in the red pyridine solutions, where Garner et al.[18] have indicated some partial replacement of trifluoroacetate ligands by pyridine has occurred. The weak absorption in the crystals may therefore result from the incorporation of a very minor impurity component with additional pyridine substitution into the molecules.

Polarized single-crystal spectra never prove transition assignments absolutely. At best, one establishes the molecular polarizations. For the carboxylate dimers of molybdenum(II) the rather uncommon and spectacular resolution of vibrational structure in the lowest electronic absorption band at low temperatures has provided convincing evidence that the major component of this band is a weak electric-dipole-allowed transition derived from molecular z polarization. The intensity is sufficiently weak that vibronically excited lines have intensities comparable to the 0–0 progressions. The polarization of the band is that expected for a $\delta \rightarrow \delta^*$ transition. The exceptionally low intensity does pose some questions. It may result from some electron density transfer from metal to carboxylate orbitals. The empty carboxylate π^* orbitals can form a B_{2g} symmetry-adapted LCAO, which can interact with the filled δ-bonding orbitals. Since the transition is essentially an intermetallic electron transfer between the Mo d_{xy} orbitals, this removes electron density from between the metals where the overlap in the transition moment integral occurs. Evidence is also accumulating that at least one other transition occurs in the vicinity of this weak dipole-allowed transition.

The studies of the molybdenum(II) carboxylate dimers have emphasized the need to investigate a number of closely related systems. This is especially true because of the low-symmetry crystal sites that have been encountered. It has been clearly demonstrated that intermolecular interactions can shift transition moment vectors away from the expected molecular axes in specific cases. Also defect components in crystals of individual compounds have only been recognized when results from several systems have been compared. The present evidence indicates that this observed transition is a weak but electric-dipole-allowed ${}^1A_{1g} \rightarrow {}^1A_{2u}$ transition under D_{4h} symmetry. Such an assignment is also consistent with the most recent theoretical treatments of orbital energies. However, the uncertainties present in this assignment and questions about possible additional transitions in this energy region clearly indicate that further experimental and theoretical studies of these interesting systems should be very worthwile.

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Registry No. Tetrakis(μ-trifluoroacetato)dimolybdenum, 36608-07-8; tetrakis(μ-trifluoroacetato)bis(pyridine)dimolybdenum, 39176-71-1.

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Infrared Spectra of Molecular Oxygen Adducts of (Tetraphenylporphyrinato)manganese(II) in Argon Matrices

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The infrared spectra of Mn(TPP) and Mn(TPP)O_2 were measured in Ar matrices at ~15 K. Splittings of the Mn(TPP) vibrations upon oxygenation are attributed to the lowering of symmetry from D_{4h} to C_{2v}. The O_2 stretching bands of Mn(TPP)${}^{16}O_2$ and its ${}^{18}O_2$ analogue are located at 983 and 933 cm^{-1}, respectively. Oxygen isotope scrambling experiments confirmed the symmetric, side-on coordination of the O_2 in Mn(TPP)O_2. All attempts to synthesize superoxo adducts of Mn(TPP) and Mn(TPP)Cl via matrix cocondensation reactions were not successful.

In 1976, Hoffman, Weschler, and Basolo[2] first discovered the reversible oxygenation of (tetraphenylporphyrinato)manganese(II) (Mn(TPP)py + $O_2 \rightleftharpoons$ Mn(TPP)O_2 + py) in toluene solution at low temperatures using electronic and ESR spectroscopy. They proposed the $Mn^{IV}(O_2^{2-})$ formulation with a side-on coordination of the peroxide ion. Although their formulation and structure were challenged by Dedieu and Rohmer,[3] subsequent ESR studies on molecular oxygen adducts of Mn(p-substituted-TPP) and Mn(OEP) (OEP = octaethylporphyrinato anion) by Hoffman et al.[4] confirmed their original report. Furthermore, recent charge iterative extended Hückel MO calculations by Hanson and Hoffman[5] suggest that the most probable geometry of the Mn(TPP)O_2 core is one in which the Mn atom is ca. 0.5 Å above the pyrrole plane with the peroxo O–O bond staggered with respect to the pyrrole nitrogens. Jones et al.[6] attempted to determine the $\nu(O_2)$ (ν, stretch) of Mn(TPP)O_2 in toluene solution as well as in Nujol mulls using IR difference spectroscopy. The 803-cm^{-1} band, which was obtained by subtracting the IR spectrum of Mn(TPP) from that of Mn(TPP)(${}^{18}O_2$), was assigned to the $\nu({}^{18}O_2)$ of the dioxygen complex. Unfortunately, the corresponding $\nu({}^{16}O_2)$ band could not be observed because of overlap with the solvent band at 844 cm^{-1}.

