the case of *cis*-$[(PhCH_2)_2Co(bpy)_2]^+$, however, $PhCH_2CoTPP$ is obtained exclusively (Table I). Such selective formation of $PhCH_2CoTPP$ may be ascribed to the slow reductive elimination of two benzyl ligands as compared with the other alkyl ligands of *cis*-$[R_2Co(bpy)_2]^{2+}$ (R = Me and Et), as reported previously.[9]

A quantitative evaluation of the contribution of such electron-transfer processes in the reductive alkylation of $CoTPP^+$ by alkylcobalt(III) complexes may be achieved by comparing the observed rate constants with those predicted by the Marcus theory for the rates of outer-sphere electron-transfer reactions.[18] The second-order rate constants for the reduction of $Co(TPP)ClO_4$ by alkylmetals in MeCN at 298 K were determined by monitoring the disappearance and rise of the absorption bands at 434 and 407 nm due to the decay of $CoTPP^+$ and the formation of RCoTPP, respectively.[19,20] The reported values of self-exchange rate constants of alkylcobalt(IV/III) complexes[9] and a cobalt(III/II) porphyrin[21] together with the electron-transfer equilibrium constants, obtained from the one-electron oxidation potentials of the alkylcobalt(III) complexes[9] and the one-electron reduction potential of $CoTPP^+$ in MeCN,[21] constitute a satisfactory basis for accounting for the k_{obs} values in light of the Marcus relation.[18] The calculated electron-transfer rate constants k_{calc} and the observed second-order rate constants are listed in Table II. The k_{calc} values are about the same order of magnitude as the corresponding k_{obs} values, although most k_{obs} values are somewhat smaller than the k_{calc} values.[22] Such agreement indicates that the rate-determining step for the reductive alkylation of $CoTPP^+$ by alkylcobalt(III) complexes mainly consists of the electron-transfer process, as shown in Scheme I.[22]

The k_{calc} values of R_4Sn are also evaluated by the same manner as the case of alkylcobalt(III) complexes, using the reported values of self-exchange rate constants and the one-electron-oxidation potentials of R_4Sn,[13] and are listed in Table I, together with the k_{obs} values for the reduction of $CoTPP^+$ by R_4Sn. In contrast with the case of alkylcobalt(III) complexes, the k_{calc} values of R_4Sn are 10^2–10^{13} times smaller than the k_{obs} values, as shown in Table II. A close scrutiny of the data reveals that the deviation from the calculated values of outer-sphere electron transfer is the most pronounced with the least hindered tetraalkyltin, i.e., Me_4Sn. The magnitude of the deviation decreases with increasing the size of the alkyl group (Table II). Such a trend must reflect steric effects that perturb the inner-sphere coordination of R_4Sn to $CoTPP^+$ in the transition state for the reductive alkylation, which is clearly distinguished from the outer-sphere electron-transfer processes involved in the corresponding reactions of alkylcobalt(III) complexes.[23]

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(17) The bis complex $[Co(bpy)_2]^{2+}$ shown in Scheme I may be converted to the tris complex $[Co(bpy)_3]^{3+}$, which was identified by ^1H NMR spectroscopy, since thermodynamic considerations indicate that the tris complex is more stable than the bis complex: Fukuzumi, S.; Ishikawa, K.; Tanaka, T. *Organometallics* **1987**, *6*, 358.

(18) The Marcus relation for the rate constant of the electron transfer from the reductant (1) to the oxidant (2), k_{12}, is given by $k_{12} = (k_{11}k_{22}k_{12}f)^{1/2}$, where k_{11} and k_{22} are the rate constants of the corresponding self-exchanges and K_{12} is the equilibrium constant for the electron-transfer reaction. The K_{12} value is obtained from the oxidation potential of the reductant, $E°_{\mathrm{ox}}$, and the reduction potential of the oxidant, $E°_{\mathrm{red}}$ by using the following equation: $\log K_{12} = (-2.3RT/F)^{-1}(E°_{\mathrm{ox}} - E°_{\mathrm{red}})$. The parameter f is given by $\log f = (\log K_{12})^2/[4 \log (k_{11}k_{22}/Z^2)]$, where Z, the frequency factor, is taken to be 1×10^{11} M^{-1} s^{-1}: Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.

