Inorg. Chem. **1980**, *19*, 2822–2824

Contribution from the Todd Wehr Chemistry Building, Marquette University, Milwaukee, Wisconsin 53233,
and Department of Chemistry, Faculty of Science, Kyushu University 33, Fukuoka, 812 Japan

Resonance Raman Spectra of Molecular Oxygen Adducts of *N,N'*-Ethylenebis(salicylideniminato)cobalt(II), $[BCo(salen)]_2O_2$ (B = Pyridine, Pyridine *N*-Oxide, and Dimethylformamide)

K. NAKAMOTO,* M. SUZUKI, T. ISHIGURO, M. KOZUKA, Y. NISHIDA, and S. KIDA

Received February 6, 1980

Resonance Raman spectra have been measured for the dimeric molecular oxygen adducts, $[BCo(salen)]_2O_2$, where B represents pyridine, pyridine *N*-oxide, and dimethylformamide. The O_2 and CoO stretching vibrations of these compounds are in the ranges 910–888 and 542–535 cm^{-1}, respectively. The Co–O_2 charge-transfer bands have been located near 500 nm on the basis of the excitation profiles of these vibrations. The origin of these charge-transfer bands has been discussed on the basis of an approximate MO energy level diagram.

Introduction

Since Tsumaki[1] discovered the reversible oxygenation of *N,N'*-ethylenebis(salicylideniminato)cobalt(II), [Co(salen)], in the solid state, a number of structural and spectroscopic investigations have been carried out on molecular oxygen adducts of Schiff base complexes.[2,3] These include X-ray analysis,[4-7] ESR,[8-10] electronic,[11-13] and vibrational[14,15] spectra. According to X-ray analysis,[5] [Co(salen)] in dimethylformamide (DMF) forms a 2:1(Co/O_2) complex, $[(DMF)Co(salen)]_2O_2$ which contains the Co–O_2–Co bridge. Although X-ray analysis has not been carried out on analogous pyridine (py) and pyridine *N*-oxide (pyO) complexes, their diamagnetism suggests similar 2:1 bridging structures for these compounds.[16]

As originally observed by Tsumaki,[1] the color of [Co(salen)] is deepened dramatically when it absorbs oxygen in air. However, the origin of this color change has not been understood even in terms of rudimentary MO theory. The formation of molecular oxygen adducts causes the red-shift of the ligand $\pi-\pi^*$ transitions[17] or the emergence of a new Co–O_2 CT band[12] in the visible region. Either one or a combination of both may be responsible for the deepening of color upon oxygenation. Resonance Raman (RR) spectroscopy has proved to be very useful in locating metal–ligand CT transitions:[18] the $\nu(O_2)$ and/or ν(CoO) are most strongly resonance enhanced when the exciting frequency is tuned within the region of the Co–O_2 CT absorption.

In the present work, we have measured the RR spectra of three $[BCo(salen)]_2O_2$ type complexes mentioned above and assigned their $\nu(O_2)$ and ν(CoO) vibrations. Furthermore, we have located their Co–O_2 CT bands on the basis of excitation profiles of these vibrations.

Experimental Section

The dimeric molecular oxygen adducts, $[BCo(salen)]_2O_2$ (B = py, pyO, and DMF), were prepared by the literature method.[16] The $^{18}O_2$ gas (93% enriched) was purchased from Monsanto Research Corp., Miamisburg, OH. The RR spectra were recorded on a Spex Model 1401 double monochromator. Detection was made by using a cooled RCA C31034 photomultiplier in conjunction with a Spex digital photometer system. Excitations at 457.9, 476.5, 488.0, 496.5, and 514.5 nm were made by a Spectra-Physics Model 164 Ar-ion laser and those at 579 and 589 nm were made by a Spectra-Physics Model 365 CW dye-laser (Rhodamine 6G) pumped by the above 4W Ar-ion laser. The spectra were measured as pellets by using the rotating sample technique. To plot an excitation profile, we measured the relative intensities of the bands against the 983-cm^{-1} band of K_2SO_4(internal standard) which was mixed homogeneously with the sample in a KBr pellet. The corrections for spectrometer sensitivity and the ν^4 law were made for each band. The average error of the relative intensities is about ±10%. The electronic absorption spectra were measured by using a Simadzu multipurpose spectrophotometer, Model MPS-5000.

