Inorganica Chimica Acta, 61 (1982) 77–81

Infrared Spectra of Octaethylporphinatocobalt(II) and its Dioxygen Adduct in Argon Matrices

MAREK W. URBAN, KAZUO NAKAMOTO

Todd Wehr Chemistry Building, Marquette University, Milwaukee, Wis. 53233, U.S.A.

and JAMES KINCAID

Department of Chemistry, University of Kentucky, Lexington, Ky. 40506, U.S.A.

Received Novemher 23, 1981

The infrared spectra of octaethylporphinatocobalt(II), Co(OEP), have been measured in argon matrices as well as in KBr pellets and as thin films. Vibrational assignments have been made based on those obtained for Ni(OEP). Cocondensation reactions of Co(OEP) with $^{16}O_2$ *and* $^{18}O_2$ *diluted in argon at ~15 K have produced 'base-free'* O_2 *adducts, Co(OEP)*$^{16}O_2$ *and Co(OEP)*$^{18}O_2$ *which exhibit their* O_2 *stretching bands at 1275 and 1202 cm*$^{-1}$*, respectively. Similar experiments with Co(OEP-d*$_4$*) confirm these assignments. These frequencies are very similar to those observed previously for Co(TPP)*$^{16}O_2$ *(1278 cm*$^{-1}$*) and Co(TPP)*$^{18}O_2$ *(1209 cm*$^{-1}$*) (TPP: tetraphenylporphinato anion), indicating that the electronic effect of OEP on the* O_2 *is similar to that of TPP. The Co(OEP) vibrations show little shifts upon the adduct formation.*

Introduction

The matrix cocondensation technique provides a unique means to observe the vibrational spectra of 'base-free' molecular oxygen adducts which are too unstable to prepare by ordinary methods. We have already applied this technique to Co(TPP)O_2 (TPP: tetraphenylporphinato anion) [1], Co(acacen)O_2(acacen: N,N′-ethylene-bis(acetylacetoniminato)-anion) [2] and Co(J-en)O_2(J-en: N,N′-ethylenebis-(2,2-diacetylethylideneiminato) anion) [3]. It was found that the $\nu(O_2)$ (ν: stretching) of Co(J-en)O_2 (1260 cm^{-1}) is much higher than that of Co(acacen)O_2 (1146 cm^{-1}). This result was interpreted as indicating that the electron-withdrawing acetyl group in Co(J-en) reduces the negative charge on the O_2 considerably relative to that in Co(acacen). However, such an in-plane ligand effect is not known for a series of Co(II) porphyrins. The main purpose of this work is to examine this effect by comparing the $\nu(O_2)$ of Co(OEP)O_2 with that of Co(TPP)O_2 (1278 cm^{-1}) studied previously [1].

Experimental

Preparation of Compounds

Co(OEP) and Co(OEP-d$_4$) were prepared according to the procedure previously described [4]. OEP-d$_4$ was prepared by deuteration of OEP in D_2SO_4 [4].

Matrix Cocondensation Reactions

Co(OEP)O_2 and Co(OEP-d$_4$)O_2 were prepared *via* cocondensation of respective Co-chelate vaporized in a Knudsen cell at 420 K with $^{16}O_2$ or $^{18}O_2$ diluted in Ar on a CsI window which was cooled to ~15 K by a CTI Model 21 closed cycle helium refrigerator. The thin films of Co(OEP) and Co(OEP-d$_4$) were prepared by the same procedure without O_2 and Ar gases. The gases, $^{16}O_2$ (99.99%), $^{18}O_2$ (99.88%) and Ar (99.9995%) were purchased from Matheson or Monsanto Research.

Spectral Measurements

IR spectra were measured on a Beckman Model 4260 infrared spectrophotometer using a 25 cm^{-1}/in chart expansion and 5 cm^{-1}/min chart speed. Rotation–vibration bands of standard molecules and polystyrene bands were used for calibration of frequency reading.

Results and Discussion

Co(OEP) and Co(OEP-d$_4$)

As the first step to interpret the IR spectrum of Co(OEP)O_2, we have studied the IR spectra of Co(OEP) and Co(OEP-d$_4$) in various physical states.

