Table I. X-ray Line Positions for Monoclinic $MoO_3 \cdot {}^1/_2H_2O$

I/I_0[a]	*hkl*	2θ, deg calcd	2θ, deg exptl[b]	*d*, Å exptl[c]
1	100	9.369	9.38	9.42
100	001	12.782	12.79	6.916
0.6	$10\bar{1}$	14.139	14.15	6.254
12	101	17.436	17.48	5.069
89	200	18.803	18.82	4.711
0.7	$20\bar{1}$	20.364	20.46	4.337
79	201	25.014	25.04	3.553
64	002	25.725	25.72	3.461
11	$11\bar{1}$	27.932	27.92	3.192
95	$20\bar{2}$ $30\bar{1}$	28.499 28.523	28.49	3.130
28	102	29.320	29.31	3.045
5	111	29.789	29.79	2.997
1	301	33.729	33.74	2.654
1	211	34.915	35.02	2.560
8	$40\bar{1}$	37.527	37.51	2.396
3	400	38.137	38.15	2.357
35	003	39.013	38.99	2.308
70	$20\bar{3}$	39.593	39.58	2.275
12	$40\bar{2}$	41.407	41.38	2.180
27	302	42.788	42.73	2.114
47	401	43.075	43.07	2.099
2	$11\bar{3}$	45.498	45.48	1.993
2	013	46.306	46.29	1.960
5	$50\bar{1}$	47.093	47.04	1.930
13	203	47.415	47.40	1.916
20	500	48.205	48.21	1.886
7	$40\bar{3}$	48.895	48.90	1.861
8	$31\bar{3}$	50.122	50.07	1.820
5	$12\bar{1}$ 402	51.324 51.330	51.37	1.777
11	004	52.875	52.85	1.731
9	303	54.090	54.01	1.696
15	$50\bar{3}$	55.886	55.93	1.643
4	$60\bar{1}$	57.188	57.13	1.611
9	$11\bar{4}$ 320	57.634 57.647	57.63	1.598
12	$40\bar{4}$	58.983	58.98	1.565
22	$31\bar{4}$	60.581	60.65	1.526
12	321	60.864	60.88	1.520
6	$51\bar{3}$	61.664	61.72	1.502
4	$61\bar{1}$	62.891	62.86	1.477
4	$61\bar{2}$	64.640	64.68	1.440
11	$10\bar{5}$ 205	66.024 66.081	66.05	1.413
5	$32\bar{3}$	67.507	67.49	1.387

[a] Preferred orientation effects render these values somewhat variable (see discussion). [b] Estimated measurement error 0.011 ± 0.008°. [c] Based upon λ(Cu Kα_1) = 1.540 598 1 Å (see: Deslattes, R. D.; Henins, A. *Phys. Rev. Lett.* **1973**, *31*, 972).

from ~50 to 70 °C. It precipitates under these conditions even in the presence of submolar concentrations of thorium, uranium, and plutonium.

The experimental procedure used by Vorob'ev and Davydov[8] to prepare a molybdenum oxide containing 0.5 mol of water/mol of MoO_3 falls within the range of conditions used in our study to prepare monoclinic $MoO_3 \cdot {}^1/_2H_2O$. The hemihydrate prepared by Vorob'ev and Davydov and that prepared in this work may be the same compound. Work is currently under way on the characterization of a different hemihydrate phase that can be formed under slightly modified conditions.

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Contribution from the Department of Chemistry,
Marquette University, Milwaukee, Wisconsin 53233

Matrix-Isolation Infrared Spectra of (Octaethylporphyrinato)manganese(II) and (Phthalocyaninato)manganese(II) and Their Dioxygen Adducts

