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Electronic Structure and Spectra of μ-Superoxo-dicobalt(III) Complexes

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The electronic spectra of the μ-superoxo complexes $[(NH_3)_5CoO_2Co(NH_3)_5]^{5+}$ and $[(CN)_5CoO_2Co(CN)_5]^{5-}$ have been subjected to detailed analysis. The electronic spectroscopic properties conclusively establish the presence of low-spin d^6 Co(III) centers in the ground states of both the decaammine and decacyanide. The $\pi^*(O_2^-)$ level is split into a filled, in-plane component involved in strong σ bonding with Co(III) and a weakly π-bonding, half-filled, out-of-plane component. Ligand-field, ligand-to-metal charge-transfer, and superoxide-localized transitions have been identified. The characteristic low-energy bands (decaammine, 672 nm; decacyanide, 486 nm) have been reassigned to metal-to-ligand charge-transfer transitions terminating in the out-of-plane $\pi^*(O_2^-)$ orbital.

Introduction

Many Co(II) complexes take up molecular oxygen in aqueous solution, and binuclear complexes often can be isolated. One-electron oxidation of these complexes yields products that are now usually formulated as μ-superoxo-dicobalt(III) species.[1] The accurate X-ray determination by Schaefer and Marsh of the crystal structure of the sulfate tris(bisulfate) salt of $[(NH_3)_5CoO_2Co(NH_3)_5]^{5+}$ (which we will hereafter refer to as the "decaammine") revealed a planar (C_{2h}) CoO_2Co unit, with an O–O distance (1.31 Å) very close to the 1.28-Å value typical of alkali metal superoxides.[2] Further, Co–N distances were found to be in good agreement with those of other Co(III) complexes.[2] A very similar CoO_2Co structure has also been established for the potassium salt of the cyanide analog, $[(CN)_5CoO_2Co(CN)_5]^{5-}$ (hereafter referred to as the "decacyanide").[3] EPR studies of the decaammine and decacyanide suggest that in each case there is very little delocalization of the unpaired electron into cobalt orbitals.[4] Both X-ray structural and EPR spectral data, therefore, are fully consistent with a formulation of oxidation state III for the cobalt centers in these complexes.

We report here the results of a thorough investigation of the electronic spectra of the decaammine and the decacyanide. These spectra are extremely complex and present a monumental problem of interpretation. Indeed, several radically different assignment schemes have already been proposed.[5-8] In our analysis we will rely primarily on detailed comparisons with the d–d and charge-transfer bands in $Co(NH_3)_5X^{2+}$ and $Co(CN)_5X^{3-}$ complexes, which have been extensively studied.[9,10] Additionally, we will examine the electronic spectra of the μ-peroxo analogs of the decaammine and decacyanide. Throughout the discussion of the results, we intend to place major emphasis on the question of the ground-state electronic structural formulation of the CoO_2Co unit in these complexes.

Experimental Section

Preparation of Compounds. The compound $[(NH_3)_5CoO_2Co(NH_3)_5]SO_4(HSO_4)_3 \cdot H_2O$ was prepared by a literature procedure.[2] Anal. Calcd for $[Co_2O_2(NH_3)_{10}]SO_4(HSO_4)_3 \cdot H_2O$: Co, 16.28; S, 17.66; N, 19.31; H, 4.82. Found: Co, 16.43; S, 17.30; N, 19.11; H, 4.90. The chloride salt $[(NH_3)_5CoO_2Co(NH_3)_5]Cl_5 \cdot 4H_2O$ was prepared by the method of Linhard and Weigel;[5] the purity of the compound was verified by electronic spectroscopic comparison to the sulfate tris(bisulfate) salt.

The compound $K_5[(CN)_5CoO_2Co(CN)_5] \cdot H_2O$ was prepared by a published method,[4] using $[(NH_3)_5CoO_2Co(NH_3)_5]SO_4(HSO_4)_3 \cdot H_2O$ as a starting material. Very careful fractional recrystallization of the compound from aqueous solutions by addition of ethanol and methanol in the dark at −5° afforded large, dendritic magenta crystals. We were unable to obtain crystalline products with any other cation. The compound is somewhat hygroscopic and very photosensitive, and all experiments were performed using freshly prepared samples. Anal. Calcd for $K_5[Co_2O_2(CN)_{10}] \cdot H_2O$: Co, 18.90; C, 19.26; H, 0.32; N, 22.46; K, 31.35. Found: Co, 17.81; C, 19.53; H, 0.77; N, 20.89; K, 28.81.

