the triazine ring, and the reaction stops at this point. More rigorous conditions might further hydrolyze the imide to an amide and a carboxylic acid. Consistent with this proposed mechanism is the fact that metals that form long metal–nitrogen bonds and therefore do not induce large amounts of angular strain do not facilitate the hydrolysis of the triazine ring. Examples of such complexes are (TPymT)$Pb_2(NO_3)_4 \cdot 2H_2O$, (TPymT)$Pb_3Cl_6 \cdot 3H_2O$, and (TPymT)$UO_2(NO_3)_2 \cdot 7H_2O$, all of which can be boiled in water with no apparent decomposition.[1]

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Registry No. $[Cu(C_{10}H_6N_5O_2)(H_2O)_3](NO_3) \cdot 2H_2O$, 62264-17-9; $[Cu(C_{12}H_8N_3O_2)(H_2O)_3](NO_3)$, 62264-16-8; 2-picolinamide, 527-85-5; TPymT, 60681-68-7; TPyT, 3682-35-7.

Supplementary Material Available: Tables S1–S3 giving structure factor amplitudes, rms thermal amplitudes, and least-squares best planes (25 pages). Ordering information is given on any current masthead page.

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Notes

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Comparative Electronic Spectra and Structure of Mononuclear and Binuclear Dioxygen Complexes[1]

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The complexation of molecular oxygen by transition metals has attracted wide interest primarily for its importance as a biological model.[3a] Thus, cobalt–dioxygen complexes have been particularly useful in formulating some of the basic principles of metal–dioxygen chemistry. It is widely accepted that the reaction of cobalt(II) complexes with molecular oxygen leads to an adduct best described as containing formally oxidized cobalt and reduced dioxygen. The stoichiometry of this reaction depends strongly on reaction conditions, so that the 1:1 Co–O_2 "superoxo" complexes initially formed may rapidly react with excess cobalt to give binuclear "μ-peroxo" ($Co^{III}–O_2^{2-}–Co^{III}$) complexes. Quite recently the electronic structures of some μ-peroxo[3b,c] and μ-superoxo complexes[3c] (formed by the one-electron oxidation of the corresponding peroxo complexes) have been examined in some detail. No such studies have been reported for the analogous mononuclear species, however, perhaps due to the strong ligand → ligand bands generally associated with such systems (e.g., cobalt porphines, and cobalt–Schiff base complexes[3a,4]) which obscure the metal associated bands of interest. Recently, however, the $(Et_4N)_3[Co(CN)_5]$ complex has been shown to react with dioxygen in nonaqueous solvents (e.g., DMF[5]) to generate the mononuclear dioxygen complex $[Co(CN)_5O_2]^{3-}$ for which the crystal structure is now known.[6] This system exhibits well-resolved ligand field spectra which may be interpreted by comparison to analogous $[Co(CN)_5X]^{4-}$ complexes and compared with the corresponding binuclear μ-superoxo complex $[Co(CN)_5O_2Co(CN)_5]^{5-}$ so that the effects of the complex stoichiometry may be evaluated.

Materials and Methods

Tetraethylammonium cyanide was prepared by ion exchange on an Amberlite IR 400 resin, passing tetraethylammonium chloride over a column presaturated with KCN. All chemicals used were reagent grade. All spectra were run in spectral grade solvents which were dried and redistilled before use. $[N(C_2H_5)_4]_3[Co(CN)_5O_2]$ was prepared by the method of White et al.[5] and characterized by ESR. Nonaqueous solutions of $K_5[Co(CN)_5O_2Co(CN)_5]$ were obtained by dissolving the compound in the presence of an external electrolyte, Bu_4NClO_4. ESR spectra were obtained on a Varian E6S spectrometer using a flat quartz cell. Visible spectra were obtained on a Cary 14 spectrophotometer using matched quartz cells.

Conductance measurements were performed on a YSI Model 300 conductance bridge, for which a cell constant was obtained using standard KCl solutions.

