

their importance. In this sense, the results from the vaporization of arsenic bear more closely upon gas-surface reactions, corrosion, dissolution, heterogeneous catalysis, and retarded sublimation, than they do upon "normal" sublimation ( $\alpha_v^\circ \approx 1$ ) or the vaporization of liquids. It is fascinating that recent studies of catalysis using single crystals<sup>31</sup> show that, although heterogeneous chemical reactions do not occur on low-index surface planes, they do take place at ledges and kinks similar to those which play such

(31) G. A. Somorjai and L. L. Kesmodel, *MTP Int. Rev. Sci.*, in press. G. A. Somorjai, *Proc. Battelle Conf. Heterogeneous Catal.*, in press.

an important role in retarded molecular vaporization.

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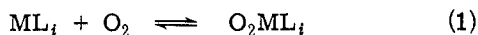
## Dioxygen-Metal Complexes: Toward a Unified View<sup>1</sup>

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This Account is concerned with the question of the nature of dioxygen bound to the metal atom in a molecular compound, and some consequences arising from these observations. This question is important not only in its own right but also because it must be answered before one can hope to understand the factors which influence the reversible oxygenation of metal complexes (eq 1), notably hemoglobin and re-



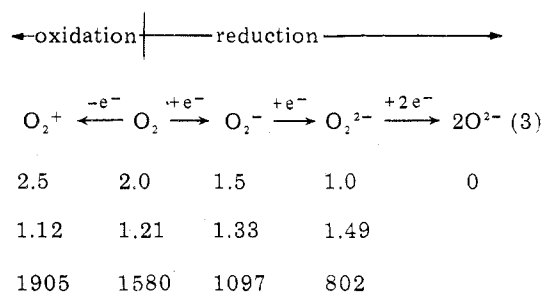
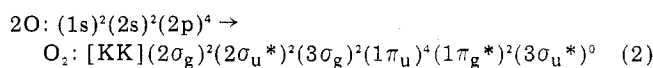
M = central metal atom;  $L_i =$

"permanent" (auxiliary) ligands

lated hemoproteins, which continue to provide a primary inspiration for the study of the title compounds.

Several reviews of dioxygen-metal complexes,  $O_2ML_i$ , have appeared in recent years,<sup>2</sup> and countless other papers and books contain analogous review type material. These writings, however, have mainly been confined to certain types of dioxygen compounds, compilations of data, or citations from articles preceding them. The present Account has thus been prompted by a need for an overall and reasonably current version of the subject, and also to show that some data which have been considered representative<sup>3</sup> have become exceptions.

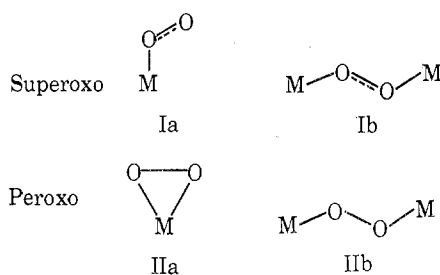
Some properties and reactions of molecular oxygen pertinent to the discussion of dioxygen-metal complexes are summarized below. The ground-state electronic structure is given in eq 2, and eq 3 schemati-



