

tuted benzenes these transitions are not described by an electron promoted from HOMO to LUMO. Rather, the T_1 transitions involve a mixing between the excitation from the HOMO to the second unoccupied orbital and the excitation from the second occupied π orbital to the LUMO.

Anions in Solution. The ground-state anions of most unsaturated hydrocarbons can be prepared as stable species in solution or in hydrocarbon glasses by alkali reduction or by means of gamma radiation.³⁴ Numerous studies of the absorption spectra of these stable ions have been carried out. A detailed comparison between the condensed-phase excitation energies and the gas phase values, determined by subtracting from the first EA the higher EAs of a molecule, will yield valuable information concerning solvation effects.

For styrene and naphthalene, we have found that the agreement is within 0.15 eV for those excitations predominantly involving transitions between π^* orbitals and for which the gas-phase anions are sufficiently long-lived. The agreement is poorer for those transitions to very short-lived anion states, indicating that solvation effects are quite different for these anion states. We note that certain transitions may not be seen in the condensed-phase studies if they are dipole-forbidden or only weakly allowed. The electron transmission method does not suffer from this limitation. It may happen, however, that an anion which is relatively long-lived in solution may have such a short lifetime in the gas phase that its energy cannot be determined.

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Conclusions

In this account, we have described the electron transmission technique and illustrated a few of the areas which will benefit from its application to hydrocarbon molecules. Without doubt the most important data resulting from transmission studies are the temporary anion energies. As a convenient reference, a table of the values which we regard as being most reliable is included. A complete bibliography of published work using electron transmission is available from one of the authors (P.D.B.).

We have also emphasized the close connection between orbital symmetry and anion lifetime and have pointed out the sensitivity of lifetime to substituents. This is an area which deserves detailed theoretical exploration.

Space has permitted only a discussion of those anions associated with the capture of electrons into vacant π^* orbitals. Other anion states, with two electrons in Rydberg orbitals, are also known to exist in some hydrocarbons. For most molecules the σ^* orbitals are sufficiently high in energy that the corresponding anions are too short-lived to be detected in transmission. We anticipate, however, that these states will be evident as broad enhancements of the cross sections for vibrational excitation of the neutral molecule by electron impact.

This paper is respectfully dedicated to the late George J. Schulz, whose pioneering contributions to the field of temporary anions made this work possible. We gratefully acknowledge the help of our colleague J. A. Michejda. Part of this article was written while K.D.J. was a Visiting Scholar at the University of Nebraska.

Electronic Spectra of Metal-Dioxygen Complexes

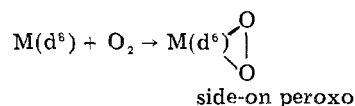
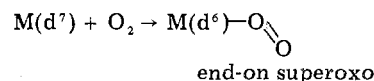
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The electronic nature of coordinated dioxygen has been the subject of many lively discussions in recent years. Most investigators now agree that binding of one dioxygen molecule to a single metal atom or ion yields a ground state in which either one or two electrons have been transferred to a π^* orbital of the O_2 unit.² The following two cases, which have been studied in detail,

serve to illustrate this point:



Although it may be too much to expect all dioxygen-metal complexes to fall into these limiting geometrical and electronic structural categories, nevertheless the

Biographical information about Harry B. Gray appears in *Acc. Chem. Res.*, **11**, 232 (1978).

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(2) L. Vaska, *Acc. Chem. Res.*, **9**, 175 (1976), and references cited therein; also see I. Hyla-Kryspin, L. Natkaniec, and B. Jejuowska-Trzebiatowska, *Chem. Phys. Lett.*, **35**, 311 (1975), and *Bull. Acad. Pol. Sci.*, **25**, 193 (1977).

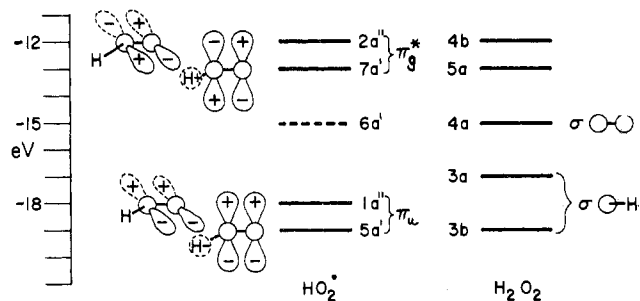


Figure 1. Orbital energy levels in the hydroperoxy radical, HO_2 , and hydrogen peroxide, H_2O_2 , based on electronic and photoelectron spectroscopic measurements.

utility of the superoxo and peroxy formulations, as well as end-on and side-on geometries, is well established.

Given that we now have a reasonable understanding of $\text{M}-\text{O}_2$ ground states, it would seem timely to turn our attention to the nature of the low-lying excited states in various metal-dioxygen complexes. Information concerning the electronic excited states has come mainly from the few detailed studies of absorption spectra that have been made. It is our purpose here to develop a unified interpretation of the electronic spectra of the well-characterized 1:1 and 1:2 superoxo- and peroxy-metal complexes. To provide a foundation for this development, we will draw heavily on the well-studied electronic structural properties of related protonated derivatives, HO_2 and H_2O_2 .

Interest in the electronic structures of metal-dioxygen units is intense for many reasons. One reason for this interest is a desire to understand the bonding of O_2 to the metal centers in the oxygen-carrying proteins hemoglobin, myoglobin, hemerythrin, and hemocyanin. Another relates to the important question of the nature of the electronic interaction of O_2 with the metal atoms in homogeneous oxidation and oxygenation catalysts and in metalloenzymes. Still another is the need to develop reasonable models for the bonding of O_2 to catalytic surfaces. Our treatment of the electronic structures and spectra of well-characterized metal-dioxygen complexes should provide a good foundation for the formulation of $\text{M}-\text{O}_2$ electronic interactions in these important but highly complicated systems.

