someric sultine **8** was not detected even after prolonged standing at −60 °C. At −40 °C, the sulfolene **9** was formed. The structure of **7** was deduced from its ^{1}H- and ^{13}C-NMR spectra.[13] The homoallylic coupling constants $^5J_{H,H}$ between the methylene protons at C(3) and C(6)[14] and the $^3J_{H,H}$ coupling constants between the olefinic proton at C(5) and the vicinal H_a and H_e protons at C(6) were consistent with the half-chair conformation shown in Scheme I.

When a 0.3 M solution of **10** in CD_2Cl_2/SO_2, 2/3 v/v, containing 0.2 M CF_3COOH was allowed to stand at −80 °C, the sultine **11** was formed. At −60 °C, **11** was decomposed to **10** and SO_2 and the more stable sultine **12** was generated (equilibrium constant $K \cong 4 \times 10^{-3}$ mol^{-1} dm^3 after ca. 6 h). When CF_3COOD (0.5−1 equiv) was used as the catalyst, no deuterium incorporation in either **11** or **12** was detected, thus demonstrating that the $[_\pi 4_s + {}_\pi 2_s]$-cycloaddition of SO_2 to **10** does not require the protonation of the diene to engender an allylic carbocation intermediate that would react with SO_2. The structures of sultines **11** and **12** (Scheme II) were elucidated from their NMR spectra.[15,16] The δ_H and δ_C values of the C(6) methylene groups[17] were consistent with the expected axial position of the S→O moiety.[18]

These results demonstrate that the hetero-Diels–Alder addition of SO_2 to **10** obeys the Alder (endo) rule as the less stable sultine **11** (with the S→O and Me groups in axial positions) is formed more rapidly than the thermodynamically more stable isomer **12** (axial S→O, equatorial Me–C(6)). When (*E*,*E*)-1-deuteriopiperylene (**13**)[19] was allowed to react with SO_2 under identical conditions, the sultine **14** was obtained at −80 °C, and the isomeric adduct **15** was formed at −60 °C. Less than 5% of any other isomeric compounds was detected (360-MHz ^{1}H-NMR), thus demonstrating the suprafaciality of the acid-catalyzed cycloadditions of (*E*)-piperylene to SO_2.

Under the above conditions (0.2 M CF_3COOH, CD_2Cl_2/SO_2, −80 to 50 °C), butadiene, (*Z*)-piperylene, and (*E*,*Z*)-hexa-2,4-diene did not give the expected sultines. The lack of an electron-releasing methyl group in butadiene makes its cycloaddition to SO_2 too slow. In the case of (*Z*)-piperylene and (*E*,*Z*)-hexa-2,4-diene, the acid-catalyzed hetero-Diels–Alder addition of SO_2, which is probably a concerted (nearly synchronous) process,[20] is drastically retarded because the s-cis conformers of these dienes are destabilized through steric repulsions.[21]

Acknowledgment. We are grateful to the Swiss National Science Foundation, the Fonds Herbette, and the Fonds Agassiz (Lausanne, Switzerland), for financial support.

Supplementary Material Available: NMR spectra of **7** and **11–15** (14 pages). Ordering information is given on any current masthead page.

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(13) Data of **7**: ^{1}H-NMR (360 MHz, CD_2Cl_2/SO_2, −60 °C) δ_H 5.58 (H-5), 4.48 (H-6$_a$), 4.38 (H-6$_e$), 3.42 (H-3$_a$), 2.89 (H-3$_e$), 1.66 ppm (Me), ^2J(H-6$_a$,H-6$_e$) = 16.0, ^2J(H-3$_a$,H-3$_e$) = 17.0, ^3J(H-5,H-6$_a$) = 2.5, ^3J(H-5,H-6$_e$) = 3.5, ^4J(H-5,H-3$_a$) = 2.5, ^4J(H-5,H-3$_e$) = 1, ^4J(H-5,Me) < 1, ^5J(H-3$_a$,H-6$_a$) = 4.0, ^5J(H-3$_a$,H-6$_e$) = 3.0, ^5J(H-3$_e$,H-6$_a$) = 2.5, ^5J(H-3$_e$,H-6$_e$) < 1 Hz (with irradiation of the methyl signal at δ_H = 1.66 ppm); ^{13}C-NMR (62.9 MHz, −60 °C) δ_C 121.0 (s, C_4), 116.0 (d, C_5, ^1J(C,H) ~ 170), 59.0 (t, C_6, ^1J(C,H) = 150), 48.0 (t, C_3, ^1J(C,H) = 135), 23.0 (q, CH_3, ^1J(C,H) = 135 Hz).