Our previous studies report the preparation and IR spectra of "base-free" adducts such as Co(TPP)O_2,[7] Co(OEP)O_2,[8] Co(J-en)O_2 (J-en = N,N'-ethylenebis(2,2-diacetylethylideneaminato)anion),[9] and Co(acacen)O_2 (acacen = N,N'-ethylenebis(acetylacetone iminato)anion)[10] using the matrix cocondensation method. The advantages of this method

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are threefold: (1) air-sensitive compounds such as Mn(TPP) can be prepared in a Knudsen cell of the evacuated matrix-isolation system by heating air-stable parent compounds such as Mn(TPP)(py), followed by evaporation of "base-free" complexes at higher temperatures; (2) highly unstable O_2 adducts can be stabilized in inert-gas environments at ~15 K; (3) the IR spectra thus obtained are free from interference by solvent bands.

The main objectives of the present investigation were to locate the $\nu(O_2)$ of Mn(TPP)($^{16}O_2$), which was not observed previously, and to find out whether the unstable, end-on species $Mn^{III}(TPP)(O_2^-)$ proposed by Dedieu and Rohmer[3] could be stabilized in Ar matrices.

Experimental Section

The complex, Mn(TPP)py, was prepared according to the literature method.[11] It was placed in the Knudsen cell of our matrix-isolation system and heated in a vacuum of 10^{-6} torr at 480 K for 4 h until the vacuum gauge indicated complete dissociation of pyridine from the complex. So that complete dissociation could be ensured, heating was continued for another 2 h. The resulting Mn(TPP) was vaporized from the Knudsen cell at ~510 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. A thin film of Mn(TPP) was prepared by the same procedure in the absence of Ar and O_2 gases.

IR spectra were measured on a Beckman Model 4260 infrared spectrophotometer with 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 the frequency reading. The IR spectra of Mn(TPP) and its O_2 adduct did not exhibit any Mn(TPP)py or py bands.

The gases, Ar (99.9995%), $^{16}O_2$ (99.99%), and $^{18}O_2$ (99.88%), were purchased from Matheson and Monsanto Research. A mixture of $^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$ in the 1:2:1 ratio was prepared by electrical discharge of an equimolar mixture of $^{16}O_2$ and $^{18}O_2$.

Results and Discussion

As the first step to interpret the IR spectrum of Mn(TPP)O_2, we have measured the IR spectra of Mn(TPP) as a thin film and in an Ar matrix at ~15 K. Although both spectra are similar, the bands in an Ar matrix are sharper and slightly shifted to higher frequencies relative to those of the film. Table I lists the observed frequencies in both states, and trace A of Figure 1 shows the IR spectrum obtained in an Ar matrix. In general, the spectrum of Mn(TPP) is similar to that reported for Co(TPP),[7] except that several metal-sensitive bands[12] show small shifts. At present, complete vibrational assignments of the TPP complexes cannot be made due to lack of normal-coordinate calculations and sufficient isotopic data.

When Mn(TPP) is cocondensed with $^{16}O_2$/Ar (1:10), several bands due to Mn(TPP) split into two bands as shown in trace B of Figure 1 and Table I. According to X-ray analysis,[13] the molecular symmetry of Mn(TPP) is approximated by D_{4h}, since the Mn atom is only slightly displaced (0.19 Å) from the pyrrole plane. On the other hand, MO calculations[5] coupled with ESR studies[4] show that the most probable structure for Mn(TPP)O_2 would be the one in which the Mn atom is ca. 0.5 Å above the pyrrole plane and the peroxo O–O bond is staggered with respect to the pyrrole nitrogens. This results in an overall symmetry of the O_2 adduct of C_{2v}. Thus, the observed band splittings resulting from oxygenation may be attributed to the lowering of symmetry from D_{4h} to C_{2v} (E_u to $A_1 + B_1$).

Earlier studies showed very little changes in the IR spectra of Co(TPP)[7] and Co(OEP)[8] when they form end-on O_2 adducts in Ar matrices. Similar observations were made for resonance Raman spectra of cobalt(II) myoglobins,[14] which form end-on O_2 adducts. These results seem to suggest that the band splittings such as those observed for Mn(TPP)O_2 can occur only when the central metal forms relatively strong metal-oxygen bonds with a side-on oxygen molecule.

