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(12) Clearly if one started with Co(III) and coordinated superoxide ion to it, a complex with a nearly neutral O_2 fragment could result from an essentially covalent bond. In the present case, since one starts with O_2 and Co(II), a description of this sort would be analogous to describing the interaction of a hydrogen and fluorine atom as involving electron transfer to fluorine to form fluoride ion and then coordination of fluoride ion to the proton to form HF. Clearly, unless the bond is essentially ionic, this practice is not followed.

(13) W. L. Masterton and E. J. Slowinski, "Chemical Principles", 4th ed., W. B. Saunders, Philadelphia, Pa., 1977, p 525.

(14) In CO_2 the carbon oxidation state is +4, and no one worries about what the electronegativity of carbon is in CO. Similarly, there is no doubt that iron has an oxidation state of IV in the doubly spin paired adduct. The two bonds cannot be distinguished in the doubly spin paired interaction. If the bonding in the case of the iron adduct involved electron pair donation from a singlet O_2 molecule, the iron oxidation state would be +2.

(15) Oxidation state considerations would suggest that the dioxygen adducts of iron(II) be named iron(IV) peroxo complexes, just as the O_2 adducts of cobalt(II) would be called cobalt(III) superoxo complexes.[6] It is clearly incorrect to push this nomenclature further and state, as has been often done, that the bound oxygen closely corresponds to a peroxide ion in the first case or a superoxide ion in the second case. In many adducts, the electronic charge on the bound O_2 more closely resembles that in free O_2 (vide infra), but one could still call it superoxo or peroxo.

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Position of the $^3T_{1g} \leftarrow {}^1A_{1g}$ Transition in Hexacyanocobaltate(III). Analysis of Absorption and Emission Results

Sir:

In 1974 Hipps and Crosby published[1] a study of the low-temperature electronic emission of crystalline $K_3Co(CN)_6$. The emission peak at 14 000 cm^{-1} was attributed to the $^3T_{1g} \rightarrow {}^1A_{1g}$ transition and was marked by a long progression assigned as the totally symmetric Co–C stretching mode. Of relevance to the present correspondence is that Hipps and Crosby located the 0–0 line of this progression at 17 000 cm^{-1} and calculated that the maximum of the corresponding transition in absorption should be at 20 300 cm^{-1}. This result is inconsistent with the data obtained from quenching experiments. The $Ru(bpy)_3^{2+}$ triplet ($E_T \simeq 17\,000$ cm^{-1}) in aqueous solution is reported[2] not to be measurably quenched by $Co(CN)_6^{3-}$. Further, whereas $Co(CN)_6^{3-}$ quenches acetone triplets ($E_T \simeq 27\,000$ cm^{-1}) at a diffusion-controlled rate, biacetyl triplets ($E_T \simeq 20\,000$ cm^{-1}) are quenched at a rate 10^3 times slower.[3] The classical interpretation[4] of these data would be that the 0 vibronic level of the $^3T_{1g}$ state of aqueous $Co(CN)_6^{3-}$ lies about 1000 cm^{-1} higher than triplet biacetyl, at ~21 000 cm^{-1}. This disagreement cannot be explained simply as a solvent effect on the triplet state energy, since the singlet → singlet ligand field transitions of crystalline $K_3Co(CN)_6$ at room temperature occur at precisely the same energies as those of hexacyanocobaltate(III) in aqueous solution (32 100 cm^{-1} ($^1T_{1g} \leftarrow {}^1A_{1g}$) and 38 500 cm^{-1} ($^1T_{2g} \leftarrow {}^1A_{1g}$)),[5] suggesting that the triplets, which differ from the singlets only by a spin–flip, should be similarly unaffected by the solvent.

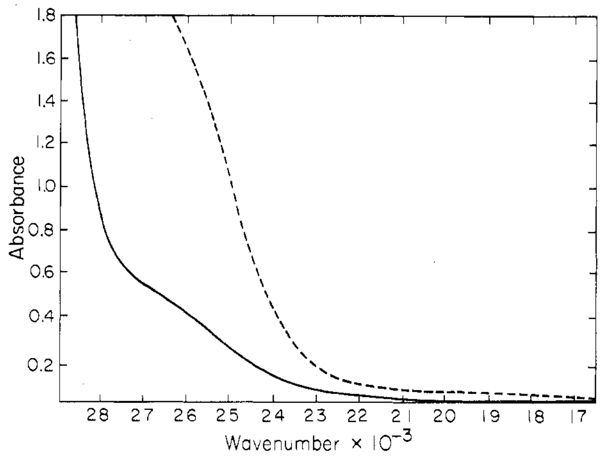

Figure 1. Electronic absorption spectra of $K_3Co(CN)_6$ single crystals at 15 K: (—) 3.0 mm thick crystal; (- - -) 14.0 mm thick crystal.