(19) Kinetic measurements were carried out by using a Union RA-103 stopped-flow spectrophotometer and a Union SM-401 spectrophotometer under the pseudo-first-order conditions where the concentrations of alkylmetals were maintained at >10-fold excess of the $CoTPP^+$ concentration with half-lives shorter than 10 s and much longer than 10 s, respectively. The second-order rate constants were determined with $Co(TPP)ClO_4$ in MeCN instead of Co(TPP)Cl in $CHCl_3$/MeCN (5:1 v/v), since the thermodynamic parameters required for calculation of the electron-transfer rate constants have been obtained in MeCN.[9,13,21]

(20) The absorption maximum of RCoTPP (λ_{max} = 407 nm)[7b] is different from λ_{max} of CoTPP (412 nm).[19]

(21) Fukuzumi, S.; Mochizuki, S.; Tanaka, T. *Inorg. Chem.* **1989**, *28*, 2459.

(22) The rate of cleavage of the cobalt–carbon bond following the electron transfer may also be involved partially in the rate-determining step, when the k_{obs} values of the overall reactions become smaller than the k_{calc} values of the electron-transfer processes. In the case of *trans*-$[Me_2Co(DpnH)]$, the k_{obs} value is somewhat larger than the k_{calc} value, indicating contribution of an inner-sphere process.[13,21,23]

(23) For comparison between outer-sphere and inner-sphere electron-transfer processes, see: Reference 13. Klingler, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 5839. Kochi, J. K. *Angew. Chem.* **1988**, *100*, 1331. Haim, A. *Prog. Inorg. Chem.* **1983**, *30*, 273. Seaman, G. C.; Haim, A. *J. Am. Chem. Soc.* **1984**, *106*, 1319.

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Facile α/β Diastereomerism in (2,2,2-Trifluoroethyl)cobalt Corrins

In a recent publication,[1] unequivocal evidence was presented that reductive alkylation of cobinamides (Cbi's) with $^{13}CH_3I$ leads essentially exclusively to formation of the β-alkylcobinamide (i.e., CH_3 in the "upper" axial position). We now wish to report a startlingly different result upon reductive alkylation of cobinamide with CF_3CH_2I.

When Factor B[2,3] was reduced with zinc/acetic acid and alkylated with CF_3CH_2I,[4] the monocationic alkylcobinamide fraction from cation-exchange chromatography showed two bands by HPLC[5] (mobility relative to CNCbl, R_{CN} = 1.23 and 1.48), both of which were readily converted to diaquocobinamide ($(H_2O)_2Cbi$, R_{CN} = 0.77) upon aerobic photolysis. The two compounds were readily separated by semipreparative HPLC. The more slowly migrating compound had a UV–visible spectrum (Figure 1A, dashed line) essentially identical, above 300 nm, with that of the base-off species of the previously characterized[6] CF_3CH_2Cbl (Figure 1B, dashed line). Moreover, its ^{19}F NMR spectrum consisted of a triplet at 57.38 ppm (Table I), J = 13.9 Hz, again essentially identical with that of the base-off CF_3CH_2Cbl (Table I). We conclude that this compound is the β-diastereomer of CF_3CH_2Cbi, i.e. α-(H_2O)-β-$(CF_3CH_2)Cbi$ (hereafter β-CF_3CH_2Cbi). The other compound (R_{CN} = 1.23) had a UV–visible spectrum (Figure 1A, solid line) quite similar to that of β-CF_3CH_2Cbi, except that its longest wavelength band (i.e. the α-band) is red-shifted 27 nm (Table I). Its spectrum was cleanly converted to that of $(H_2O)_2Cbi$[7] upon aerobic photolysis and to that of $(CN)_2Cbi$[8] upon aerobic photolysis in excess cyanide. Its ^{19}F NMR resonance (δ = 59.52 ppm, J = 14.7 Hz) was distinctly downfield from those of base-off CF_3CH_2Cbl and base-on CF_3CH_2Cbl (Table I). Both compounds were also characterized by FAB-MS (glycerol matrix). The positive-ion mass spectra were virtually identical, with a parent ion mass 1072.8 for β-CF_3CH_2Cbi and 1072.9 for the other compound (calculated for $M^+ - H_2O$[9]

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(1) Brown, K. L.; Peck-Siler, S. *Inorg. Chem.* **1988**, *27*, 3548–3555.

