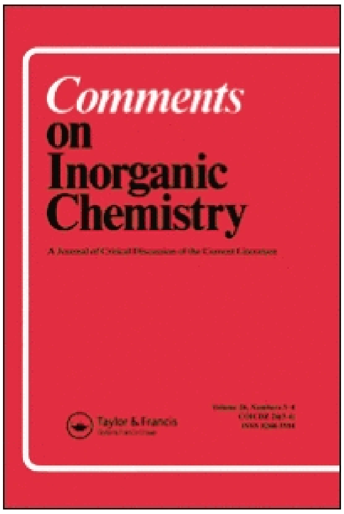

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The Electronic Spectra of μ-Peroxodicobalt(III) Complexes

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The Electronic Spectra of μ-Peroxodicobalt(III) Complexes

Some of the problems encountered in the determination of the electronic spectra of μ-peroxodicobalt(III) complexes are discussed. After account is taken of the common formation of mixtures of different μ-peroxocomplexes upon oxygenation of Co(II)-ligand solutions, it can be concluded that three classes of spectra exist. Planar single-bridged complexes exhibit a strong ($\varepsilon \simeq 12{,}500$) $\pi_h^* \rightarrow d\sigma^*$ peroxide LMCT band at 300–310 nm, with a weak ($\varepsilon \simeq 600$) $\pi_v^* \rightarrow d\sigma^*$ band at 425–430 nm. Nonplanar (dihedral angle near 145°) single-bridged complexes exhibit two strong ($\varepsilon \simeq 6000$) $\pi^*(O_2^{2-}) \rightarrow d\sigma^*$ bands near 320 and 390 nm. Dibridged μ-(OH^-,O_2^{2-}) complexes, with a dihedral angle near 60°, exhibit one broad peroxide LMCT band at ≃355 nm ($\varepsilon \simeq 6000$). The latter compounds have an additional band near 280 nm which is not due to peroxide. All of the peroxide LMCT spectra are shown to be consistent with a simple model that assumes a sinusoidal dependence of $\pi^*(O_2^{2-})$ energies and σ-overlaps upon the dihedral angle.

INTRODUCTION

In this Comment will be presented the end result of fifteen years of experience as to the electronic spectra of μ-peroxo-dicobalt(III) complexes. A model for interpreting these spectra was first suggested in Ref. 1, and considerably expanded upon later.[2] The typically intense near UV absorptions of the complexes are attributed to ligand-to-metal charge-transfer (LMCT) transitions from the two highest-energy occupied O_2^{2-} orbitals, derived from the π^* orbital of O_2, into empty Co(III) $d\sigma^*$ orbitals (see Fig. 1). This assignment is highly consistent with the observation[3] that irradiation into these bands results in loss of O_2. The problem of assign-

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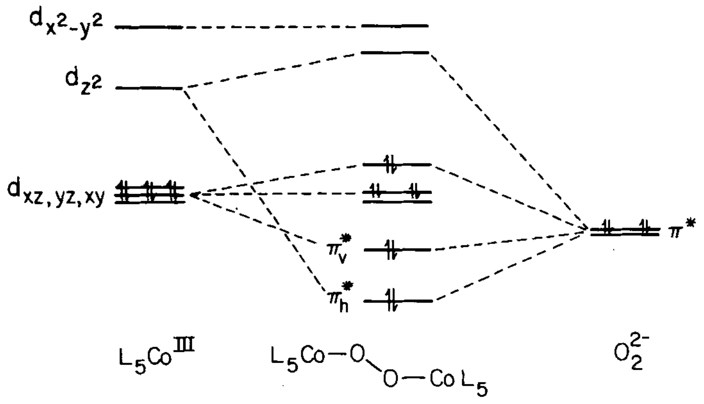

FIGURE 1 Molecular orbital diagram for a planar μ-peroxo dicobalt(III) complex.

ment of oxidation states[1,2] will not be considered here, as structural[4] and vibrational[5] studies appear to unambiguously favor a Co(III) formation. The Co(III) formulation of the analogous μ-superoxo complexes has been strongly supported by a single-crystal polarized electronic spectral study.[6]

Of long-standing concern was that the electronic spectra of the μ-peroxo complexes were very sensitive both to ligand variations and to the details of sample preparation. With the accumulation of considerable data, and with the aid of the extensive x-ray crystallographic work now available, a much firmer understanding of the electronic spectra has eventually been reached. The interpretation of these spectra is of prime importance because the complexes are much more easily accessible than those of biologically important metals such as iron and copper. Thus, the interpretation of the spectra[2a] of metalloprotein-O_2 complexes must largely rely upon analogy to the interpretation of the spectra of model complexes such as the cobalt complexes.

In the following section, some of the difficulties involved in studying these spectra will be identified. In the remaining sections, the spectra will be analyzed in depth.