(1) Some terminology used in this paper: (a) dioxygen—generic designation of diatomic oxygen ( $O_2$ ); it comprises all states and forms of  $O_2$  in which there is an "oxygen-oxygen covalent bond", regardless of whether dioxygen is free, part of another compound, or carries an electronic charge, etc; (b) dioxygen-metal complex—includes one or more covalent bonds between dioxygen and metal atom(s) in a molecular unit, without further specification of bonding and structure; (c) molecular oxygen—free or isolated neutral  $O_2$ ; refers usually to the ground-state configuration, but does not exclude other states of the molecule; (d) superoxide— $O_2^-$  ion; superoxo—covalently bound dioxygen resembling  $O_2^-$ ; superoxo-metal complex: contains metal-bound superoxo ligand(s); (e) peroxide— $O_2^{2-}$  ion; peroxo—covalently bound dioxygen resembling  $O_2^{2-}$ ; peroxo-metal complex—contains metal-bound peroxo ligand(s); (f) oxide— $O^{2-}$  ion; oxo: covalently bound monatomic oxygen resembling  $O^{2-}$  (the term dioxo,  $(O)_2$ , is not to be confused with dioxygen,  $O_2$ ); (g) oxygenation—dioxygen (usually molecular  $O_2$ ) addition; deoxygenation—dioxygen (usually molecular oxygen) subtraction from a dioxygen compound; (h) dioxygen carrier or dioxygen-carrying compound, = oxygen carrier—refers to dioxygen transport by a (metal) compound, i.e., uptake, transport, release. This process, specifically a biological one, is also called reversible oxygenation, which is a more general chemical term (eq 1); (i) oxygen—generic term for the element and its various forms; since it is widely used for several oxygen species, it cannot be avoided as a synonym for some of the terms cited above.

(2) (a) L. H. Vogt, Jr., H. M. Faigenbaum, and S. E. Wiberley, *Chem. Rev.*, **63**, 269 (1963); (b) J. A. Connor and E. A. V. Ebsworth, *Adv. Inorg. Chem. Radiochem.*, **6**, 279 (1964); (c) E. Bayer and P. Stretzmann, *Struct. Bonding*, **2**, 181 (1967); (d) A. G. Sykes and J. A. Weil, *Prog. Inorg. Chem.*, **13**, 1 (1970); (e) R. Wilkins, *Adv. Chem. Ser.*, **No. 100**, 111 (1971); (f) V. J. Choy and C. J. O'Connor, *Coord. Chem. Rev.*, **9**, 145 (1972/73); (g) J. Valentine, *Chem. Rev.*, **73**, 235 (1973); (h) L. Klevan, J. Peone, Jr., and S. K. Madan, *J. Chem. Educ.*, **50**, 670 (1973); (i) G. Henrici-Olivé and S. Olivé, *Angew. Chem., Int. Ed. Engl.*, **13**, 29 (1974).

Lauri Vaska was born in Rakvere, Estonia. He attended the Baltic University in Hamburg and the University of Göttingen in Germany in 1946–1949, and obtained his Ph.D. from the University of Texas with Professor George W. Watt in 1956. After a postdoctoral year at Northwestern University with Professor P. W. Selwood, he was a Fellow of Independent Research at Mellon Institute until 1964, when he joined the faculty at Clarkson College of Technology, where he is Professor of Chemistry.



**Figure 1.** Principal types of presently known metal-dioxygen geometries (for references, see Table II). The diagrams for type *b* complexes are oversimplified: they do not show dihedral angles which are vastly different in the two cases (Ib, IIb) and also vary from compound to compound (see ref 5). Other ligands (including additional bridging groups in some *b* species) are omitted; for  $O_2$ -metal stoichiometries, see Table I. Bond orders: — = 1 (single bond); - - = 0.5 (one-half bond). MOO angles: ca.  $120^\circ$  in Ib, IIb, and Ia (but see ref 6, 7b):  $67^\circ$  in IIa.

cally depicts the reactions of  $O_2$  in simple terms, together with some data for the species shown.<sup>4</sup> It is important to remember that the electrons added to the oxygen molecule (eq 3) enter the partially vacant antibonding orbitals ( $1\pi_g^*$ , eq 2) and thus decrease the O-O dissociation energy and the vibrational frequency ( $\nu_{O_2}$ ) and increase the interatomic distance (O-O, Å). Several excited states of molecular oxygen are well established, and their properties have recently been discussed and tabulated.<sup>4a</sup>

### Nature of Dioxygen-Metal Complexes

Contrary to custom, but to clarify presentation, the conclusions of this Account are given first, followed by a summary of experimental evidence for the statements made in this section.