Takeshi Watanabe, Tomoharu Ama, and Kazuo Nakamoto*

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The symmetric side-on coordination of dioxygen in (dioxygen)(tetraphenylporphyrinato)manganese Mn(TPP)O_2, is well established by electronic[1] and ESR[1,2] studies and MO calculations.[3] We have recently provided further support for this structure through an IR study on Mn(TPP)O_2, which was prepared via cocondensation of Mn(TPP) vapor with isotopically scrambled dioxygen ($^{16}O_2$ + $^{16}O^{18}O$ + $^{18}O_2$) diluted in argon on a cold window at ~15 K.[4] Furthermore, we have located the $\nu(O_2)$ (ν: stretching) of Mn(TPP)O_2 at 983 cm^{-1}, which is between those of superoxo (1200–1100/cm^{-1}) and peroxo (900–750 cm^{-1}) and is much higher than that previously assigned (ca. 840 cm^{-1}).[5] This result has led us to conclude that the negative charge on the O_2 of Mn(TPP)O_2 is between those of superoxo (O_2^-) and peroxo (O_2^{2-}) adducts. The main objective of this investigation is to determine whether (dioxygen)(octaethylporphyrinato)manganese, Mn(OEP)O_2, and (dioxygen)(phthalocyaninato)manganese, Mn(Pc)O_2, prepared by matrix cocondensation techniques exhibit $\nu(O_2)$ in a range similar to that of Mn(TPP)O_2. Previous researchers[6] reported the isolation of crystalline Mn(Pc)O_2 from a DMA (*N*,*N*-dimethylacetamide) solution. They assigned a weak IR band at 1094 cm^{-1} to the $\nu(^{18}O_2)$ of Mn(Pc)$^{18}O_2$ and suggested the end-on coordination of a superoxo type dioxygen. However, the corresponding $\nu(^{16}O_2)$ was not distinct and assumed to be hidden under the tail of a strong Pc band at 1167 cm^{-1}. It is, therefore, of great interest to determine whether the $\nu(^{16}O_2)$ of Mn(Pc)O_2 prepared in inert-gas matrices appears near 980 cm^{-1} as found for Mn(TPP)O_2 or near 1167 cm^{-1} as assigned for the solid compound obtained from a DMA solution.

Experimental Section

The complex Mn(OEP)$(py)_2$ was prepared by the literature method.[7] It was placed in the Knudsen cell of our matrix-isolation system and heated under 10^{-6} torr at ~320 K for 4 h until the vacuum gauge indicated complete dissociation. The resulting Mn(OEP) was vaporized from the Knudsen cell at ~400 K and cocondensed with pure Ar or O_2 diluted in Ar at various ratios on a CsI window that was cooled to ~15 K by a CTI Model 21 closed-cycle helium refrigerator. Similar experiments were also carried out by using pure Kr or O_2 diluted in Kr. The complex Mn(Pc) was purchased from Eastman Kodak and used without purification. Procedures similar to those described above were used to deposit Mn(Pc) and Mn(Pc)O_2 onto the cold window. Mn(Pc) was preheated at ~450 K for 14 h to remove impurities adsorbed on the sample and evaporated on the cold window by heating at 500 K.

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

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(1) Hoffman, B. M.; Weschler, C. J.; Basolo, F. *J. Am. Chem. Soc.* **1976**, *98*, 5473.
(2) Hoffman, B. M.; Szymanski, T.; Brown, T. G.; Basolo, F. *J. Am. Chem. Soc.* **1978**, *100*, 7253.
(3) Hanson, L. K.; Hoffman, B. M. *J. Am. Chem. Soc.* **1980**, *102*, 4602.
(4) Urban, M. W.; Nakamoto, K.; Basolo, F. *Inorg. Chem.* **1982**, *21*, 3406.
(5) Jones, R. D.; Budge, J. R.; Ellis, P. E.; Linard, J. E.; Summerville, D. A.; Basolo, F. *J. Organomet. Chem.* **1979**, *181*, 151.
(6) Lever, A. B. P.; Wilshire, J. P.; Quan, S. K. *J. Am. Chem. Soc.* **1979**, *101*, 3668; *Inorg. Chem.* **1981**, *20*, 761.
(7) Bonnett, R.; Dimsdale, M. J. *J. Chem. Soc., Perkin Trans. 1* **1972**, 2540.

