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)$_5$O$_2$]$^{3-}$ 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

$$2[Co(CN)_5O_2]^{3-} \rightarrow [Co_2(CN)_{10}O_2]^{5-} + O_2^-\cdot$$
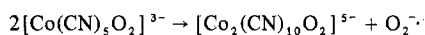
i.e., formally a superoxide displacement reaction. (Simple deoxygenation and dimerization would yield a diamagnetic μ-peroxo complex.) Kinetic studies will be necessary to clarify the mechanism of this unusual reaction.

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References and Notes

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(2) (a) Texas A&M University Health Fellow, 1974–1976. (b) Texas A&M University Health Fellow, 1976–1977. This work was taken in part from a dissertation of S.R.P. to be submitted to the Faculty of Texas A&M University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.
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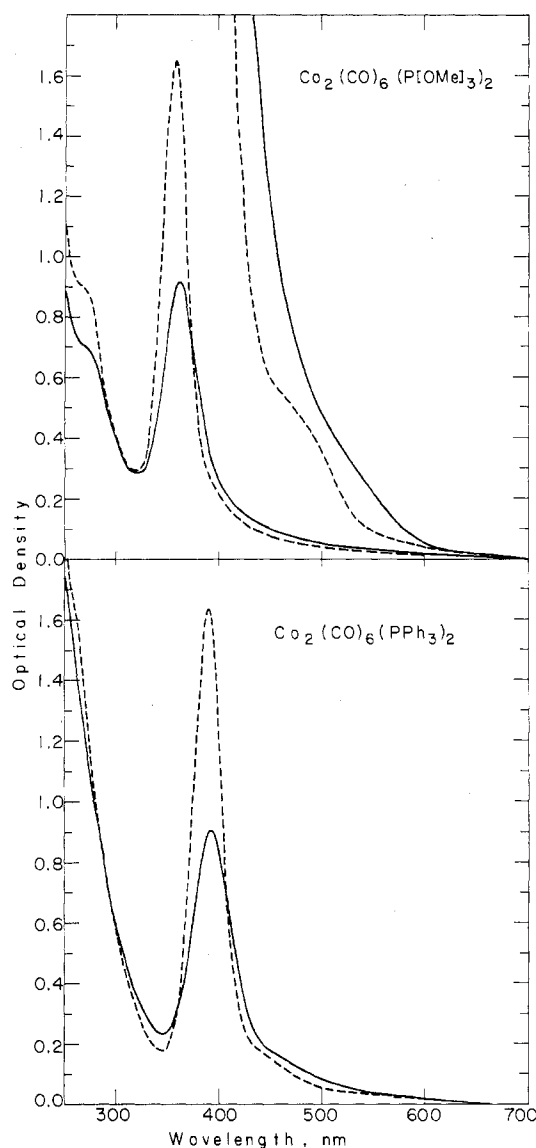

Electronic Spectra of Dinuclear Cobalt Carbonyl Complexes

Harmon B. Abrahamson,[1,2] Claude C. Frazier,[3] David S. Ginley,[1] Harry B. Gray,*[3] Jane Lilienthal,[3] David R. Tyler,[3] and Mark S. Wrighton*[1,4]

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]

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.

and extended to a number of other systems, including (η^5-C$_5$H$_5$)$_2$M$_2$(CO)$_6$ (M = Mo, W),[12,13] (η^5-C$_5$H$_5$)M(CO)$_3$M'-(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]

The electronic spectra of Co$_2$(CO)$_6$L$_2$ (L = P(OMe)$_3$, PPh$_3$) are shown in Figure 1. These spectra may be interpreted with

