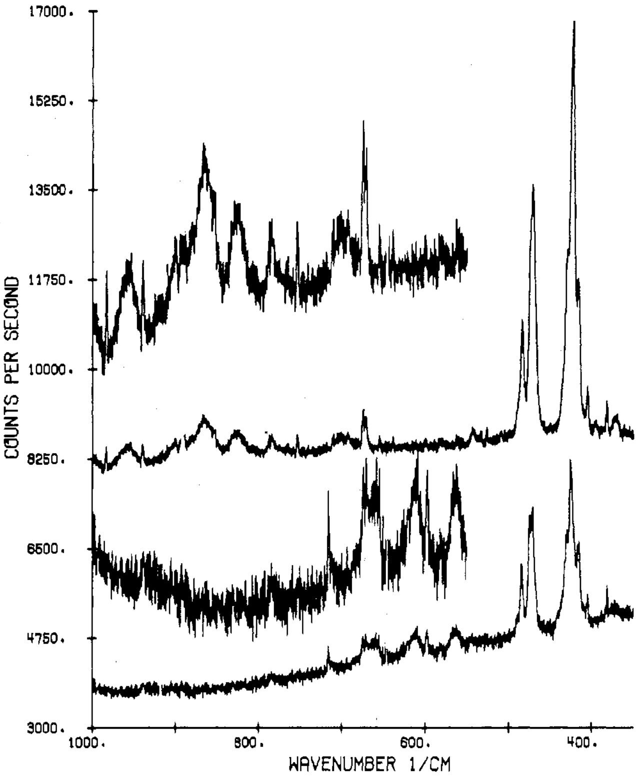

**Figure 2.** Low-temperature Raman spectra of oxygen-18-containing $[Et_4N][HW_2(CO)_{10}]$ (upper two curves) and $[Et_4N][DW_2(CO)_{10}]$ (lower two curves).

and used as obtained. The isotopic $W(C^{18}O)_6$ was prepared by oxygen-exchange techniques.[8] $[Et_4N][H(\text{and } D)W_2(CO)_{10}]$ were synthesized by a slightly modified version of Hayter's procedure.[9] The compounds were recrystallized once, and the purity was checked by infrared and Raman spectra.

The Raman spectrometer was a Spex 1401. Raman samples were cooled in an Air Products Displex unit, and spectra were recorded either on pressed pellets attached to the cold finger with a thin layer of Apiezon N grease or on samples deposited on the cold finger from a THF solution. Either the 676.4-nm Kr-ion laser line or the 514.5-nm Ar-ion laser line was used to irradiate the samples, with 10-mW maximum power at the sample. The temperature was measured just above the sample block, but the actual temperature in the region being irradiated is considerably above the measured temperature. For example, in one run a temperature of 80 K was calculated from the Stokes and anti-Stokes Raman spectra for the pellet in contact with the cold finger cooled to 10 K.

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**Registry No.** $[Et_4N][HW_2(CO)_{10}]$, 12083-01-1; $[Et_4N][HW_2(C^{18}O)_{10}]$, 69551-87-7; $[Et_4N][DW_2(CO)_{10}]$, 55971-52-3; $[Et_4N][DW_2(C^{18}O)_{10}]$, 69551-89-9.

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## Comments on the Description of Dioxygen Bound End-On to Transition Metals

*Sir:*

Considerable discussion has occurred regarding the nature of the binding of dioxygen to first-row transition-metal complexes.[1-6] Unrecognized difficulties in interpreting infrared results have led to the rejection of our position[2] on the nature of the bound dioxygen. Attempts to translate our arguments into an oxidation state description have led to a misquoting of our position. In this communication, we clarify these problems.

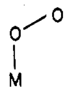
Our interest in the binding of dioxygen to cobalt(II) complexes began with the interpretation of their EPR spectra. The original interpretations[7] were based on a Fermi contact analysis, and the cobalt hyperfine splitting was rationalized in terms of direct delocalization of the unpaired electron on the metal. On the basis of the information available at the time, this was a viable rationalization of the spectral results. In our first publication[8] on this subject, we stated that the data did not conclusively prove an essentially ionic $Co(III)-O_2^-$ formulation but could be rationalized equally well with a Fermi contact interpretation by utilizing a coordinated singlet $O_2$ formulation. Since neither interpretation was conclusive nor able to explain all of the spectral results, information regarding $^{17}O$ anisotropic hyperfine coupling parameters was considered essential. In the course of making preparations to carry out this experiment, a publication appeared in which the key results were presented[9] but not properly interpreted. We concluded from the results[2b] that the cobalt hyperfine coupling must be arising via an indirect mechanism and could not be attributed to the unpaired electron being delocalized on cobalt.[10] The earlier interpretations[7,8] of the EPR spectra based on direct delocalization of the electron cannot be correct, for the summation of the cobalt and $^{17}O$ anisotropic hyperfine coupling parameters would suggest more than one unpaired electron in a system which contains only one unpaired electron. A new interpretation of the EPR results was offered and a spin-pairing model[2b] was employed to describe the interaction of the metal center with $O_2$. This spin-pairing model is an extension, which accommodates a wide range of electron transfer into $O_2$, of the molecular orbital description of these adducts proposed by Wayland et al.[11] Contrary to earlier interpretations, the spin-pairing model and our EPR interpretation[2b] lead to the conclusion that regardless of whether the charge on the bound $O_2$ were slightly positive, neutral, or negative, the unpaired electron would be localized mainly on $O_2$.