0020-1669/83/1322-2470$01.50/0

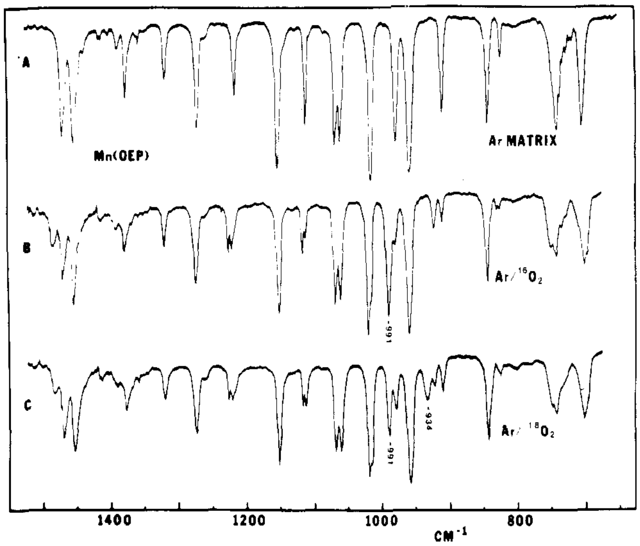

Figure 1. Infrared spectra of (A) Mn(OEP) in an Ar matrix, (B) Mn(OEP) cocondensed with $^{16}O_2$/Ar (1/10), and (C) Mn(OEP) cocondensed with $^{18}O_2$/Ar (1/10), all at ~15 K.

polystyrene bands were used for calibration of frequency reading. The gases, Ar (99.9995%), Kr (99.995%), $^{16}O_2$ (99.99%), and $^{18}O_2$ (99.88%), were purchased from Matheson, Airco and Monsanto Research.

Results and Discussion

Mn(OEP) and Mn(OEP)O$_2$. Since Mn(OEP) itself is air sensitive, it was prepared in our matrix-isolation system by heating Mn(OEP)(py)$_2$ as described in the Experimental Section. The IR spectrum (1500–700 cm^{-1}) of Mn(OEP) thus obtained is shown in trace A of Figure 1. As expected, it is very similar to those of Co(OEP),[8] Fe(OEP),[9] and Ni(OEP)[10] in the high-frequency region where OEP vibrations are dominant. Previously, Abe et al.[11] reported normal-coordinate analyses and band assignments of in-plane vibrations of Ni(OEP) and its OEP-$^{15}N_4$ and OEP-d_4 analogues. Recently, we revised their vibrational assignments of the E$_u$ species on the basis of a detailed IR study.[10] The band assignments shown in Table I are taken from this work.

When Mn(OEP) was cocondensed with $^{16}O_2$/Ar (1/10) on a cold window, a new rather strong band was observed at 991 cm^{-1} (trace B), next to the 980-cm^{-1} band of pure Mn(OEP) (trace A). Similar experiments with $^{18}O_2$/Ar (trace C) decreased the intensity of the 991-cm^{-1} band and produced a new band at 934 cm^{-1}. These results suggest the 991-cm^{-1} band in trace B is an overlap of the $\nu(^{16}O_2)$ of Mn(OEP)O$_2$ and a split component of the Mn(OEP) vibration at 980 cm^{-1}. The 1217-cm^{-1} band of Mn(OEP) also shows a similar splitting (1228 and 1222 cm^{-1}) upon oxygenation. Thus we conclude that, in both Mn(TPP)O$_2$ and Mn(OEP)O$_2$, the $\nu(^{16}O_2)$ bands appear in the same region (983–991 cm^{-1}) with low or medium intensity.