0020-1693/82/0000-0000/$02.75

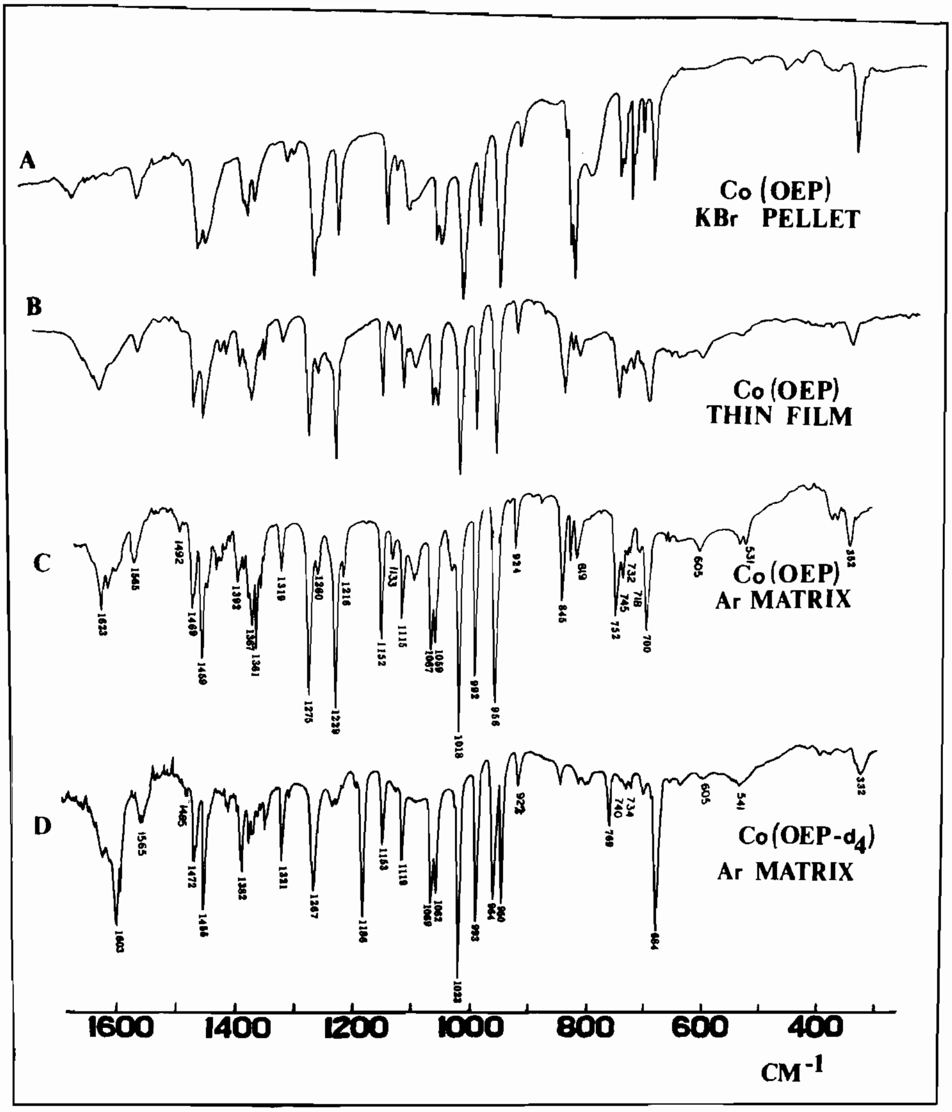

Fig. 1. Infrared spectra of Co(OEP) and Co(OEP-d$_4$) in various physical states. The thin film and Ar matrix spectra were measured at ~15 K.

Figure 1 shows the IR spectra of Co(OEP) in a KBr pellet (trace A), as a thin film (trace B) and in an Ar matrix at ~15 K (trace C). Although the general features of these spectra are similar, the Ar matrix spectrum shows more and sharper bands than the other two spectra. Distinction between the matrix isolated state and the film can be made by the appearance of several extra bands in the former. This and other characteristics of the matrix spectrum are useful in estimating the degree of matrix isolation. In general, the bands in the KBr pellet are broader than those of the film. Furthermore, several bands in the former show marked shifts relative to those of the other states. The most conspicuous shift is seen in the doublet at *ca.* 820 cm^{-1} of the KBr pellet which is shifted to 845 cm^{-1} in the film and Ar matrix obtained at ~15 K.