Results and Discussion

Spectra of the superoxo complexes $[Co(CN)_5–O_2–Co(CN)_5]^{5-}$ and $[Co(CN)_5O_2]^{3-}$ are presented in Figure 1. Convincing band assignments for the binuclear complex have already been made by Gray and co-workers.[3c] The band at 310 nm corresponds to an LMCT ($\pi_h^*(O_2^-\cdot) \rightarrow d_{z^2}$), the shoulder at 380 nm to the $^1A_1 \rightarrow {}^1E$ tetragonal component of the "$^1A_{1g} \rightarrow {}^1T_{1g}$" (d → d) transition, and the intense band at 526 nm to an MLCT ($d\pi \rightarrow \pi_v^*(O_2^-\cdot)$). Attempts at finding a weak $\pi_h^*–\pi_v^*$ band at about 10 000 cm^{-1} in the mononuclear complex have not thus far met with success.) Upon examination, the transition energies for the mononuclear complex are found to be quite similar to those for the binuclear complex (Table I). Thus the band assignments made by Gray for the binuclear complex are probably also valid for the mononuclear complex.

The spectra show a substantial medium dependence, as indicated by the solvent variation study summarized in Table I. Since the more negatively charged $[Co(CN)_5–(\mu\text{-}O_2)–Co(CN)_5]^{5-}$ might be expected to be differently solvated from $[Co(CN)_5O_2]^{3-}$, one might expect the various bands in the former complex to be solvent shifted from the corresponding bands in the latter. The observed shifts, however, are too small for a comparison of band positions to be very meaningful. It

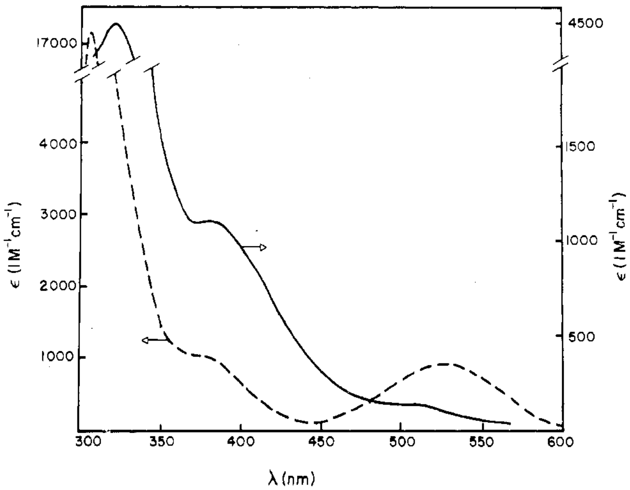


Figure 1. Spectra of $(NEt_4)_3[Co(CN)_5O_2]$ (—) and of $K_5[Co(CN)_5O_2Co(CN)_5]$, (- - -) in DMF solution.

is interesting, however, to compare the intensities of the analogous bands in the binuclear and mononuclear complexes. The low-energy MLCT band in particular is notably more intense in the binuclear complex (ϵ_{520} 900) than in the mononuclear (ϵ_{540} 90). This may perhaps be explained by the fact that the transition moment integral for the MLCT transition will be sharply dependent on the covalency of the Co–O bond. For the transition moment integral, intensity $\propto \langle \Psi_{ex}|M|\Psi_{gr}\rangle$, the ground-state wave function, Ψ_{gr} may be approximated as a linear combination of a cobalt π (d_{yz}, see Figure 2) orbital, Φ_{Co}, and dioxygen π^* orbital, Φ_{O_2}:$\Psi_{gr} = a\Phi_{O_2} + b\Phi_{Co}$. The excited-state wave function is then the orthogonal combination $\Psi_{ex} = b\Phi_{O_2} - a\Phi_{Co}$, and the transition moment integral becomes

Table I. Summary of Spectral Data for $[Co(CN)_5O_2]^{3-}$ and $[Co(CN)_5(\mu\text{-}O_2)Co(CN)_5]^{5-}$ in Various Solvents