(2) Factor B is a mixture of the diastereomeric cyanoaquocobinamides α-(CN)-β-(H_2O)Cbi and α-(H_2O)-β-(CN)Cbi.

(3) Renz, P. *Methods Enzymol.* **1971**, *18*, 82–92.

(4) Typical preparative-scale conditions: 100 mg of Factor B (0.09 mmol) in 25 mL of 10% acetic acid was purged with argon for 1 h. Zinc wool, 2.0 g (briefly freshed by swirling in 1.0 N HCl), was introduced and reduction allowed to proceed for 30 min under argon. A 1.0-mL aliquot of CF_3CH_2I (10 mmol) was injected, and after 2 min the reaction mixture was desalted by either passage through an Amberlite XAD-2 column or extraction through phenol. Purification of the alkylcobinamides was effected by ion-exchange chromatography on SP-Sephadex, Na^+ form, the RCbi's eluting in 0.1 M sodium acetate, pH 5.0.

(5) Jacobsen, D. W.; Green, R.; Brown, K. L. *Methods Enzymol.* **1986**, *123*, 14–22.

(6) Brown, K. L.; Hakimi, J. M.; Nuss, D. M.; Montejano, Y. D.; Jacobsen, D. W. *Inorg. Chem.* **1984**, *23*, 1463–1471.

(7) Baldwin, D. A.; Betterton, E. A.; Pratt, J. M. *J. Chem. Soc., Dalton Trans.* **1983**, 217–233.

(8) Barker, H. A.; Smyth, R. D.; Weissbach, H.; Toohey, J. I.; Ladd, J. N.; Volcani, B. E. *J. Biol. Chem.* **1960**, *235*, 480–488.

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Table I. HPLC Mobilities and Spectroscopic Properties of (2,2,2-Trifluoroethyl)cobalt Corrins

compd[a]	R_{CN}[b]	$\delta_{^{19}F}$,[c] ppm	J_{HF}, Hz	λ_{max},[d] nm
β-CF_3CH_2Cbi	1.48	57.38	13.9	455
α-CF_3CH_2Cbi	1.23	59.52	14.7	482
β-CF_3CH_2Cbl	1.41			
base-on[e]		58.97	14.4	530
base-off[f]		57.40	13.5	454
α-CF_3CH_2Cbl	1.35	59.53	14.5	482

[a] β signifies the upper axial ligand; α, the lower. [b] HPLC mobility relative to that of CNCbl.[5] [c] Nicolet NT200 superconducting NMR spectrometer operating at 188.239 MHz. Chemical shifts are relative to external fluorobenzene; positive shifts, downfield. [d] Maximum of the longest wavelength (or α) band in the visible spectrum. [e] In water. [f] In 0.5 M HCl (pH 0.30) or 0.21 M H_2SO_4 (pH 0.50) $pK_{base\text{-}off}$ 2.60.[6]

1073.2). Both products were further characterized by GC-MS analysis of the gaseous products formed from their organic ligands upon anaerobic photolysis and pyrolysis.[11] Pyrolysis of both compounds produced only 1,1-difluoroethylene (ca. 95%) and 1,1,1-trifluoroethane, while photolysis produced the same two products with the alkane predominating (ca. 75%). We conclude that the slower migrating organocobinamide product from reductive alkylation of Factor B with CF_3CH_2I is the α-diastereomer α-(CF_3CH_2)-β-(H_2O)Cbi (hereafter α-CF_3CH_2Cbi).

