SSCE) of the H-cell type. The SSCE was separated from the sample solution via a salt bridge that was constructed from heat-shrink Teflon tubing with a Vycor plug. The salt bridge contained 0.4 M supporting electrolyte

† University of Cincinnati.
‡ Present address: National Bureau of Standards, Washington, DC 20234.
§ Purdue University.
‖ Present address: Department of Chemistry, Queen Mary College, London E1 4NS, England.

(1) Williams, R. J. P. *Inorg. Chim. Acta, Rev.* **1971**, *5*, 137.
(2) Freeman, H. C. in "Inorganic Biochemistry"; Eichhorn, G. L., Ed.; Elsevier: New York, 1973; Vol. I, Chapter 4.
(3) Burke, P. J.; McMillin, D. R. *J. Chem. Soc., Dalton Trans.* **1980**, 1794.
(4) Holm, R. H.; Everett, G. W.; Chakravorty, A. *Prog. Inorg. Chem.* **1966**, *7*, 83.
(5) Elder, R. C.; Hill, M. C. *Inorg. Chem.* **1979**, *18*, 729.
(6) Engeseth, H. R.; McMillin, D. R.; Ulrich, E. L. *Inorg. Chim. Acta* **1982**, *67*, 145.
(7) Hughes, M. N. "The Inorganic Chemistry of Biological Processes", 2nd ed.; Wiley: New York, 1981; Chapter 4.
(8) Hauenstein, B. L.; Jr.; McMillin, D. R. In "Metal Ions in Biological System"; Sigel, H., Ed.; Marcel Dekker: New York, 1981; Vol. 13, Chapter 10.
(9) Zeppezauer, M. In "The Coordination Chemistry of Metalloenzymes"; Bertini, I., Drago, R. S., Luchinat, C., Eds.; Reidel Press: Boston, MA, 1983; Chapter 8, pp 99–122.
(10) Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd ed.; Wiley: New York, 1978.
(11) Hurst, R. W. Ph.D. Thesis, University of Cincinnati, 1980.
(12) Rohrbach, D. F.; Deutsch, E.; Heineman, W. R. In "Characterization of Solutes in Nonaqueous Solvents"; Mamantov, G., Ed.; Plenum Press: New York, 1978.

0020-1669/83/1322-2777$01.50/0

Table II. Electrochemical Results in DMF (V vs. SSCE)

compd	ligating atoms	voltammetry E_{red}	voltammetry E_{ox}	voltammetry $E^{\circ\prime}$	spectroelectrochemistry $E^{\circ\prime}$	spectroelectrochemistry n	ref
$[Cu(slppy)]NO_3$	N_3O	−0.760	−0.480	−0.620	−0.622	0.93	*a*
Cu(sltsl)	N_2O_2	−0.788	−0.550	−0.669	−0.657	0.95	*b*
Cu(plppl)	N_4	−1.050	−0.675	−0.863	−0.841	1.06	*a*
Cu(slppl)	N_3O	−1.100	−0.850	−0.975			*a*
Cu(slpsl)	N_2O_2	−1.150	−0.825	−0.988			*a*
Cu(slesl)	N_2O_2	−1.255	−1.060	1.158			*c*
$[Cu(pyppy)](ClO_4)_2$	N_4	−0.289	−0.139	−0.214			*d, e*
$[Ni(slppy)]NO_3$	N_3O	−0.85					*a*
$[Ni(slppy)]BF_4$	N_3O	−0.90					*a*
Ni(slppl)	N_3O	−1.67	1.40	−1.54	−1.527	1.04	*a*
Ni(plppl)	N_4	−1.82	−1.37	−1.60	−1.562	0.98	*a*

[a] This work. [b] Reference 5. [c] Reference 12. [d] Measured in acetonitrile. [e] Nikles, D. E.; Powers, M. J.; Urbach, F. L. *Inorg. Chim. Acta* 1979, *37*, L499.