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(15) Data of **11**: ^{1}H-NMR δ_H 6.00 (H-5), 5.80 (H-4), 4.60 (H-6$_e$), 3.37 (H-3$_e$) (vanishes in **14**), 3.25 (H-3$_a$), 1.32 (Me), ^2J(H-3$_a$,H-3$_e$) = 16.5, ^3J(H-3$_e$,H-4) = 7.0, ^3J(H-3$_a$,H-4) = 2.5, ^3J(H-5,H-6$_e$) = 2.0, ^3J(H-4,H-5) = 11.5, ^3J(H-6$_e$,Me) = 7.0, ^4J(H-3$_a$,H-5) = 2.5, ^4J(H-3$_e$,H-5) < 0.5, ^4J(H-4,H-6$_e$) = 3.0, ^5J(H-3$_a$,H-6$_e$) = 3.0, ^5J(H-3$_e$,H-6$_e$) < 0.5 Hz; ^{13}C-NMR δ_C 130 (d, C_5, ^1J(C,H) ≅ 166), 114 (d, C_4, ^1J(C,H) = 175), 74 (d, C_6, ^1J(C,H) = 150), 45 (t, C_3, ^1J(C,H) = 138), 22.5 (q, CH_3, ^1J(C,H) = 128 Hz).

(16) Data of **12**: ^{1}H-NMR δ_H 5.8 (H-5), 5.6 (H-4), 4.65 (H-6$_a$), 3.45 (H-3$_a$) (vanishes in **15**), 2.95 (H-3$_e$), 1.3 (Me), ^2J(H-3$_a$,H-3$_e$) = 17, ^3J(H-4,H-5) = 11.0, ^3J(H-3$_e$,H-4) = 5.5, ^3J(H-5,H-6$_a$) = 1.0, ^3J(H-3$_a$,H-4) = 2.0, ^4J(H-3$_e$,H-5) = 1.5, ^4J(H-3$_a$,H-5) = 2, ^5J(H-3$_a$,H-6$_a$) = 4.0, ^5J(H-3$_e$,H-6$_a$) = 2.5, ^3J(H-6$_a$,Me) = 7.0 Hz; ^{13}C-NMR δ_C 129 (d, C_5, ^1J(C,H) ≅ 166), 114 (d, C_4, ^1J(C,H) = 175), 65 (d, C_6, ^1J(C,H) = 150), 45 (t, C_3, ^1J(C,H) = 138), 19 (q, Me, ^1J(C,H) = 128 Hz).

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Extraordinarily Intense Vibrational Circular Dichroism of a Metmyoglobin Cyanide Complex

Junji Teraoka,*[†] Keiji Nakamura,[†] Yumi Nakahara,[†]
Yoshimasa Kyogoku,[‡] and Hiromu Sugeta*[‡]

Department of Chemistry, Osaka City University
Sugimoto, Osaka, Japan 558
Institute for Protein Research, Osaka University
Suita, Osaka, Japan 565