DIFFICULTIES IN OBTAINING ELECTRONIC SPECTRA

The overwhelming majority of crystallographically characterized μ-peroxo-dicobalt(III) amine complexes fall into either of two classes:

complexes with a single transplanar CoO_2Co bridge,[4] and di-bridged complexes,[7] where the second bridge is usually OH^- or NH_2^-, and the CoO_2Co unit is highly nonplanar. The electronic spectra of well-characterized examples of each class of compound are shown in Figs. 2 and 3, in both cases chosen for their very high stability.

The μ-peroxo complexes usually exist in fairly labile equilibrium

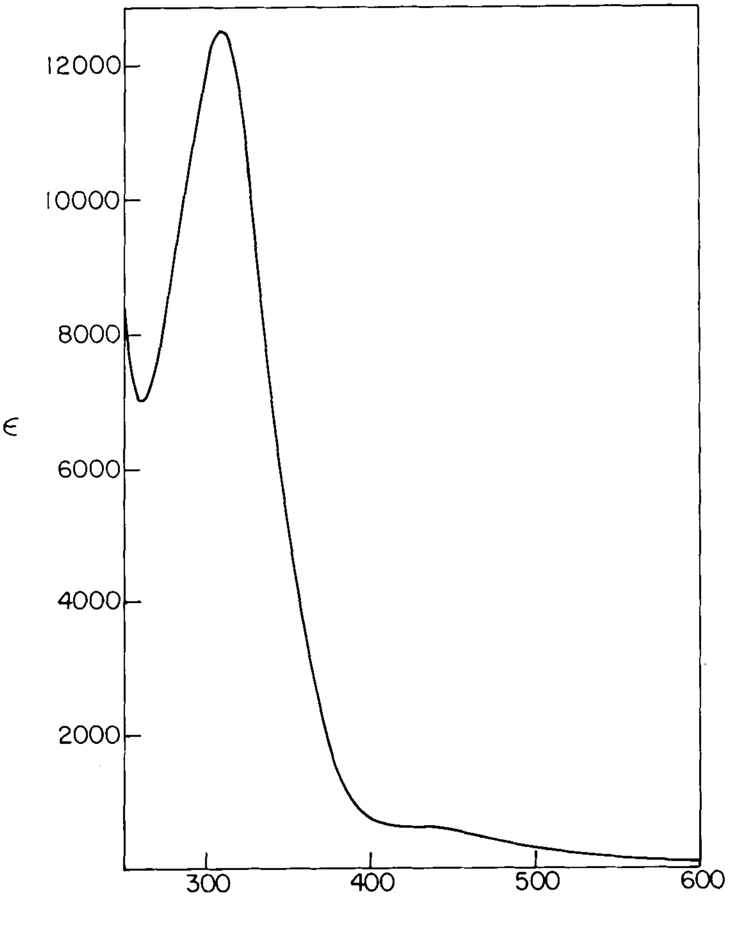

FIGURE 2 Electronic spectrum of $[(Co(tetren))_2O_2]^{4+}$ in 0.01 M borate buffer, pH 9.2.

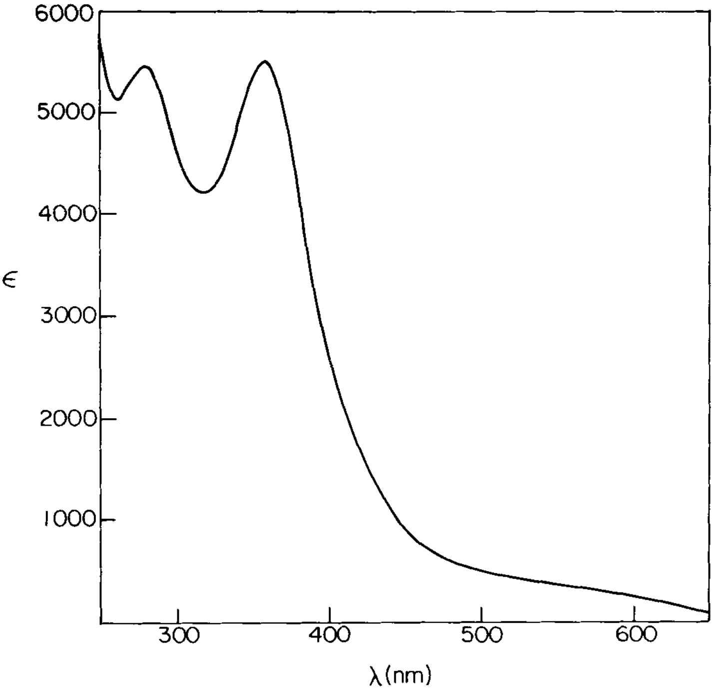

FIGURE 3 Electronic Spectrum of *meso*-$[(Co(en)_2)_2(O_2,OH)]^{3+}$ in 0.02 M borate buffer, pH 9.

with O_2 and Co(II) species, and also decompose to yield mononuclear Co(III) complexes. The rates of these reactions are now well understood,[7c–7e,8] and in many cases they are slow enough that the electronic spectrum of a pure compound can be obtained simply by dissolving crystalline material in buffered solution (and working rapidly). In some cases, reactions are too fast for this to be feasible, or a pure crystalline compound may not be obtainable. In these cases, spectra must be obtained directly from oxygenated Co(II)-ligand solutions, and here we meet several complications.