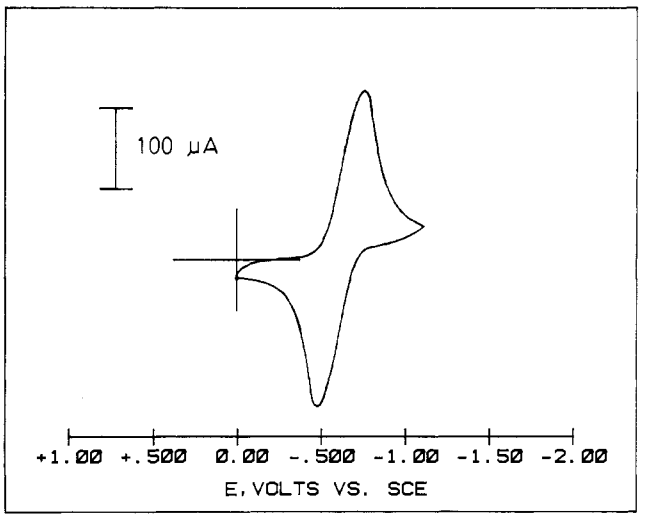

Figure 1. Thin-layer cyclic voltammogram of 1.0 mM $[Cu(slppy)]^+$ in 0.4 M TEAP/DMF (scan rate 5 mV/s).

in DMF. All potentials are vs. the SCCE.

Procedure. Solutions of the Schiff base complexes were prepared in dimethylformamide (DMF) (Fisher Certified/MCB) with 0.4 M polarographic grade tetraethylammonium perchlorate (TEAP) or 0.4 M tetraethylammonium tetrafluoroborate (G. F. Smith). The DMF was slurried over 3-Å molecular sieves ($^1/_{16}$-in "pellets" MCB) for 24 h. The solvent was then transferred to a vacuum distillation flask and slurried with calcium hydride (MCB) for 24 h. The solvent was subsequently distilled with the middle 50% fraction being kept. The solvent was handled under high-purity nitrogen (Linde) and stored in an inert-atmosphere (argon) drybox where all solutions were prepared and stored. Sample solutions were transferred to a gas train and thoroughly deoxygenated by extended argon bubbling with subsequent transfer to the electrochemical cell via Teflon tubing under a positive argon pressure.[13] The Lucite box was positioned in the sample chamber of the spectrophotometer, and an internal blanket of argon was maintained in the box throughout the experiment. The spectropotentiostatic experiment was performed as previously described.[12,14,15]

Results and Discussion

The electrochemical results obtained in this study as well as relevant results from the literature are compiled in Table II. Cyclic voltammograms have been run for each compound; representative results obtained in a thin-layer cell are depicted in Figure 1 for the case of $[Cu(slppy)]^+$. The peak separation of 280 mV is attributed to *iR* drop within the OTTLE and possible quasi-reversbility of the redox process. In most instances repetitive scans yielded superimposable voltammograms, indicating stability of the M(II) and M(I) forms of the couple where M denotes either copper or nickel depending on the complex involved.

Table III. Spectrophotometric Data for Electrogenerated M(I) Species

M(I)	ligand	λ_{max}, nm (ϵ, M^{-1} cm^{-1})	ref
Cu	slppy	397 (2500)	*a*
Cu	sltsl	405 (13 000), 450 (24 150)	*b*
Cu	plppl	<350	*a*
Ni	plppl	<325	*a*
Ni	slppl	325 (28 500)	*a*

[a] This work. [b] Reference 5.

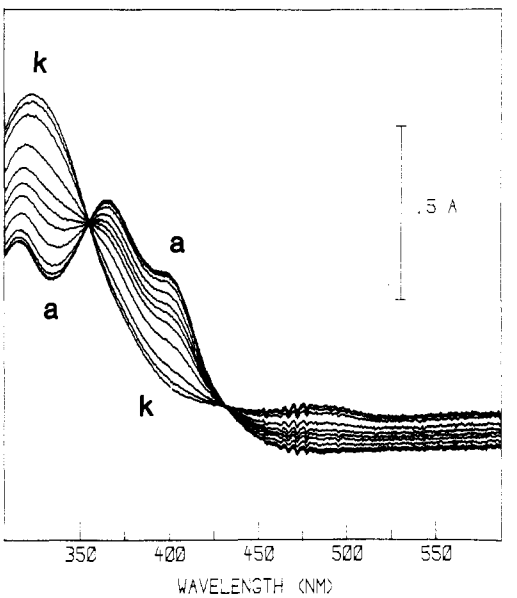

Figure 2. Spectra of 1.0 mM Ni(slppl) in 0.4 M TEAP/DMF in an OTTLE for the following potentials (V vs. SSCE): (a) −1.435; (b) −1.460; (c) −1.485; (d) −1.510; (e) −1.525; (f) −1.535; (g) −1.545; (h) −1.560; (i) −1.585; (j) −1.610; (k) −1.635. Spectrum a has the maximum absorbance and spectrum k the minimum absorbance at 400 nm.