Energy Levels in HO_2 and H_2O_2 (Figure 1)

The highest occupied orbitals in the free superoxide ion are the degenerate π_g^* set lying at -0.44 eV.³ Addition of a proton to form the hydroperoxy radical, the analogue for 1:1 superoxometal complexes, stabilizes these orbitals by some 12 eV⁴ and the loss of cylindrical symmetry lifts the degeneracy. The hydroperoxy radical exhibits^{5,6} an absorption band at about 7100 cm^{-1} , which is assigned as a transition between the split π_g^* levels. The $\pi-\pi^*$ transition in this species occurs⁷ at $47\,620$ cm^{-1} , implying that the bonding π_u level lies at about -18 eV. The highest filled levels in the free peroxide ion lie above zero. Addition of two protons, to form H_2O_2 , the analogue for the bridging peroxy

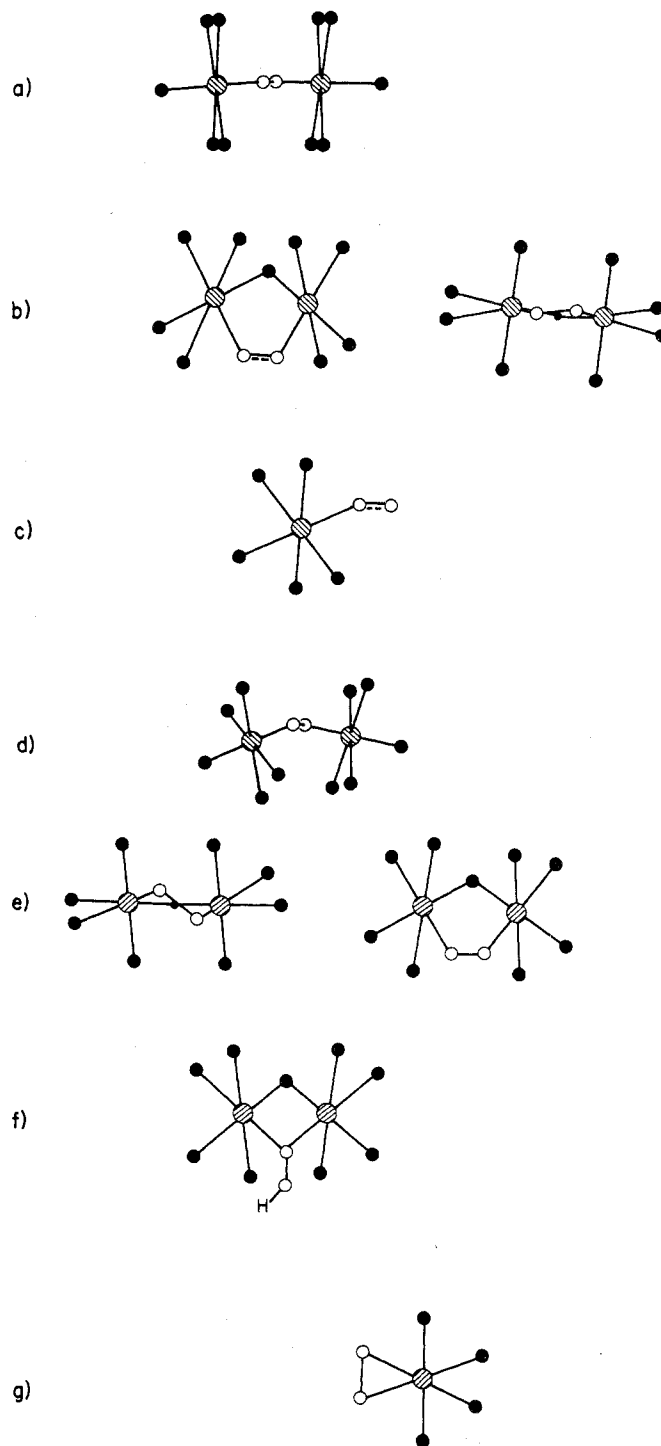


Figure 2. Modes of binding for superoxo and peroxy complexes: (a) bridging superoxo, (b) doubly bridging superoxo, (c) 1:1 end-on superoxo, (d) bridging peroxy, (e) doubly bridging peroxy, (f) bridging hydroperoxy, (g) side-on peroxy.

complexes, stabilizes and splits these highest filled (π^* -like) orbitals. Measurements of the photoelectron spectrum of hydrogen peroxide suggest that these levels lie at -11.69 and -12.69 eV, a splitting of some 8000 cm^{-1} .⁸ The other two p orbitals, which are involved in the OH σ bonds, lie at -17.4 eV. No data are available for H_2O_2^+ , the analogue for the 1:2 bridging superoxo derivatives. However, we suggest that the system is similar to H_2O_2 , but with the levels stabilized to some degree by the positive charge.