Previous studies have also been in disagreement as to the position of the $^3T_{1g} \leftarrow {}^1A_{1g}$ absorption band.[6] A careful investigation of the spin-triplet region of the absorption spectrum of crystalline $K_3Co(CN)_6$ was therefore initiated. In contrast to the low-temperature emission results, no vibronic structure was observed in the absorption spectrum at either 15 or 4.2 K.[7] However, cooling did eliminate the thermal broadening of the singlet bands, revealing a weak (ϵ ~0.25) shoulder on the low-energy side of the $^1T_{1g} \leftarrow {}^1A_{1g}$ transition (Figure 1). The apparent absorption maximum is at ~26 000 cm^{-1}. No significant polarization was observed.

We were concerned that the 26 000 cm^{-1} absorption could be due to impurities.[8] Intentional doping of $K_3Co(CN)_6$ with $Fe(CN)_6^{3-}$, a likely impurity, did lead to an absorption band at 24 000 cm^{-1}. However, this impurity band is structured and much narrower than the absorption of undoped samples and is easily distinguished. Another likely impurity is $Co(CN)_5H_2O^{2-}$, a photoproduct of $Co(CN)_6^{3-}$, which has a $^1E^a \leftarrow {}^1A_1$ (C_{4v}) absorption band (ϵ ~280) at 26 300 cm^{-1}.[9] However, three very different lattices[10] ($InCo(CN)_6$, $Cd_3[Co(CN)_6]_2 \cdot xH_2O$, and $K_3Co(CN)_6$) all show the shoulder to a similar extent, whereas the amount of impurity would be expected to be different in these compounds. Furthermore, the extinction coefficient of the 26 000-cm^{-1} absorption band was found not to vary in measurements on several different samples of $K_3Co(CN)_6$. Finally, the isoelectronic $Fe(CN)_6^{4-}$ ion in the salt $K_4Fe(CN)_6 \cdot 3H_2O$ shows a completely analogous absorption system (Figure 2). The maximum is shifted to lower energy relative to $K_3Co(CN)_6$ by about 2000 cm^{-1}, similar to the shift in the singlet–singlet ligand field transitions.[5]

This assignment of the 26 000 cm^{-1} shoulder as the $^3T_{1g} \leftarrow {}^1A_{1g}$ transition is also strongly supported by ligand field theory. In the strong field limit, the $^3T_{1g}$–$^1T_{1g}$ splitting is 2*C*. Upon consideration of the free ion value of *C* for Co^{3+} (5120 cm^{-1}) and the position of $^1T_{1g} \leftarrow {}^1A_{1g}$ as 32 100 cm^{-1}, it is clear that

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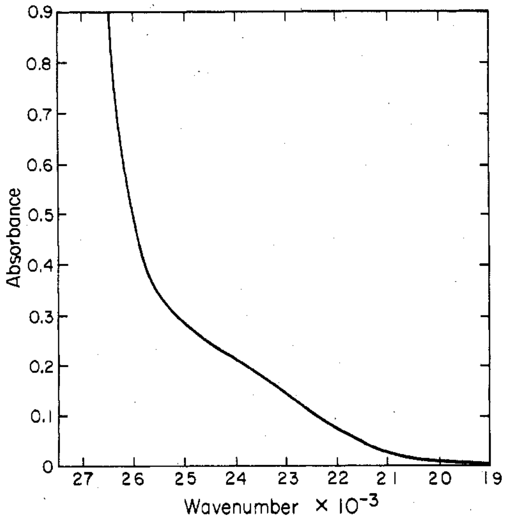

Figure 2. Electronic absorption spectrum of a crystal (1.8 mm thick) of $K_4Fe(CN)_6{\cdot}3H_2O$ at 15 K.

${}^3T_{1g} \leftarrow {}^1A_{1g}$ must fall well above 22 000 cm^{-1} to be consistent with the expected reduction in the Racah C parameter. And the reduction of C necessary to fit the 26 000 cm^{-1} transition [C'(complex)/C(free ion) = 0.53] is entirely consistent with results for other d^6 hexacyanides [$Fe(CN)_6^{4-}$, $C'/C = 0.64$; $Ru(CN)_6^{4-}$, $C'/C = 0.69$].[5b] Further, assuming that the transition to ${}^3T_{1g}$ gains intensity (I) through spin-orbit coupling to ${}^1T_{1g}$, we calculate[11]

$$I({}^3T_{1g} \leftarrow {}^1A_{1g}) \simeq \left[\frac{2^{1/2}(\zeta/2)}{E({}^3T_{1g}) - E({}^1T_{1g})}\right]^2 I({}^1T_{1g} \leftarrow {}^1A_{1g})$$

or, since the bandwidths are approximately equal, $\epsilon({}^3T_{1g} \leftarrow {}^1A_{1g}) \simeq 10^{-3}\epsilon({}^1T_{1g} \leftarrow {}^1A_{1g})$. Taking $\epsilon({}^1T_{1g} \leftarrow {}^1A_{1g}) \simeq 140$, we find reasonable agreement with the 26 000 cm^{-1} shoulder.