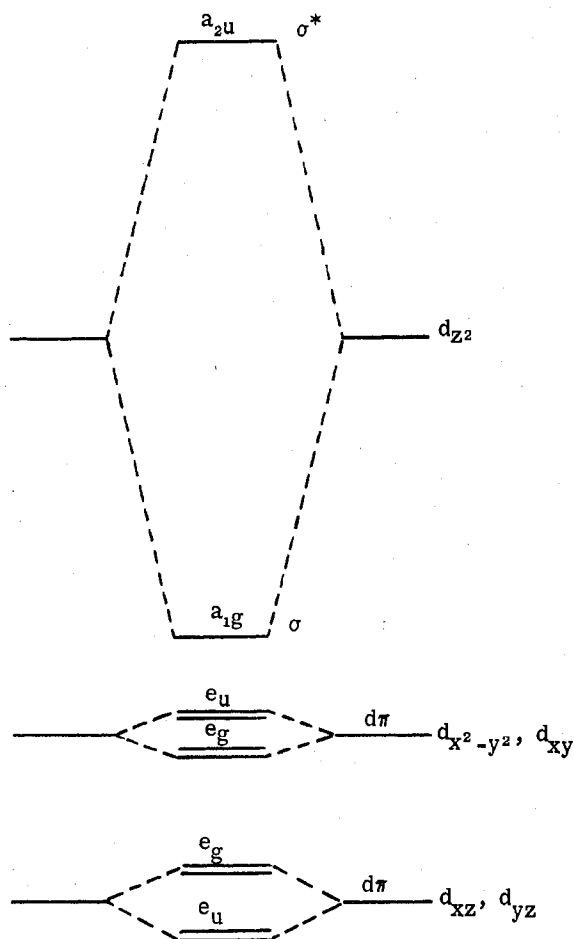**Figure 2.** Relative energies of the molecular orbitals of D_{3d} $Co_2(CO)_6L_2$. The ground state is $^1A_{1g}(e_u^4e_g^4e_g^4e_u^4a_{1g}^2)$.

the aid of an MO diagram for a D_{3d} $Co_2(CO)_6L_2$ molecule (Figure 2). The $Co_2(CO)_6L_2$ complexes studied here show no appreciable quantity of any bridged isomer and the infrared data are consistent with either D_{3d} or D_{3h} symmetry.[18] The intense absorptions at 393 nm in $Co_2(CO)_6(PPh_3)_2$ and 360 nm in $Co_2(CO)_6(P(OMe)_3)_2$ are assigned to allowed $\sigma \rightarrow \sigma^*$ [$^1A_{1g}(a_{1g}^2) \rightarrow {}^1A_{2u}(a_{1g}a_{2u})$] transitions. These assignments are supported by the temperature-dependent behavior of the absorption bands. In each case cooling results in an increase in absorbance, a sharpening, and a slight shift of the band to higher energy. Such behavior has previously been noted for the $\sigma \rightarrow \sigma^*$ band in related complexes.[6] By analogy to the interpretation of the electronic spectrum of $Mn_2(CO)_{10}$,[6] the weak, low-energy shoulder observed on the $\sigma \rightarrow \sigma^*$ band in each of the $Co_2(CO)_6L_2$ complexes is attributed to a $d\pi \rightarrow \sigma^*$ transition [$^1A_{1g}(e_g^4) \rightarrow {}^1E_u(e_g^3a_{2u})$].

Infrared spectral studies have shown that solutions of $Co_2(CO)_8$ at 298 K contain roughly a 50:50 mixture of bridged and nonbridged isomers; it has also been established that cooling such solutions converts the mixture exclusively to the bridged form.[17a] Consequently, we have measured the electronic spectra of 2-methylpentane solutions of $Co_2(CO)_8$ at 298 and 50 K (Figure 3). Large changes are found and we draw attention to the fact that the 298-K solution exhibits a well-resolved band at 350 nm, which is absent at 50 K. Also, the low-temperature spectrum exhibits a more well-defined, intensified band at 280 nm compared to the 298-K spectrum.