Previously, Abe *et al.* [5] made complete band assignments for all the in-plane skeletal modes of Ni(OEP), Ni(OEP-d$_4$) and Ni(OEP-^{15}N) based on normal coordinate calculations. However, detailed assignments of the ethyl group and out-of-plane skeletal vibrations were not included. We have undertaken a thorough investigation of IR spectra of matrix-isolated Ni(OEP) and Ni(OEP-d$_4$) in which we proposed alternative band assignments [6]. Table I lists the observed IR frequencies and our assignments for the E$_u$ (IR active) vibrations of Co(OEP) and Co(OEP-d$_4$). Figure 2 shows the symbols used for the assignments given in Table I.

TABLE I. Observed Frequencies (cm^{-1}) and Band Assignments for Co(OEP) and Co(OEP-d_4).

Co(OEP)	Co(OEP-d_4)	Assignment*
1623	1623	
1604	1603	$\nu_{37} - \nu(C_{\beta}C_{\beta})$
1592	1592	
1565	1559	$\nu_{38} - \nu(C_{\alpha}C_{m})$
1492	1485	$\nu_{39} - \nu'(C_{\alpha}C_{m}), \nu'(C_{\alpha}N)$
1469	1472	Et
1459	1455	
1415	1415	
1392	1382	$\nu_{40} - \nu'(C_{\alpha}C_{\beta}), \nu'(C_{\beta} - Et)$
1367	1393	Et
1361	1352	
1319	1321	Et
1275	1267	$\nu_{41} - \nu(C_{\alpha}N), \delta(C_{\alpha}C_{m})$
1229	1186	$\nu_{42} - \nu'(C_{\beta} - Et)$
1152	1153	$\nu_{43} - \nu'(C_{\alpha}N), \nu'(C_{\beta}-Et)$
1133	964	$\nu_{44} - \delta(C_{m}-H)$
1115	1119	Et
1067	1069	Et
1059	1062	
1018	1023	Et
992	993	$\nu_{45} - \nu'(C_{\alpha}N), \nu'(C_{\alpha}C_{m})$
956	950	Et
924	920	$\nu_{46} - \nu'(C_{\beta}-Et), \delta'(C_{\alpha}C_{m})$
845	684	$\pi(C_{m}-H)$
831		
819		
752	769	
745	740	Et
732	734	$\nu_{47} - \nu(C_{\beta} - Et), \nu(C_{\alpha}C_{\beta})$
718		
700	715	
605	605	$\nu_{48} - \delta'(C_{\beta}-Et), \nu(C_{\alpha}C_{m})$
544	541	$\nu_{49} - \delta'(C_{\alpha}C_{\beta}C_{\beta}), \delta(C_{\alpha}C_{m}C_{\alpha})$
531		
352	332	π(skeletal)

*ν, symmetric stretch; ν', antisymmetric stretch; δ, symmetric bending; δ', antisymmetric bending; π, out-of-plane bending; Et, ethyl group vibration. $\nu_{37} \cdots \nu_{47}$ refer to those of Abe *et al.* (Ref. 5) which were modified by our study on Ni(OEP) (Ref. 6).

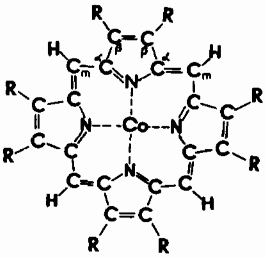

Fig. 2. Structure of Co(OEP). – – – R denotes the ethyl group.