**State of Coordinated Dioxygen.** If we first focus our attention on the ligated dioxygen only, two prominent pictures, shown in Figure 1, emerge. Nearly all currently known  $O_2$ -metal compounds can conveniently be divided into two types according to the characteristics of the dioxygen ligand: superoxo (I) and peroxo (II) complexes. That is to say that  $O_2$  exhibits or approaches one or the other discrete state when attached to a metal center. In view of continuing debates regarding the nature of several dioxygen complexes, synthetic as well as biological, this principal conclusion needs emphasis. The coordinated  $O_2$  shows, or at least strongly tends to show, a *constant state* in either class of compounds.

Each type of complexes (I, II) can further be categorized according to whether the dioxygen ligand is

(3) (a) R. Mason, *Nature (London)*, 217, 543 (1968); (b) R. Mason, *Chem. Soc. Rev.*, 1, 431 (1972); (c) R. Ugo in "Proceedings of the Fifth International Congress on Catalysis", Vol. 1, J. W. Hightower, Ed., American Elsevier Publishing Co., Inc., New York, N.Y., 1973, p B-19; (d) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3rd ed, Wiley-Interscience, New York, N.Y., 1972, p 635 ff.

(4) Data in eq 3 are from (a) P. H. Krupenie, *J. Phys. Chem. Ref. Data*, 1, 423 (1972); (b) "Tables of Interatomic Distances and Configuration in Molecules and Ions. Supplement 1956-1959", L. E. Sutton, Ed., *Chem. Soc., Spec. Publ.*, 18, M38s (1965); O-O (Å) in  $O_2^{2-}$  ( $Na_2O_2$ ); (c) G. A. Ozin, private communication:  $\nu_{O_2}$  in  $O_2^{2-}(Li_2O_2)$  and  $O_2^{2-}(Li_2O_2)$ .

(5) J. R. Fritch, G. G. Christoph, and W. P. Schaefer, *Inorg. Chem.*, 12, 2170 (1973).

(6) In  $[(O_2)Co(CN)_5]^{3-}$ ,  $\angle CoOO = 174^\circ$ : L. D. Brown and K. N. Raymond, *J. Chem. Soc. Chem. Commun.*, 470 (1974).

(7) (a) J. P. Collman, R. R. Gagne, C. A. Reed, T. Halbert, G. Lang, and W. T. Robinson, *J. Am. Chem. Soc.*, 97, 1427 (1975). This recent paper describes a novel Fe-O<sub>2</sub> complex, and its derivatives, with these interesting properties: (b) "end-on"  $O_2$  coordination,  $\angle FeOO$ ,  $136^\circ$ ; (c)  $\nu_{O_2} = 1385\text{ cm}^{-1}$  at  $-175^\circ$  which disappears at  $25^\circ$ ; this value is not included in Table III. (d) One derivative shows  $\mu = 2.4\text{ BM}$  at  $25^\circ$ .

**Table I<sup>8</sup>**  
Metals in Dioxygen Complexes: Modes of Formation and  $O_2$ -Metal Stoichiometries<sup>a</sup>

Ti	V	Cr	Mn	Fe	Co	Ni	Cu
1	1, 2	1, 2, 4	0.5	0.5, 1	0.5, 1	1, 2	0.5
Zr	Nb	Mo		Ru	Rh	Pd	
	1, 2, 3, 4	0.5, 1, 2, 4		1	1	1, 2	
Hf	Ta	W		Os	Ir	Pt	
		2		1	1	1, 2	

U  
1, 3

<sup>a</sup> The symbols and numbers in the table convey the following information: (i) the characters of the symbol for the element refer to the formation of dioxygen complexes by reaction with (a)  $O_2^{2-}$  ( $H_2O_2$ ), *italic*; (b)  $O_2$ , roman; (c)  $O_2$ ,  $O_2^-$ , and/or  $O_2^{2-}$  ( $H_2O_2$ ), **boldface**; (ii) the numbers below the elemental symbol show the number of dioxygens coordinated to a single metal center.

coordinated to one or two metal atoms. The principal M-O bonding properties of the four subclasses, relevant to this interpretative summary, are evident from Figure 1 (see caption).