Figure 4 shows a set of spectra for freshly oxygenated Co(II)-NH_3(aq) solutions. At 3M NH_3 the spectrum is very similar to Fig. 2, and we infer the predominant presence of a planar $[((Co(NH_3)_5)_2O_2]^{4+}$ complex. At 1M NH_3 the spectrum is similar to that of Fig. 3, which suggests predominant presence of a dibridged $[(Co(NH_3)_4)_2(O_2,OH)]^{3+}$ complex. At still lower NH_3 concentrations, oxygenation becomes incomplete.

Formation of dibridged complexes is a persistent feature of solution oxygenation. Since, in general, dibridged complexes are kinetically more stable than monobridged complexes,[8] they are very difficult to avoid, and their occurrence in nominally pure solutions of single-bridged complexes very likely accounts for 300 nm extinction coefficients in the literature that are[2,9] often lower than those of Table I, as well as for most claims[2] of absorption shoulders near 360 nm.

There are other types of "isomers" which can result in spectral variation. One obvious possibility is that ligands such as tetren can adopt several different conformations about the metal atom. Fortunately, these isomers appear to have nearly identical CT electronic spectra.[10]

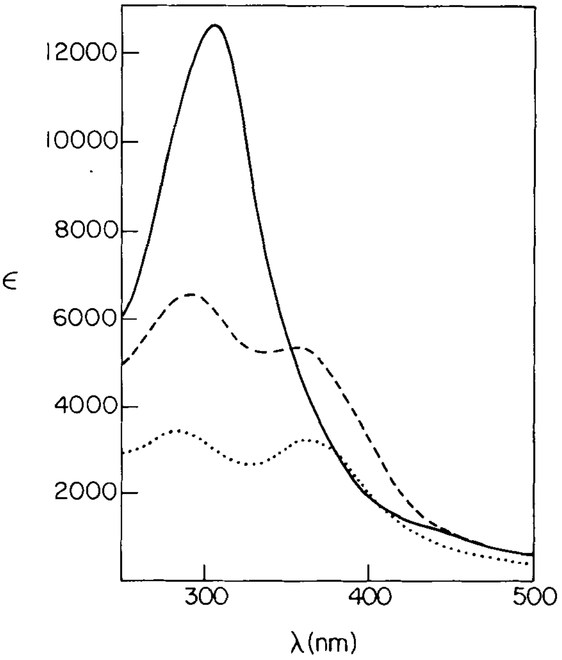

FIGURE 4 Oxygenation of Co^{2+} in NH_3(aq) solution, pH 10. (—): 3M NH_3; (---): 1M NH_3; (· · · ·) 0.5M NH_3.

TABLE I

Charge-transfer electronic spectra of μ-peroxo-dicobalt(III) complexes. Ligands on cobalt other than bridging groups are listed under the column heading L_5 or L_4. Table entries are of the form λ_{max}(nm) (ε_{max}). Solutions are borate buffer, pH = 9, and ligands are in stoichiometric ratio, unless otherwise noted. All ε's are per Co_2 unit

A. *Planar Single-Bridged*

L_5	LMCT Absorption
[a]$(NH_3)_5$	304(12,500); 430(1000,sh)
[b]$(en)_2(NH_3)$	303(12,500); 430(600,sh)
(dien)(en)	304(12,100); 430(800,sh)
tetren	301(12,200); 425(600,sh)
papd	307(12,500); 425(600,sh)
(dien)(gly)	303(10,500); 430(700,sh)

B. *Nonplanar Single-Bridged*

L_5	LMCT Absorption
[c](dien)(ox)	317(6200); 393(6000)
[d]$(histidine)_2$	327(7200); 386(6600)
[e]$(l\text{-}2,4,\text{-diaminobutyrate})_2$	314(3890); 370(2950)

C. *Di-Bridged (O_2,OH)*

L_4	LMCT Absorption
trien	275(5750); 355(7270)
meso-$(en)_2$	278(5300); 357(5500)
DTMA	289(6500); 350(6600)
EDDA	298(5200); 355(4900)

[a] 3M NH_3.

[b] 5 equivalents en, 0.3M NH_3.

[c] 4 equivalents ox.

[d] Data from: S. Bagger and K. Gibson, Acta Chem. Scand. **26**, 3788 (1972).

[e] Data from: L. G. Stadherr, R. Prados and R. B. Martin, Inorg. Chem. **12**, 1815 (1983).

[f] pH 11.2.