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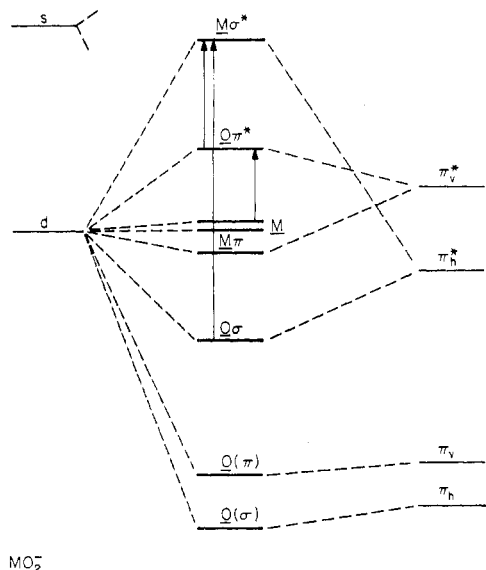


Figure 3. Simplified molecular orbital energy level diagram for a 1:1 superoxometal complex. The principal metal and dioxygen levels and the relevant LMCT and MLCT transitions are shown. If the M–O axis is z , then $d\sigma^*$ is derived from the d_{z^2} metal orbital. The $d\sigma^*(d_{z^2})$ orbital in most of the complexes discussed in this paper is more energetic; it is not shown in the diagram. This diagram is also applicable to bridging superoxo complexes after allowance is made for the fact that the $d\sigma^*$ levels are now appropriate combinations of orbitals on each metal atom (see ref 10). The ground state for a low-spin d^6 superoxometal complex is $(\pi_h)^2(\pi_v)^2(\pi_h^*)^2(d\pi)^6(\pi_v^*)^1$.

Bridging Superoxodimetal (1:2) Complexes (Figure 2a,b)

The energy levels for the HO_2 radical shown in Figure 1 may be used as a basis of discussion for both the 1:1 and 1:2 superoxometal complexes. (The latter complexes possess⁹ a planar MO_2M unit (Figure 2a).) The π_g^* level splits into an in-plane orbital (π_h^*), which has strong σ bonding character, and an out-of-plane orbital, which is designated π_v^* . The electrons in the π_u orbitals are bound firmly to the O_2^- unit; for this reason $\pi_u(\text{O}_2^-) \rightarrow d\sigma^*$ transitions are expected to occur only at very high energies (i.e., outside the conventional ultraviolet region). The relative energies of the metal and dioxygen orbitals as well as the expected ligand-to-metal charge-transfer (LMCT) and metal-to-ligand charge-transfer (MLCT) transitions are shown in Figure 3.

Electronic spectra of bridging superoxo complexes exhibit a single intense band in the region $25\,000\text{--}33\,000\text{ cm}^{-1}$ ^{10–16} that has been assigned¹⁰ as a charge-transfer transition from the π_h^* orbital to an appropriate $d\sigma^*$ level on the metal center (Table IA). The molar extinction coefficient of this band generally lies in the range $1\text{--}3 \times 10^4\text{ L mol}^{-1}\text{ cm}^{-1}$ (Figure 4). A very weak feature observed near $12\,500\text{ cm}^{-1}$ in the absorption spectra of some complexes has been assigned¹⁰ to the

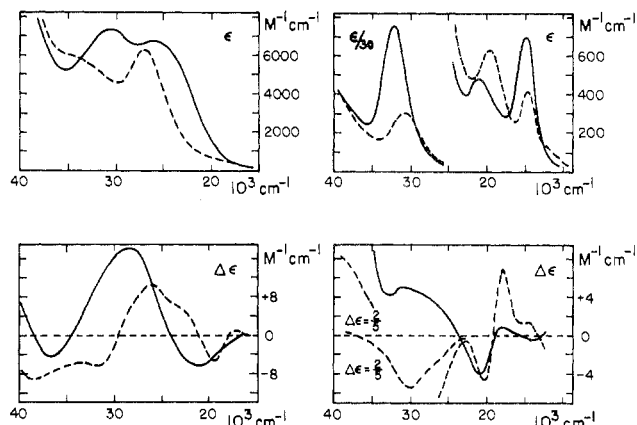


Figure 4. Aqueous solution absorption spectra of dioxygen adducts of Co(II)-L-histidine complexes. Top left: bridging peroxo, —; doubly bridging peroxo ($\text{OH}, \text{O}_2^{2-}$), ---. Top right: bridging superoxo, —; doubly bridging superoxo (OH, O_2^-), ---. Lower left and right boxes show the corresponding circular dichroism spectra for these species. (Adapted with permission from Bagger and Gibson.¹¹)

transition between the split components of the π_g^* level ($\pi_h^* \rightarrow \pi_v^*$). It appears that interaction with the metal rather than a proton^{4,5} causes a somewhat larger splitting of π_g^* .

Another prominent absorption system in the spectra (Figure 4) of bridging superoxodicobalt(III) species falls in the region $13\,000\text{--}20\,000\text{ cm}^{-1}$ ($\epsilon \sim 10^3\text{ L mol}^{-1}\text{ cm}^{-1}$); this band has been attributed to a $d\pi \rightarrow \pi_v^*$ charge-transfer transition,¹⁰ but an alternative assignment that should be considered is $\pi_v^* \rightarrow d\sigma^*$. We have adopted the former assignment because it alone is consistent with the band positions in the spectra of the μ -superoxo-decaammine- and μ -superoxo-decacyanodicobalt(III) species.¹⁰ The $\pi_h^* \rightarrow d\sigma^*$ and $\pi_h^* \rightarrow \pi_v^*$ transitions in these two species are at about the same energies, whereas the band in question is strongly blue-shifted in the decacyanide relative to the decaammine. If in fact the band were due to $\pi_v^* \rightarrow d\sigma^*$, no such blue shift should occur.