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Vibrational circular dichroism (VCD) has become one of the most powerful means of investigating the structures of chiral molecules in solution.[1,2] This technique has been used to elucidate the structures of polypeptides and proteins and has provided a new insight into their conformations in solution.[3,4] Marcott et al. reported that the antisymmetric stretching vibration of the azide in azidomethemoglobin A at 2025 cm^{-1} gives rise to an extraordinarily strong VCD band with an anisotropy ration, $g = 0.02$, of 2 orders of magnitude greater than that normally observed for VCD.[5] They suggested that the exceptionally great rotational strength may be due to the presence of the chirally arranged lone pairs of the ligated N_3. Freedman and Nafie tried to explain the great rotational strength of the azide antisymmetric stretching in a chiral environment in terms of vibrationally generated ring currents, originating from the large region of delocalizable electron density in the porphyrin ring and low-lying electronic states.[1,6] However, there is still no experimental evidence for the proposed mechanism. Therefore, we investigated the VCD spectra of azidometmyoglobin (metMbN_3) and a reconstituted azidometmyoglobin with an iron–octaethylporphyrin (FeOEP), metMb(OEP)N_3, and a variety of ligands of metMbL (L = SCN^-, OCN^-, CN^- and CO) in order to clarify the VCD enhancement mechanism of the azide ligand. New interesting observations are presented in this paper. The first is that no VCD band for the

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* Authors to whom correspondence should be addressed.

[†] Department of Chemistry, Osaka City University.

[‡] Institute for Protein Research, Osaka University.

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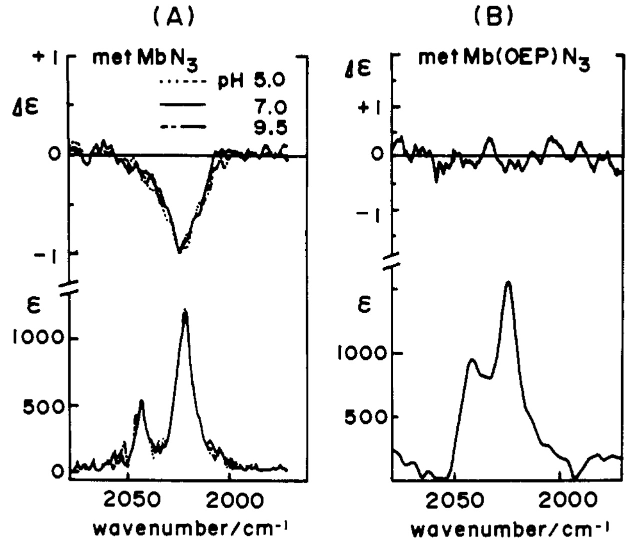

Figure 1. Absorption and VCD spectra of (A) 13.4 mM metMbN$_3$ (horse skeletal muscle metMb) in 0.1 M phosphate buffer at pH 5.0 (···), 7.0(—), and 9.5 (-·-) and (B) 2.3 mM metMb(OEP)N$_3$ reconstituted with iron-octaethylporphyrin at pH 7.0 in a 50.8 μm path length cell with CaF$_2$ windows. The IR absorption spectra were measured on a JASCO A-302 spectrometer with 4 cm^{-1} resolution, and VCD spectra were measured on a J-200E dispersive VCD instrument,[13] with 20 cm^{-1} resolution, time constant 1 s, scanning speed 100 cm^{-1}/min, and 130 scans.

metMb(OEP)N$_3$ reconstituted with Fe(OEP) was observed for the antisymmetric stretching of the azide covalently bound to iron, although the dipole strength was as great as that of the native metMbN$_3$ with an iron-protoporphyrin IX, which exhibits a considerably strong VCD band; the second is that the CN stretching vibration of the metMb cyanide complex exhibited an extraordinarily strong VCD positive band, i.e., opposite to the case of the azide complex, while no VCD band was observed for metMbL with L = SCN$^-$, OCN$^-$, or CO.