This surprising result prompted us to reexamine the products formed upon reductive alkylation of H_2OCbl with CF_3CH_2I, previously reported to yield the expected β-isomer of CF_3CH_2Cbl.[6] Upon cation-exchange chromatography of a desalted reaction mixture, a red band eluting with water was closely followed by a yellow band. The mobility of the yellow band could be significantly retarded by lowering the pH of the desalted reaction mixture to 5.0. The yellow material had a UV-visible spectrum (Figure 1C) which was identical, above 300 nm, with that of α-CF_3CH_2Cbi. It was readily converted to H_2OCbl by aerobic photolysis (UV-vis and HPLC, R_{CN} = 0.82) and to $(CN)_2$Cbl by aerobic photolysis in the presence of excess cyanide (by UV-vis).[8] Its UV-visible spectrum (Figure 1C) was pH-independent above 300 nm, unlike that of the red CF_3CH_2Cbl (Figure 1B), but showed spectral changes in the UV region consistent with the protonation of a pendent, but uncoordinated, dimethylbenzimidazole nucleotide.[6] The pK_a for this acid dissociation reaction was 5.54 by potentiometric titration (ionic strength 1.0 M, 25.0 °C). The ^{19}F NMR resonance of the yellow material was virtually identical with that of the α-diastereomer of CF_3CH_2Cbi (Table I). Also, its FAB mass spectrum (parent ion mass 1412.8, calculated for $MH^+ - H_2O$[12] 1413.4) was identical with that of the red CF_3CH_2Cbl (parent ion mass 1413.4). The yellow material was also further characterized by GC-MS analysis of the organic products of its anaerobic pyrolysis and photolysis.[11] Again, CF_2CH_2 was the predominant product (ca. 84%) of anaerobic pyrolysis while photolysis produced a 60:40 mixture of CF_3CH_3 and CF_2CH_2. Similar results were obtained with the red CF_3CH_2Cbl. We conclude that this yellow organocobalt corrin is the α-isomer of CF_3CH_2Cbl (hereafter α-CF_3CH_2Cbl), in which coordination of the pendent dimethylbenzimidazole nucleotide is blocked by the α-organic ligand. In two independent preparations, the total yield of CF_3CH_2Cbl's was 40%, of which 17% was α-CF_3CH_2Cbl and 83% was β-CF_3CH_2Cbl.