According to the spin-pairing model, the metal–dioxygen interaction involves the pairing of the electron(s)[5] on the oxygen molecule with the metal electron(s) in a manner very similar to, but much weaker in magnitude than, the interaction that occurs when two hydrogen atoms combine. In the superoxide model, the interaction is attributed to the electrostatic interaction of the cobalt(III) center for an ionic superoxide ion; accordingly, the formula is written as $Co^{III}O_2^-$. In some instances, this latter formula is a reasonably good description of the $O_2$ adduct. However, in many others where electron transfer is small, it is not. Our objection to this formulation has been in placing the minus sign on the $O_2$ fragment[2] because, in coordination chemistry nomenclature, ligands are not given a sign unless the bonding is essentially ionic. In the original Fermi contact interpretation of the EPR, 90% electron transfer was proposed and the $Co^{III}O_2^-$ formulation is a consistent description of this incorrect conclusion. In the more recent literature, several authors now claim[1,3-5] only the "formal oxidation states" are being described. Accordingly, the $Co^{III}O_2^-$ representation should be replaced with $Co^{III}O_2$, $Co^{III}O_2(-I)$, or $(d^6)Co–O_2$ as satisfactory ways to indicate the formula depending upon the information which one wishes to convey.[12]

It is not this author's intent to get involved in an oxidation state controversy. However, the essential arguments we have presented have been recast and misinterpreted in this formalism. As stated by Masterton and Slowinski,[13] the concept of oxidation state is introduced to refer to the charge an atom would have if the bonding electrons were assigned *arbitrarily* to the more electronegative element. The concept of oxidation state is a formalism; hence, the term "formal oxidation state" is redundant. Oxidation states have pedagogical utility; however, there is a tendency in recent articles to imply more meaning to the concept of oxidation state (for example, electron transfer) than that described above without defining what phenomenon is involved. The difficulty in trying to ascertain an author's conclusion when the conventions are disregarded is illustrated by recent[1] descriptions of the iron–dioxygen bond as either $Fe^{II}(O_2)$ or $Fe^{III}(O_2^-)$. There can be no controversy about a formalism as well defined as the application of oxidation state to this system. When both of the unpaired electrons of dioxygen are involved in a direct spin-pairing interaction with the iron, the oxidation state of the iron is +4, since oxygen is more electronegative than iron.[14] If the "formal oxidation states" in the $Co–O_2$ system are[1,3,4] Co(III) and $O_2(-I)$, consistency demands that iron is II[14] or IV in its dioxygen adducts.[1,4] In a similar fashion, the oxidation states of the $O_2$ adducts of Mn(II) and Cr(II) are not as claimed,[4] but are also IV. With the spin-pairing model and with the similarity in the conclusions from various types of molecular orbital calculations, our understanding of the binding of dioxygen is well beyond any insights that can be provided by an oxidation state classification; however, effective communication requires adherence to the conventions.[15]

Knowledge of the extent of electron density transferred into the dioxygen fragment upon coordination is important for an understanding of the reactivity of this particular species with electrophiles and nucleophiles. Any conclusions regarding this property are best expressed in terms of electron transfer into the bound $O_2$. It is not clear what a description such as $Fe^{III}O_2^-$ means in terms of electron transfer or oxidation state. If it is meant to imply roughly a one-electron transfer into oxygen, this representation flaunts conventions and is unfortunate.