(a) $[Co(CN)_5O_2]^{3-}$

λ_{max}, nm (ϵ)			
CH_3CN	MeOH	DMF	Assignment[a]
530 (~80)	510 (~110)	520 (~90)	MLCT ($d_{yz} \rightarrow \pi_v^*$)
400 (1000)	380 (900)	390 (1150)	"$^1A \rightarrow {}^1E$" (d → d)
320 (2800)	315 (4600)	320 (4800)	LMCT ($\pi_h^* \rightarrow d_{z^2}$)

(b) $[Co(CN)_5(\mu\text{-}O_2)Co(CN)_5]^{5-}$

λ_{max}, nm (ϵ)			
H_2O	MeOH[b]	DMF[c]	Assignment
487 (800)	500 (800)	526 (900)	MLCT ($d_{yz} \rightarrow \pi_v^*$)
370 (1600)	376 (940)	380 (1050)	"$^1A \rightarrow {}^1E$" (d → d)
310 (17 000)	~310 (6200)	312 (7000)	LMCT ($\pi_h^* \rightarrow d_{z^2}$)

[a] See ref 3. [b] In presence of Et_4NCl supporting electrolyte. [c] In presence of Bu_4NClO_4 supporting electrolyte.

$$\begin{aligned}\langle \Psi_{ex}|M|\Psi_{gr}\rangle &= \langle b\Phi_{O_2} - a\Phi_{Co}|M|a\Phi_{O_2} + b\Phi_{Co}\rangle \\ &= (b^2 - a^2)\langle \Phi_{Co}|M|\Phi_{O_2}\rangle + ab\langle \Phi_{O_2}|M|\Phi_{O_2}\rangle \\ &\quad - ab\langle \Phi_{Co}|M|\Phi_{Co}\rangle\end{aligned}$$