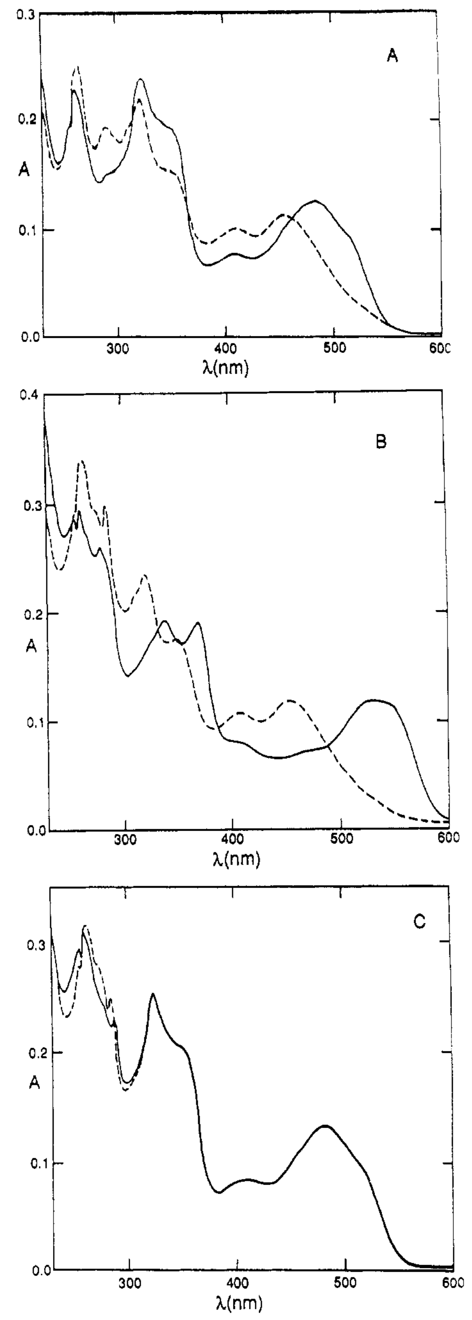

Figure 1. (A) Electronic spectra of the (2,2,2-trifluoroethyl)cobinamides, 1.25 × 10^{-5} M, in water: (solid line) α-CF_3CH_2Cbi; (dashed line) β-CF_3CH_2Cbi. (B) Electronic spectra of β-(2,2,2-trifluoroethyl)cobalamin, 1.25 × 10^{-5} M: (solid line) base-on β-CF_3CH_2Cbl, pH 6.8 in 0.1 M potassium phosphate buffer; (dashed line) base-off β-CF_3CH_2Cbl, pH 0.50 in 0.3 M HCl. (C) Electric spectra of α-(2,2,2-trifluoroethyl)cobalamin, 1.25 × 10^{-5} M: (solid line) pH 6.8 in 0.1 M potassium phosphate buffer; (dashed line) pH 0.5 in 0.3 M HCl.

Careful analytical HPLC determinations of CF_3CH_2Cbi product ratios from both preparative-scale and analytical-scale[13] reaction mixtures show that the RCbi product fraction from reductive alkylation of Factor B with CF_3CH_2I is 87.4 ± 3.7% α-CF_3CH_2Cbi (average of 35 determinations). This is in stark contrast to reductive alkylation of Factor B with CH_3I, which gives

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(9) As reported by Hay and Finke[10] for 5′-deoxyadenosylcobinamide, the parent cation is a 5-coordinate RCbi (i.e. $M^+ - H_2O$).

(10) Hay, B. P.; Finke, R. G. *J. Am. Chem. Soc.* **1987**, *109*, 8012–8018.

(11) Finnigan MAT TSQ70 tandem mass spectrometer equipped with a 30 m × 0.539 mm GS-Q megabore column, temperature programmed from 40 to 200 °C at 16 °C/min. Samples (ca. 1 mg) for anaerobic photolysis (in 0.5 mL of 5% isopropanol) and pyrolysis (dry solid) were prepared in 1.0-mL Reactivials (Pierce) closed with Teflon Mininert valves (Pierce) as described previously.[6] Photolysis was effected by illumination with a 275-W incandescent lamp for 3 h at a distance of 5.0 cm, and pyrolysis, by heating the vials for 60 s in a 220 °C oil bath. CF_2CH_2: retention time 1.8 min; mass spectrum *m/e* (relative abundance, ion) 64 (100%, M^+), 63 (15%, $M^+ - H$), 45 (59%, $M^+ - F$), 44 (48%, $M^+ - HF$), 33 (23%, $M^+ - CF$), 31 (35%, $M^+ - CH_2F$). CF_3CH_3. Retention time 2.6 min. Mass spectrum (*m/e*, relative abundance, ion) 84 (1.5%, M^+), 69 (100%, $M^+ - CH_3$), 65 (30%, $M^+ - F$), 64 (9.0%, $M^+ - HF$), 45 (9.0%, $M^+ - HF_2$).

(12) For the zwitterionic RCbl's, the positive-ion parent mass contains a proton from the matrix. As was the case with AdoCbi[10] and the CF_3CH_2Cbi's, the parent ion of the α-isomer of CF_3CH_2Cbl is missing the (presumed) axial H_2O ligand.

(13) Factor B varied from 2.0 × 10^{-5} to 3.3 × 10^{-3} M, and CF_3CH_2I varied from 2.0 × 10^{-3} to 0.39 M, representing an excess of alkylating agent ranging from 11.2-fold to 19 511-fold.