Table I. Observed IR Frequencies (cm^{-1}) of Co(TPP), Mn(TPP), and Mn(TPP)O_2

Co(TPP) Ar matrix	Mn(TPP) thin film	Mn(TPP) Ar matrix	Mn(TPP)$^{16}O_2$ Ar matrix
1605	1600	1603	1602
1522	1516	1517	1519
1497			1497
	1477	1477	1480
1444	1442	1444	1446
1358	1350	1352	1353
			1349
	1339	1339	1342
1317	1333	1333	1336
			1213
1209	1203	1206	1206
1180	1180	1181	1182
1157	1159	1160	1160
1077	1072	1072	1076
			1022
1026	1012	1013	1014
1009	1005	1007	1009
1001	999	999	1001
			983
837	835	836	834
			806
804	801	801	802
			760
757	759	759	756
737	737	738	739
728	728	729	728
715	723	722	718
703	704	704	705
669	670	670	668
659	662	662	661
			656
621	615	615	616
560	560	560	561
523	521	522	522
466	460	457	457
414	425	425	423
306	315	316	315

The new band that appears at 983 cm^{-1} upon oxygenation (trace B) was first thought to be a splitting of an E_u mode as discussed above. However, a similar experiment with $^{18}O_2$/Ar (1:10) yielded a new distinct band at 933 cm^{-1} (trace C). The observed shift of 50 cm^{-1} is close to that expected for the perturbed diatomic molecule (56 cm^{-1}). Thus, these two bands must be assigned to the $\nu(^{16}O_2)$ and $\nu(^{18}O_2)$ of Mn(TPP)O_2, respectively. The 1:1 (Mn(TPP)/O_2) stoichiometry of the adduct is supported by the observation that no significant spectral changes occurred when the O_2/Ar dilution ratio was changed from 1:950 to 1:250 to 1:10 or when pure O_2 was used as the matrix gas. All that happened was that the $\nu(O_2)$ band became stronger in pure O_2 than it was in Ar matrices.

Although the side-on coordination of O_2 in Mn(TPP)O_2 was suggested earlier on the basis of ESR[4] and MO studies,[5] we carried out the oxygen isotope scrambling experiment to provide further evidence on the structure of the dioxygen adduct. As is seen in trace D of Figure 1, three new bands were observed at 983, 958, and 933 cm^{-1} when Mn(TPP) was cocondensed with a mixture of $^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$ in approximately 1:2:1 ratio. The bands at 983 and 933 cm^{-1} correspond to the $\nu(O_2)$ of the $^{16}O_2$ and $^{18}O_2$ adducts, respectively. The remaining band at 958 cm^{-1} must be assigned

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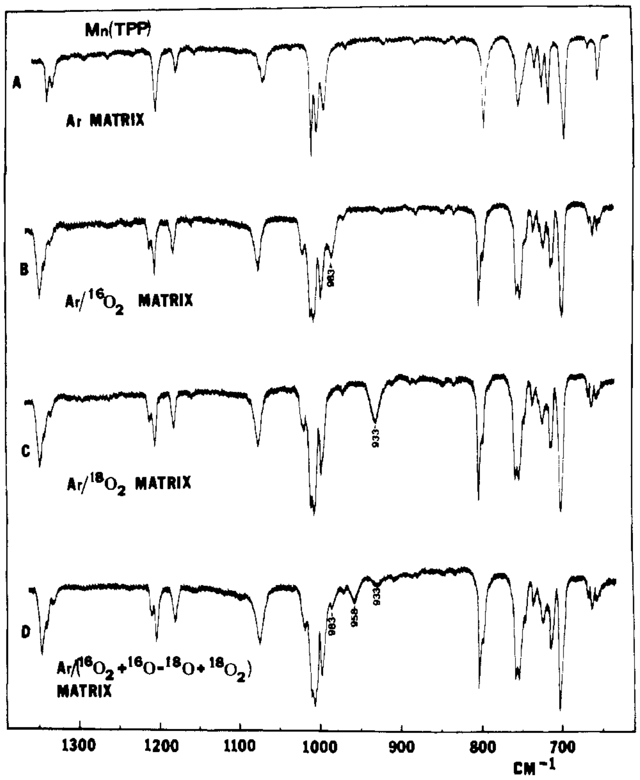

Figure 1. Infrared spectra of (A) Mn(TPP) in an Ar matrix, (B) Mn(TPP) cocondensed with $^{16}O_2/Ar$ (1:10), (C) Mn(TPP) cocondensed with $^{18}O_2/Ar$ (1:10), and (D) Mn(TPP) cocondensed with ($^{16}O_2$ + $^{16}O^{18}O$ + $^{18}O_2$)/Ar, all at ~15 K.

to the $^{16}O^{18}O$ species. This frequency is again very close to that expected for the isolated diatomic molecule (955 cm^{-1}). The observed three-peak pattern definitely confirms the symmetric side-on coordination of the O_2 in Mn(TPP)O_2. Previously, we have carried out a similar experiment on Co(TPP)O_2 which exhibited a four-peak pattern: 1278 (Co–$^{16}O^{16}O$), 1252 (Co–$^{16}O^{18}O$), 1241 (Co–$^{18}O^{16}O$), and 1209 cm^{-1} (Co–$^{18}O^{18}O$) in agreement with its end-on structure. If the O_2 in Mn(TPP)O_2 were of end-on type, we would expect the separation of the central peak to be approximately 8 cm^{-1} on the basis of the ratio of the $\nu(^{16}O^{18}O)$ bands (1247:958).