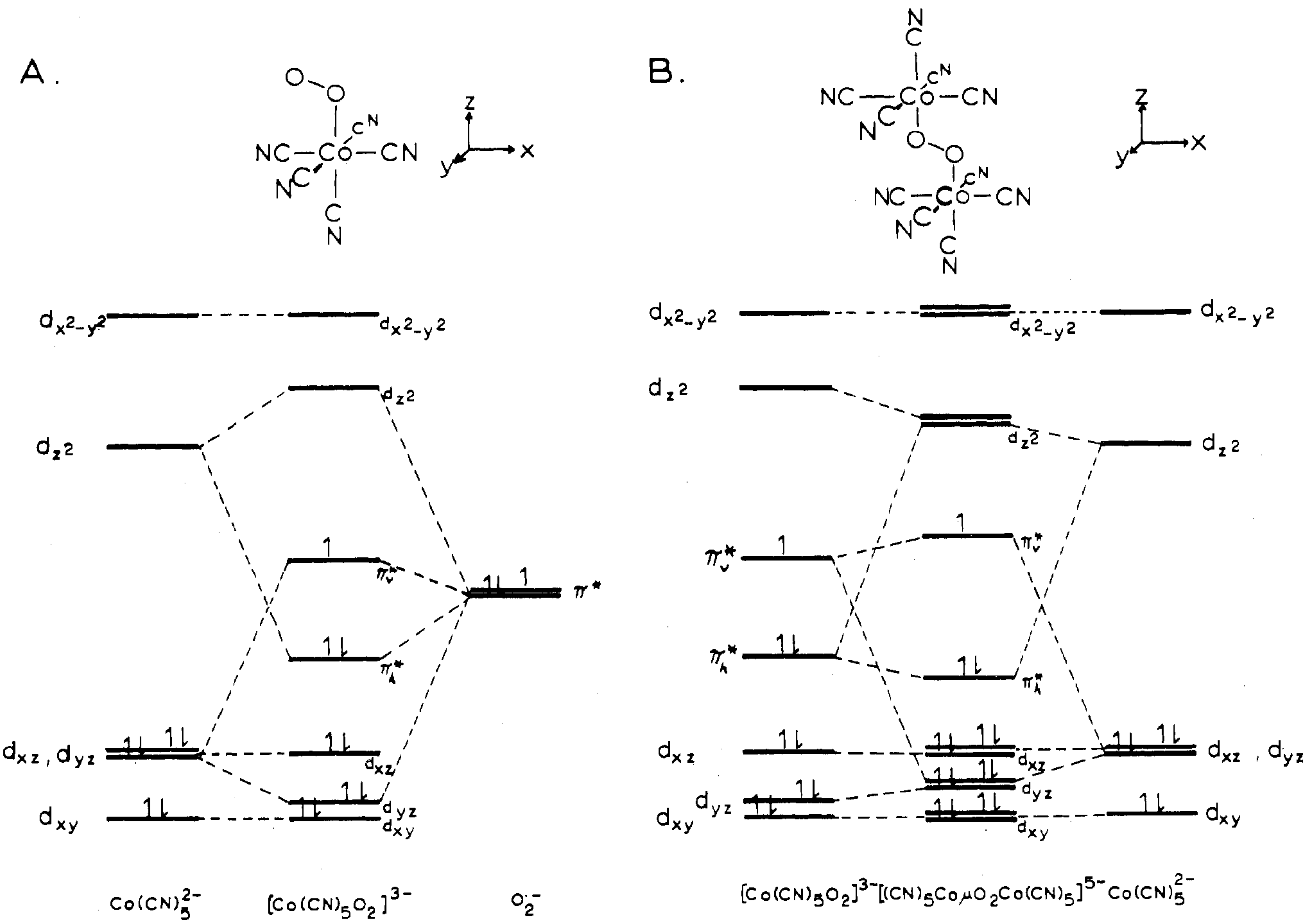


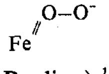
Figure 2. Molecular orbital diagrams showing (A) the interaction of $O_2^{-}\cdot$ with $[Co(CN)_5]^{2-}$ to yield $[Co(CN)_5O_2]^{3-}$ and (B) further interaction with another $[Co(CN)_5]^{2-}$ to yield $[Co(CN)_5(\mu\text{-}O_2)_2Co(CN)_5]^{5-}$. Tetragonal and rhombic splittings of the metal orbitals have been exaggerated for the sake of clarity.

Due to symmetry a Co d–d transition is electronically forbidden so that the term $\langle \phi_{Co}|M|\phi_{Co}\rangle$ is negligibly small as is the $\langle \phi_{O_2}|M|\phi_{O_2}\rangle$ term when compared with $\langle \phi_{O_2}|M|\phi_{Co}\rangle$. Thus, to a first approximation, the intensity of the transition is proportional to the term $(b^2 - a^2)\langle \Phi_{O_2}|M|\Phi_{Co}\rangle$. Given this, it is apparent that the intensity of the MLCT band will drop sharply as covalency increases. (In the limiting case $a = b = {}^1/_2$, so $\langle \Psi_{ex}|M|\Psi_{gr}\rangle = {}^1/_2|\langle \Phi_{O_2}|M|\Phi_{O_2}\rangle - \langle \Phi_{Co}|M|\Phi_{Co}\rangle|$).

From the above, we infer that in the mononuclear complex the cobalt–oxygen π bond is significantly more covalent than in the binuclear complex. Several lines of independent evidence support this hypothesis. First of all, the observed isotropic hyperfine coupling constant, A_{iso}, is 11.5 G for the mononuclear complex, whereas it is 8 G for the binuclear complex. This difference is consistent with, though not in itself proof of, a different degree of covalency in the two types of complex. Available x-ray results are also consistent with such an argument. Structural data are available for both $[Co(CN)_5O_2](N(C_2H_5)_4)_3$[6] and $K_5[Co(CN)_5O_2Co(CN)_5]$.[7] The Co–O_2 bond distance in these adducts decreases from 1.94 Å in the binuclear complex to 1.91 Å in the mononuclear complex, consistent with a more covalent Co–O_2 bond in the mononuclear complex. Furthermore, similar phenomena have been observed[8] in the $[Co(Me_2en)_2Cl(O_2)]^+$ system (Me_2en = *N,N'*-dimethylethylenediamine), which has an isotropic coupling constant, A_{iso}, of 14 G (as compared with A_{iso} of 10–11 G for comparable dinuclear complexes) and a correspondingly low intensity for the MLCT transition (ϵ_{630} 80).