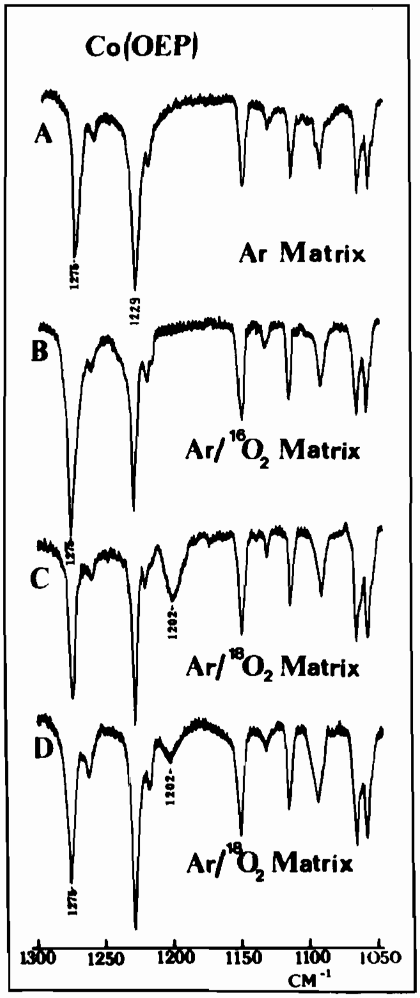

Fig. 3. Infrared spectra of Co(OEP (A) and its cocondensation products with Ar/$^{16}O_2$ (B) and Ar/$^{18}O_2$ (C and D). The Ar/O_2 ratio was 10/1 for B and C, and 100/1 for D.

Co(OEP)O_2 and Co(OEP-d_4)O_2

Traces, A, B, C and D of Fig. 3 show the IR spectra of Co(OEP) cocondensed with pure Ar, Ar/$^{16}O_2$ (10/1), Ar/$^{18}O_2$ (10/1) and Ar/$^{18}O_2$ (100/1), respectively. Co(OEP) (trace A) exhibits two strong bands at 1275 and 1229 cm^{-1} which are similar to those observed at 1275 and 1231 cm^{-1} of Ni(OEP) [6]. When Co(OEP) was cocondensed with Ar/$^{16}O_2$-(10/1), no spectral changes were observed except for the relative intensities of these two bands (trace B); the 1275 cm^{-1} band became stronger than the 1229 cm^{-1} band. However, cocondensation with Ar/$^{18}O_2$ produced a new band at 1202 cm^{-1} (trace C) which

TABLE II. O_2 Stretching Frequencies of Base-Free Molecular Oxygen Adducts (cm^{-1}).

	$\nu(^{16}O_2)$	$\nu(^{18}O_2)$	$\Delta\nu$	Ref.
$Co(TPP)O_2$	1278	1209	69	1
$Co(OEP)O_2$	1275	1202	73	*
$Co(J\text{-}en)O_2$	1260	1192	68	3
$Co(acacen)O_2$	1146	1098	48	2

*This work.

became weaker as the $Ar/^{18}O_2$ ratio was decreased to 100/1 (trace D). Thus, the 1202 cm^{-1} band has been assigned to the $\nu(O_2)$ of Co(OEP) $^{18}O_2$. In the case of $Co(TPP)O_2$, the $\nu(O_2)$ is shifted from 1278 to 1209 cm^{-1} by $^{16}O_2-^{18}O_2$ substitution. If a shift of a similar magnitude occurs for $Co(OEP)O_2$, the $\nu(O_2)$ of its $^{16}O_2$ adduct is expected to be hidden by the strong band at 1275 cm^{-1}. To confirm this possibility, we have carried out similar experiments with Co(OEP-d_4).

Trace A of Fig. 4 shows the IR spectrum of Co(OEP-d_4) in an Ar matrix. It is seen that the two strong bands at 1275 and 1229 cm^{-1} of Co(OEP) are shifted to 1267 and 1186 cm^{-1}, respectively, by deuterium change of the four meso-hydrogens. When Co(OEP-d_4) was cocondensed with $Ar/^{16}O_2$ (10/1), two bands appeared at 1275 and 1267 cm^{-1} as is shown by trace B of Fig. 4. The former is absent in Co(OEP-d_4) whereas the latter is at the same frequency as that observed for Co(OEP-d_4). Thus, the band at 1275 cm^{-1} has been assigned to the $\nu(O_2)$ of Co(OEP-d_4)$^{16}O_2$. This result also confirms our interpretation that the $\nu(O_2)$ of Co(OEP)$^{16}O_2$ is hidden under the strong Co(OEP) band at 1275 cm^{-1}.