Figure 1A presents the IR absorption and VCD spectra of metMbN$_3$ at different pH's. There is virtually no change in either the VCD or the absorption spectrum in the pH range of 5.0–9.5, where the distal heme environment is expected to change.[7] It is, however, quite interesting that VCD is observable only for the absorption band at 2021 cm^{-1} as mentioned by Asher et al.,[8] which is attributed to the covalently bound azide in the low-spin Fe(III) species in metMbN$_3$, but the absorption band at 2043 cm^{-1} due to the rather ionically bound azide in the high-spin Fe(III) complex[9] does not show any VCD. Consequently, a good overlapping between the Π^* molecular orbitals of the ligand and the porphyrin ring through the iron d$_\pi$ orbitals seems to be important for the appearance of the VCD band.

Freedman and Nafie pointed out, in their ring current model, that the asymmetric orientation of vinyl groups in protoporphyrin IX plays a critical role in determining the direction of the ring current which induces the transition magnetic moment.[1] Thus, an artificial myoglobin, in which the porphyrin exhibits no difference as to the head and tail, was prepared by incorporating an iron-octaethylporphyrin into apomyoglobin.[10,11] Figure 1B shows the absorption and VCD spectra of the artificial metMb(OEP)N$_3$. It is hard to recognize a definite VCD band within the signal to noise ratio although two absorption bands can be observed at 2042 and 2024 cm^{-1}, the same as seen in native metMbN$_3$. This observation suggests that asymmetry of the porphyrin ring may be an important factor for the strong VCD signal. Recently, Asher et al.[8] asserted that VCD is very sensitive to the small interaction between the azide ligand and distal globin amino acid residues on the basis of the observation of a drastic decrease in the VCD intensity of the azide stretching in a variety of metMbN$_3$ whose distal histidine was replaced by other amino acids. Yamamoto et al.[12] very recently pointed out the possibility of the rotation of the vinyl substituents in shark Mb, whose distal amino acid is replaced by Gln. Such racemization through the rotation of the vinyl groups in metMbN$_3$ without a distal histidine may be the origin of the quenching of the VCD intensity found by Asher et al.

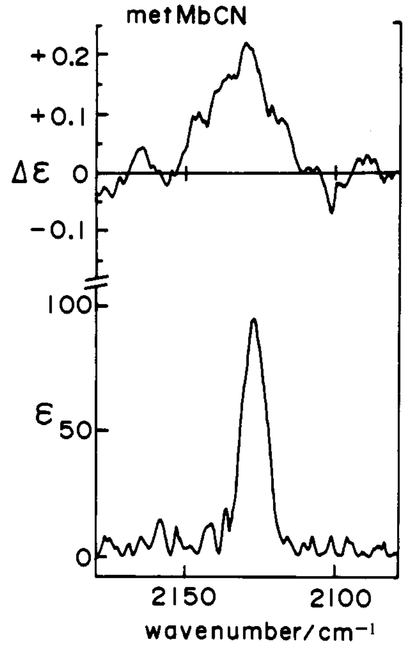

Figure 2. Absorption and VCD spectra of 13.5 mM (KCN) metMbCN at pH 7.0 in a 50.8 μm path length cell with CaF$_2$ windows. The IR spectrum was recorded on a Nicolet 5ZDX FTIR spectrometer with 4 cm^{-1} resolution and 1000 scans, because the intensity of the ligated CN stretching is very weak at 2127 cm^{-1} (ϵ = 100 cm^{-1} mol^{-1} L). VCD spectra were measured on a J-200E dispersive VCD instrument,[13] with 20 cm^{-1} resolution, time constant 1 s, scanning speed 100 cm^{-1}/min, and 300 scans.