Both traces B and C show that the reaction of Mn(OEP) with O$_2$ causes splittings of some OEP bands. This is clearly seen for the Mn(OEP) bands at 1473, 1217, 1113, 1016, 980, 911, 826, and 744 cm^{-1}. Exactly the same splittings were observed when Kr was used as a matrix gas. Thus, the observed splittings are not due to the matrix-site effect. As stated in our previous paper,[4] the side-on coordination of dioxygen to Mn(TPP) lifts the Mn atom by ca. 0.5 Å from the pyrrole plane and lowers the overall symmetry from D_{4h} to C_{2v}. Such symmetry lowering should split the IR-active (E$_u$) porphyrin core vibrations. Thus, the Mn(TPP) bands at 1206, 801, and 759 cm^{-1} must be assigned to porphyrin core vibrations.[4] In the case of Mn(OEP), the available band assignments (Table I)[10,11] show, in fact, that most of the split bands originate in porphyrin core vibrations. Exceptions are the ethyl group vibrations at 1113, 1016, and 826 cm^{-1}, which are probably coupled with porphyrin core vibrations.

Table I. Observed IR Frequencies (cm^{-1}) and Band Assignments of Mn(OEP), Mn(OEP)$^{16}O_2$, and Mn(OEP)$^{18}O_2$ in Ar Matrices[a]

Mn(OEP)	Mn(OEP)$^{16}O_2$	Mn(OEP)$^{18}O_2$	assignment[a]
1604	1604	1604	ν_{37}: $\nu(C_\beta-C_\beta)$
1551	1551	1551	ν_{37}: $\nu(C_\alpha-C_m)$
1473[c]	1485	1484	ν_{39}: $\nu(C_\alpha-C_m)$
	1472[c]	1471[c]	
1473[c]	1472[c]	1471[c]	Et
1456	1456	1455	Et
1391	1391	1390	ν_{40}: $\nu(C_\alpha-C_\beta)$, $\nu(C_\beta-Et)$
1379	1380	1378	Et
1321	1321	1320	Et
1273	1276	1274	ν_{41}: $\nu(C_\alpha-C_\beta)$, $\nu(C_\beta-C_\beta)$
1217	1228	1226	ν_{42}: $\nu(C_\alpha-C_m)$, $\nu(C_\alpha-N)$, $\delta(C_m-H)$
	1222	1220	
1154	1154	1152	ν_{43}: $\nu(C_\alpha-N)$
1127	1131	1129	ν_{44}: $\delta(C_m-H)$, $\nu(C_\alpha-N)$
1113	1118	1117	Et
	1113	1113	
1069	1071	1069	Et
1062	1063	1062	
1016	1021	1019	Et
	1018	1017	
	991[c]		$\nu(^{16}O_2)$
980	991[c]	991	ν_{45}: $\nu(C_\alpha-N)$, $\nu(C_\alpha-C_m)$
	980	980	
959	960	960	Et
		934	$\nu(^{18}O_2)$
911	924	924	ν_{46}: $\nu(C_\alpha-C_m)$, $\nu(C_\beta-Et)$
	912	912	
845	845	844	$\pi(C_m-H)$
826	830	830	$\pi(C_m-H)$
	826	827	
744	751	750	π(skeletal)
	744	744	
722	(hidden)	(hidden)	ν_{47}: $\nu(C_\alpha-N)$
707	701	702	π(skeletal)
	697	698	

[a] Only the bands in the 1650–650-cm^{-1} region are listed.
[b] Band assignments are based on ref 10. Abbreviations: ν, stretching; δ, in-plane bending; π, out-of-plane bending. C_α, C_β, and C_m refer to the α-, β-, and meso-carbon atoms, respectively.
[c] Overlapped band.

Mn(Pc) and Mn(Pc)O$_2$. Metallophthalocyanines exist in several crystalline modifications of which the α and β forms are well characterized by IR spectra and X-ray powder patterns.[12,13] Regardless of the central metal atom, the α form exhibits bands near 1173, 1110, 877, and 780 cm^{-1} whereas the β form lacks all these bands.[12] According to Sidorov and Kotlyar,[12] the α form is obtained by sublimation and the α to β transition occurs when the sublimate thus obtained is heated in vacuo. X-ray studies[13] have shown that the metal atom in the β form is coordinated by two nitrogen atoms of the adjacent Pc molecules while such intermolecular interaction does not exist in the α form. As expected, the matrix-isolation IR spectrum of Mn(Pc) shown in trace A of Figure 2 is similar to those of metallophthalocyanines in the α form, except that all the bands are sharper and the two bands near 1296 and

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(8) Urban, M. W.; Nakamoto, K.; Kincaid, J. *Inorg. Chim. Acta* **1982**, *61*, 77.