The lower covalency in the π orbital of the binuclear complex is not unreasonable in view of the bonding picture presented in Figure 2. It is shown there how an O_2^- π^* orbital interacts with a metal dπ orbital to produce an elevated antibonding orbital, $\pi_v^*(O_2^-)$, and a depressed dπ-bonding (d_{yz}) orbital, which were referred to above as Ψ_{ex} and Ψ_{gr}, respectively. If the elevated $\pi_v^*(O_2^-)$ orbital now interacts with a second metal dπ (d_{yz}) orbital, the interaction will be more ionic since there is a greater energy difference between these new basis orbitals (i.e., the $\pi_v^*(O_2^-)$ orbital from the mononuclear complex and the d_{yz} orbital of the new metal) than between the original basis orbitals (i.e., an O_2^- π^* orbital and a metal d_{yz} orbital).

Gray has previously noted the apparent insufficiency of an Fe^{III}–$O_2^-\cdot$ ligand field model to explain the observed properties of oxyhemoglobin since $Dq(O_2^-\cdot) \approx Dq(NCS^-)$ (our own results suggest $Dq(NH_3) \geq Dq(O_2^-\cdot) \geq Dq(NCS)$), and metal thiocyanatohemoglobin is high spin, whereas oxyhemoglobin is low spin.[9] As the present results suggest that the covalency of the metal "superoxo" bond may vary with complex composition (so that the Racah parameters *B*, *C*, and the orbital splitting would vary), such a simple comparison based on the binuclear μ superoxo data may not be valid, as the π-acceptor nature of $O_2^-\cdot$ responsible for this bonding is not matched by NCS^-. On going from cobalt to iron, the relevant metal orbitals will be raised in energy, approaching the $\pi^*(O_2)$ orbitals and further increasing the covalency of the system (approaching in the limiting case the VB



$$\overset{\quad O-O^-}{\underset{Fe}{//}}$$

description advanced by Pauling).[10]

Finally, the marked solvent dependence of the spectra merit comment. Pauling has previously emphasized the possibility of strong hydrogen bonding between the "distal" imidazole of hemoglobin and coordinated oxygen, presumably acting to stabilize complexed dioxygen.[10] No experimental data have previously tested this postulate, however. Gray[3c] has already noted the strong medium dependence of the spectra of $[Co(CN)_5O_2Co(CN)_5]^{5-}$, which is orange in aqueous solution but magenta in the solid potassium salt.[11] In the present paper more extensive solvent variations demonstrate the strong dependence of the spectra on solvent composition, such observations being consistent with strong ion pairing in nonaqueous solution between the highly charged cyano complex and alkylammonium ions. (Thus $K_5[Co_2CN_{10}O_2]$ is insoluble in pure DMF but is readily solubilized in the presence of excess tetrabutylammonium perchlorate.) Conductance measurements for $(Et_4N)_3[Co(CN)_5O_2]$ in DMF at 10^{-3} M give Λ = 160 Ω^{-1} cm^{-1}, well below the range expected for a 3:1 electrolyte ($\Lambda \approx 220$ Ω^{-1} cm^{-1}),[12] consistent with strong ion-pair formation. As solvent polarity decreases, the MLCT bands for both binuclear and mononuclear complexes undergo pronounced red shifts (thus $[Co_2(CN)_{10}O_2]^{5-}$ gives magenta solutions in DMF with Bu_4NClO_4 supporting electrolyte), while the MLCT transition is only slightly blue shifted. Most surprisingly, there is a small but definite red shift in the $^1A_1 \rightarrow {}^1E$ tetragonal component of the $^1A_{1g} \rightarrow {}^1T_{1g}$ d–d band on going to solvents of decreasing polarity. As the complexes studied are coordinatively saturated, any solvent effects must be secondary and probably involve ion-pairing interaction.