To date, only the azide ligand has been reported to exhibit strong VCD. Then we investigated VCD of several ligands, L = CN$^-$, SCN$^-$, OCN$^-$, and CO, in metMbL, in order to elucidate the VCD enhancement mechanism of the ligand in hemeproteins. For metMbCN among them, a very intense VCD band of $g = 2.8 \times 10^{-3}$, in comparison with the g values of 10^{-4}–10^{-5} normally observed, was observed for the first time as shown in Figure 2. It is almost 4 times stronger than that of metMbN$_3$ ($g = -7.8 \times 10^{-4}$) and just opposite in sign. The g values were evaluated from the integrated intensities, and the experimental uncertainty was estimated within 50%. No VCD band was observed for either the isocyanide or thiocyanide complex of metMb, even though they exhibited intense absorption bands at 2162 (ϵ = 1900) and 2006 cm^{-1} (ϵ = 1050 cm^{-1} mol^{-1} L), respectively (data not shown). This might be comprehensible because they are in ferric high-spin states like the metMbN$_3$ which gives an absorption band at 2043 cm^{-1}. Little VCD was detected for metMbCO, even though its electronic state of iron is low-spin Fe(II). From these results it may be deduced that either a magnetic dipole moment nearly

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perpendicular to the electric dipole moment or little magnetic moment is induced by the stretching of the ligands in the ferric high-spin state and CO in the ferrous low-spin state. The relative orientation of the electric and magnetic dipole moments induced by the stretching of a ligand is approximately parallel for the cyanide but antiparallel for the azide in the ferric low-spin state. The orientation of the electric dipole moment depends on the coordination geometry of the ligand. Therefore, VCD is promising as to new insights into the electronic states as well as the coordination geometry of hemeproteins. Further studies on the VCD enhancement mechanism of porphyrin ligands are currently in progress.

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High-T_c Molecular-Based Magnets: A Ferromagnetic Bimetallic Chromium(III)–Nickel(II) Cyanide with T_c = 90 K

V. Gadet, T. Mallah, I. Castro,[1] and M. Verdaguer*

Laboratoire de Chimie des Métaux de Transition
URA CNRS 419, Université Pierre et Marie Curie
4 Place Jussieu, 75252 Paris, France

P. Veillet

Institut d'Electronique Fondamentale
URA CNRS 22, Université de Paris Sud
91405 Orsay, France

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$CsNi[Cr(CN)_6]\cdot 2H_2O$ obtained by slow addition of a dilute aqueous solution of a Ni^{II} salt to a concentrated aqueous solution of freshly prepared $Cs_2K[Cr(CN)_6]$ (1/1 molar ratio) exhibits a spontaneous magnetization at T_c = 90 K, due to a genuine short-range *ferromagnetic exchange interaction*. The elemental analysis fits with the proposed formula. The powder diffraction data display patterns of a face centered cubic cell with a unit cell parameter a = 10.57 Å. X-ray absorption data show octahedral Cr^{III} and Ni^{II} ions surrounded respectively by six carbon atoms at 2.06 Å and six nitrogen atoms at 2.10 Å. The $Cr(CN)_6$ group appears unchanged in the solid. The heavy atom peak in the Fourier transform, at $a/2$, at both edges confirms the presence of a three-dimensional (3D) bimetallic network with CN^- as a bridging ligand.

In the last few years, different groups have obtained encouraging results in the field of molecular-based ferromagnets, either with organic (i.e., fullerene),[2] metal–organic,[3,4a] metal–radical,[4b] or bimetallic[4c] systems. Among the data with an available crystal structure, the true molecular systems present the lowest T_c. One way to enhance the T_c value is to deal with bimetallic one-dimensional (1D) systems,[4b,c] with a strong and controlled interaction along one direction. However, the problem of inducing 1D–3D crossover in order to obtain the wanted magnets remains. Our approach is to build directly 3D frameworks through mild chemistry methods using *molecular* precursors specially chosen to achieve a 3D covalent bonding network between spin-bearing species. One of the simplest and most convenient molecular building blocks can be found in the hexacyanometalate family $[B(CN)_6]^{n-}$.

