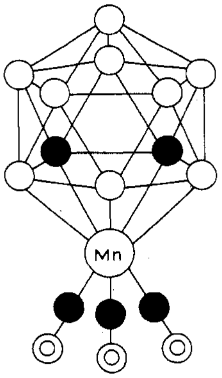

Figure 1. (π-(3)-1,2-Dicarbollyl)tricarbonylmanganese anion where ○ = boron, ● = carbon, and ◎ = oxygen.

as well as in complexes without carbonyl groups. Thus, one may regard the dangling orbitals of the dicarbollide dianion as essentially σ orbitals with respect to any 12th atom of a cluster.

Registry No. CpMn(CO)$_3$, 12079-65-1; [CbMn(CO)$_3$]$^-$, 73333-88-7.

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Electron Transfer in Metal–Dioxygen Adducts

Sir:

The conventional delineation of metal–dioxygen adducts into "superoxides" and "peroxides" is a convenient formalism which conveys no information concerning the actual negative charge residing on the dioxygen unit. "Superoxides" are characterized by having an ν(O–O)stretching frequency in the range 1075–1195 cm^{-1}.[1] X-ray studies reveal a (O–O) bond length of about 133 pm, and, so far, all structures show the dioxygen bound end-on to a metal atom. Thus the observation of a ν(O–O) frequency in this range in an oxygen adduct conveys a bond order of about 1.5 and almost certainly end-on binding.

The "peroxides" are closed shell and are characterized by an ν(O–O) frequency in the range 790–932 cm^{-1}.[1] X–ray studies show an (O–O) bond length of about 146 pm and sideways bonding for 1:1 complexes. Thus an infrared frequency in the range indicated implies a bond order of about 1.0 and, for 1:1 complexes, probably sideways bonding.

Neither of these descriptions in themselves provides any information about net electronic charge on oxygen.[2] Molecular orbital and valence-bond descriptions have inferred that the net charge in superoxides may be quite small.[3,4] Drago[5] has shown that the ESR spectra of some cobalt–dioxygen adducts may be interpreted in terms of 0.1–0.8 electron net transfer to dioxygen. Several oxygen-17 ESR studies[6,7] may be similarly, and perhaps more directly, interpreted. With the exception of such ESR studies, direct experimental evidence for net-electron transfer is sparse.

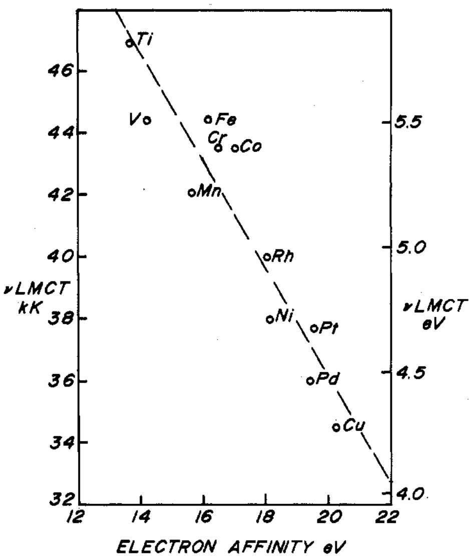

Figure 1. A plot of the more intense oxygen to metal LMCT band (maximum) energy vs. the electron affinity of M(II) for a series of M(O$_2$)$_2$ species. Most of the M(O$_2$)$_2$ species included here have been reported by Ozin and co-workers.[8] Ogden[17] has reported Cr(O$_2$)$_2$ and Cu(O$_2$)$_2$. The Ti, V, Fe, and Mn species were prepared in pure oxygen[18] and are presumed, though not as yet proven, to be M(O$_2$)$_2$ moieties. The best line through these data is (LMCT) = 8.88 − 0.22(EA) (11 points) with both (LMCT) and (EA) in eV.

We now report additional experimental information and show that infrared spectra in combination with electronic spectra can be interpreted in terms of net negative charge residing on oxygen. Ozin and co-workers[8] have synthesized two series of binary metal dioxygen complexes, M(O$_2$) and M(O$_2$)$_2$, by using cryogenic matrix techniques.[9] In the absence of any other ligands any electron density, $\delta-$, transferred to (O$_2$) must leave $\delta+$ on the metal. It should therefore be possible to correlate charge properties on the metal with those on dioxygen. These species all exhibit an electronic spectrum consisting of one strong band and one weak band usually seen as a lower energy shoulder on the principal peak. In most cases these two bands are the only absorption noted in the 200–800-nm region. A simple group theoretical treatment[10] predicts one strong LMCT (σ–σ*) transition[10] and one weaker LMCT (π–σ*) transition irrespective of whether end-on or sideways bound dioxygen is assumed.[11] The spectrum is assigned accordingly. As inferred above, there is no evidence, in most of these species, for any band assignable to an internal π–π* transition within the oxygen ligand. Studies on 1:1 "superoxo" cobalt(III) complexes reveal that this band, observed near 250 nm in free superoxide ion, blue shifts at least to 215 nm in the terminally bound 1:1 superoxides.[12,13] It will clearly be absent from the peroxy derivatives.

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(3) R. F. Kirchner and G. H. Loew, *J. Am. Chem. Soc.*, **99**, 4639 (1977).