A more serious problem is illustrated by Fig. 5. Oxygenation of solutions of $Co(dien)^{2+}$ and glycine produces a spectrum with a strong shoulder at 390 nm. The complex $[(Co(dien)(gly))_2O_2]^{2+}$ can be crystallized as the perchlorate salt; the spectrum of a solution of the crystalline material, also shown in Fig. 5, is a completely normal planar single-bridged spectrum. Thus, solution oxygenation evidently gives a mixture of complexes, including the planar single-bridged complex.

What is the complex responsible for the 390 nm band of the solution oxygenation spectrum? The absorption is at too long a wavelength to be attributable to a μ-(OH^-,O_2^{2-}) complex. A possible answer is suggested by Fig. 6. When the solution contains oxalate instead of glycine, a distinct "two-band" CT spectrum is obtained, which we attribute to the complex $(Co(dien)(ox))_2O_2$. Since high concentrations of glycine are required for complete solution oxygenation in the diene/glycine system, it is very possible that dioxygen adducts with more than one carboxylate bound to each Co (analogous to the oxalate complex) may be present in the mixture.

An explanation for the unusual spectrum of the oxalate adduct is presented below. Whether or not the explanation is correct, it should be emphasized that the problems exhibited by the glycine-dien system are common to most amino acid ligand systems that have been examined, and absorption spectra for such complexes

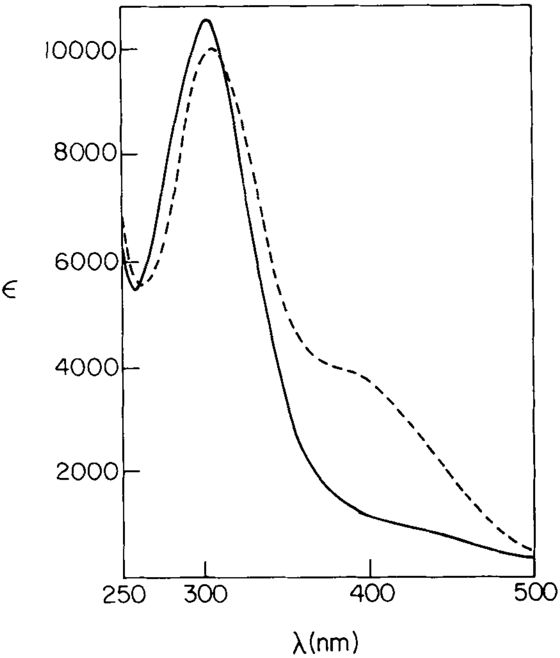

FIGURE 5 Electronic spectra of: (—) $[((dien)(gly)Co)_2O_2]^{2+}$, perchlorate salt; (---) oxygenated solution of $Co(dien)^{2+}$ in the presence of 10 equivalents of glycine.

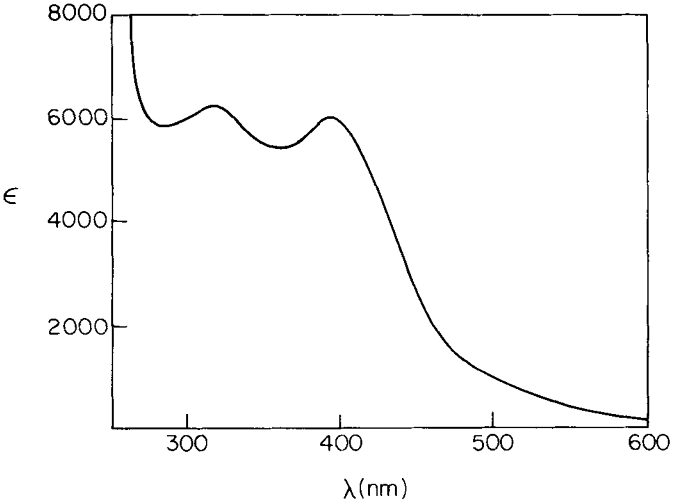

FIGURE 6 Electronic spectrum of aqueous $[((\mathrm{dien})(\mathrm{ox})\mathrm{Co})_2\mathrm{O}_2]$, pH 8.

as obtained from solution oxygenation should always be considered *cum grano salis.*

INTERPRETATION OF ELECTRONIC SPECTRA

Planar Single-Bridged. Spectra of some well-characterized examples of planar μ-peroxo complexes are given in the first section of Table I. Solid state absorption spectra (an example of which appears in Fig. 6) agree well with solution spectra. There is a single strong ($\varepsilon \simeq 12{,}500$) and broad (fwhm $\simeq 6500\ \mathrm{cm}^{-1}$) band at 300–310 nm in all these spectra; it is straightforwardly assigned[1,2] to $\pi_h^* \rightarrow d\sigma^*$, the peroxide-to-cobalt LMCT transition involving the in-plane, σ-bonding, $\pi^*(\mathrm{O}_2^{2-})$ component. (Division of the π^* orbitals into in-plane (π_h^*) and out-of-plane (π_v^*) components in the planar case was introduced in Ref. 1.)