(9) Watanabe, T.; Ama, T.; Nakamoto, K., submitted for publication in *J. Phys. Chem.*

(10) Kincaid, J.; Urban, M. W.; Watanabe, T.; Nakamoto, K., submitted for publication in *J. Phys. Chem.*

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

(12) Sidorov, A. N.; Kotlyar, I. P. *Opt. Spectrosc.* (*Engl. Transl.*) **1961**, *11*, 92.

(13) Stymne, B.; Sauvage, F. X.; Wettermark, G. *Spectrochim. Acta, Part A* **1979**, *35A*, 1195; **1980**, *36A*, 397.

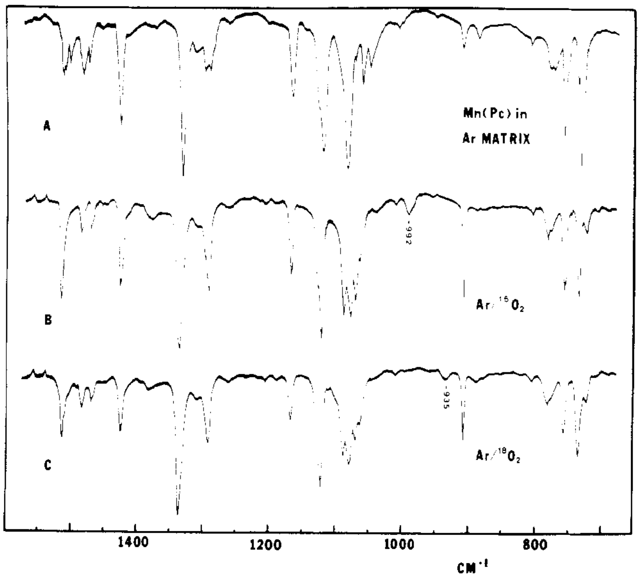

Figure 2. Infrared spectra of (A) Mn(Pc) in an Ar matrix, (B) Mn(Pc) cocondensed with $^{16}O_2$/Ar (1/10), and (C) Mn(Pc) cocondensed with $^{18}O_2$/Ar (1/10), all at ~15 K.

1056 cm^{-1} split in Ar matrices. Table II lists the observed frequencies and probable band assignments based on previous work.[12,13]

Different from Mn(TPP) and Mn(OEP), Mn(Pc) in the β form is stable and does not react with oxygen under ambient conditions. However, several regions of the IR spectra exhibit marked changes when Mn(Pc) vapor is cocondensed with $^{16}O_2$ diluted in Ar (1/10). This is demonstrated by trace B of Figure 2. These changes may be due to the lowering of symmetry of the Pc band and/or the emergence of a new $\nu(O_2)$ band as a result of oxygenation. To distinguish these two possibilities, we have measured the IR spectrum of Mn(Pc) vapor cocondensed with $^{18}O_2$ diluted in Ar (1/10) (trace C). It is seen that traces B and C are almost identical except for the region from 1000 to 900 cm^{-1} where a weak band at 992 cm^{-1} in the former disappears completely and a new weak band emerges at 935 cm^{-1} in the latter. Thus, these weak bands must be assigned to the $\nu(^{16}O_2)$ and $\nu(^{18}O_2)$ of Mn(Pc)O$_2$, respectively. On the basis of the similarity of its $\nu(O_2)$ to those of Mn(TPP)O$_2$ (980 cm^{-1}) and Mn(OEP)O$_2$ (991 cm^{-1}), we may conclude that the structures and bondings of the MnO$_2$ moiety in all these compounds are similar.