The disappearance of the band at 350 nm upon cooling to 50 K suggests that it is the $\sigma \rightarrow \sigma^*$ transition of the nonbridged species. The band at 280 nm, which gains intensity, is assigned
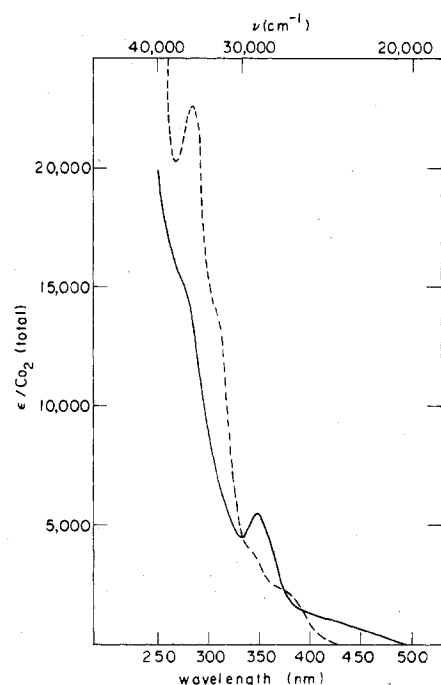

Figure 3. Electronic spectra of $Co_2(CO)_8$ in 2-methylpentane solutions: at 298 K, —; after cooling to 50 K, - - -. The spectral changes are not corrected for solvent contraction.

to $\sigma \rightarrow \sigma^*$ in the bridged dimer. This higher energy $\sigma \rightarrow \sigma^*$ transition is consistent with a shorter Co–Co bond in the bridged form inferred from the Co–Co stretching frequencies.[17d] The band lower in energy than the $\sigma \rightarrow \sigma^*$ absorption in the nonbridged dimer is attributed to a $d\pi \rightarrow \sigma^*$ transition, by analogy to the assignments proposed for the $Co_2(CO)_6L_2$ and $Mn_2(CO)_{10}$ species. From the electronic spectral measurements, we have been unable to identify features attributable to more than two isomers. However, it is likely that the spectra will be similar for the possible nonbridged isomers, and their presence might not be as easily detectable as in vibrational spectroscopic studies.[17b–e]

The effect of ligand substitution on the energy of the $\sigma \rightarrow \sigma^*$ transition has been well documented for the $Mn_2(CO)_{10}$ dimer.[6] The $\sigma \rightarrow \sigma^*$ transition decreases in energy from 29 740 cm^{-1} in $Mn_2(CO)_{10}$ to 27 400 cm^{-1} in $Mn_2(CO)_8(PPh_3)_2$ (both at 77 K). A similar decrease in the $\sigma \rightarrow \sigma^*$ transition energy is observed in the Co_2 analogue, i.e., a shift from 28 570 cm^{-1} in nonbridged $Co_2(CO)_8$ to 27 780 cm^{-1} in $Co_2(CO)_6(PPh_3)_2$. Electronic spectral assignments for the various metal–metal bonded dimers are summarized in Table I.

The position of the $\sigma \rightarrow \sigma^*$ band in certain heterodinuclear metal–metal bonded complexes reinforces our assignment of the band near 350 nm in $Co_2(CO)_8$ as the $\sigma \rightarrow \sigma^*$ transition in the nonbridged form. The position of the $\sigma \rightarrow \sigma^*$ absorption band in each of several complexes is set out in Table II. Table II also gives calculated values of the $\sigma \rightarrow \sigma^*$ band position for several heterodinuclear complexes, under the assumption that $\sigma \rightarrow \sigma^*(M-M') = [\sigma \rightarrow \sigma^*(M-M) + \sigma \rightarrow \sigma^*(M'-M')]/2$. The point is that the position of the band for $(\eta^5-C_5H_5)M(CO)_3Co(CO)_4$ (M = Mo, W) is fairly accurately predicted from the assigned $\sigma \rightarrow \sigma^*$ energies of $(\eta^5-C_5H_5)_2M_2(CO)_6$ and nonbridged $Co_2(CO)_8$. Similarly, the $\sigma \rightarrow \sigma^*$ position in $Co(CO)_3(PPh_3)Mn(CO)_5$ falls between the values for $Mn_2(CO)_{10}$ and $Co_2(CO)_6(PPh_3)_2$. These relationships establish a measure of internal consistency in the $\sigma \rightarrow \sigma^*$ assignments of the dinuclear carbonyls involving cobalt carbonyl fragments. Since the position of the $\sigma \rightarrow \sigma^*$ transition has been correlated with M–M bond strength,[7] we