Spectroscopic Measurements. Ultraviolet, visible, and near-infrared spectral measurements were made on a Cary Model 17 spectrophotometer. For solution measurements, the solvent used in most cases was a 1:1 mixture of saturated aqueous LiCl and water, pH being adjustable with HCl. This solvent forms a good glass at low temperatures. Spectra at 78 K were measured in a quartz dewar with optical quality windows. Solution cells for the measurements were made by molding round quartz tubing on a square molybdenum frame; the rounded corners help to prevent cracking of the glass and/or cell. Samples were completely immersed in liquid nitrogen. Prior to measurements, the liquid nitrogen was cooled by pumping or by blowing helium gas through the liquid, in order to avoid bubbling. Spectra were routinely corrected by taking baseline measurements using solvent alone at both room temperature and 78 K. Measurements on the same solutions were also made using commerical Suprasil cells at room temperature, in order to correct for path length variability in the other experiments. Molar extinction coefficients at 78 K were corrected for volume contraction, the correction factor being 2.5% for 1:1 LiCl(satd aq)–H_2O. Solid samples were very finely ground with KBr (~300–400 mg), and in each case the mixture was pressed into a pellet, which gave little scattering at $\lambda > 250$ nm if prepared carefully. Spectra were measured using KBr reference pellets of the same thickness. The pellets were cooled to ~80 K using the same quartz dewar employed in the solution measurements.

Photochemical Measurements on $[(CN)_5CoO_2Co(CN)_5]^{5-}$. Samples were irradiated using merry-go-rounds.[11] Filter systems were used to isolate the mercury lamp lines at 254, 313, and 366 nm. Light intensities were measured using ferrioxalate actinometry[12] and were of the order of 10^{-7} einstein min^{-1} (3-ml samples). Correction was made for thermal aquation rates, which were measured spectrophotometrically in the sample compartment of the Cary 17, employing a cell holder adapted to circulate water from a thermostated bath continuously around the cell. For both the photochemical and thermal reactions, the concentration of $[(CN)_5CoO_2Co(CN)_5]^{5-}$ was monitored by following the decrease in absorbance at 495 nm.

Results and Discussion

μ-Peroxo Complexes. The electronic spectra of μ-peroxo-dicobalt(III) complexes generally are poorly resolved, owing to the presence of very broad charge-transfer bands in the near-ultraviolet region.[1] The lowest energy ligand-field (LF) band of $[(NH_3)_5CoO_2Co(NH_3)_5]^{4+}$, for example, appears only as an ill-defined shoulder near 450 nm.[13] The best resolved spectra in the literature are those reported by Bosnich et al.[14,15] for the complexes $[(Co(cyclam)X)_2O_2]^{2+}$. Here the positions and intensities of the lowest energy bands accord well with expectation for LF transitions in tetragonal, low-spin d^6 Co(III) complexes. Analysis of these spectra by standard LF procedures gives decreasing *Dq* values of the axial groups according to $NH_3 > NCS^- > O_2^{2-} > OH_2$.[13] It is apparent, therefore, that O_2^{2-} coordinated to Co(III) possesses normal spectrochemical properties for an oxygen donor.

Ligand-to-metal charge-transfer (LMCT) transitions from filled $\pi^*(O_2^{2-})$ to empty Co(III) $d\sigma^*$ orbitals are expected at relatively low energies.[10] The relative and absolute energies and intensities of these bands should be a strong function of the dihedral angle of the CoO_2Co unit,[16] which determines the degree of splitting of the $\pi^*(O_2^{2-})$ level. An empirical correlation has been noted for various μ-peroxo-dicobalt(III) complexes, namely, that monobridged species show two