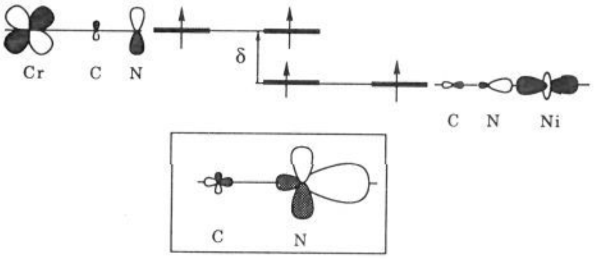

Figure 1. Orthogonality between t_{2g} (xy) Cr^{III} and e_g (z^2) Ni^{II} magnetic orbitals in $Cs^INi^{II}[Cr^{III}(CN)_6]\cdot 2H_2O$.

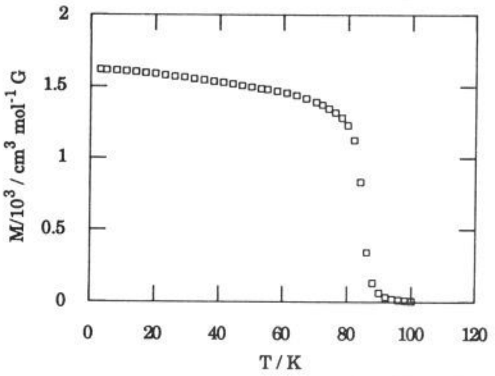

Figure 2. Field cooled magnetization curve $M = f(T)$ at H = 10 G.

The old but evergreen family of Prussian blue like bimetallic complexes leads to various k/l stoichiometries, $A_k[B(CN)_6]_l\cdot mH_2O$.[5] When $k/l > 1$, the structure presents $B(CN)_6$ vacancies and high water content. Ten years ago, among a series of uncoupled paramagnetic systems, Babel et al.[6] reported on the *ferrimagnetic* system $Cs^IMn^{II}[Cr^{III}(CN)_6]\cdot 1H_2O$, with T_c *value* = 90 K. Using $[Fe^{III}(CN)_6]^{3-}$ (d^5, $(t_{2g})^5$, low-spin $S = {}^1/_2$) as a precursor, we obtained *ferrimagnetic* (with $A^{II} = Mn^{II}$ and Co^{II}) and *ferromagnetic* (with $A^{II} = Cu^{II}$ and Ni^{II}) systems and a $k/l = {}^3/_2$ stoichiometry, with T_c ranging from 9 to 23 K.[7] However, using chromicyanide instead of ferricyanide, we obtain a spectacular enhancement of T_c[8] (in the 55–65 K range), still with the ${}^3/_2$ stoichiometry. The presence of $B(CN)_6$ vacancies probably hinders a full interaction through the whole compound. To avoid such vacancies, a cesium cation Cs^I was used to stabilize ${}^1/_1$ stoichiometric compounds. We report here the magnetic properties of $Cs^INi^{II}[Cr^{III}(CN)_6]\cdot 2H_2O$, which orders ferromagnetically at 90 K.

The susceptibility and magnetization measurements were performed using a SQUID magnetometer. Upon cooling down from room temperature to 90 K, χ_MT increases continuously, expressing a short-range *ferromagnetic exchange interaction* between nearest metallic ions. Such a short-range interaction, expected from the strict orthogonality of the t_{2g} orbitals of Cr^{III} and the e_g orbitals of Ni^{II} (Figure 1), had already been predicted by Ginsberg[9] and experimentally demonstrated by Pei et al.[10] At 90 K, χ_MT diverges, suggesting a long-range *ferromagnetic order*. The field-cooled magnetization vs temperature plot at H = 10 G in the 3–100 K range (Figure 2) presents a break at T_c = 90 K confirming the onset of a 3D long-range *ferromagnetic order* within the compound. The value is well above that observed for the ${}^3/_2Ni_3[Cr(CN)_6]_2\cdot 12H_2O$ compound (T_c = 60 K),[8] showing the importance of a lack of $[Cr(CN)_6]^{3-}$ vacancies in these com-

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(1) Permanent address: Departament de Quimica Inorganica, Facultat de Quimica, Dr Moliner 50, Burjassot, Valencia, Spain.

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