Table I. Electronic Spectral Data and Transition Assignments

Complex	ν, cm^{-1}	ϵ, M^{-1} cm^{-1}	Assignment
Mn$_2$(CO)$_{10}$[a]	26 700	2 900	d$\pi \rightarrow \sigma^*$
	29 740	33 700	$\sigma \rightarrow \sigma^*$
Mn$_2$(CO)$_8$(PPh$_3$)$_2$[a]	27 400	31 800	$\sigma \rightarrow \sigma^*$
Co$_2$(CO)$_8$[b]	23 470[c]	980	d$\pi \rightarrow \sigma^*$ (nonbridged)
	28 570[c]	5 500	$\sigma \rightarrow \sigma^*$ (nonbridged)
	35 460[c]	14 400	$\sigma \rightarrow \sigma^*$ (bridged)
	26 460[d]	2 200	d$\pi \rightarrow \sigma^*$ (bridged)
	(29 000)[d]	(3 700)	e
	(32 100)[d]	(13 500)	e
	35 460[d]	22 600	$\sigma \rightarrow \sigma^*$ (bridged)
Co$_2$(CO)$_6$(PPh$_3$)$_2$[f]	22 200(sh)	5 300	d$\pi \rightarrow \sigma^*$
	25 450	23 800	$\sigma \rightarrow \sigma^*$
Co$_2$(CO)$_6$(P(OMe)$_3$)$_2$[g]	20 800[h]	h	d$\pi \rightarrow \sigma^*$
	27 780[g]	24 000[g]	$\sigma \rightarrow \sigma^*$

[a] In 3-pip at 77 K; from ref 6. [b] In 2-methylpentane; ϵ/Co$_2$ (total) values are reported. [c] 298 K. [d] 50 K; uncorrected for solvent contraction. [e] Not assigned. [f] In dichloromethane at 298 K. [g] In isooctane at 298 K. [h] Shoulder, observable only in low-temperature spectrum; cf. Figure 1.

Table II. Near-UV $\sigma \rightarrow \sigma^*$ Band Maxima for Several Metal–Metal Bonded Complexes

Complex	Calcd $\bar{\nu}$, cm^{-1} [a]	Obsd $\bar{\nu}$, cm^{-1} [a,b]
Mn$_2$(CO)$_{10}$		29 240 (342)[c]
Re$_2$(CO)$_{10}$		31 950 (313)[c]
(η^5-C$_5$H$_5$)$_2$Mo$_2$(CO)$_6$		25 770 (388)[d]
(η^5-C$_5$H$_5$)$_2$W$_2$(CO)$_6$		27 620 (362)[d]
(η^5-C$_5$H$_5$)Mo(CO)$_3$Mn(CO)$_5$	27 505 (364)	26 810 (373)[e]
(η^5-C$_5$H$_5$)Mo(CO)$_3$Re(CO)$_5$	28 860 (347)	27 400 (365)[e]
(η^5-C$_5$H$_5$)W(CO)$_3$Mn(CO)$_5$	28 430 (352)	27 620 (362)[e]
(η^5-C$_5$H$_5$)W(CO)$_3$Re(CO)$_5$	29 785 (336)	30 210 (331)[e]
Co$_2$(CO)$_8$ [bridged]		35 460 (282)[f]
Co$_2$(CO)$_8$ [nonbridged]		28 570 (350)
Co$_2$(CO)$_6$(P(OMe)$_3$)$_2$		27 780 (360)
Co$_2$(CO)$_6$(PPh$_3$)$_2$		25 450 (393)[g]
Co(CO)$_3$(PPh$_3$)Mn(CO)$_5$	27 345 (366)	26 600 (376)
(η^5-C$_5$H$_5$)Mo(CO)$_3$Co(CO)$_4$	27 170 (368)	28 170 (355)
(η^5-C$_5$H$_5$)W(CO)$_3$Co(CO)$_4$	28 095 (356)	29 240 (342)