It is satisfying that the observed wavelength is the same as that of the (completely equivalent in terms of assignment and orbital occupancy) analogous transition of planar μ-superoxo dicobalt(III) complexes.[1,2,6] It is still more satisfying that the oscillator strengths are now found to be equivalent at 0.30–0.35. The $\pi_h^* \rightarrow d\sigma^*$ band of μ-superoxo complexes is more intense[1,2] at the maximum ($\varepsilon \simeq 20{,}000$) but proportionately narrower (fwhm $\simeq$ 3500 cm^{-1}). The equivalency of oscillator strengths would be expected in view of the equivalency of Co–O bond lengths (hence, bonding interaction) in the two types of complex.

The difference in band widths can be understood in terms of the formally one-electron oxidized bridging ligand of the LMCT excited state. For the μ-peroxo complexes the excited state is superoxo-like, and the change in equilibrium O_2 bond length in the electronic transition should then be about 1.48–1.30 = 0.18 Å. This is much larger than the analogous change for μ-superoxo complexes, about 1.30–1.21 = 0.09 Å, with a "μ-dioxygen"-like excited state. According to theory,[11] band widths vary with the square of the change in equilibrium bond distance (diatomic approximation), so a much broader band is indeed expected for the μ-peroxo complexes. The LMCT excited state also[5,6] involves changes in equilibrium Co–O and Co–N bond lengths, which contribute to the total width of the electronic transition; these changes should be similar for the μ-superoxo complexes, which accounts for the fact that the difference in bandwidths is smaller than predicted solely on the basis of the O_2 bond length changes.

A second LMCT transition is predicted for these μ-peroxo complexes, involving the out-of-plane π_v^* component of $\pi^*(O_2^{2-})$. In planar geometry this component is purely π-bonding to cobalt d orbitals. Accordingly, we can predict both its energy and intensity by comparison to the very well-established LMCT spectra of mononuclear halopentaamine cobalt(III) complexes,[12] where σ/π separation is rigorous. Thus, for example, $Co(NH_3)_5Br^{2+}$ shows bromide σ and π LMCT at, respectively, 39,500 cm^{-1} ($\varepsilon \simeq 12{,}600$) and 31,800 cm^{-1} ($\varepsilon \simeq 560$). The 8000 cm^{-1} splitting is very characteristic,[12] and it is therefore reasonable that the $\simeq$425–430 nm ($\varepsilon \simeq 600$) shoulder of the planar μ-peroxo spectra be assigned to $\pi_v^* \rightarrow d\sigma^*$.

The wavelength of this band is *not* reasonable for assignment to a ligand-field (d-d) transition. The ligand-field strength of peroxide has been established[1,3] near that of H_2O. The lowest-energy ligand-field transition (components of the octahedral ${}^1A_{1g} \rightarrow {}^1T_{1g}$) is then expected[13] at 500–550 nm (no *shorter* wavelength than 475 nm, the value for $Co(NH_3)_6^{3+}$), while the second set of ligand-field

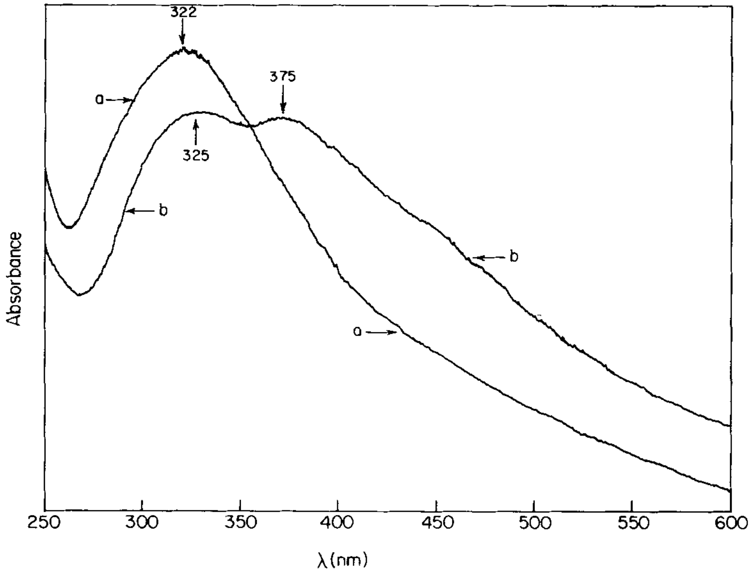

FIGURE 7 Solid state spectra (hydrocarbon mulls) of: (a) $[(Co(NH_3)_5)_2O_2](NCS)_4$; (b) $[(Co(NH_3)_5)_2O_2](SO_4)_2 \cdot 4H_2O$.

transitions (derived from $^1A_{1g} \rightarrow {}^1T_{2g}$) should be[6,13] near 350 nm. We do observe a long non-Gaussian tail through the visible (see Fig. 2) and this is likely to contain the lowest-energy d-d transitions, at about their expected wavelengths.[14]

Nonplanar Single-Bridged. The classic example of a nonplanar single-bridged μ-peroxo-dicobalt(III) complex is the salt[15] $[(Co(NH_3)_5)_2O_2](SO_4)_2 \cdot 4H_2O$, containing a cation with a dihedral angle (ω) of 146° about the O–O bond, versus 180° for the planar complexes. The nonplanarity has been proposed[4b] to result from very strong hydrogen bonding to peroxide in this lattice.