Indeed, the expected $\pi_v^* \rightarrow d\sigma^*$ transition was not identified in the previous study.¹⁰ Being a transition from an out-of-plane to an in-plane orbital, it is expected to be weak in absorption but could give rise to a strong feature in the circular dichroism spectrum. Study of the absorption and CD curves for a range of superoxo complexes^{11,13–14} reveals a candidate for this transition. Most of these spectra show a shoulder in absorption on the low energy edge of the $\pi_h^* \rightarrow d\sigma^*$ band (Table IA). In this same region there is a well-developed shoulder in the CD spectrum of the one complex that has been investigated.¹¹ Although d–d transitions may occur in this region, they would be components of $^1A_{1g} \rightarrow ^1T_{2g}$, which is magnetic-dipole-forbidden and therefore unlikely to give rise to a strong CD band. This shoulder could therefore be due to a $\pi_v^* \rightarrow d\sigma^*$ component, rather than to a d–d transition as previously surmised.¹⁰

Several 1:2 superoxo derivatives contain an additional bridging group, usually amido or hydroxo. The two bridging groups and the two metal atoms are approximately planar.^{16,17} The geometric structure of

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Table I
Electronic Spectra of Superoxometal Complexes^a

A. Bridging Superoxodimetal Complexes, $[L_x M(O_2^-) M L_x]^{n+}$						
M	L	$\pi_h^* \rightarrow \pi_v^*$	$d\pi \rightarrow \pi_v^*$	$\pi_v^* \rightarrow d\sigma^*$	$\pi_h^* \rightarrow d\sigma^*$	ref
Co	NH ₃	12.5 (2.04)	14.89 (2.97)	28.9sh (3.54)	33.1 (4.30)	10
Co	en, NH ₃		14.1 (3.05)	26.7sh (3.3)*	33.1 (4.29)	13
Co	trien		14.1 (3.11)		32.5 (4.29)	13
Co	dien, 1-pn		14.0 (3.19)		32.6 (4.36)	13
Co	tetren		14.1 (3.15)	27.0sh (3.3)*	31.9 (4.28)	13
Co	L-histidine		15.1 (2.85)*		31.9 (4.36)*	11
Co	CN	12.2 (1.1)	CD 14.2 (-0.5)*	26.8 (+3.5)*	31.0 (+5.5)*	11
			20.59 (2.87)		32.2 (4.24)	10
Rh	Cl, pyridine		16.6 (3.46)		37.7 (3.72) ^b	
Rh	Cl, 4-picoline		16.37 (3.43)	27.0sh (3.33)	34.72 (4.28) ^c	12
					33.90 (4.36) ^c	12
B. Doubly Bridged Complexes, $[L_x Co(X)(O_2^-) Co L_x]^{n+}$						
L	X	$d\pi \rightarrow \pi_v^*$	$\pi_v^* \rightarrow d\sigma^*$	$\pi_h^* \rightarrow d\sigma^*$		ref
en	NH ₂	14.6 (2.64)	28.5 (3.2)sh*	32.5 (3.87)		13, 18
			CD 26.7 (-1.05)	30.3 (+3.82)		
NH ₃	NH ₂	14.3 (2.45)		33.0 (3.61)		13
1-pn	NH ₂	14.4 (2.61)	28.0sh (3.3)*	32.4 (3.82)		18, 20
			CD 26.5 (-0.45)	30.3 (+5.52)		
en	OH	14.8 (2.72)	27.8 (3.7)*	~32.8 (2.7)*		13
1-pn	OH	14.9 (2.71)				13
L-histidine	OH	14.9 (2.6)*		30.7 (4.0)*		11
		CD 14.8* (+1.5)	26.8 (-3.0)sh	30.1 (-5.5)*		
C. 1:1 Superoxometal Complexes, $[L_x XCoO_2]^{n+}$						
L	X	$d\pi \rightarrow \pi_v^*$	$\pi_h^* \rightarrow d\sigma^*$			ref
CN	CN	18.87 (1.9) ^d	31.25 (3.45) ^d			26
S-Me ₂ en	Cl	20.79 (2.81) ^e	28.98 (3.72) ^e			24
S-Et ₂ en	Cl	20.32 ^e	26.95sh ^e			f
Co(II) (4,11-dienN ₄)			41.6 (4.39)*			27

^a In Tables I-III band positions in the absorption and CD spectra are reported in 10^3 cm^{-1} . These are followed by $(\log \epsilon)$ and $(\epsilon_1 - \epsilon_2)$ in parentheses, respectively. For solvents, see the cited literature. Data marked with an asterisk are estimated from graphical spectra in the article cited. ^b $\pi_h^* \rightarrow d_{x^2-y^2}$. ^c Assignment is uncertain. ^d In acetonitrile solution; the position of the $d\pi \rightarrow \pi_v^*$ band is solvent dependent. ^e 20% MeOH/EtOH at 10 K. ^f A. B. P. Lever and H. B. Gray, unpublished results.

these complexes differs from a singly bridged system in that the stereochemistry about the superoxo group is necessarily cis, whereas it is trans in the latter. For these two quasi-planar systems, however, the electronic structure and the splitting of the π^* level should not be very different.⁸ In accord with this idea, the spectroscopic characteristics of the two series of complexes do not differ markedly (Table IAB).^{11,13,18-21} Note, however, that the spectra of complexes containing -OH- and -NH₂- bridges also exhibit absorption bands in the 25 000-33 000 cm^{-1} region ($\pi \rightarrow d\sigma^*$ LMCT). The CD characteristics are often rather different and may allow absorptions attributable to the coordinated superoxo group to be identified.