Table I. Vibrational Frequencies of $[BCo(salen)]_2O_2$ (cm^{-1})

B	$\nu(O_2)$	ν(CoO)
py	888	542
DMF	897	*a*
pyO	910	535

[a] Hidden by a ligand band.

Results and Discussion

Figure 1 shows the RR spectra of the $[BCo(salen)]_2O_2$ series obtained by using the 476.5-nm excitation. To locate the $\nu(O_2)$ and ν(CoO) (ν = stretch) vibrations, we have compared the RR spectra of $[(py)Co(salen)]_2O_2$ and its $^{18}O_2$ analogue in the solid state. As is seen in trace A, the $^{16}O_2$ complex exhibits two strong bands at 888 and 542 cm^{-1}. When the complex was prepared by using $^{18}O_2$ (trace A'), the intensities of these two bands decreased markedly and new bands appeared at 833 and 529 cm^{-1}. It was not possible to eliminate the $^{16}O_2$ peaks completely from the $^{18}O_2$ spectrum due to rapid exchange of $^{16}O_2$–$^{18}O_2$ caused by laser irradiation. This exchange process was completed within 1 h and the spectrum became identical with that of the $^{16}O_2$ complex (trace A). These results clearly indicate that the vibrations at 888 and 542 cm^{-1} of the $^{16}O_2$ complex involve the motions of the oxygen atoms. The analogous pyO complex (trace B) exhibits similar bands at 910 and 535 cm^{-1}. The DMF complex (trace C) shows a

---

*To whom correspondence should be addressed at Marquette University.

(1) T. Tsumaki, *Bull. Chem. Soc. Jpn.*, **13**, 252 (1938).
(2) G. McLendon and A. E. Martell, *Coord. Chem. Rev.*, **19**, 1 (1976).
(3) R. W. Erskine and B. O. Field, *Struct. Bonding (Berlin)*, **28**, 1 (1976).
(4) G. A. Rodley and W. T. Robinson, *Nature (London)*, **235**, 438 (1972).
(5) M. Calligaris, G. Nardin, L. Randaccio, and A. Ripamonti, *J. Chem. Soc. A*, 1069 (1970).
(6) R. S. Gall, J. F. Rogers, W. P. Schaefer, and G. G. Christoph, *J. Am. Chem. Soc.*, **98**, 5135 (1976).
(7) A. Avdeef and W. P. Schaefer, *J. Am. Chem. Soc.*, **98**, 5153 (1976).
(8) B. M. Hoffman, D. L. Diemente, and F. Basolo, *J. Am. Chem. Soc.*, **92**, 61 (1970).
(9) B. S. Tovrog, D. J. Kitko, and R. S. Drago, *J. Am. Chem. Soc.*, **98**, 5144 (1966).
(10) R. S. Drago, T. Beugelsdijk, J. A. Breese, and J. P. Cannady, *J. Am. Chem. Soc.*, **100**, 5374 (1978).
(11) M. J. Carter, D. P. Rillema, and F. Basolo, *J. Am. Chem. Soc.*, **96**, 392 (1974).
(12) K. Kubokura, H. Okawa, and S. Kida, *Bull. Chem. Soc. Jpn.*, **51**, 2036 (1978).
(13) L. S. Chen, M. E. Koehler, B. C. Pestel, and S. C. Cummings, *J. Am. Chem. Soc.*, **100**, 7243 (1978).
(14) A. L. Crumbliss and F. Basolo, *J. Am. Chem. Soc.*, **92**, 55 (1972).
(15) J. D. Landels and G. A. Rodley, *Synth. Inorg. Met.-Org. Chem.*, **2**, 65 (1972).
(16) C. Floriani and F. Calderazzo, *J. Chem. Soc. A*, 946 (1969).
(17) D. V. Stynes, H. C. Stynes, B. R. James, and J. A. Ibers, *J. Am. Chem. Soc.*, **95**, 1796 (1973).
(18) N. Ohta, W. Scheuermann, K. Nakamoto, Y. Matsuda, S. Yamada and Y. Murakami, *Inorg. Chem.*, **18**, 457 (1979).