Table I. Electronic Spectra of μ-Superoxo-dicobalt(III) Complexes

	300 K			78 K			
Complex	λ_{max}, nm	ν_{max}, kK	ϵ	λ_{max}, nm	ν_{max}, kK	ϵ	Assignment
$[(NH_3)_5CoO_2Co(NH_3)_5]Cl_5 \cdot 4H_2O$ in 1:1 LiCl(satd aq)-HCl(1 *M* aq)	~800	~12.5	~110 sh	~790	~12.7	~830 sh	$\pi_h^*(O_2^-) \rightarrow \pi_v^*(O_2^-)$
	671.5	14.89	927	675.5	14.80	1249	$d\pi \rightarrow \pi_v^*(O_2^-)$
	480	20.8	309	472.0	21.19	291	"$^1A_{1g}$" → "$^1T_{1g}$"
	~345	~28.9	~3,450 sh	~342	~29.2	~3,460 sh	"$^1A_{1g}$" → "$^1T_{2g}$"
	302	33.1	20,160	301	33.2	23,960	$\pi_h^*(O_2^-) \rightarrow d_{z^2}$
	~225	~44.4	~21,000 sh	~225	~44.4	~21,000 sh	$\pi_v(O_2^-) \rightarrow \pi_v^*(O_2^-)$
$K_5[(CN)_5CoO_2Co(CN_5] \cdot H_2O$ in 1:1 LiCl(satd aq)-H_2O	~817	12.2	12.7	*a*	*a*	*a*	$\pi_h^*(O_2^-) \rightarrow \pi_v^*(O_2^-)$
	485.5	~20.59	745	491.0	20.35	1,120	$d\pi \rightarrow \pi_v^*(O_2^-)$
	~373	~26.8	~1,500 sh	362	27.6	670	"$^1A_1$" → "^1E"
	310.5	32.20	17,250	301.5	33.16	16,750	$\pi_h^*(O_2^-) \rightarrow d_{z^2}$
	268	37.7	5,230	266	37.6	5,400	$\pi_h^*(O_2^-) \rightarrow d_{x^2-y^2}$
	~228	~44.4	~13,800 sh	~225	~44.4	~12,800 sh	$\pi_v(O_2^-) \rightarrow \pi_v^*(O_2^-)$
	208	48.1	23,450	*a*	*a*	*a*	$d\pi \rightarrow \pi^*(CN)$

[a] Not measured.

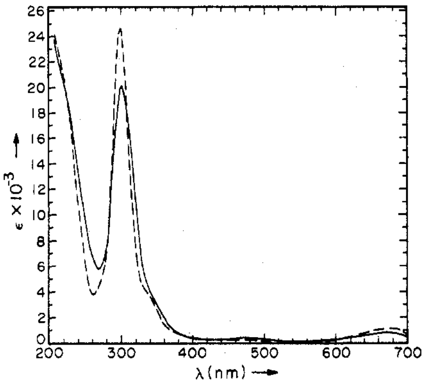

Figure 1. Electronic spectra of $[(NH_3)_5CoO_2Co(NH_3)_5]Cl_5 \cdot 4H_2O$ in 1:1 LiCl(satd aq)-HCl(1 *M* aq) at 300 (——) and 78 K (- - - -).

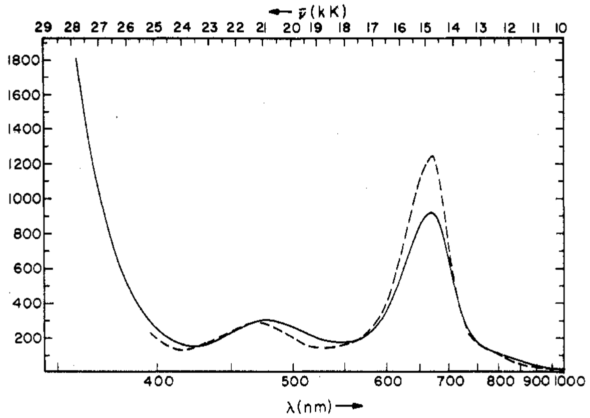

Figure 2. Low-energy bands of $[(NH_3)_5CoO_2Co(NH_3)_5]Cl_5 \cdot 4H_2O$ in 1:1 LiCl(satd aq)-HCl(1 *M* aq) at 300 (——) and 78 K(- - - -).