The $Fe^{III}O_2^-$ description has arisen in part from the similarity in the O–O stretching frequency of the dioxygen bound end-on to a metal with that of superoxide ion. As we emphasized earlier,[2b] in order to gauge the extent of electron transfer from infrared evidence, one would need to interpolate the measured value between that for a neutral coordinated dioxygen and a coordinated superoxide ion. There is dispute over what constitutes a neutral bound $O_2$[3a] so this interpolation has not been possible, and we have attached little significance to the infrared results in terms of electron transfer. This position can be strengthened. The O–O infrared stretching frequency for end-on-bonded dioxygen is found to be remarkably insensitive to ligand and metal variation. For example, the infrared stretching vibration of the bound $O_2$ in the solid $O_2$ adduct FeTp1vPP·*N*-methylimidazole occurs[16] at 1159 $cm^{-1}$ and the enthalpy of $O_2$ adduct formation is −15.6 ± 0.2 kcal/mol. In $Co^{II}$TpsvPP·*N*-MeIm, the enthalpy of dioxygen binding in the solid is 13.3 ± 0.9 $kcal/mol^{-1}$ and $\nu(O_2)$ in the adduct occurs at 1150 $cm^{-1}$. The conclusion from these experiments is that either the electron transfer into the $O_2$ is similar in all instances (and thought by many to be nearly complete) or else the O–O stretching vibration is insensitive to the variation in electron transfer in these adducts. The assumption of nearly constant electron transfer is at odds with an EPR study,[2b] indicating that the amount of electron transfer varies extensively with ligand variations. It is also in conflict with molecular orbital results[17] that indicate more extensive electron transfer into $O_2$ by a cobalt(II) complex than by the analogous iron(II) complex. Also, if the bound dioxygen is neutral in the iron complexes, as has been proposed from several recent molecular orbital calculations, $\nu$(O–O) is nearly the same for a neutral bound dioxygen as it is for the ionic superoxide ion (1145 $cm^{-1}$). The hypothesis that the O–O stretching frequency is insensitive to the nature of the metal–oxygen bond receives strong support from evaluation[18,19] of reported matrix isolation frequencies of $HO_2$ and its isotopic variants. The Lewis acidity of a bare proton and the covalency expected in the O–H bond preclude viewing the O–O fragment in $HO_2$ as an ionic superoxide. Through use of the reported[18] force constant of 6.1 mdyn/Å, the uncoupled O–O stretching frequency in $HO_2$ can be calculated to occur at 1138 $cm^{-1}$. The observed $\nu(O_2)$ in $HO_2$ occurs at 1101 $cm^{-1}$ so both the observed and uncoupled values occur at *even lower* frequencies than that usually quoted for $O_2^-$. The uncoupled value for $HO_2$ falls near the middle of the range of O–O stretching vibrations for metal–dioxygen adducts and is very close to the value of 1145 $cm^{-1}$ for free[3a] superoxide ion. Not only do the infrared spectra not support previous conclusions of extensive electron transfer into metal-bound dioxygen but they also provide no information about the extent of electron transfer in the metal–dioxygen adducts. At our present level of understanding of the factors influencing the O–O force constant, the O–O stretching frequency appears to be generally diagnostic only of the structural aspects of end-on bonding of $O_2$ (**1**) on the one hand and either a divalent, ring-bonding interaction (**2**) or a divalent bridging interaction (**3**) on the other. The latter two modes are not readily distinguished from each other on the basis of $\nu$(O–O).



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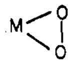

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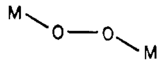

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We hope this discussion has made clear our position on the significant question of the electronic nature of dioxygen coordinated to transition-metal ions.

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**Registry No.** $O_2$, 7782-44-7.

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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.

(16) J. P. Collman, J. I. Brauman, K. M. Doxsee, T. R. Halbert, and K. S. Suslick, *Proc. Natl. Acad. Sci. U.S.A.*, **75**, 564 (1978).

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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.

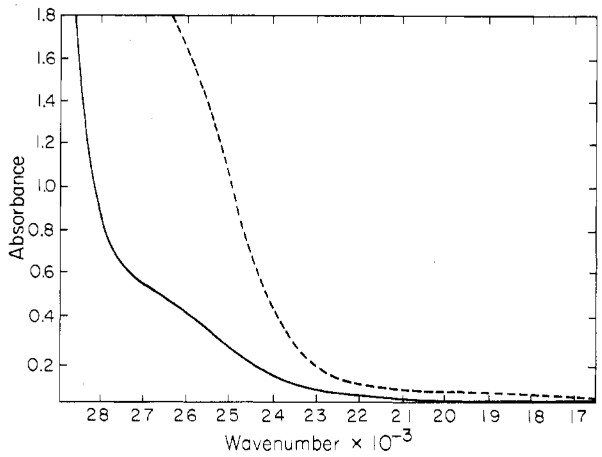

**Figure 1.** Electronic absorption spectra of $K_3Co(CN)_6$ single crystals at 15 K: (—) 3.0 mm thick crystal; (---) 14.0 mm thick crystal.

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 ($\epsilon$ ~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 ($\epsilon$ ~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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