Table II. Observed IR Frequencies (cm^{-1}) and Band Assignments of Mn(Pc), Mn(Pc)$^{16}O_2$, and Mn(Pc)$^{18}O_2$ in Ar Matrices

no.[a,b]	Mn(Pc)	Mn(Pc)$^{16}O_2$	Mn(Pc)$^{18}O_2$	assignment[a]
32	1615	1617	1615	ν(C=N), ν(C=C)
31	1594	1598	1595	
30	1514	1516	1515	
	1511			
	1504			
29	1484	1487	1485	
28	1475	1472	1470	
27	1428	1428	1428	
		1426	1426	
26	1334	1339	1339	
		1338	1338	
23	1300			
	1293	1293	1293	
21	1167	1168	1168	δ(C–H)
20	1120	1124	1123	
18		1089	1088	ν(C=N)
	1084	1079	1079	
		1071	1070	
17	1062	1065	1064	δ(C–H)
	1008			
	1008	1010	1009	
		992		$\nu(^{16}O_2)$
14	951	955	955	
			935	$\nu(^{18}O_2)$
13	911	907	908	
11	888	888	888	π(C–H)
10	807	804	803	
8	776	782	780	
	772	776	776	
6	757	757	757	
		756	756	
5	732	735	734	π(C–H)
		723	723	
3	570	570	569	π(ring)
	527	529	529	
2	511	512	511	
1	435	432	432	

[a] Numbering of observed bands and band assignments are based on ref 12 and 13. [b] Bands characteristic of the β-form (no. 9, 12, 15, 19, and 22) are not observed.

Previous workers[6] found that Mn(Pc) reacts with O$_2$ reversibly in DMA solution and were able to isolate a very stable solid from it, which they formulated as Mn(Pc)O$_2$. Their compound is definitely different from our Mn(Pc)O$_2$ since the latter decomposes when the matrix is warmed to ~200 K. This discrepancy may suggest that the solid compound isolated from a DMA solution is (1) a structural isomer with respect to the mode of oxygen binding, (2) a solvated complex similar to Mn(Pc)O$_2$(DMF),[14] or (3) a 1/2 adduct, [Mn(Pc)]$_2$O$_2$. In our view, (1) is ruled out since the end-on structure is expected to be less stable than the side-on structure.[3] (2) is unlikely because the IR spectrum of the solid we prepared by the reported procedure[6] did not show any DMA bands.[15] (3) is most probable since a 1/2 adduct such as [Mn(Pc)]$_2$O$_2$ is expected to be stable, and previous IR evidence to support the 1/1 end-on structure is not clear-cut. The $\nu(O_2)$ of the 1/2 adduct should be in the 900–750-cm^{-1} (peroxo) region. However, it may be very weak or forbidden in IR spectra due to its symmetrical bridging structure. It should be noted that the 1/1 (superoxo, end-on) and 1/2 (peroxo, bridging) adducts cannot be distinguished unequivocally by microanalysis and magnetic measurements. Thus, we conclude that the solid compound obtained from a DMA solution is the 1/2 adduct although the 1/1 adduct may predominate in solution.

In summary, all the $\nu(^{16}O_2)$ of Mn(TPP)O$_2$, Mn(OEP)O$_2$, and Mn(Pc)O$_2$ prepared in Ar matrices appear in the 992–983-cm^{-1} region of IR spectra with weak or medium intensity. These results combined with the previous $^{16}O_2$–$^{18}O_2$ isotope scrambling experiments on Mn(TPP)O$_2$ suggest that all three adducts contain symmetric side-on dioxygen and that the negative charge on the dioxygen is between those of typical superoxo (O_2^-) and peroxo (O_2^{2-}) adducts.

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Registry No. Mn(OEP), 51321-25-6; Mn(OEP)O$_2$, 86323-15-1; Mn(OEP)$^{18}O_2$, 86323-16-2; Mn(Pc), 14325-24-7; Mn(Pc)O$_2$, 68027-09-8; Mn(Pc)$^{18}O_2$, 86323-17-3.

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(14) Uchida, K.; Naito, S.; Soma, M.; Onishi, T.; Tamaru, K. *J. Chem. Soc., Chem. Commun.* **1978**, 217.

(15) The IR spectrum we obtained was almost identical with that reported previously in the 1175–1075-cm^{-1} region.