The terms *superoxo* and *peroxo*,<sup>1</sup> although familiar to all chemists, require clarification and more adequate definition than is usually afforded to them. "Superoxo" is *not* a superoxide ion ( $O_2^-$ ), and "peroxo" is *not* a peroxide ion ( $O_2^{2-}$ ), as for example, the  $CN^-$  ligand in a cyano-metal complex is not a cyanide ion (there is, for instance, a toxicity difference between them!). Thus, coordinated  $O_2$  may not be expected to exhibit properties identical with those of dioxygen ions. Yet, it is perhaps remarkable that the *covalently* bound dioxygen does, in many respects, resemble either of the two ionic species.

**Summary of General Characteristics: A Diverse Family of Compounds Containing Inflexible Dioxygen.**<sup>8</sup> Table I displays the metal atoms which have been reported to form dioxygen complexes. The items listed in Table I and those cited below summarize the observations that coordinated  $O_2$  is, in either of the two types of compounds (I, II), insensitive to the nature of its intimate neighbors and other components present, as well as to the electronic and stereochemical properties of the overall complex.

(1) Nearly all transition metals bind dioxygen. (2) The formal oxidation states of the metals in these species range from II through VI: they represent common or "higher than common" valences for the element. (3) The number of formally nonbonding d electrons ( $d^n$ ) ranges from 0 to 9. (4) While the vast majority of the compounds are diamagnetic, several paramagnetic complexes are well established. (5) The coordination number (CN) of the central atom varies from 2 to 8, and some metals exhibit more than one CN. (6) The  $O_2$ -metal stoichiometries are also diverse, ranging from less than 1<sup>9</sup> up to 4. (7) The charges of the complexes include numbers from 4- through 0 to 5+. (8) Ligands other than  $O_2$  are familiar types found throughout the diverse coordination chemistry of transition metals, i.e., they include "hard" (e.g. F,  $NH_3$ ) and "soft" (CO,  $AsPh_3$ , etc.),

(8) Data compiled from ref 2, and those given in Tables II and III and text.

(9)  $O_2:Mo = 2:7$  in  $K_6[(O_2)_2Mo_7(O)_{22}] \cdot 8H_2O$ : I. Larking and R. Stomberg, *Acta Chem. Scand.*, 26, 3708 (1972).

Table II  
Summary of Pertinent Bond Lengths in Crystalline Dioxygen-Metal Complexes<sup>a, b</sup>