1:1 Superoxo Complexes (Figure 2c)

Although a substantial number of 1:1 superoxo complexes are known,^{2,22,23} they are generally either fleeting intermediates on the way to bridging species or involve complex organic ligands whose electronic absorptions obscure the characteristic metal-dioxygen bands. Recently, however, some sterically hindered ethylenediamines bound to Co(II) have been used to

form 1:1 dioxygen adducts. Not only are the ligands in these cases ultraviolet transparent, but the formation of bridging species is inhibited by the steric hindrance.²⁴ The electronic spectra of such complexes have been measured and interpreted.²⁵ The electronic spectrum of $Co(CN)_5(O_2)^{3-}$ has also been reported.²⁶ All of these systems exhibit spectra that are closely related to those of their 1:2 analogues. The removal of a metal ion from one end of the superoxo group, relative to the bridging species, should cause some destabilization of the π^* set, with the effect on π_h^* being more pronounced. This should lead to red shifts in the $\pi_h^* \rightarrow \pi_v^*$ and the $\pi_h^* \rightarrow d\sigma^*$ ($\sigma \rightarrow \sigma^*$ LMCT) bands, and indeed the latter is observed (Table IC). Additional evidence of the LMCT character of this $\sigma \rightarrow \sigma^*$ transition may be drawn from the spectrum of the transient cobalt(II) macrocyclic derivative²⁷ (4,11-dieneN₄)Co(II)(O₂⁻), where the band in question is greatly blue-shifted relative to those in the spectra of the cobalt(III) systems previously discussed (Table I). The $d\pi \rightarrow \pi_v^*$ band in the 1:1 complexes should blue shift relative to the 1:2 series. In the ethylenediamine 1:1 series,²⁵ the d-d absorption near 20 000 cm^{-1} is appreciably stronger than expected, suggesting that the MLCT band has blue-

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shifted into this region. In the pentacyanosuperoxo derivative, however,²⁶ the MLCT band is observed at about 19000 cm⁻¹, representing a small red shift relative to the position of the transition in the bridging analogue (Table IA,C). Note that in common with many charge-transfer absorptions, this band shows considerable solvent dependence in both the 1:1²⁶ and 1:2¹⁰ series. Neither the $\pi_h^* \rightarrow \pi_v^*$ transition nor the weak LMCT feature ($\pi_v^* \rightarrow d\sigma^*$) has been detected in the 1:1 series.

Before leaving the superoxo systems we note that, for the 1:2 complexes, there is sufficient spectroscopic information to map the various electronic states quite accurately. It is of interest to point out that after correction for crystal field and mean spin pairing energy contributions²⁸ the transition energies cannot be reconciled without assuming that considerable electron repulsion is involved in the addition and/or subtraction of an electron from dioxygen. In particular, it is illuminating to note the nature of the dioxygen molecule generated in the excited states of the LMCT transitions, $(O_2^-)Co(d_{z^2}) \rightarrow (O_2)Co(d_{z^2})$. Transfer of a π_h^* electron leaves behind a spin-triplet dioxygen, whereas transfer of the π_v^* electron leaves a spin singlet. It is well known that spin-singlet dioxygen has a much higher interelectronic repulsion energy than the spin triplet,²⁹ thereby aiding our understanding of why the two LMCT bands are so close together (Table I) when the originating π^* components are of the order of 8000–12000 cm⁻¹ apart. Similarly, the addition of an electron to superoxide (second electron affinity of dioxygen) is highly unfavorable, thereby explaining the relatively high energy of the MLCT band.

1:2 Bridging Peroxo Complexes (Figure 2d)

In addition to the longer O–O bond length associated with the coordinated peroxo group, these complexes differ from the bridging superoxo species in that the Co–O₂–Co unit is frequently nonplanar.³⁰ The cobalt atoms are trans to the O–O bond and the torsional (twisting) angle is generally of the order of 145°. The addition of an electron to the O₂⁻ π^* levels to form the peroxide ion (O₂²⁻) does not seriously perturb the nature of these orbitals. Although the O–O bond length increases, the highest occupied orbitals still have π^* character.

In a nonplanar Co–O₂–Co unit, the distinction between π_h^* and π_v^* is lost, and both of the π^* levels (now labeled π_a^* and π_b^*) will possess some σ bonding character. Neither, however, will have the degree of σ bonding character that is present in the π_h^* component of a planar superoxometal unit. This line of argument leads us to expect two closely spaced LMCT systems (in the 25 000–33 000 cm⁻¹ region for cobalt(III)), each having lower intensity than the $\pi_h^* \rightarrow d\sigma^*$ band in the analogous superoxo case. This indeed turns out to be the situation^{10,11,31,32} (Table II). The energy separation between these bands is essentially the same as that of

the split π^* levels in hydrogen peroxide,⁸ providing support for their assignment. The two transitions are magnetic-dipole-allowed; consistent with theory, intense CD absorption is observed with shoulders being evident. However, the two main components are not resolved.^{11,31} No other absorption bands attributable to transitions involving dioxygen are expected nor observed, in the conventional region, because of the closed-shell nature of the coordinated peroxo group.

In some circumstances the Co–O₂²⁻–Co unit is planar.³⁰ The electronic situation then parallels the superoxo case where there are in-plane and out-of-plane π^* orbitals. As expected, two LMCT bands, one strong and one weak, are observed in the spectra of such complexes.¹³

The addition of a second bridge, commonly hydroxide or amide, causes the metal atoms to be bound in a cis fashion about the O–O bond^{16,33} (Figure 2e). The torsional angle is now near 60°,¹⁶ implying greater distortion from planarity than in the simple peroxo-bridged species, and certainly greater distortion than in the doubly bridged superoxo species.