It seemed highly unlikely that the emission, on the other hand, could be spurious, since several different lattices containing the $Co(CN)_6^{3-}$ moiety have similar emissions, the lifetimes ranging over an order of magnitude.[10] We considered it possible that a $Co(CN)_5H_2O^{2-}$ or $Co(CN)_5OH^{3-}$ trapped species could be responsible for emission of the pure material through energy transfer. Therefore, crystals of $K_3Co(CN)_6$ were grown from both D_2O and H_2O under similar conditions, and it was found that their measured emission lifetimes were identical (τ = 650 μs at 77 K). Doping $K_3Co(CN)_6$ crystals with $K_3Co(CN)_5Cl$ and $K_3Co(CN)_5I$ also left the emission unchanged.

Accepting then the observed emission as ${}^3T_{1g} \rightarrow {}^1A_{1g}$ and the absorption band at 26 000 cm^{-1} as ${}^3T_{1g} \leftarrow {}^1A_{1g}$, our problem was to reconcile these assignments with the Franck–Condon (FC) least-squares analysis of the emission spectrum reported by Hipps and Crosby.[1]

$$I(E) = C\sum_n e^{-S}\frac{S^n}{n!}g(E - E_0 - n\hbar\omega)$$

Using a simplified FC formula, we performed a similar analysis and verified the published results[1] (subject to small differences in the final parameters due to a different fitting function). We found, however, that an equally good fit could be obtained by using our observed FC maximum for ${}^3T_{1g} \leftarrow {}^1A_{1g}$.

The approximate position of the electric-dipole-forbidden, pure electronic 0–0 transition (${}^3T_{1g} \leftarrow {}^1A_{1g}$) was estimated to be ~20 000 cm^{-1}, midway between the FC maxima of the absorption and emission bands. Allowing for a t_{1u} odd-parity vibronic origin to generate the observed intensity, we arrived at the fit depicted in Figure 3. The required parameters are

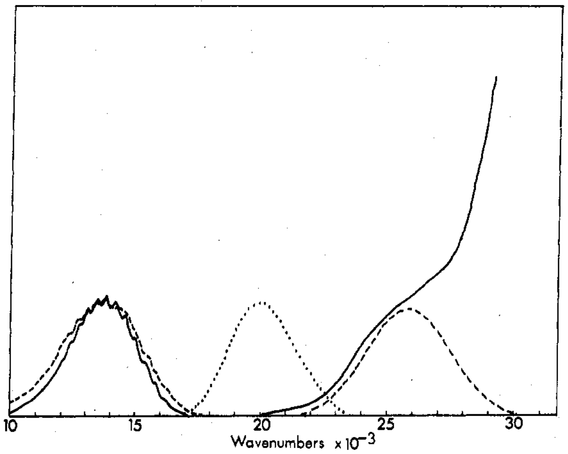

Figure 3. Experimental emission (${}^3T_{1g} \rightarrow {}^1A_{1g}$) and absorption (${}^3T_{1g} \leftarrow {}^1A_{1g}$) spectra of a single crystal of $K_3Co(CN)_6$ at 4.2 K (—), calculated emission and absorption band shapes (S = 14, $\hbar\omega$ = 420 cm^{-1}) from a least-squares fit to the emission and absorption data (- -), and calculated absorption band shape (S = 8.9, $\hbar\omega$ = 420 cm^{-1}) from a least-squares fit to the emission data only (···).

$\hbar\omega$ = 420 cm^{-1} and $S \approx 14$. The high value of S required does not necessarily imply a huge distortion in one totally symmetric mode[1] but can be the result of several progressional modes of equal energy (in the Huang–Rhys approximation with $S = \sum_i S_i$).[12] We suggest that both a_{1g} and e_g Co–C stretching vibrations are involved. These modes have nearly identical frequencies and force constants.[13,14]

Straightforward theoretical considerations suggest that the ${}^3T_{1g}$ excited state will distort significantly from octahedral geometry, owing to the strong σ-antibonding effect of the e_g electron in a $t_{2g}{}^5e_g$ configuration. Examination of the known structures of low-spin d^7 ($t_{2g}{}^6e_g$) complexes is relevant to this point. Perhaps the best ground-state analogue is low-spin $Co(CNPh)_6^{2+}$, which is a strongly tetragonally distorted (D_{4h}) ion, according to an interpretation of EPR measurements.[15] More commonly in low-spin d^7 cases, five-coordinate square-pyramidal geometry is observed; the prototypal $Co(CN)_5^{3-}$ ion exhibits this geometry, with an apical Co–C that is 0.117 Å longer than each of the basal Co–C bonds.[16] Such a distortion of the ${}^3T_{1g}$ excited state of $Co(CN)_6^{3-}$ would lead to a long e_g progression in the ${}^3T_{1g} \leftrightarrow {}^1A_{1g}$ electronic transition.