0020-1669/80/1319-2822$01.00/0

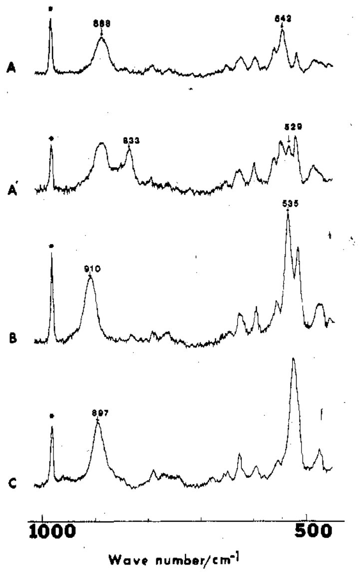

Figure 1. Resonance Raman spectra obtained by using 476.5-nm excitation: A, $[(py)Co(salen)]_2{}^{16}O_2$; A′, $[(py)Co(salen)]_2{}^{18}O_2$; B, $[(pyO)Co(salen)]_2O_2$; C, $[(DMF)Co(salen)]_2O_2$. The asterisks indicate the 983-cm^{-1} band of K_2SO_4 (internal standard).

strong band at 897 cm^{-1} although the band corresponding to the 542-cm^{-1} band of the py complex is not seen because it is probably hidden by a Co(salen) band.

Two bands at 910–888 and 542–535 cm^{-1} observed for the $[BCo(salen)]_2O_2$ series can be assigned to $\nu(O_2)$ and $\nu(CoO)$, respectively, due to the following reasons: (1) These frequencies are in the ranges expected for the peroxo complexes of the 2:1 ($metal/O_2$) type.[19–21] The ν(Co–B) are expected to be below 350 cm^{-1}.[22,23] (2) The intensities of these two bands are sensitive to the exciting frequency in the region where the $Co–O_2$ CT band is expected (Figure 3). (3) These frequencies are moderately sensitive to the change in the base ligand (Table I). (4) The $\nu(O_2)$ of the py complex at 888 cm^{-1} is insensitive to pyridine deuteration. Previously Barraclough et al.[24] assigned the $\nu(O_2)$ of $[(DMF)Co(salen)]_2O_2$ at 800 cm^{-1}. This band is probably due to a Co(salen) vibration since Co(salen) as well as analogous py and pyO complexes exhibit similar bands near 800 cm^{-1}.

Figure 2 shows the RR spectra of $[(pyO)Co(salen)]_2O_2$ as a function of the exciting frequency. It is seen that the intensities of the two bands at 910 and 535 cm^{-1} change markedly as the exciting frequency changes. Similar spectra have been obtained for the analogous oxygen adducts containing py and DMF. In Figure 3, we have plotted the excitation profiles of these bands together with its electronic spectrum. It was found that, in all three cases, the intensities of $\nu(O_2)$ and $\nu(CoO)$ are maximized near 500 nm, indicating that their $Co–O_2$ CT bands are near 500 nm. The maximum positions may be shifted slightly by changing the base ligand although these shifts are too small to be determined accurately.