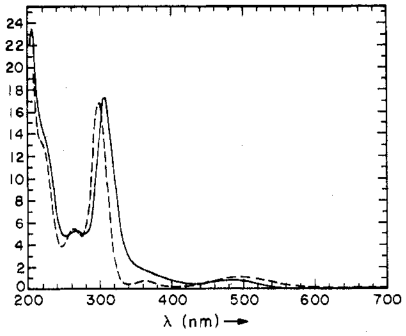

Figure 3. Electronic spectra of $K_5[(CN)_5CoO_2Co(CN)_5] \cdot H_2O$ in 1:1 LiCl(satd aq)-H_2O at 300 (——) and 78 K (- - - -).

charge-transfer maxima near 320 and 380 nm, whereas dibridged ones (where the other bridging ligand is, e.g., OH^-) show only a single maximum, near 360 nm.[17] The two maxima of the monobridged species presumably are associated with charge-transfer transitions involving the two components of the split $\pi^*(O_2^{2-})$ level, having roughly the same intensity because the large dihedral angle[1] allows both orbitals to engage in strong σ-bonding interactions with cobalt dσ* functions. For the dibridged species, the dihedral angle must necessarily be considerably smaller, and the charge-transfer band arising from excitation involving the "out-of-plane" component of the π* level should therefore be weaker than that associated with the "in-plane" orbital. We suggest that the former transition is obscured by the broad, intense "in-plane" charge-transfer band.

The electronic spectrum of $[(CN)_5CoO_2Co(CN)_5]^{6-}$, which is also very broad and poorly resolved, shows an intense band at ~315 nm ($\epsilon \simeq 10{,}000$) and a pronounced shoulder at ~370 nm ($\epsilon \simeq 5000$).[13,18] Again, we suggest that these bands be assigned to LMCT transitions originating in the two $\pi^*(O_2^{2-})$ components. Such an assignment is consistent with our earlier observation that the energies of the X^-–Co(III) LMCT transitions in $Co(NH_3)_5X^{2+}$ and $Co(CN_5)X^{3-}$ complexes are nearly equal.[10] By analogy to the ammines, the lowest energy LF band of the cyanide complex would be expected near 370 nm,[10] and it is presumably obscured by charge-transfer absorption.

μ-Superoxo Complexes. Electronic spectra of the decaammine in solution at room temperature and 78 K are displayed in Figures 1 and 2. Band positions observed in spectra recorded for KBr pellets of $[(NH_3)_5CoO_2Co(NH_3)_5]Cl_5 \cdot 4H_2O$ are in excellent agreement with those found in solution. The most striking difference in the spectrum of the decaammine from that of its μ-peroxo analog is the appearance of a moderately intense band at 672 nm. The decacyanide also exhibits an absorption band at relatively low energy (486 nm), which probably is attributable to the same type of electronic transition. We shall refer to the 672- and 486-nm features as the "low-energy" bands.

As the decacyanide is not very stable, we have performed a number of experiments to make certain that none of the bands in the solution spectra shown in Figure 3 results from the presence of impurities. One check involved irradiation of the decacyanide at 313 nm, which yields[19] efficient production of very weakly absorbing products (primarily $[Co(CN)_5(OH_2)]^{2-}$). By means of comparison of disappearance rates of the various spectral features to that of the 486-nm peak, we have been able to confirm that all the bands arise from the same species.[20] Furthermore, we have recorded electronic spectra of KBr pellets of $K_5[(CN)_5CoO_2Co(CN)_5] \cdot H_2O$ (Figure 4). These spectra do not differ significantly from

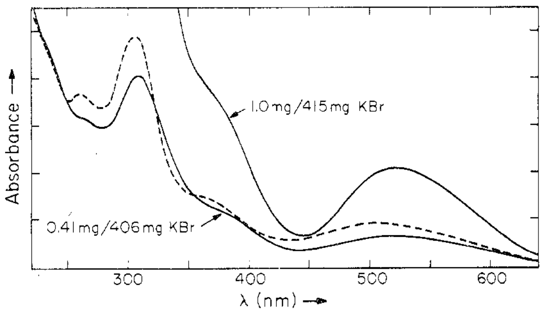

Figure 4. Electronic spectra of $K_5[(CN)_5CoO_2Co(CN)_5]\cdot H_2O$ dispersed in KBr at 300 (——) and 80 K (- - - -).

those of Figure 3 (with one exception, to be noted later).

The positions and intensities of the bands observed in solutions for both the decaammine and the decacyanide are set out in Table I. Proposed assignments for the bands, to be discussed in subsequent sections, are also given. We shall take up first the bands that appear to be analogous to features in the μ-peroxo complexes.

