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Y. OZAKI
K. IRIYAMA
Division of Biochemistry
The Jikei University School of Medicine
Nishi-Shinbashi, Minato-ku, Tokyo 105
Japan
T. KITAGAWA
Institute for Molecular Science
Myodaiji, Okazaki, Aichi 444
Japan
H. OGOSHI
T. OCHIAI
Department of Chemistry and Chemical Engineering
Technological University of Nagaoka
Nagaoka, Niigata 940-21
Japan

COMPARATIVE STUDY OF METALLOCHLORINS AND METALLOPORPHYRINS BY RESONANCE RAMAN SPECTROSCOPY

Basic studies on metallochlorins have recently become increasingly important, because it was found that not only chlorophylls but also some hemoproteins contain the metallochlorin as a prosthetic group (*e.g.* [1]). In order to elucidate the reason for the existence of chlorin prosthetic groups in some hemoproteins it is essential to investigate what features of molecular and electronic structures of metallochlorins are different from those of metalloporphyrins. Thus we have undertaken comparative study of metallochlorins and metalloporphyrins using resonance Raman (RR) spectroscopy [2] which is known to be a powerful structure probe for hemoproteins as well as their model compounds [3,4].

RESULTS AND DISCUSSION

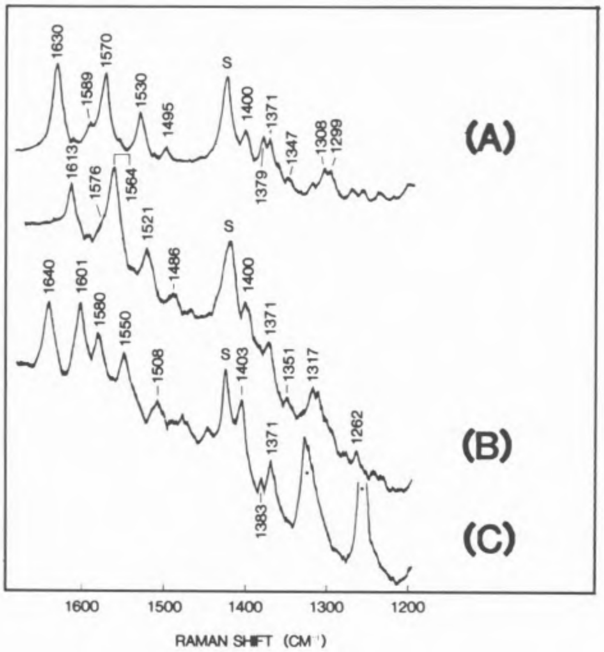

Fig. 1
Resonance Raman spectra of (A) Fe(OEC)Br, (B) Fe(OEC)($Me_2SO)_2$, and (C) Fe(OEC)($Im)_2$Br.
Experimental conditions: excitation wavelength, 488.0 nm; laser power, 200 mW; spectral slit width, 6 cm^{-1}. S denotes Raman lines due to solvents (CH_2Cl_2 for Fe(OEC)Br and Fe(OEC)($Im)_2$Br and 1:1 mixture (V/V) of CH_2Cl_2/Me_2SO for Fe(OEC)($Me_2SO)_2$). Bands marked with an asterisk are due to imidazole

Fig. 1 shows the 488.0 nm-excited RR spectra of Fe(OEC)Br (5-coordinate, high-spin; OEC = octaethylchlorin), Fe(OEC)($Me_2SO)_2$ (6-coordinate, high-spin; Me_2SO = dimethyl sulfoxide), and Fe(OEC)($Im)_2$Br (6-coordinate, low-spin; Im = imidazole). RR bands at 1630, 1570, and 1494 cm^{-1} of Fe(OEC)Br can be assigned to the modes involving mainly the methine bridge stretching vibration, that is, ν_{10}, ν_{19}, and ν_3 modes [2], respectively. These frequencies are very close to those of the corresponding modes of Fe(OEP)Br. Since the frequencies of ν_{10}, ν_{19}, and ν_3 modes are correlated with the center-to-pyrrole-N distance of the porphyrin cavity [4], the close similarities in the frequencies of these modes between Fe(OEC)Br and Fe(OEP)Br indicate the similarity in their core sizes. RR bands of Fe(OEC)Br at 1589 and 1530 cm^{-1} may be due to the modes involving substantially the $C_\beta C_\beta$ stretching character [2]. The corresponding modes of Fe(OEP)Br were observed at 1581 and 1558 cm^{-1}. Although it was expected that the two $C_\beta C_\beta$ stretching modes would show large downward shifts upon saturation of one of $C_\beta C_\beta$ bonds, the 1581 cm^{-1} band did exhibit an upward shift by 8 cm^{-1}. Two $C_\beta C_\beta$ stretching modes of Fe(OEP)Br with