In Fig. 7 are shown solid state (hydrocarbon mulls between quartz disks) spectra for this salt and for the salt $[(Co(NH_3)_5)_2O_2]$ $(SCN)_4$, containing[4b] a rigorously planar Co_2O_2 group. The spectrum of this compound is typical of our mull data for crystallographically characterized planar μ-peroxo complexes; the spectrum is very similar to solution spectra, but scattering effects somewhat distort the intense peaks. The spectrum of the sulfate salt is different; it shows *two* intense peaks in the CT region. This result was reproducible, even when the mull was prepared from one large single crystal of the sulfate salt.

The above result can be explained in terms of the original[1] LMCT model. If the CoO_2Co group is nonplanar, then *both* $\pi^* \rightarrow d\sigma^*$ transitions have σ-LMCT character and can be intense. A crude quantification of this argument is presented in Fig. 8. The right-hand side is established by assignments for the planar single-bridged complexes; it is assumed that the two π^* energies will become equal (an "accidental" degeneracy) at a dihedral angle of 90° and that the energies of the π^* orbitals will vary as $\sin^2\omega$. This is obviously an over-simplification, but it does roughly describe the ω dependence of the π^* derived levels of H_2O_2 predicted by calculations[16]; in particular, an accidental degeneracy does appear near 90°. At this point, each π^* component would be equally σ-bonding, and, according to Fig. 8, two equally intense transitions would be superimposed at the same wavelength, ≈355 nm. The predicted situation for the sulfate salt of the decamine salt is in-

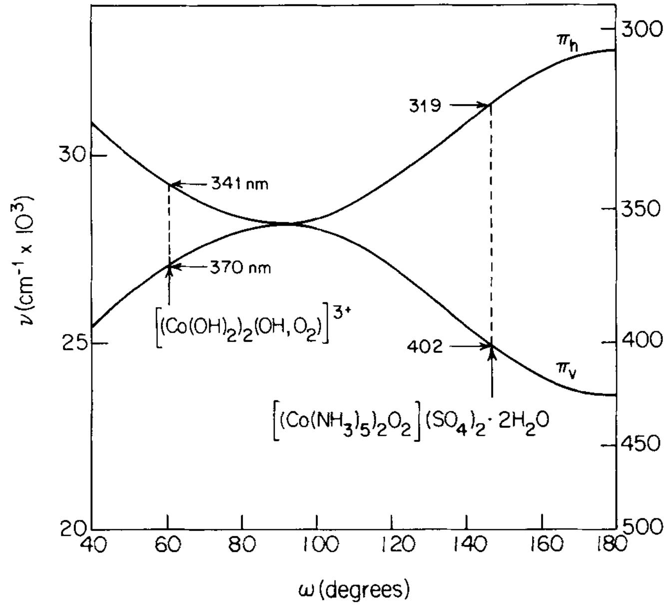

FIGURE 8 Proposed dependence of $\pi^*(O_2^{2-}) \rightarrow d\sigma^*$ LMCT transition energies on Co-O-O-Co dihedral angle (ω).

dicated with an arrow at $\omega = 146°$. At this intermediate point, two well-separated LMCT transitions are predicted; both should have considerable σ-LMCT character, hence intensity. The fair agreement with experiment is encouraging.

The spectrum of $(Co(dien)(ox))_2O_2$ (Fig. 6) probably represents a second example of a nonplanar μ-peroxo complex with ω near 145°; since there is minimal charge-repulsion between the cobalt centers in this neutral complex the small[17] but real[18] preference of the X_2O_2 unit for nonplanarity can manifest itself. It is likely that the well-known[2] spectra of μ-peroxo complexes of cobalt with certain tridentate amino acids (two of which are included in the second section of Table I) are also examples of nonplanar single-bridged spectra. However, none of these latter materials has yet been crystallographically characterized, so their integrity as single isomers remains questionable.

Dibridged. The dibridged μ-(X,O_2^{2-}) complexes, where X is usually OH^-, are extremely stable,[8] and our data for them (third section of Table I) are in good agreement with literature data,[2,9] where available. Their electronic spectra all show two moderately intense bands near 360 nm and 280 nm. Lever and Gray[2a] suggested that these be assigned as the two $\pi^*(O_2^{2-}) \rightarrow d\sigma^*$ LMCT transitions.