Ligand Field Bands. The decaammine exhibits a broad band at 480 nm (ϵ 309), whose intensity is diminished at 78 K (Figure 2). The low-temperature spectrum of the decaammine also reveals a shoulder at ~342 nm (Figure 1). For comparison, $Co(NH_3)_6^{3+}$ exhibits LF transitions, ${}^1A_{1g} \rightarrow {}^1T_{1g}$ and ${}^1A_{1g} \rightarrow {}^1T_{2g}$, at, respectively, 475 (ϵ 60) and 339 nm (ϵ 55).[5] The temperature behavior of the intensities and the compelling energy match with $Co(NH_3)_6^{3+}$ strongly suggest that the 480- and 342-nm decaammine bands correspond to spin-allowed LF transitions in isolated Co(III) centers. Although the ground state of the entire complex is ${}^2B_g$, each Co(III) unit is effectively "${}^1A_{1g}$", as the unpaired electron resides primarily on the $\pi_v{}^*$ orbital of O_2^- (vide infra). The logical assignments for the 480- and 342-nm bands, therefore, are "${}^1A_{1g}$" → "${}^1T_{1g}$" and "${}^1A_{1g}$" → "${}^1T_{2g}$", respectively. Furthermore, the LF strength of O_2^- apparently is only slightly less than that of NH_3, as evidenced by the lack of observable splitting of the "${}^1T_{1g}$" and "${}^1T_{2g}$" excited states.

The spectrum of the decacyanide similarly shows one band which clearly decreases in integrated intensity and is well resolved at 78 K. The band maximum, 362 nm (ϵ 670), may be compared to the positions of LF bands in $[Co(CN)_5(NH_3)]^{2-}$ (345 nm) and $[Co(CN)_5(NCS)]^{3-}$ (363 nm).[10] Assuming effective C_{4v} symmetry about each isolated Co(III) center, the assignment of the 362-nm band is to the "${}^1A_1$" → "${}^1E$" component of the "${}^1A_{1g}$" → "${}^1T_{1g}$" octahedral transition. Consistency of interpretation with the decaammine band is apparent, and a ligand-field strength of O_2^- closely comparable to that of N-bonded thiocyanate is inferred. A large splitting of the "${}^1T_{1g}$" octahedral state is to be expected[10] for the decacyanide, in view of the high ligand-field strength of CN^- relative to O_2^-.

Charge-Transfer and Intraligand Bands. The charge-transfer and intraligand bands may be interpreted by reference to the molecular orbital energy level diagram shown in Figure 5. The MO diagram is appropriate for a C_{2h} superoxo complex in which the CoO_2Co unit is planar, and it takes into account the above LF band analysis, which suggests that the Co(III) centers interact negligibly with each other. The $\pi^*(O_2^-)$ orbitals are designated as in plane, $\pi_h{}^*(O_2^-)$, or out of plane, $\pi_v{}^*(O_2^-)$, and the $\pi(O_2^-)$ orbitals are similarly classified. Considering the $\pi^*(O_2^-)$ orbitals, only $\pi_h{}^*(O_2^-)$ is situated properly for strong σ-bonding interactions with Co(III). This results in the energy order $\pi_h{}^*(O_2^-) < \pi_v{}^*(O_2^-)$ and predicts the ground state to be ${}^2B_g(a_g{}^2b_g)$. The nonbonding nature of $\pi_v{}^*(O_2^-)$ accounts for the localized character of the unpaired electron observed in EPR experiments.[4,21] Furthermore, the strong σ-bonding interactions engaged in by $\pi_h{}^*(O_2^-)$ provide a rationale for the observed tendency of CoO_2Co to be planar,[2,3] as the half-filled $\pi_v{}^*(O_2^-)$ component would be a much poorer σ donor.