Table II lists the $\nu(O_2)$ of all four 'base-free' O_2 adducts we have studied. In the Schiff base complex series, the $\nu(O_2)$ of $Co(J\text{-}en)O_2$ is much higher than that of $Co(acacen)O_2$ since the strong electron-withdrawing acetyl groups in Co(J-en) result in a much less negatively charged O_2 relative to that of $Co(acacen)O_2$. On the other hand, the present result shows that the $\nu(O_2)$ of $Co(OEP)O_2$ is almost identical to that of $Co(TPP)O_2$, indicating that their Co–O_2 bond strength is similar. This may be due to two reasons. First, the electronic effect of the phenyl group on the Co atom does not differ appreciably from that of the ethyl group since the phenyl groups in Co(TPP) are perpendicular to the porphyrin core and the ethyl groups in Co(OEP) are only weakly electron-donating. Second, the effect of peripheral groups on the Co atom is more 'diluted' in metalloporphyrins than in Schiff base complexes due to a more extended π-electron system in the former. To determine which is the main factor responsible for the present result, it is necessary to extend our study to Co(II) porphyrins containing a variety of substituents and to Co(II) chelates having larger π-systems than porphyrins (*e.g.*, tetrabenzporphin, tetrazaporphin, phthalocyanine, *etc.*).

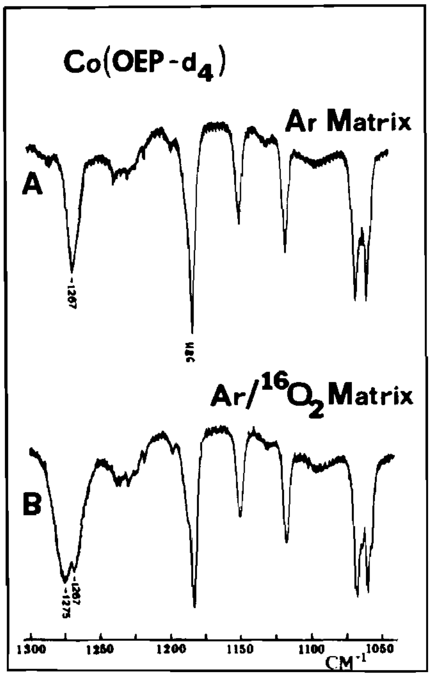

Fig. 4. Infrared spectra of Co(OEP-d_4) (A) and its cocondensation product with $Ar/^{16}O_2$ (B). The Ar/O_2 ratio was 10/1 for B.

The vibrational frequencies of Co(OEP) and Co(OEP-d_4) show almost no changes upon oxygenation. Similar observations were made previously for Co(TPP) [1] and Co(II) myoglobins [7]. These results indicate that coordination of molecular oxygen to the axial position causes no appreciable changes in the electronic and molecular structures of Co(II) porphyrins. This should be contrasted to deoxyhemoglobin whose vibrational frequencies change markedly by oxygenation due to changes in its oxidation, spin state and core geometry [8].

Acknowledgments

The work performed at Marquette University was supported by the National Science Foundation (CHE-7915169). Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and Research Corporation for partial support of the work performed at University of Kentucky.

References

1 M. Kozuka and K. Nakamoto, *J. Am. Chem. Soc.*, *103*, 2162 (1981).

2 M. W. Urban, Y. Nonaka and K. Nakamoto, *Inorg. Chem.*, *20*, (1982).

3 K. Nakamoto, Y. Nonaka, T. Ishiguro, M. W. Urban, M. Suzuki, M. Kozuka, Y. Nishida and S. Kida, *J. Am. Chem. Soc.*, submitted for publication.

4 K. M. Smith, 'Porphyrins and Metalloporphyrins', Elsevier, Amsterdam, 1975.

5 M. Abe, T. Kitagawa and Y. Kyogoku, *J. Chem. Phys.*, *69*, 4526 (1978).

6 J. Kincaid, M. W. Urban and K. Nakamoto, to be published in *J. Phys. Chem.*

7 W. H. Woodruff, D. H. Adams, T. G. Spiro and T. Yonetani, *J. Am. Chem. Soc.*, *97*, 1695 (1975).

8 T. G. Spiro and T. M. Loehr, 'Resonance Raman Spectra of Heme Proteins and Other Biological Systems', in 'Advances in Infrared and Raman Spectroscopy' (edited by R. J. H. Clark and R. E. Hester), vol. 1, 1975.