In these complexes, the dihedral angle is[7] very near 60°. The molecular orbital model, Fig. 8, is then obviously inconsistent with the Ref. 2 assignments, as it predicts two closely spaced transitions near 355 nm. Moreover, regardless of the details of the model, it is very hard to explain how one of the $\pi^*(O_2^{2-})$ LMCT transitions could occur to *higher* energy of the planar, single-bridged $\pi_v^* \rightarrow d\sigma^*$ transition at 300–310 nm.

In fact, there are better reasons to doubt the Ref. 2(a) assignment. As shown in Fig. 9, $[(Co(en)_2)_2(OH)_2]^{4+}$, lacking peroxo groups, nonetheless shows an intense band at 290 nm. Indeed, polynuclear Co(III) complexes with one to three hydroxo bridges,[19] or amido bridges[14,20] all show intense (ε 1–5000) bands at 260–310 nm. Evidently, the assignment of the ≃280-nm band of the dibridged μ-peroxo complexes to peroxide LMCT is very questionable.[21]

It is suggested here that the observed spectra may be consistent with Fig. 8, both peroxide LMCT transitions being near 355 nm,

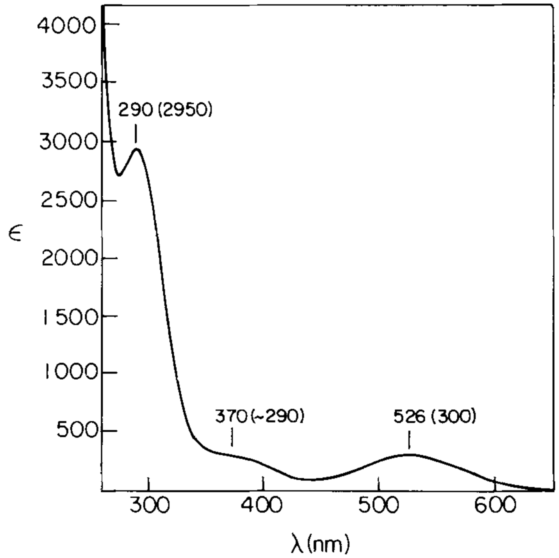

FIGURE 9 Electronic spectrum of $[(Co(en)_2)_2(OH)_2]^{4+}$ 0.02 M borate buffer, pH 9.

their superposition resulting in a single very broad band. One prediction of this interpretation is that, for optically active dibridged compounds, no CD extrema should coincide with CT absorption maximum, except by sheer accident, and observed[2,14] CD spectra in the CT region are indeed much more complex than absorption spectra.

The dibridged complexes show a fairly well-resolved shoulder at ≈550 nm ($\varepsilon \approx 300$) (see Fig. 3). By comparison to analogue complexes[19] lacking peroxo groups (see Fig. 9, for example), this is very reasonably assigned as the lowest-energy ligand-field transition(s). The breadth of this band is consistent with the poor resolution of ligand field transitions in the planar μ-peroxo spectra such as Fig. 2. CD spectra of the optically active complex $[(l\text{-}pn)_2Co)_2(\mu\text{-}OH,O_2)]^{3+}$ reported by Sasaki *et al.*[14] indicate at least three electronic transitions in this region, which are possibly the components of the octahedral $^1A_{1g} \rightarrow {}^1T_{1g}$ transition.

This Comment has tried to show that the electronic spectra of many μ-peroxo dicobalt(III) complexes can be described within the confines of a very simple model. It is furthermore suggested that spectra which do not fit this model are symptomatic of mixtures of isomers which, individually, do fit it. The interpretation of these (simple?) spectra provides benchmarks for the interpretation of metalloprotein-dioxygen adduct electronic spectra, and will, hopefully, aid in their interpretation.

APPENDIX

Uncommon ligand abbreviations used in this paper are as follows: dien: 1,4,7-triazaheptane; trien: 1,4,7,10-tetraazadecane; tetren 1,4,7,10,13-pentaazatridecane; papd: 1,5,8,11,15-pentaazapentadecane; DTMA: dien-1-acetate; EDDA: en-1,1-diacetate; l-pn: l-1,2-diaminopropane.

Acknowledgments

It is a pleasure to acknowledge the contributions of Harry B. Gray and Silvio Fallab to this work over the years. Some of the previously unpublished data presented here were measured by Prof. Fallab and his research group and are used with his kind permission. This work was performed at the Jet Propulsion Laboratory for the U.S. Department of Energy, Energy Conversion and Utilization Technologies Program, through an agreement with the National Aeronautics and Space Administration.