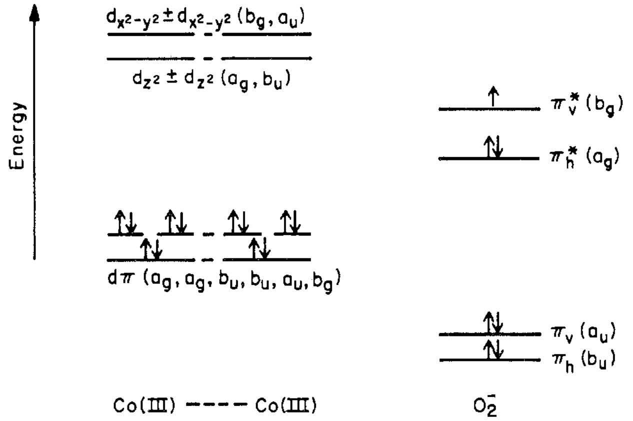

Figure 5. Relative energies of the molecular orbitals in a C_{2h} μ-superoxo-dicobalt(III) complex containing a planar CoO_2Co unit. Symmetry designations of the $d\pi$ and $d\sigma^*$ orbitals refer to the observed conformation of the decaammine in the sulfate tris(bisulfate) salt.[2]

There are a number of formally allowed LMCT transitions of the type $\pi^*(O_2^-) \rightarrow d\sigma^*$. Only one, however, $\pi_h{}^*(O_2^-) \rightarrow d_{z^2}$ ($a_g \rightarrow b_u$), possesses sufficient $\sigma \rightarrow \sigma^*$ character to give rise to an intense absorption band. Therefore, the band in the decaammine at 302 nm (ϵ 20,160) may be assigned to the transition $\pi_h{}^*(O_2^-) \rightarrow d_{z^2}$. The band in the decacyanide at 311 nm (ϵ 17,250), which shows a fairly large blue shift to 302 nm at 78 K, is clearly analogous. An additional band at 268 nm (ϵ 5230) is readily explained by the large splitting of the cobalt $d\sigma^*$ orbitals in the cyanide complex.[10] Thus the higher energy band is assigned to $\pi_h{}^*(O_2^-) \rightarrow d_{x^2-y^2}$, whereas the lower energy feature is $\pi_h{}^*(O_2^-) \rightarrow d_{z^2}$. The relative intensities of the bands are consistent with the expected larger overlap of d_{z^2} with the $\pi_h{}^*(O_2^-)$ orbital.

The out-of-plane component, $\pi_v{}^*(O_2^-)$, is expected to give rise to LMCT bands that are considerably weaker, as a consequence of very poor overlap with the $d\sigma^*$ orbitals. The 345-nm shoulder of the decaammine could conceivably be attributed to such an LMCT transition, but the decacyanide has no analogous feature. Thus we prefer our previous ligand-field assignment.

Low-Energy Bands. Early workers assigned the 672-nm peak of the decaammine and the 486-nm band of the decacyanide to "perturbed" d–d transitions.[5,6] However, Garbett and Gillard pointed out that optically active μ-superoxo-dicobalt(III) complexes failed to show strong circular dichroism (CD) in these bands,[7] in contrast to the situation expected for d–d transitions. Very recently, Strekas and Spiro have found that the low-energy bands of both the decaammine and decacyanide show strong resonance Raman enhancement of O–O stretching (near 1105 cm^{-1}, appropriate for O_2^-) and Co–O stretching modes.[22] In contrast, the 480-nm absorption of the decaammine does not exhibit an appreciable resonance effect, which is quite typical behavior for LF bands.[22] It should also be noted that a standard calculation based on the assignment of these bands to "${}^1A_1$" → "${}^1E$" LF transitions results in negative values of *Dq* for O_2^-.[13] Thus there is an overwhelming case against a ligand-field interpretation of the low-energy bands.

The CD effect was used by Garbett and Gillard as evidence for an assignment to an internal O_2^- transition.[7] In view of the fact that the transition must terminate in the half-filled $\pi_v{}^*(O_2^-)$ component, it must presumably be $\pi_v(O_2^-) \rightarrow \pi_v{}^*(O_2^-)$, as $\pi_h{}^*(O_2^-) \rightarrow \pi_v{}^*(O_2^-)$ is LaPorte forbidden in

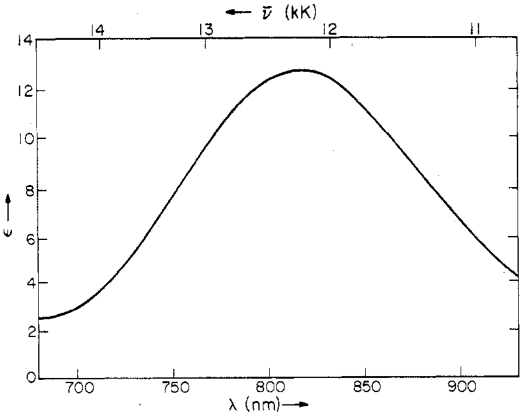

Figure 6. Near-infrared spectrum of an aqueous solution of $K_5[(CN)_5CoO_2(CN)_5]\cdot H_2O$ at 300 K.