By analogy with previous arguments, we anticipate two LMCT bands, whose intensities will depend upon the degree of distortion in the ring. It has been frequently observed, e.g., that the spectra of doubly bridged peroxo species exhibit only one band near 27 600 cm⁻¹ (for cobalt(III)),³¹ in distinction to the two-band system observed in the case of the singly bridged peroxo species. Closer examination shows that this generalization is not correct, as doubly bridged complexes do indeed exhibit a second LMCT band. This is at higher energy than the two bands observed with the singly bridged species and generally appears only as a broad intense shoulder in absorption. In CD spectra, this feature is quite clearly observed with a rotation that is opposite to that of the lower energy band.³¹

The peak intensities in the doubly bridged systems appear always to be lower, and sometimes much lower, than observed with the corresponding LMCT bands in singly bridged systems. This may be associated with the increasing distortion (twisting) of the ring. The band shape is related to the overlap between the ground- and excited-state vibrational wave functions (Franck–Condon factors). If the nuclear configuration of the ground state differs appreciably from that of the equilibrated excited state, then a number of vibrational levels may be excited, leading to a broad band. The integrated intensity will not change, but the apparent intensity, as measured by the extinction coefficient at the band maximum, will decrease. It is not unreasonable to expect that the greater the distortion from planarity, the greater will be this apparent decrease. This will certainly be true if the excited state prefers a planar configuration, which is expected for some configurations of the Co(II)–O₂⁻ type. A similar argument allows us to understand the broad bands that are observed in the spectra of the singly bridged peroxo species.

1:2 Bridging Hydroperoxo Complexes

As illustrated in Figure 2f, the hydroperoxo group can act as a bridge linking both metal atoms through a

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Table II
Electronic Spectra of Peroxometal Complexes

A. Bridging Peroxodimetal Complexes, $[L_xM(O_2^{2-})ML_x]^{n+}$					
M	L	CD	abs ^a	ref	
Co	CN		27.0sh (3.7) 31.75 (4.0)	10	
Co	en, dien		27.3sh (3.26)* 33.3 (3.98)	13	
Co	dien, 1-pn			13	
Co	tetren		33.2 (4.00) 27.6sh (3.53) 32.2 (4.10)	13	
Co	L-histidine	28.1 (+1.8) ^b	25.9 (3.82) 30.6 (3.86)	11	
Co	L-2,3-diamino-propionate	27.55 (-2.8)	25.97 (3.48) 31.75 (3.54)	31	
Co	L-2,4-diamino-butyrates	29.24 (-0.7)	27.03 (3.47) 31.85 (3.59)	31	
Rh	Cl, 4-picoline		27.02 (3.6) ^c 32.47 (4.2) ^c	12	
Rh	Cl, pyridine		27.78 (3.63) ^c 32.15 (4.18) ^c	12	
Cr	H ₂ O		36.76 (3.07) ^d 42sh*(3.1) ^d	32	
B. Doubly bridged Complexes, $[L_xCo(X)(O_2^{2-})CoL_x]^{n+}$					
L	X	CD ^a	abs ^a	ref	
en	NH ₂	27.8 (-10.33)	29.8 (3.59)	13, 18	
1-pn	NH ₂	27.8 (-8.61)	29.7 (3.52) 33.7sh (3.61)*	13, 18	
en	OH		28.0 (3.69) 36.2* (3.68)	13	
1-pn	OH		28.6 (3.76) 36.8* (3.75)	13	
L-histidine	OH	25.7 (+1.1)* 31.5 (-0.6)*	26.9 (3.79)* 33.3 (3.74)*	11	
L-2-3-diamino-propionate	OH	26.45 (-2.2) 32.89 (+2.8)	27.93 (3.40)	31	
L-1,2-diamino-propane	OH	27.03 (-6.5) 32.79 (+4.4)	28.09 (3.34)	31	

^a For the Co complexes, the two components, if observed, are $\pi_a^* \rightarrow d\sigma^*$ and $\pi_b^* \rightarrow d\sigma^*$. ^b Broad, ill-resolved band containing several components. ^c Probably $\pi^*(O_2^{2-}) \rightarrow d\sigma^*$ transitions, but the assignment is uncertain. ^d Probably $\pi^*(O_2^{2-}) \rightarrow d\pi$ transitions, but the assignment is uncertain.

single oxygen atom. Such complexes are obtained through protonation of the bridging peroxo species.³⁴⁻³⁷ These complexes, which have been known a long time³⁶ and have been characterized by X-ray analysis,³⁷ are best regarded as derivatives of the hydroperoxide ion, HO₂⁻, rather than the hydroperoxo radical, HO₂[•], since the O-O distance is 1.42 Å.³⁷ We note that complexes of the hydroperoxy radical are known,³⁸ but are very unstable.

Miskowski has managed to obtain a good spectrum of the sulfate salt of (NH₃)₅Co(O₂H)Co(NH₃)₅⁵⁺ in a Nujol mull.¹⁵ In addition to a well-resolved d-d absorption band at 20 620 cm⁻¹, the spectrum exhibits an intense absorption peak at 33 330 cm⁻¹, with a shoulder at 27 780 cm⁻¹. The 33 330-cm⁻¹ band is attributed to a $\pi^*(O_2H) \rightarrow d\sigma^*$ transition, and the weaker 27 780 cm⁻¹ feature probably has a similar origin. If both oxygen atoms of the HO₂⁻ group lie in the same plane as the Co-O-Co unit, then the π^* orbital involved in the lower energy LMCT transition would have no σ character and a very weak band would be anticipated. In fact, the

X-ray data are consistent with a structure in which the HO₂⁻ group is tilted out of the Co-O-Co plane.³⁷ Such tilting would give the highest occupied OOH⁻ molecular orbital some degree of σ character and be consistent with the relatively small $\pi^*(O_2^{2-})$ splitting observed and the moderate intensity of the lower energy LMCT component.