C_{4v} symmetry belong to different symmetry species (A_1 for 1581 cm^{-1} and B_1 for 1558 cm^{-1}), but they belong to the same symmetry species (A_1) for Fe(OEC)Br with C_{2v} symmetry. Therefore it seems very likely that vibrational coupling of two A_1 modes causes a large splitting of the two $C_\beta C_\beta$ stretching modes for Fe(OEC)Br. The so-called oxidation-state marker (ν_4) is seen at 1371 cm^{-1} in the RR spectrum of Fe(OEC)Br.

The middle spectrum of Fig. 1 was obtained by dissolving Fe(OEC)Br in a 1:1 mixture (V/V) of CH_2Cl_2/Me_2SO. The RR spectrum resembles that of $Fe(OEP)(Me_2SO)_2$ regarding the frequencies of the methine bridge stretching modes [5], suggesting that ferric chlorin forms the hexa-coordinated high-spin complex with dimethyl sulfoxide at two axial positions as in the case of porphyrin.

Upon the high- to low-spin conversion of ferric chlorins all the RR bands above 1450 cm^{-1} showed large upward shifts. The ν_{10}, ν_{19}, and ν_3 modes of $Fe(OEC)(Im)_2Br$ were observed at 1640, 1580, and 1508 cm^{-1}, respectively. These frequencies are again close to those of the corresponding modes of $Fe(OEP)(Im)_2Br$.

The reduction of the iron atom resulted in numerous changes in both positions and intensities of RR bands. However, the frequency shift of the ν_4 mode was rather small (*ca.* 4 cm^{-1}) compared with porphyrins (7-17 cm^{-1}) [3,4]. The frequency decrease of the ν_4 mode upon the change from Fe^{3+} to Fe^{2+} has been attributed to the increased π-back donation of d_π electrons to porphyrin π^* orbital [3,4]. Therefore, the relatively small frequency shift of ν_4 mode indicates that π-back donation is less significant in ferrous chlorins than in ferrous porphyrins.

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M.A. CINELLU
M.L. GANADU
G. MINGHETTI
Istituti Chimici
Università di Sassari
07100 Sassari
Italy
F. CARIATI
Dipartimento di Chimica Inorganica e Metallorganica
Università di Milano
20133 Milano
Italy
F. DEMARTIN
M. MANASSERO
Laboratorio di Strutturistica
Facoltà di Scienze, Centro CNR
Università di Milano
20133 Milano
Italy

PALLADIUM(II) DERIVATIVES OF SOME 1,4-BENZODIAZEPIN-2-ONES

The reaction of $PdCl_2$ and $Na_2[PdCl_4]$ with two 1,4-benzodiazepin-2-ones, L, (DIAZEPAM and PRAZEPAM) has been investigated. Complexes of the types trans-*$(L)_2PdCl_2$, $[(L-H)PdCl]_2$, $(L-H)(Ph_3P)PdCl$ and (L-H)Pd(acac) have been characterized by IR and NMR spectroscopy. An X-ray structure determination of $(PRAZEPAM)_2PdCl_2$ has shown that the ligand is coordinated to the metal through the 4-nitrogen atom.*

RESULTS

Previously we have shown that the reaction of some 1,4-benzodiazepin-2-ones, (L) (*e.g.* DIAZEPAM, PRAZEPAM, NIMETAZEPAM, LORAZEPAM, NITRAZEPAM) with gold(III) chloride affords 1:1 adducts $(L)AuCl_3$. For the complex $(PRAZEPAM)AuCl_3$ the coordination mode of the ligand has been ascertained by an X-ray structure determination and found to occur through the 4-nitrogen atom [1].

We report now some preliminary results on the interaction of $PdCl_2$ and $Na_2[PdCl_4]$ with DIAZEPAM and PRAZEPAM (scheme I):