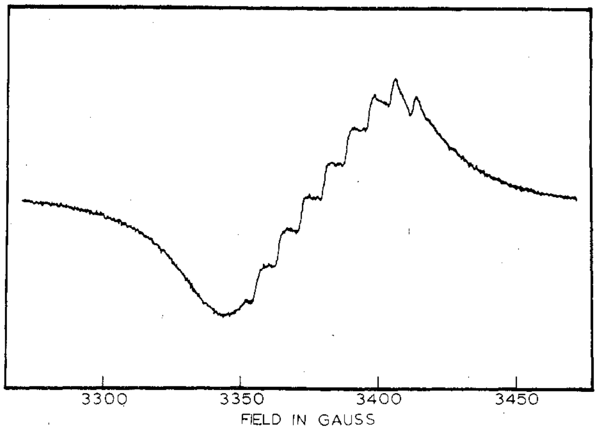


Figure 3. Isotropic EPR spectrum of $[Co(CN)_5O_2](Et_4N)_3$ in DMF solution at 23 °C. g_{iso} = 2.002; A_{iso} = 11.5 G.

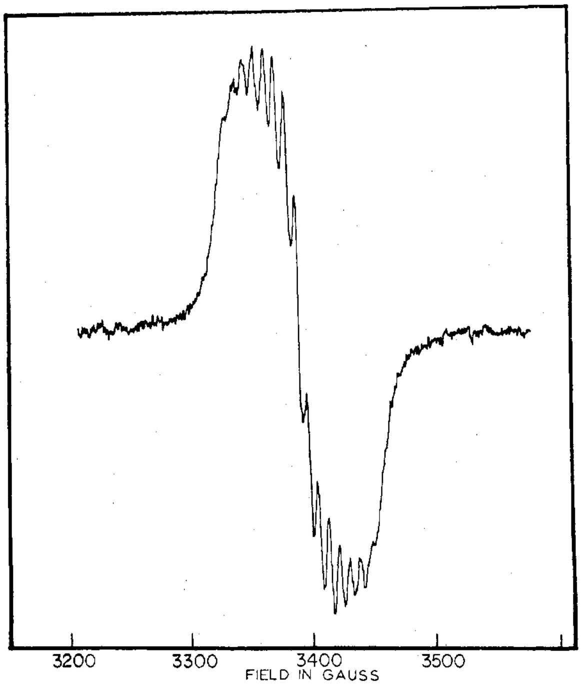


Figure 4. Isotropic EPR spectrum of $[Co(CN)_5O_2](Et_4N)_3$ in H_2O solution, demonstrating formation of the binuclear complex $[Co_2CN_{10}O_2]^{5-}$.

Apparently, then, strong ion pairing in a nonpolar environment serves to decrease the metal orbital splitting, thus *destabilizing* the dioxygen complex. By controlling the degree of ion pairing (varying $N-H-O_2$ bond length by conformational changes) it may be possible to affect metal–ligand bond strength in a manner which is opposite to that envisioned by Pauling but which might contribute to cooperativity in hemoglobin. Further studies will be necessary to test this possibility.[13]

On extension of solvent variation studies on $[Co(CN)_5O_2]^{3-}$ to water, the EPR spectrum is transformed from the poorly resolved 8-line spectrum (Figure 3) to a 15-line spectrum typical of a binuclear adduct (Figure 4). This change implies the occurrence of a reaction with the stoichiometry

$$2[Co(CN)_5O_2]^{3-} \rightarrow [Co_2(CN)_{10}O_2]^{5-} + O_2^{-\cdot}$$

i.e., formally a superoxide displacement reaction. (Simple deoxygenation and dimerization would yield a diamagnetic μ-peroxo complex.) Kinetic studies will be necessary to clarify the mechanism of this unusual reaction.

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Registry No. $(NEt_4)_3[Co(CN)_5O_2]$, 53908-43-3; $K_5[Co(CN)_5O_2Co(CN)_5]$, 12557-90-3.