It is well established that, as more electrons drift from the metal to O_2, the O_2 bond order is reduced, the O_2 distance becomes longer, and the $\nu(O_2)$ shifts to a lower frequency. This is clearly seen in the following series (bond order, bond distance, $\nu(O_2)$): O_2^+ (2.5, 1.12 Å, 1905 cm^{-1}) > O_2 (2.0, 1.21 Å, 1580 cm^{-1}) > O_2^- (1.5, 1.33 Å, 1097 cm^{-1}) > O_2^{2-} (1.0, 1.49 Å, 802 cm^{-1}).[25] The $\nu(O_2)$ of the three compounds studied here (Table I) are close to that of O_2^{2-}, indicating the presence of the peroxo O_2 in all cases. It should be noted, however, that the O_2 distance in $[(DMF)Co(salen)]_2O_2$ (1.339 Å)[5] is rather close to that of O_2^-. The average O_2 distance of 49 peroxo complexes is 1.45 Å, and their $\nu(O_2)$ are in the range from 932 to 790 cm^{-1}.[25] Therefore, the above compound is a rare example for which the bond distance and vibrational frequency give different classifications of the O_2 moiety. In Table II, we have compared the O_2 and CoO distances with $\nu(O_2)$ for three compounds containing the bridging O_2 group. Although both $[(DMF)Co(salen)]_2O_2$ and $[(NH_3)_5CoO_2Co(NH_3)_5](SO_4)_2 \cdot 4H_2O$ are regarded as peroxo complexes, the $\nu(O_2)$ of the former (897 cm^{-1}) is much higher than that of the latter (808

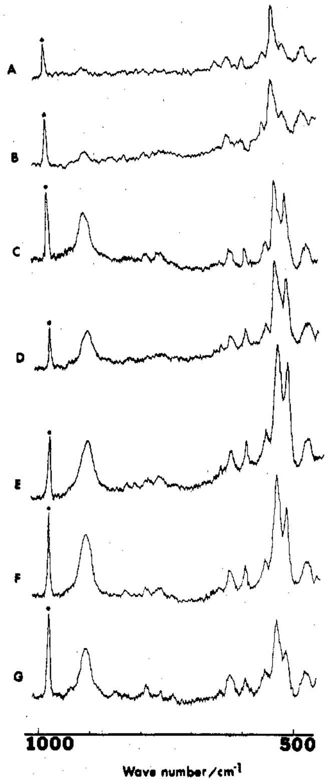

Figure 2. Resonance Raman spectra of $[(pyO)Co(salen)]_2O_2$ obtained by excitations at (A) 589 nm, (B) 579 nm, (C) 514.5 nm, (D) 496.5 nm, (E) 488.0 nm, (F) 476.5 nm, and (G) 457.9 nm. The asterisks indicate the 983-cm^{-1} band of K_2SO_4 (internal standard).

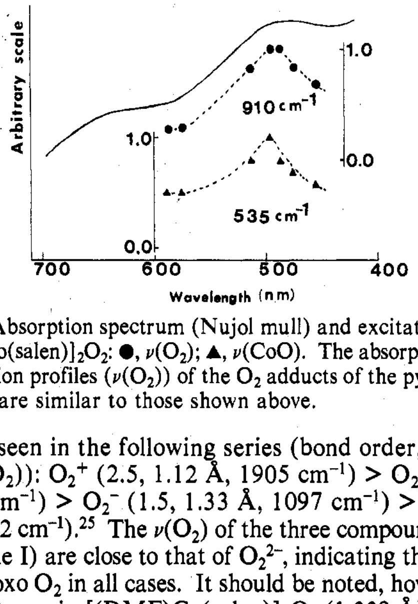

Figure 3. Absorption spectrum (Nujol mull) and excitation profiles of $[(pyO)Co(salen)]_2O_2$: ●, $\nu(O_2)$; ▲, $\nu(CoO)$. The absorption spectra and excitation profiles ($\nu(O_2)$) of the O_2 adducts of the py and DMF complexes are similar to those shown above.

---

(19) T. B. Freedman, C. M. Yoshida, and T. M. Loehr, *J. Chem. Soc., Chem. Commun.*, 1016 (1974).

(20) T. Shibahara and M. Mori, *Bull. Chem. Soc. Jpn.*, **51**, 1374 (1978).