the C_{2h} symmetry of the μ-superoxo complexes. However, assignment of the 672- and 486-nm bands to $\pi_v(O_2^-) \rightarrow \pi_v^*(O_2^-)$ may be ruled out on energetic grounds. This conclusion follows from the observation that the vertical $\pi \rightarrow \pi^*$ transition of the superoxide ion in alkali halide crystals occurs near 285 nm.[23] Bonding interactions of $\pi(O_2^-)$ with cobalt orbitals will tend to *increase* the $\pi \rightarrow \pi^*$ transition energy, and perturbations of $\pi_v^*(O_2^-)$ by the cobalt dπ orbitals should not be very large.[13] It is likely, therefore, that the intense shoulders observed near 225 nm in both the decaammine and decacyanide[24] are attributable to $\pi_v(O_2^-) \rightarrow \pi_v^*(O_2^-)$ and that we must look elsewhere for an explanation of the low-energy bands.

We suggest that the low-energy bands be assigned to a metal-to-ligand charge-transfer (MLCT) transition of the type $d\pi \rightarrow \pi_v^*(O_2^-)$. Indeed, given the open-shell character of O_2^-, it would be surprising if such a transition were not observed at relatively low energies. The observed intensities of the bands ($\epsilon < 1000$) are reasonable, assuming a fairly small amount of π interaction occurs. Furthermore, it is encouraging to note that it is possible to understand the medium dependence of the 486-nm band of the decacyanide in terms of an MLCT transition terminating in the $\pi_v^*(O_2^-)$ orbital. That this medium dependence is substantial may be inferred from the observation that the crystalline potassium salt of the decacyanide is magenta, whereas aqueous solutions are orange. Potassium bromide pellets of the salt are the same color as pure crystalline material, and the band maximum is observed to be at 523 nm (Figure 4), a shift of nearly 1500 cm^{-1} from the solution peak. In addition, the solution band shows a definite *red shift* at 78 K (Figure 3), which is an unusual effect. The absence of any large medium effects for the other absorption bands implies that the red shift involves specific stabilization of the excited state associated with one particular transition. Also, the lack of an analogous effect on any of the bands of the decaammine suggests that some type of interaction with cations is involved. Such interactions would presumably be reduced greatly by the high positive charge of the decaammine. An MLCT transition terminating in the $\pi_v^*(O_2^-)$ orbital thus fits our observations on the low-energy bands, as a peroxo-like excited state should be stabilized by close association with cations. The temperature behavior of the decacyanide band could simply be explained as increased ion pairing at 78 K.[25]

Near-Infrared Bands. The decacyanide exhibits a weak (ϵ 13), well-resolved band at 817 nm (Figure 6). This band has previously been noted by other workers,[18] and our photolysis experiments confirm that it is attributable to the decacyanide. The spectrum of the decaammine also shows a weak shoulder near 800 nm (Figure 2). At least in the case of the decacyanide, the band is much too low in energy to be a spin-forbidden counterpart of one of the higher energy transitions. The small intensity indicates a LaPorte-forbidden transition, the logical assignment being $\pi_h^*(O_2^-) \rightarrow \pi_v^*(O_2^-)$. If this assignment is correct, then the implied stabilization of $\pi_h^*(O_2^-)$ is large enough to account for most of the bonding of the bridging group to the cobalt(III) centers.

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Registry No. $[(NH_3)_5CoO_2Co(NH_3)_5]Cl_5$, 12526-59-9; $K_5[(CN)_5CoO_2Co(CN)_5]$, 12557-90-3.

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(24) The intense band at 208 nm in the decacyanide may be assigned to an allowed $d\pi \rightarrow \pi^*(CN)$ transition. Similar features are observed in a wide variety of $Co(CN)_5X^{n-}$ complexes.[10]
(25) We would not expect LF transition energies to be affected significantly. Furthermore, LMCT excited states should be destabilized, which may account for the large blue shift of the 311-nm band of the decacyanide at 78 K.