Side-on Peroxo Complexes (Figure 2g)

Many complexes are known, or most reasonably believed, to contain side-on dioxygen,³⁹⁻⁴¹ and yet little definitive spectroscopic information has been published. Nevertheless, sufficient information is available to establish the main energy-level pattern.

In the early days of spectrophotometric analytical chemistry, it was recognized that the addition of hydrogen peroxide to a wide range of metal ions, especially those to the left of the various transition series, resulted in coloration. Electronic spectra for such solutions were reported.⁴¹⁻⁴⁸ Although the species in question were

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Table III
Electronic Spectra of Side-on Peroxometal Complexes, $L_xM(O_2^{2-})_y$

M(ox)	L or formula	$\pi_v^* \rightarrow d$	other bands	ref
Cr(VI)	$NH_4[Cr(OH)(O_2)_2O]$	18.83 (2.64)	<i>a</i>	48
Cr(VI)	$PyCrO_5$	13.7* (2.69) 17.6* (2.86)		50
Cr(VI)	CrO_5	13.5 (2.60) 17.3 (2.78)	46.9 (3.78)	51
Cr(V)	K_3CrO_8	18.2* 19.2* 19.6 sh*		49
Cr(IV)	$Cr(en)(H_2O)(O_2)_2$	27.03 (2.70)	40.00 (3.69)	52
Cr(IV)	$Cr(dien)(O_2)_2$	26.18 (2.66)	40.00 (3.73)	52
Cr(IV)	$Cr(NH_3)_2(O_2)_2$	27.03 (2.74)	39.06 (3.73)	52
Ti(IV)	H_2O/SO_4^{2-}	23.25 (2.1)	<i>b</i>	45
V(V)	H_2O/SO_4^{2-}	22.22 (2.41)		45
Nb(V)	H_2O/SO_4^{2-}	27.40 (2.93)	>38.5	45
Mo(VI)	H_2O/SO_4^{2-}	24.10 (2.64)		45
Ta(V)	H_2O/SO_4^{2-}	35.09 (2.98)	>41.5	45
W(VI)	H_2O/SO_4^{2-}	33.90 (2.75)		45
Re(VII)	H_2O/SO_4^{2-}	25.64 (2.91)		45
Pt(II)	$Pt(PPh_3)_2O_2$	29.8 (3.04)		55

^a Absence of UV absorption was specifically mentioned. ^b There are no peaks below the UV cut-off: A. B. P. Lever, unpublished results.

not well defined at the time, it is now rather certain that they contain side-on peroxo groups. Spectroscopic data for more well-defined species, often with X-ray structural information, have been published, without detailed comment, in more recent times.⁴⁹⁻⁵² The spectra of all these complexes, without exception, exhibit a weak absorption band (ϵ 10^2 – 10^3 L mol⁻¹ cm⁻¹) as the lowest energy identifiable charge-transfer feature. In some cases there is a shoulder or additional weak peak. This absorption is quite variable in position and may be in the near-infrared, visible, or ultraviolet region, depending upon the oxidation level of the metal ion (Table III). This dependence upon oxidation level identifies the transition as charge transfer in nature, and comparison (Table III) of the data for Cr(VI), Cr(V), and Cr(IV), or for V(V), Nb(V), and Ta(V), reveals that it is LMCT, as surmised by Evans.⁵⁰

There is no hydrogen analogue for side-on dioxygen. We may reasonably assume that the in-plane π_h^* orbital on O_2^{2-} forms a strong σ bond to the metal, leaving the π_v^* orbital at higher energy. The latter has no σ character. The weak absorptions are assigned to transitions from the π_v^* orbital into the d shell, i.e., $\pi_v^* \rightarrow d$ LMCT.

There must necessarily be an intense absorption band associated with the $\sigma \rightarrow \sigma^*$ LMCT transition from the bonding π_h^* orbital to its $d\sigma^*$ partner. However, because of the stabilization of the π_h^* σ -bonding orbital, this transition will lie at very high energy. Indeed, when these peroxo complexes contain only UV transparent ligands, they often show no additional absorption of any significance before the UV cut-off, implying that the $\pi_h^* \rightarrow d\sigma^*$ transition occurs above 50 000 cm⁻¹. There

is absorption near 45 000 cm⁻¹ in some high oxidation state chromium complexes (Table III),^{51,52} but in the absence of a systematic spectroscopic study it would be unwise to assign these bands.

Included within the side-on dioxygen class are many derivatives to the right in the transition groups. These usually contain additional ligands, which are rarely UV transparent. Definitive studies of phosphine⁵³ and arsine⁵⁴ cobalt(III) complexes containing side-on peroxo groups revealed no absorption bands assignable to peroxo-to-metal transitions. Despite the wealth of data on derivatives of Vaska's dioxygen complex² and the multitude of heavy metal systems,⁴¹ there appears to be only one assignment of a dioxygen-to-metal transition in these series, namely in $Pt(PPh_3)_2(O_2)$. An SCF-X α -SW calculation⁵⁵ of this system is consistent with the LMCT assignment. Our expectation is that, in most of these complexes, weak absorption attributable to the LMCT transition $\pi_v^* \rightarrow d\sigma^*$ will fall in the ultraviolet region, and it will usually be obscured by more intense bands.

Other Cobalt-Dioxygen Complexes

Dioxygen adducts of Co(II) porphyrins have been well characterized,⁵⁶ however, because of intense absorption arising from transitions within the porphyrin itself, bands attributable to excitations involving the dioxygen molecule have only rarely been detected. Both vitamin B₁₂ and dimethyl((mesoporphyrin IX)ato)pyridine-cobalt(II) form dioxygen adducts which, by analogy with other Co(II) 1:1 dioxygen adducts,²² may be presumed to contain an end-on superoxocobalt(III) unit. The former adduct exhibits a well-defined shoulder,⁵⁷ on the Soret band, at about 30 300 cm⁻¹, which could be the $\pi_h^* \rightarrow d\sigma^*$ LMCT absorption. The weak LMCT band that should fall in the visible region is undoub-

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tedly obscured. The MCD spectrum of the latter derivative is similar to that of oxyhemoglobin; there is, however, an extra component near $28\,570\text{ cm}^{-1}$,⁵⁸ which could be associated with the expected LMCT transition.