at least 95% of the β-diastereomer.[1] The latter observation prompted speculation that in the case of CH_3Cbi the products were under kinetic control, with alkylation of the β-face being sterically favored due to congestion at the α-face from the b, d, and e propionamide side chains and the f secondary amide side chain. We have consequently attempted to determine if for the CF_3CH_2Cbi's the products are under equilibrium control, with initial alkylation occurring at the β-face followed by equilibration of the diastereomers via a pathway that is not available (or more likely of too high energy) in the case of CH_3Cbi. Time-resolved determination of the product ratios for the CF_3CH_2Cbi's under a variety of conditions[13] showed that the final product ratio (i.e. 6.9:1, α:β) is established within 10-20 s of introduction of alkylating agent and remains unchanged throughout the reaction period (up to 30-60 min). Interestingly, both diastereomers of CF_3CH_2Cbi proved to be quite unstable with respect to reductive dealkylation by zinc/acetic acid ($T_{1/2} \sim 1$ min) so that net alkylation in this system represents a steady-state situation. Consequently, at long reaction times (30-60 min) the total yield of alkylcobinamides is reduced, presumably due to depletion of alkylating agent. At 0 °C, the net alkylation yield rose from about 25% to 46% over the first 4 min and then gradually declined to less than 20% at 1 h, while the ratio of diastereomers remained constant throughout. These observations are consistent with kinetic control of products, with the rate of α-face attack exceeding that of β-face attack by about 7-fold, but this conclusion is difficult to accept in light of the contrary results with CH_3Cbi. The results are also consistent with the CF_3CH_2Cbi products being under equilibrium control, provided that the rate of equilibration of the diastereomeric CF_3CH_2Cbi's is quite fast, even exceeding the rate of initial alkylation at 0 °C. The exact mechanism of formation of the diastereomeric CF_3CH_2Cbi's and the extreme difference in behavior of the CF_3CH_2Cbi's and CH_3Cbi are currently under intense investigation.[14]

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(14) Kraütler and Caderas[15] have reported that treatment of heptamethyl cob(I)yrinate in toluene/tetrahydrofuran with methyl tosylate leads exclusively to the heptamethyl β-methylcobyrinate (75% yield) while treatment with CH_3I yields the heptamethyl α-methylcobyrinate (71% yield) along with 7% of the β-isomer. The reasons for the different outcomes when cobinamide in water and cobester in an organic medium are reductively alkylated with CH_3I are not at all clear. As yet, we have been unable to obtain any products by reductive alkylation of cobinamides with trifluoroethyl tosylate.

(15) Kraütler, B.; Caderas, C. *Helv. Chim. Acta* **1984**, *67*, 1891-1896.

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Sulfur L-Edge XANES Study of Zinc-, Cadmium-, and Mercury-Containing Metallothionein and Model Compounds

We report the first sulfur L-edge (150-250 eV), X-ray absorption near-edge structure (XANES) spectra for the metallothionein (MT) species Zn_7-MT, Cd_7-MT, Hg_7-MT, and Hg_{18}-MT 2. These data are compared with sulfur L-edge spectra obtained for PbS (galena) and ZnS (sphalerite) and the model compounds $[Zn_4(SPh)_{10}](Me_4N)_2$ and $[Cd_4(SPh)_{10}](Me_4N)_2$. The detail in these XANES spectra illustrates the considerable utility of a technique that can provide geometric data for a range of different metal complexes from the same thiolate groups within the metal binding site. Analysis of the data for Zn_7-MT 1, Cd_7-MT 1, and Hg_7-MT 1 shows that Hg_7-MT 1 adopts a similar structure in terms of the sulfur environment, with the same thiolate oxidation state and nearest-neighbor distances as those for the well-known Cd and Zn metallothioneins. The substantially different spectrum for the recently described Hg_{18}-MT 2 species shows that it adopts a significantly different structure in terms of the thiolate environment. Although the XANES spectra of $[Zn_4(SPh)_{10}](Me_4N)_2$ and $[Cd_4(SPh)_{10}](Me_4N)_2$ compounds, which can be considered to be analogues of the α-domain in MT, are similar to each other, these spectra do not closely resemble the data obtained for the protein samples.