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References

1. V. M. Miskowski, J. L. Robbins, I. M. Treitel and H. B. Gray, Inorg. Chem. **14**, 2318 (1975).
2. (a) A. B. Lever and H. B. Gray, Acc. Chem. Res. **11**, 348 (1978); (b) S. R Pickens and A. E. Martell, Inorg. Chem. **19**, 15 (1980).
3. M. Kikkawa, Y. Sasaki, S. Kawata, Y. Hatakeyama, F. B. Ueno, and K. Saito, Inorg. Chem. **24**, 4096 (1985).
4. (a) J. R. Fritch, G. C. Christoph and W. P. Schaefer, Inorg. Chem. **12**, 2170 (1973); (b) F. R. Fronczek, W. P. Schaefer and R. E. Marsh, Acta Crystallogr. Sect. B **30**, 117 (1974); (c) U. Thewalt, M. Zehnder and S. Fallab, Helv. Chim.

Acta **60**, 867 (1977); (d) M. Zehnder and U. Thewalt, Z. Anorg. Allg. Chem. **461**, 53 (1980).

5. C. G. Barraclough, G. A. Lawrance and P. A. Lay, Inorg. Chem. **17**, 3317 (1978).
6. V. M. Miskowski, B. D. Santarsiero, W. P. Schaefer, G. E. Ansok and H. B. Gray, Inorg. Chem. **23**, 1154 (1984).
7. (a) U. Thewalt, Z. Anorg. Allg. Chem. **393**, 1 (1972); (b) U. Thewalt and G. Struckmeier, Z. Anorg. Allg. Chem. **419**, 163 (1976); (c) M. Zehnder and U. Thewalt, Helv. Chim. Acta **63**, 1491 (1980); (d) M. Zehnder, U. Thewalt and S. Fallab, Helv. Chim. Acta **59**, 2290 (1976); (e) H. Macke, M. Zehnder, U. Thewalt and S. Fallab, Helv. Chim. Acta **62**, 1804 (1979).
8. (a) A. G. Sykes and J. A. Weil, Prog. Inorg. Chem. **13**, 1 (1970); (b) R. Caraco, D. Braun-Steinle and S. Fallab, Coord-Chem. Rev. **16**, 147 (1975); (c) S. Fallab, H.-P. Hunold, M. Maeder and P. R. Mitchell, J. Chem. Soc., Chem. Commun. 469 (1981).
9. G. A. Lawrance and P. A. Lay, J. Inorg. Nucl. Chem. **41**, 301 (1979).
10. M. Zehnder and S. Fallab, Helv. Chim. Acta **57**, 1493 (1974).
11. C. J. Ballhausen, *Molecular Electronic Structures of Transition Metal Complexes* (McGraw-Hill, New York, 1979), pp. 132–135.
12. (a) L. E. Orgel and R. S. Mulliken, J. Am. Chem. Soc. **79**, 4839 (1987); (b) H. Yamatera, J. Inorg. Nucl. Chem. **15**, 50 (1960).
13. R. A. D. Wentworth and T. S. Piper, Inorg. Chem. **4**, 709 (1965); (b) S. Yamada, Coord. Chem. Rev. **2**, 83 (1967).
14. Sasaki *et al.* (Y. Sasaki, J. Fujita and K. Saito, Bull. Chem. Soc. Japan **44**, 3373 (1971)) observed a CD extremum at ≈530 nm for a fresh solution of the compound $[((\text{dien})(l\text{-pn})\ \text{Co})_2\text{O}_2]^{4+}$, which can be assigned to the $d_{xz,yz} \rightarrow d_z^2$ component of the $^1A_{1g} \rightarrow {}^1T_{1g}$ d-d transition.
15. W. P. Schaefer, Inorg. Chem. **7**, 725 (1968).
16. (a) W. H. Fink and L. C. Allen, J. Chem. Phys. **46**, 2261, 2276 (1967); (b) K. Osafune and K. Kimura, Chem. Phys. Lett. **25**, 47 (1974).
17. T. H. Dunning, Jr. and N. W. Winter, Chem. Phys. Lett. **11**, 194 (1971).
18. P. A. Giguere and T. K. K. Srinivasan, J. Mol. Spectrosc. **66**, 168 (1977).
19. (a) A. B. Hoffman and H. Taube, Inorg. Chem. **7**, 903 (1968); (b) S. F. Mason and J. W. Wood, J. Chem. Soc., Chem. Commun. 209 (1967); (c) H. Siebert and H. Feuerhake, Chem. Ber. **102**, 2951 (1969); (d) M. R. Churchill, R. A. Lashewycz, K. Koshy and T. P. Dasgupta, Inorg. Chem. **20**, 376 (1981).
20. A. W. Chester and C. H. Brubaker, Jr., J. Inorg. Nucl. Chem. **30**, 213 (1968).
21. The most likely assignment of this band is to a bridging ligand (OH^- or NH_2^-) LMCT transition.[19] It has been noted that mononuclear analogues have no analogous absorption,[19c] but there is conceivably a "special" stabilization of some CT states for the dinuclear complexes. The interesting possibility that the band is some sort of metal–metal transition has not been eliminated, however.