For these samples the spectropotentiostatic technique has been used to obtain an independent estimate of $E^{\circ\prime}$ as well as n. This technique also provides an absorbance spectrum of the electrogenerated species. It involves applying a series of potentials to the OTTLE and recording a spectrum for each potential after equilibrium is attained.[12,15] Spectrophotometric data for the electrochemically generated species are presented in Table III. Figure 2 shows the spectral changes that accompany the reduction of Ni(slppl). Using the absorbances at 390 nm from Figure 2, a Nernstian plot gives a straight line,

(13) Rohrbach, D. F. Ph.D. Thesis, University of Cincinnati, 1980.
(14) Rohrbach, D. F.; Deutsch, E.; Heineman, W. R.; Pasternack, R. F. *Inorg. Chem.* **1977**, *16*, 2650.
(15) DeAngelis, T. P.; Heineman, W. R. *J. Chem. Educ.* **1976**, *53*, 594.

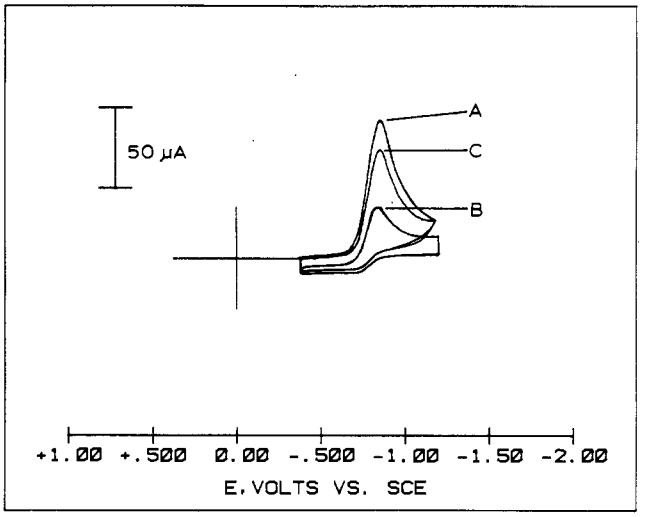

Figure 3. Thin-layer cyclic voltammograms of 1.0 mM $[Ni(slppy)]^+$ in 0.4 M TEAP/DMF (scan rate 5 mV): (A) initial cyclic voltammogram started at −0.300 V in negative direction; (B) second cycle showing a greatly diminished reduction wave; (C) cyclic voltammogram scan started after resting at −0.300 V for 15 min.

from which $E^{\circ\prime} = -1.527$ V and $n = 1.04$ are obtained. Thus, these techniques of spectroelectrochemistry allow relatively precise determination of $E^{\circ\prime}$ (to a few millivolts) and n as well as provide the spectra of otherwise rather inaccessible species.

For the copper systems the results are in accord with the general trends established by Patterson and Holm.[16] One point worth noting is that $E^{\circ\prime}$ is little changed whether the terminal group is a deprotonated phenolic oxygen or a deprotonated pyrrolic nitrogen. However, replacing either of these groups by a pyridine nitrogen gives rise to a dramatic positive shift in $E^{\circ\prime}$. Such a shift may result from a stabilization of the Cu(I) species or a destabilization of the Cu(II) moiety. Both of these may occur here. Pyridine, which is capable of significant back-bonding,[17] is expected to stabilize the Cu(I) moiety. That the $E^{\circ\prime}$ of Cu(sltsl) is significantly more positive than those of Cu(slesl), Cu(slpsl), Cu(slppl), and Cu(plppl) illustrates the fact that imposing pseudotetrahedral geometry also stabilizes Cu(I) while destabilizing Cu(II).[5,16]

Where measurable, the $E^{\circ\prime}$ values of the nickel complexes are much more negative than those of the corresponding copper systems (Table II), illustrating the fact that the Ni(I) state is much less accessible than is Cu(I). For the same reason the ligand-to-metal charge-transfer bands of Ni(II) proteins occur at much higher energies than the analogous bands of Cu(II) proteins.[8]

The thin-layer cyclic voltammogram of $[Ni(slppy)]^+$ is quite different from the normal case, as shown in Figure 3. The first scan, A, appears to represent an irreversible process. On the negative scan a reduction peak occurs, but on the positive scan no reoxidation wave is observed and no value of $E^{\circ\prime}$ may be assigned. This is most easily ascribed to some unknown chemical (or physical) reaction that occurs rapidly following electrochemical reduction to remove the reduced species so that the reverse oxidation is not electrochemically possible. Quite remarkably, the system still appears to be chemically reversible. Scan B, begun immediately after scan A, shows much less material available for reduction; however, if the system is held at a potential positive of the reduction potential for 15 min and then scan C is begun, the reduction wave, albeit somewhat reduced in magnitude relative to scan A, is again observed. Whether the ligand or the metal center is reduced and what the nature of the follow-up reaction is are questions that cannot be answered at present. Two possibilities that might explain the follow-up reaction are disproportionation of Ni(I) or precipitation of the reduced form of the complex.