(21) J. B. R. Dunn, D. F. Shriver, and I. M. Klotz, *Proc. Natl. Acad. Sci. U.S.A.*, **70**, 2582 (1973).

(22) K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd ed., Wiley, New York, 1978.

(23) Y. Kakiuti, S. Kida, and J. V. Quagliano, *Spectrochim. Acta*, **19**, 201 (1963).

(24) C. G. Barraclough, G. A. Lawrance, and P. A. Lay, *Inorg. Chem.*, **17**, 3317 (1978).

(25) L. Vaska, *Acc. Chem. Res.*, **9**, 175 (1976).

Table II. Vibrational Frequencies and Structures of Bridging O_2 Complexes

complex	approx charge on O_2	$R(O_2)$, Å	$\nu(O_2)$, cm^{-1}	R(CoO), Å	torsional angle,[g] deg
$[Co(NH_3)_5O_2Co(NH_3)_5]$-$(SO_4)_2 \cdot 4H_2O$	O_2^{2-}	1.47[a]	808[b]	1.88[a]	146[a]
$[(DMF)Co(salen)]_2O_2$	O_2^{2-}	1.339[c]	897[d]	1.91[c]	110[c]
$[Co(NH_3)_5O_2Co(NH_3)_5]$-$(HSO_4)_3SO_4$	O_2^-	1.31[e]	1110[f]	1.89[e]	180[e]

[a] Reference 32. [b] Reference 19. [c] Reference 5. [d] This work. [e] Reference 31. [f] The value obtained for analogous $[Co(NH_3)_5O_2Co(NH_3)_5](HSO_4)(SO_4)_2$ (T. Shibahara, *J. Chem. Soc., Chem. Commun.*, 864 (1973)). [g] The torsional angle of the Co-O-O-Co bond is 180° for the trans-planar linkage and decreases as the Co-O bonds are twisted around the O-O bond.

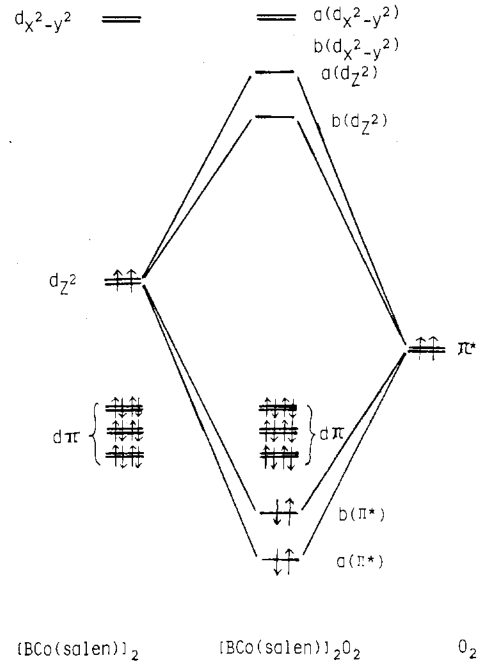

Figure 4. Approximate molecular orbital diagrams. Since the symmetry of the $[BCo(salen)]_2O_2$ type adduct is C_2, the energy levels are classified into the a and b species which are symmetric and antisymmetric about the C_2 axis, respectively.

cm^{-1}). This result suggests that the negative charge on the O_2 is probably less in the former than in the latter. The same conclusion can also be obtained from the electronic spectra of these compounds (*vide infra*). In accordance with this trend, the former has a shorter O_2 and a longer CoO bond than the latter. However, the O_2 distance of the DMF complex is unusually short for a peroxo type complex. At present, the origin of this anomaly is not clear.

As is shown in Figure 3, the electronic spectrum of the pyO complex exhibits two bands near 650 and 500 nm in the solid state. The excitation profiles of its $\nu(O_2)$ and ν(CoO) vibrations clearly indicate that the 500-nm band originates in an electronic transition involving the Co–O_2 charge transfer. It is interesting to note that $[(pyO)Co(dmg)_2]_2O_2$ (Hdmg = dimethylglyoxime) exhibits two absorption maxima at 700 and 550 nm.[26] These two bands probably correspond to the 650- and 500-nm bands of $[BCo(salen)]_2O_2$, respectively.