[a] Wavelengths in nm are given in parentheses. [b] All measurements were made at 298 K in aliphatic hydrocarbon solvents unless noted otherwise. [c] From ref 11. [d] From ref 12. [e] From ref 14. [f] 50 K. [g] Dichloromethane at 298 K.

can infer that our ability to predict the M–M' $\sigma \rightarrow \sigma^*$ position from that of M–M and M'–M' implies little ionic bonding in the heterodinuclear complexes reported here.

Experimental Section

Complexes. Co$_2$(CO)$_8$ is commercially available and was used after sublimation. Both Co$_2$(CO)$_6$(P(OMe)$_3$)$_2$ and Co$_2$(CO)$_6$(PPh$_3$)$_2$ were prepared according to published procedures[18] and infrared spectra in the carbonyl stretching region were found to be as reported previously.[18] The mixed-metal dinuclear complexes Mn(CO)$_5$Co-(CO)$_3$PPh$_3$ and (η^5-C$_5$H$_5$)M(CO)$_3$Co(CO)$_4$ (M = Mo, W) were prepared by near-UV irradiation of the homodinuclear metal–metal bonded complexes. A procedure analogous to that outlined for other M–M' complexes was used.[14] The compounds were purified by column chromatography and were characterized by infrared and UV–VIS spectra and by elemental analyses. The details are to be published in a paper concerning the photochemistry of M–Co bonded complexes.[19]

Spectra. Spectra of the complexes were recorded in optically transparent solvents using a Cary 17 UV–VIS–near-IR spectrophotometer. Low-temperature spectra were recorded in either 2-methylpentane, 2-methyltetrahydrofuran, or EPA (5:5:2 diethyl ether–isopentane–ethanol by volume). These solvents form good glasses at low temperature. The 77-K spectra were recorded using an all-quartz liquid N$_2$ Dewar fitted with optical-quality flats for windows. Lower temperature spectra were obtained using a Cryogenics Technology, Inc., cryotip assemply. All of the complexes studied here are light sensitive in solution. Special precautions were taken to exclude light. Solutions of Co$_2$(CO)$_8$ were cooled in a dry ice–acetone bath to avoid thermal decomposition.

Registry No. Co$_2$(CO)$_8$ [bridged], 10210-68-1; Co$_2$(CO)$_8$ [nonbridged], 12553-61-6; Co$_2$(CO)$_6$(P(OMe)$_3$)$_2$, 21407-15-8; Co$_2$(CO)$_6$(PPh$_3$)$_2$, 10170-27-1; Co(CO)$_3$(PPh$_3$)Mn(CO)$_5$, 61966-64-1; (η^5-C$_5$H$_5$)Mo(CO)$_3$Co(CO)$_4$, 62015-65-0; (η^5-C$_5$H$_5$)W(CO)$_3$Co-(CO)$_4$, 62015-64-9.

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Hydrogen–Deuterium Exchange in Transition Metal Hydridocarbonyl Cluster Complexes. Standardization of a Mass Spectroscopic Analytical Technique

Mark A. Andrews, Stephen W. Kirtley, and Herbert D. Kaesz*

Although hydridometal cluster complexes are thermodynamically acidic,[1] a number of these such as H$_3$Re$_3$(CO)$_{12}$[2] or H$_4$Ru$_4$(CO)$_{12}$[3] ionize or exchange protons slowly in polar solvents and thus their reactions with bases are rather slow.