Acknowledgment. P.J.B. and D.R.M. acknowledge NIH Grant No. GM 22764; W.R.H. acknowledges NSF Grant No. CHE 79-11872.

Registry No. $[Cu(slppy)]NO_3$, 75675-06-8; Cu(plppl), 21297-44-9; Cu(slppl), 75675-09-1; Cu(slpsl), 21051-65-0; Cu(slesl), 14167-15-8; $[Cu(pyppy)](ClO_4)_2$, 15772-23-3; $[Ni(slppy)]NO_3$, 75675-08-0; $[Ni(slppy)]BF_4$, 86688-20-2; Ni(slppl), 75675-10-4; Ni(plppl), 15158-90-4.

(16) Patterson, G. S.; Holm, R. H. *Bioinorg. Chem.* **1975**, *4*, 257.
(17) Elder, R. C. *Inorg. Chem.* **1968**, *7*, 2316.

Contribution from Ames Laboratory and the Department of Chemistry, Iowa State University, Ames, Iowa 50011

Reactions of Bis(dimethylglyoximato)cobalt(II) Complexes with *tert*-Butyl Hydroperoxide

James H. Espenson* and Jon D. Melton

Received December 20, 1982

The reaction of the cobalt(II) cobaloxime[1] $Co(dmgH)_2OH_2$ with various alkyl hydroperoxides $RC(CH_3)_2OOH$ leads, in aqueous or semiaqueous solution, to an organocobalt complex, $RCo(dmgH)_2OH_2$.[2] This product, the net stoichiometry (eq 5), and the rate law (eq 1) (shown here for *tert*-butyl hydroperoxide)

$$-d[Co(dmgH)_2OH_2]/dt = 2k_1[Co(dmgH)_2OH_2][(CH_3)_3COOH] \quad (1)$$

are all readily accounted for by the mechanism shown in Scheme I.

Scheme I

$$(CH_3)_3COOH + Co(dmgH)_2OH_2 \xrightarrow{k_1} HOCo(dmgH)_2OH_2 + (CH_3)_3CO\cdot \quad (2)$$

$$(CH_3)_3CO\cdot \xrightarrow{\text{fast}} (CH_3)_2CO + \cdot CH_3 \quad (3)$$

$$\cdot CH_3 + Co(dmgH)_2OH_2 \xrightarrow{\text{fast}} CH_3Co(dmgH)_2OH_2 \quad (4)$$

$$\text{net: } (CH_3)_3COOH + 2Co(dmgH)_2OH_2 = HOCo(dmgH)_2OH_2 + (CH_3)_2CO + CH_3Co(dmgH)_2OH_2 \quad (5)$$

In contrast, essentially the same reaction in benzene, carried out so as to produce the cobalt(II) complex by photolysis of an alkyl(pyridine)cobaloxime, was reported to produce (*tert*-butylperoxy)cobaloxime, $(CH_3)_3COOCo(dmgH)_2py$.[3] There can be little doubt of its identity, as the cumylperoxy analogue, obtained analogously, was characterized by single-crystal X-ray diffraction and all of the alkylperoxy compounds were characterized by spectroscopic methods.[3] A direct examination of the reaction between $Co(dmgH)_2py$ and $(CH_3)_3COOH$ in benzene was undertaken to seek an explanation for such a major effect of solvent change.

(1) Cobaloxime = $Co(dmgH)_2$ (Schrauzer, G. N. *Acc. Chem. Res.* **1968**, *4*, 97), where $dmgH^-$ represents the monoanion of dimethylglyoxime (=2,3-butanedione dioxime).
(2) Espenson, J. H.; Martin, A. H. *J. Am. Chem. Soc.* **1977**, *99*, 5953.
(3) Giannotti, C.; Fontaine, C.; Chiaroni, A.; Riche, C. *J. Organomet. Chem.* **1976**, *113*, 57.

0020-1669/83/1322-2779$01.50/0