Concluding Remarks. Spectral Expectations for Other Dioxygen-Adduct Structures

We now have a reasonable picture of the nature of the charge-transfer transitions involving d^6 low-spin metal centers and end-on superoxo, end-on bridging peroxy, and side-on peroxy groups. This foundation has been built almost entirely from detailed examination of low-spin complexes of Co(III), where the lowest acceptor orbital for LMCT transitions is of the $d\sigma^*$ type. In both superoxo and peroxy end-on complexes of Co(III), there are two observable LMCT transitions. These transitions originate in the split π^* levels of the O_2^{n-} unit and terminate in the $d\sigma^*$ orbital that is associated with the M- O_2 interaction (the d_{z^2}). In the spectra of the planar-end-on superoxo complexes, the two-band intensity pattern is weak-strong, which is attributable to the $\pi \rightarrow d\sigma^*$ ($\pi_v^* \rightarrow d_{z^2}$) and $\sigma \rightarrow d\sigma^*$ ($\pi_h^* \rightarrow d_{z^2}$) character of the LMCT transitions. A similar pattern is observed in the spectra of planar peroxy end-on complexes. In the spectra of the non-planar end-on peroxy complexes, the two bands have comparable (and medium) intensities; in this case both $\pi_a^* \rightarrow d\sigma^*$ and $\pi_b^* \rightarrow d\sigma^*$ transitions have at least a small degree of $\sigma \rightarrow \sigma^*$ character. Another major difference in the spectra of end-on superoxo and peroxy Co(III) complexes is the appearance of a relatively low energy LMCT ($d\pi \rightarrow \pi_v^*$) band in the former cases.

The splitting of the $\pi^*(O_2^{2-})$ levels due to side-on peroxy coordination as inferred by spectral comparisons is very large. In very favorable cases (d^0 metal ions, high oxidation states) one or more weak to medium-intensity spectral bands attributable to $\pi_v^* \rightarrow d$ transitions are observed. In no side-on peroxy complex, however, has it proved possible to identify with confidence a transition originating in the σ -bonding orbital derived from π_h^* , and we assume that in such cases excitations of the type $\pi_h^* \rightarrow d\sigma^*$ require very high energies.

We close with a few comments concerning the interpretation of the electronic spectra of more complex M- O_2 systems. It should be stressed that some knowledge of the ground-state geometry and electronic structure is needed in order to interpret the electronic spectrum of a complicated M- O_2 system. It would be a happy situation indeed if we could proceed in reverse with any confidence, that is, determine the geometry of an M- O_2 unit from an electronic spectroscopic analysis. Probably the most we can expect at this stage, based on the generalizations set forth above, is that certain M- O_2 geometries can be determined to be inconsistent with a given spectroscopic pattern, whereas

others remain as viable possibilities.

Two complex M- O_2 systems where some progress can be made on the interpretation of charge-transfer spectra are oxyhemerythrin (Fe_2O_2) and oxyhemocyanin (Cu_2O_2). Magnetic susceptibility^{59,60} and resonance Raman spectroscopic⁶¹⁻⁶⁴ experiments have established that the oxidation levels of the metal-dioxygen units in these proteins are $[Fe(III)]_2O_2^{2-}$ ^{59,61,62} and $[Cu(II)]_2O_2^{2-}$ (or $[Cu(I)Cu(III)]O_2^{2-}$).^{60,63,64} Thus it is certain that relatively low energy LMCT transitions originating in the $\pi^*(O_2^{2-})$ levels should be observed in each case. As the magnetic susceptibility work⁵⁹ on oxyhemerythrin shows the $[Fe(III)]_2$ unit to be an antiferromagnetically coupled ($5/2, 5/2$) system, the acceptor orbital for the lowest LMCT transitions must be of the $d\pi^*$ type. Thus the band at $20\,000\text{ cm}^{-1}$ in the oxyhemerythrin spectrum,⁶⁵ which involves an excitation in the Fe_2O_2 unit,⁶¹ must be of the $\pi_a^*(O_2^{2-}) \rightarrow d\pi^*(Fe)$ type. If the Fe_2O_2 unit has one of the end-on geometries, as seems probable,⁶⁶ then $\pi_b^*(O_2^{2-}) \rightarrow d\pi^*(Fe)$, which is predicted to be a higher energy, weaker transition, may be obscured by other bands in the oxyhemerythrin spectrum.⁶⁵

Resonance Raman spectroscopic experiments have shown that the bands at $17\,500$ and $20\,400\text{ cm}^{-1}$ in the spectrum of oxyhemocyanin are due to charge-transfer excitations in the Cu_2O_2 unit.⁶⁴ These bands may be assigned to LMCT transitions originating in split $\pi^*(O_2^{2-})$ levels. If the acceptor orbital on the Cu_2O_2 center has $d\sigma^*(Cu-O_2)$ character, then the observed band pattern is clearly inconsistent with a side-on (one Cu) peroxy geometry; rather, one of the end-on structures would appear likely, with a bridging end-on peroxy geometry being favored in view of the observed equivalence (or near equivalence) of the two oxygen atoms in the Cu_2O_2 unit.⁶⁷

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