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(9) The M(O$_2$)$_x$ binary complexes of the present study are to be regarded as the kinetically stable primary products formed and trapped under cryochemical conditions in pure dioxygen or dioxygen/inert gas mixtures. Under higher temperature reaction conditions the likely M/O$_2$ products are the thermodynamically stable metal oxides. The dioxygen complexes represent reactive intermediates which may be regarded as precursors to molecular or bulk oxide generation.

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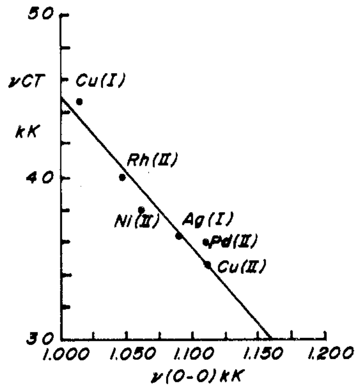

Figure 2. A plot of the more intense oxygen to metal LMCT band (maximum) energy vs. the infrared (O–O) frequency for a series of $M(O_2)$ and $M(O_2)_2$ species.

The energies of both LMCT transitions in the $M(O_2)_2$ series show an excellent linear correlation with the electron affinity of the dipositive element.[14,15] (A plot with the principal LMCT band σ–σ^* is shown in Figure 1.) There is a much poorer correlation with the electron affinity of any other reasonable valence state. This correlation confirms the LMCT nature of the transition which red shifts as the electron affinity of the metal ion increases and also leads one to conclude that these 1:2 systems are best described as M(II) species.

Furthermore there is also an excellent correlation involving both 1:1 and 1:2 series between ν(LMCT) in the UV and ν(O–O) in the IR (Figure 2). The infrared frequencies span a wide range in the superoxide region but most significantly approach values associated with a peroxide. Evidently the bond order is changing from about 1.5 with high-electron affinity ions (such as Cu(II)) to values approaching 1.0 with low-electron affinity ions such as Cu(I).[16] The most straightforward explanation for these data is that there is indeed a net increase in electronic charge on dioxygen from right to left as the electron affinity of the metal ion decreases. Moreover we may speculate that the high-electron affinity ions bind oxygen end on while in the lower electron affinity ions the oxygen molecule may bend around to approach sideways bonding.

A referee has suggested that these data may be rationalized in terms of a change in σ(M–O) bonding, with change in electron affinity. Higher electron affinity ions should cause a greater stabilization of the oxygen σ pair of electrons. This alone could lead to a blue shift rather than the observed red shift in LMCT. Evidently the stabilization of the acceptor orbital on the metal is more important. However, note that stronger σ bonding, in transferring more charge from oxygen to metal, will reduce the net transfer of charge to oxygen. This will not be offset by back-donation because of the higher electron affinity of the metal.

Acknowledgment. A.B.P.L. and G.A.O. are indebted to the Natural Sciences and Engineering Research Council (Ottawa) and H.B.G. thanks the National Science Foundation for research support. This is Contribution No. 6089 from the Arthur Amos Noyes Laboratory.

Registry No. $Ti(O_2)_2$, 73117-12-1; $V(O_2)_2$, 73117-13-2; $Fe(O_2)_2$, 58220-67-0; $Cr(O_2)_2$, 73117-14-3; $Co(O_2)_2$, 58220-68-1; $Mn(O_2)_2$, 12502-70-4; $Rh(O_2)_2$, 63904-17-6; $Ni(O_2)_2$, 40935-30-6; $Pt(O_2)_2$, 50417-49-7; $Pd(O_2)_2$, 50417-48-6; $Cu(O_2)_2$, 73117-15-4; $Cu(O_2)$, 12019-06-6; $Ag(O_2)$, 12321-65-2.

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[13] A. B. P. Lever and S. R. Pickens, to be submitted for publication.

[14] The electron affinity is equated to the ionization potential of M^+, obtained from C. E. Moore, Ed., *Natl Bur. Stand.* (*U.S.*) *Monogr.*, No. 35 (1971).

[15] These data should be corrected for changes in average spin-pairing energy upon excitation. However in the absence of firm information concerning the magnetic ground states of these species, such a correction cannot be estimated reliably. Moreover there will be a significant contribution to this term from the dioxygen unit.[11] The good linear behavior may imply that for most ions, such a correction is small.

[16] For various reasons, not all species shown in Figure 1 appear in Figure 2 and vice versa. Thus Figure 1 only considers $M(O_2)_2$ species—Ag and Au, for example, do not appear to form such species. Unequivocal dioxygen isotopic substitution infrared data are not yet available for all the species shown in Figure 1, hence their absence from Figure 2.

[17] J. H. Darling, M. B. Garton-Sprenger, and S. J. Ogden, *Faraday Symp. Chem. Soc.*, **18**, 1974 (1975).

[18] G. A. Ozin, A. J. Lee Hanlan, and W. J. Power, unpublished observations.

Additions and Corrections

1980, Volume 19

David DeMarco, Tayseer Nimry, and Richard A. Walton*: Reactions of the Gaseous Hydrogen Halides with Dimers of Molybdenum(II) and Tungsten(II) Containing the Anion of 2-Hydroxy-6-methylpyridine.

Page 576. A line is missing five lines from the end of the page. The sentence should read: The X-ray photoelectron spectra of these complexes reveal that each complex possesses a well-resolved W $4f_{5/2,7/2}$ doublet, thereby demonstrating that these products are free of any high oxidation state tungsten oxide contaminants.—Richard A. Walton