The $\nu(O_2)$ of Mn(TPP)O_2 determined by the present investigation (983 cm^{-1}) is much higher than that estimated previously for the toluene solution (near 840 cm^{-1}).[6] This discrepancy may be due to one of the following two reasons: (1) The Mn(TPP)O_2 in an Ar matrix takes a structure in which the Mn–O bond is longer (with a higher $\nu(O_2)$). (2) Previous results obtained in toluene solution could be erroneous in view of difficulties involved in applying low-temperature IR difference spectroscopy to O_2-sensitive compounds. We tend to think that (2) is responsible although repetition of similar experiments is required before we can come to a definitive conclusion.

It is interesting to note that the $\nu(^{16}O_2)$ of Mn(TPP)O_2 is intermediate between the superoxo (1200–1100 cm^{-1}) and peroxo (930–780 cm^{-1}) regions.[15] Table II lists the $\nu(O_2)$ and structures of "base-free" O_2 adducts. It should be noted that several O_2 adducts (all in side-on coordination) produced in inert-gas matrices exhibit $\nu(O_2)$ between 1100 and 920 cm^{-1}. The 2:1 adduct [Co(salen)]$_2O_2$ exhibits its $\nu(O_2)$ at 1011 cm^{-1} in the solid state.[18] Previously, we[10] have demonstrated that the $\nu(O_2)$ of Co(II) chelates can vary over a wide range (1280–800 cm^{-1}) depending upon the negative charge on the O_2, which is controlled by the nature of the in-plane and axial ligands. At present, we hold the view that this $\nu(O_2)$–O_2 charge relationship is valid for other metals as long as the nature of the metal–oxygen bond is similar. Thus, we conclude that the negative charge on the O_2 increases in the following order: Mn(phthalocyanine)O_2 (1154 cm^{-1})[23] < Mn(TPP)O_2 (983 cm^{-1}) < Ti(OEP)O_2 (898 cm^{-1}).[20] The O_2 in the first compound is close to the superoxide ion (end-on coordination).[23] The O_2 in the last compound is close to the peroxo type.[20] The negative charge on the O_2 of Mn(TPP)O_2 is somewhere between that of O_2^- and O_2^{2-}.

Table II. O_2 Stretching Frequencies of "Base-Free" O_2 Adducts (cm^{-1})[a]

compd	structure	ν-($^{16}O_2$)	ν-($^{16}O^{18}O$)	ν-($^{18}O_2$)	ref
Co(TPP)O_2	end-on	1278	1252 1241	1209	7
Co(OEP)O_2	end-on	1275		1202	8
Co(J-en)O_2	end-on	1260		1198	9
Co(acacen)O_2	end-on	1146		1098	10
LiO_2	side-on	1097	1067	1035	16
PdO_2	side-on	1024	996	967	17
[Co(salen)]$_2O_2$		1011		943	18
Mn(TPP)O_2	side-on	983	957	933	*b*
NiO_2	side-on	966	940	914	17
FeO_2	side-on	956	931	906	19
PtO_2	side-on	927	901	875	17
Ti(OEP)O_2	side-on	898			20
[Fe^{III}(OEP)O_2]$^-$ [c]	side-on	806		759	21

[a] In addition to those listed above, the O_2 adducts of Vaska complexes exhibit $\nu(O_2)$ in the range from 900 to 820 cm^{-1}.[22]
[b] Present work. [c] It is not certain whether a base ligand is coordinated at the axial position.

As stated in the introduction, one of our objectives was to search for the formation of unstable, end-on species that could be formulated as Mn^{III}(TPP)(O_2^-). Such an adduct is expected to show its $\nu(O_2)$ in the 1200–1100-cm^{-1} region. However, no new bands were observed in this range, in spite of repeated experiments under various conditions. The failure to find a band in this superoxo region had also been noted for studies of toluene solutions.[6] Further attempts were made to synthesize Mn^{IV}(TPP)Cl(O_2^-) via matrix cocondensation of Mn(TPP)Cl with O_2/Ar. However, no signs of adduct formation were noted. It must, therefore, be concluded that these superoxo type adducts are too unstable to form even in inert-gas matrices at ~15 K.

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Registry No. Mn(TPP), 31004-82-7; Mn(TPP)O_2, 61113-07-3; Mn(TPP)$^{18}O_2$, 82390-36-1.

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