Finally, we emphasize that an axially distorted ${}^3T_{1g}$ excited state is nicely consistent with the high quantum yield photosubstitution chemistry of $Co(CN)_6^{3-}$ and its derivatives in fluid solution.[17] We feel that the ${}^3T_{1g}$ excited state is dissociative or near-dissociative in the absence of a tight ionic lattice such as occurs in the potassium salt. In support of this statement, we have found that the tetra-*n*-butylammonium salt of $Co(CN)_6^{3-}$ displays no detectable emission either as a solid or in glassy solution at 77 K, whereas flash photolysis of its solutions in noncomplexing solvents such as CH_2Cl_2 leads to generation of metastable (second-order decay over seconds to tens of seconds) $Co(CN)_5(solvent)^{2-}$ species in high quantum yield, with a rise time of <10 ns.[18]

Acknowledgment. We thank C. J. Ballhausen for allowing us to make spectroscopic measurements in his laboratory in Copenhagen. Mark Wrighton is acknowledged for helpful discussions. Research at Caltech was supported by the National Science Foundation (Grant CHE75-19086). Research at MIT was supported by the Research Corporation, the Cabot Solar Energy Fund, and an Alfred P. Sloan Research Fellowship (E.I.S.).

Registry No. $K_3Co(CN)_6$, 13963-58-1; $K_4Fe(CN)_6$, 13943-58-3.

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(8) Mingardi and Porter[6b] reported a very weak (ϵ ~0.01) absorption band at 18 500 cm^{-1}. We have found this latter transition to be present in some, but not all, samples studied; it is likely associated with an impurity present in the lattice. For our experiments, large crystals of $K_3Co(CN)_6$ were grown in darkness by slow evaporation of saturated, filtered aqueous solutions of commercial material. The resultant crystals were redissolved in water and the process was repeated; crystals from several different batches were used in our studies. Very large crystals were grown from seeds.
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Acidity of Zinc Chloride Solutions

Sir:

In a recent issue of *Inorganic Chemistry* the Hammett acidity function, H_0, was reported for a series of zinc chloride solutions, and it was concluded that "highly concentrated solutions of certain metal salts must be regarded as strong protonic acids".[1] This conclusion was arrived at by comparing the H_0 of $ZnCl_2$ solutions with that of other acids at the same (high) molarities. It is the purpose of this correspondence to point out that comparisons of H_0 for the purpose of providing orders of acid strength should be made at the *same water activity*.[2-4] Figure 1 displays the H_0 values as a function of water activity for the zinc chloride solutions, as well as for several strong acids and phosphoric acid ($pK_a = 2.15$). The curve for nitric acid[5] is similar to that for the strong acids down to a water activity of 0.6.

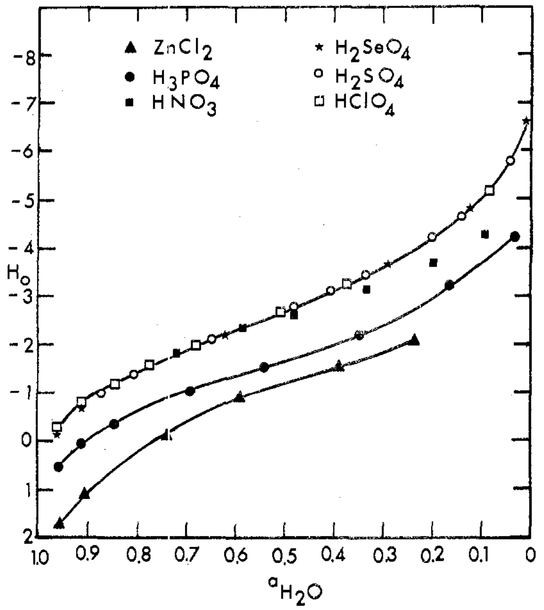

Figure 1. H_0 values of some mineral acid solutions and zinc chloride solutions vs. water activity of the solutions.[8]

From Figure 1 we may conclude that the acidity of the aquozinc ion is less than that of phosphoric acid even at high concentration. More quantitative treatments of acidity from H_0 and a_{H_2O} data are available,[6] but in view of the unknown salting-out effect[7] of concentrated $ZnCl_2$ solutions on the neutral indicator, no attempt has been made to apply them.

Registry No. $ZnCl_2$, 7646-85-7.

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