References and Notes

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Electronic Spectra of Dinuclear Cobalt Carbonyl Complexes

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The $\sigma \rightarrow \sigma^*$ assignment of the intense near-UV band in $M_2(CO)_{10}$[5,6] (M = Mn, Tc, Re) has been widely adopted[7-11] and extended to a number of other systems, including $(\eta^5\text{-}C_5H_5)_2M_2(CO)_6$ (M = Mo, W),[12,13] $(\eta^5\text{-}C_5H_5)M(CO)_3M'(CO)_5$ (M = Mo, W; M' = Mn, Re),[14] $M_2(CO)_{10}^{2-}$ (M = Cr, Mo, W),[6,15,16] and $MM'(CO)_{10}^-$ (M = Cr, Mo, W; M' = Mn, Re).[6,16] These systems are related in that each is viewed as having a two-electron metal–metal σ bond. Each complex also exhibits an intense near-UV absorption band that sharpens and intensifies upon cooling. The $\sigma \rightarrow \sigma^*$ assignment has been useful in interpreting the experimental observation that homolytic cleavage of the metal–metal bond is a very efficient photoprocess.[8-14] The aim of this note is to extend the $\sigma \rightarrow \sigma^*$ assignment to dinuclear cobalt carbonyl complexes and, in particular, to assign the spectrum of $Co_2(CO)_8$ which is known[17] to exist in solution as a mixture of bridged and nonbridged isomers. The mixture consists mainly of one bridged and one nonbridged isomer of D_{3d} symmetry,[17a] although there is recent compelling evidence showing a second nonbridged isomer.[17b-e]

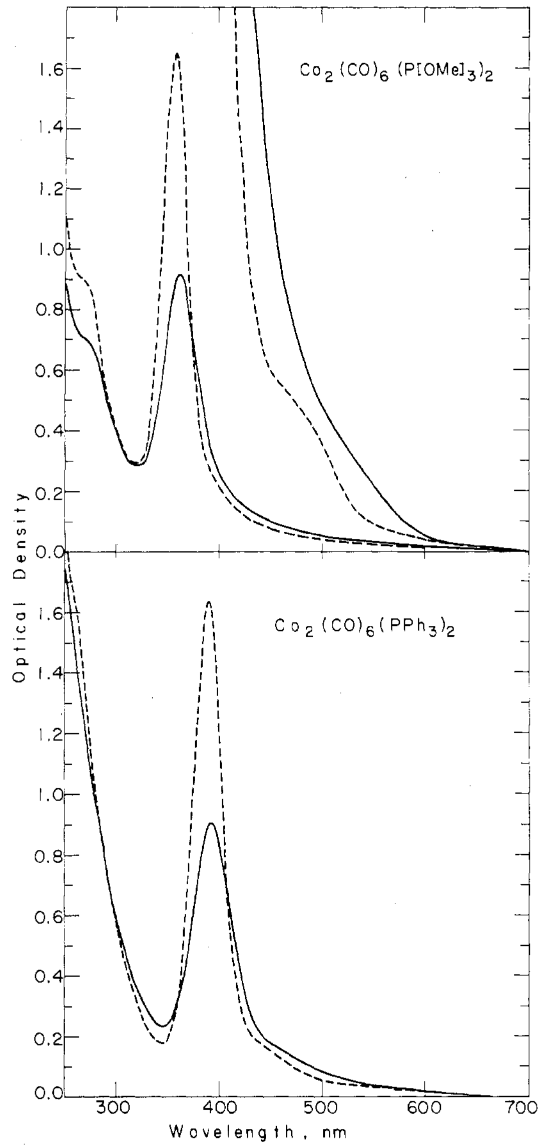

Figure 1. Electronic spectra of $Co_2(CO)_6(P(OMe)_3)_2$ in EPA solution and $Co_2(CO)_6)(PPh_3)_2$ in 2-methyltetrahydrofuran solution: at 298 K —; after cooling to 77 K, - - -. The high optical density in the $Co_2(CO)_6(P(OMe)_3)_2$ spectrum is for a higher concentration. Changes in the spectra upon cooling are not corrected for solvent contraction.

The electronic spectra of $Co_2(CO)_6L_2$ (L = $P(OMe)_3$, PPh_3) are shown in Figure 1. These spectra may be interpreted with