According to X-ray analyses, most of binuclear Co(III) complexes containing O_2 bridges take centrosymmetric structures in which the Co–O–O–Co linkage is nearly trans planar and the two equatorial ligand planes around the Co atoms are almost parallel to each other.[27-31] In this respect, the structure of the present DMF complex[5] is unusual since its two Co–O bonds form a torsional angle of 110°. A similar deviation from the trans-planar linkage is reported for $[(NH_3)_5CoO_2Co(NH_3)_5](SO_4)_2 \cdot 4H_2O$ (torsional angle = 146°).[32]

Figure 4 illustrates an approximate MO diagram for $[BCo(salen)]_2$, O_2, and $[BCo(salen)]_2O_2$. Similar to the case of the 1:1 complex,[33] only the interaction between the Co d_{z^2} and the O_2 π^* orbitals was considered. According to this diagram, the most probable transitions for the 500- and 650-nm bands are those of the $\pi^* \rightarrow d_{z^2}$ and $d\pi \rightarrow d_{z^2}$, respectively. Since the former is expected to accompany charge transfer between the Co and O_2, it can account for the strong enhancement of $\nu(O_2)$ and ν(CoO) shown in Figure 3. The latter, on the other hand, is essentially a d–d transition in agreement with the observation that the 650-nm band is relatively weak. Peroxo-bridged dicobalt(III) complexes such as $[Co_2(en)_2(dien)_2O_2](ClO_4)_4$ (en = ethylenediamine; dien = diethylenetriamine) exhibit the Co–O_2 CT bands in the region of 300–400 nm[34] with weak d–d transitions in the visible region. These results are understandable in terms of our MO diagram since a strong axial ligand such as amine raises the d_{z^2} level, resulting in the blue-shift of the Co–O_2 CT band. A larger energy gap between the d_{z^2} and π^* orbitals would bring about more electron drift from Co to O_2, resulting in an increase in the O_2 distance and a decrease in $\nu(O_2)$. Thus, the DMF complex has a shorter O_2 bond and a higher $\nu(O_2)$ than the decaammine Co complex (Table II). It is interesting to note that the O_2 binding of the DMF complex is reversible whereas that of the decaammine complex is irreversible in solution. Thus, the limit of the reversibility seems to lie somewhere between 1.339 and 1.47 Å in terms of the O_2 distance.

Acknowledgment. The work performed at Marquette University was supported by the National Science Foundation (Grant CHE-7915169) and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. $[(py)Co(salen)]_2O_2$, 23411-54-3; $[(DMF)Co(salen)]_2O_2$, 23507-67-7; $[(pyO)Co(salen)]_2O_2$, 23411-53-2.

---

(26) G. N. Schrauzer and L. P. Lee, *J. Am. Chem. Soc.*, **92**, 1551 (1970).

(27) J. R. Fritch, G. G. Christoph, and W. P. Schaefer, *Inorg. Chem.*, **12**, 2170 (1973).

(28) R. Fronczek and W. P. Schaefer, *Inorg. Chim. Acta*, **9**, 143 (1974).

(29) R. E. Marsh and W. P. Schaefer, *Acta Crystallogr., Sect. B*, **B24**, 246 (1968).

(30) L. A. Lindblom, W. P. Schaefer, and R. E. Marsh, *Acta Crystallogr., Sect. B*, **B27**, 1461 (1971).

(31) W. P. Schaefer and R. E. Marsh, *Acta Crystallogr.*, **21**, 735 (1966).

(32) W. P. Schaefer, *Inorg. Chem.*, **7**, 725 (1968).

(33) R. D. Jones, D. A. Summerville, and F. Basolo, *Chem. Rev.*, **79**, 142 (1979).

(34) A. B. P. Lever and H. B. Gray, *Acc. Chem. Res.*, **11**, 348 (1978), and references therein.