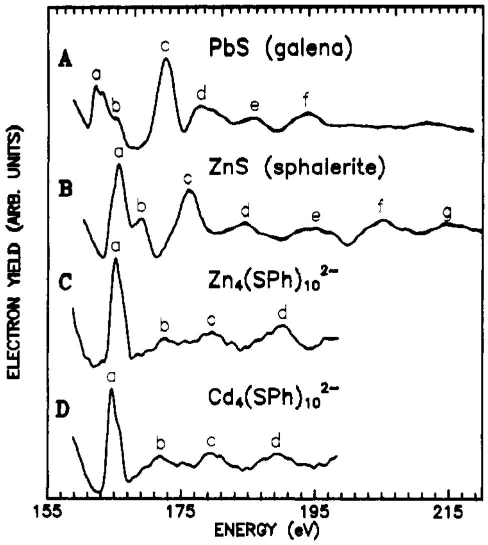

Figure 1. Sulfur L-edge XANES spectra of model compounds: (A) PbS; (B) ZnS; (C) $[Zn_4(SPh)_{10}](Me_4N)_2$; (D) $[Cd_4(SPh)_{10}](Me_4N)_2$.

Metallothioneins are low molecular weight, cysteine-rich proteins containing 20 SH groups per molecule. These proteins bind to a wide range of metal ions both in vivo and in vitro.[1] Extensive studies have been carried out in order to understand the nature of metal binding in metallothionein using ^{113}Cd NMR, ^1H NMR, X-ray crystallography, circular dichroism (CD), magnetic circular dichroism (MCD), and Raman spectroscopic techniques.[1,2]

Hasnain et al. have reviewed the available extended X-ray absorption fine structure spectroscopy (EXAFS) data for different metal environments of MT.[1,3,4] Elder et al.[5a] and Laib et al.[5b] have published results from XANES studies, in which the Au L_3 energy region (11-12 keV) was used to determine the oxidation state of Au in Au_{20}-MT. Klemens et al. have recently reported the EXAFS and XANES spectra of the Hg L_3-edge of mercury-substituted copper proteins.[6] Stephan and Hitchcock[7] have reported metal K-edge EXAFS of two model compounds of the metallothionein α-domain. To our knowledge, no sulfur L-edge XANES studies of metallothionein or any other sulfur-containing

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(1) Kagi, J. H. R.; Kojima, Y., Eds. *Metallothionein II* (*Experientia Suppl. 52*) Birkhauser: Basel, Switzerland, 1987.

(2) For example, ^{113}Cd NMR: (a) Otvos, J. D.; Armitage, I. M. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 7094-7098. ^1H NMR: (b) Neuhause, D.; Wagner, G.; Vasak, M.; Kagi, J. H. R.; Wuthrich, K. *Eur. J. Biochem.* **1985**, *151*, 257-273. X-ray crystallography: (c) Furey, W. F.; Robbins, A. H.; Clancy, L. L.; Winge, D. R.; Wang, B. C.; Stout, C. D. *Science* **1986**, *231*, 704-710. Circular dichroism: (d) Stillman, M. J.; Cai, W.; Zelazowski, A. J. *J. Biol. Chem.* **1987**, *262*, 4538-4548. EXAFS: (e) George, G. N.; Byrd, J.; Winge, D. R. *J. Biol. Chem.* **1988**, *263*, 8199-8203.

(3) Hasnain, S. S., *Top. Curr. Chem.* **1988**, *147*, 82-93.

(4) Hasnain, S. S.; Garner, C. D. *Prog. Biophys. Mol. Biol.* **1987**, *50*, 47-65.

(5) (a) Elder, R. C.; Eidsness, M. K.; Heeg, M. J.; Tepperman, K. G.; Shaw, C. F., III; Schaeffer, N. S. *ACS Symp. Ser.* **1983**, *No. 209*, 385-400. (b) Laib, J. E.; Shaw, C. F., III; Petering, D. H.; Eidsness, M. K.; Elder, R. C.; Garvey, J. S. *Biochemistry* **1985**, *24*, 1977-1986.

(6) Klemens, S.; McMillin, D. R.; Tsang, H. T.; Penner-Hahn, J. E. *J. Am. Chem. Soc.* **1989**, *111*, 6398-6402.

(7) Stephan, D. W.; Hitchcock, A. P. *Inorg. Chim. Acta* **1987**, *136*, L1-L5.

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