		Oxygen-oxygen <sup>c</sup> and metal-oxygen <sup>d</sup> distances, Å					Max diff	Av	Calcd <sup>e</sup>	
M										
Superoxo Complexes, Ia										
Fe	O-O	1.24 (8); ref 7							1.33 <sup>f</sup>	
	M-O	1.75 (2)							1.90	
Co	O-O	1.26 (4),		1.2-1.3				1.3	1.33 <sup>f</sup>	
	M-O	1.86,	1.95 (5),	1.93 (2)		0.09	1.91	1.89		
	Ref	11b	29	6						
Superoxo Complexes, Ib										
Co	O-O	1.31 (2),	1.32 (2),	1.31 (3),	1.32,	1.36 (3),	1.26	0.10	1.31 (3)	1.33 <sup>f</sup>
	M-O	1.89 (2),	1.90 (2),	1.96 (3),	1.87,	1.88	1.94	0.09	1.91 (2)	1.89
	Ref	30a	30b	30c	30d	30e	30f			
Peroxo Complexes, IIa										
Ti	O-O	1.45 (1),	1.46 (0),	1.46 (1)		0.01	1.46 (1)	1.46		
	M-O	1.89 (1),	1.85 (0),	1.85 (1)		0.04	1.86 (1)	2.05		
	Ref	31a	31b	31b						
V	O-O	1.44 (2),	1.44 (0),	1.47 (1)		0.03	1.45 (2)	1.46		
	M-O	1.87 (2),	1.87 (2),	1.88 (3)		0.01	1.87 (2)	1.95		
	Ref	32a	32b	32c						
Nb	O-O	1.48 (1),	1.50 (0),	1.50 (1),	1.51 (1)		0.03	1.50 (1)	1.46	
	M-O	1.97 (0),	2.04 (0),	1.99 (1),	1.99 (1)		0.07	2.00 (1)	2.07	
	Ref	33a	33b	33c						
Cr	O-O	1.40 (2),	1.40 (2),	1.40 (2),	1.43 (3),	1.45 (1)				
	M-O	1.81 (1),	1.85 (1),	1.83 (1),	1.88 (2),	1.89 (1)				
	Ref	23a	23b	23c	23c	23c				
	O-O	1.46 (1),	1.46 (3)			0.06	1.43 (2)	1.46		
	M-O	1.88 (1),	1.92 (2)			0.11	1.87 (1)	1.91		
	Ref	23c	23c							
Mo	O-O	1.38 (6),	1.44 (3),	1.44 (2),	1.46 (2),	1.47 (1)				
	M-O	1.91 (9),	1.94 (2),	1.93 (1),	1.94 (2),	1.94 (1)				
	Ref	9	34d	34f	34c	34e				
	O-O	1.48 (2),	1.48 (1),	1.50 (1),	1.55 (5)		0.17	1.47 (3)	1.46	
	M-O	1.96 (1),	1.96 (1),	1.94 (1),	1.97 (3)		0.06	1.94 (2)	2.03	
	Ref	34b	34e	34f	34a					
W	O-O	1.50 (3); M-O,		1.93 (2);	ref 35			2.03		
U	O-O	1.51 (6); M-O,		2.28 (4);	ref 36			2.15		
Co	O-O	1.42 (1),	1.45 (3),	1.44 (1)		0.03	1.44 (2)	1.46		
	M-O	1.89 (1),	1.87 (2),	1.90 (1)		0.03	1.89 (2)	1.89		
	Ref	20a	37a	37b						
Rh	O-O	1.42 (1),	1.43 (1),	1.47 (2)		0.05	1.44 (1)	1.46		
	M-O	2.03 (1),	2.03 (1),	2.02 (1)		0.01	2.03 (1)	1.98		
	Ref	17b	20b	20c						
Ir	O-O	1.30 (3),	1.36 (3),	1.37 (2),	1.47 (1),	1.51 (3),	1.62 (3)	0.32	1.44 (2)	1.46
	M-O	2.07 (3),	2.00 (2),	2.01 (1),	2.06 (1)	2.06 (2),	1.98 (2)	0.09	2.03 (2)	2.00
	Ref	17a	20d	20e	20f	17c	17b			
Pt	O-O	1.45 (4),	1.51 (2)			0.06	1.48 (3)	1.46		
	M-O	2.01 (3),	2.01 (1)			0.0	2.01 (2)	2.03		
	Ref	38a	38b							
Peroxo Complexes, IIb										
Co	O-O	1.34 (1),	1.45 (2),	1.47 (1),	1.49 (1),	1.45 (0)		0.13	1.44 (1)	1.46
	M-O	1.91 (1),	1.93 (3),	1.88 (1),	1.90 (0),	1.98 (0)		0.10	1.92 (1)	1.89
	Ref	39a	39b	39c	5	39d				
Rh <sup>g</sup>	O-O	1.44 (2);	M-O,	2.08 (1);	ref 40a					
Mo <sup>g</sup>	O-O	1.48;	M-O,	2.24;	ref 40b					

All 49 peroxo complexes, IIa,b: O-O

1.45 (2)

1.46

<sup>a</sup> For compositions and detailed geometries, see original papers; for MOO angles, see Figure 1. <sup>b</sup> Each pair of O-O and M-O values refers to a different complex. For uniformity, the structural parameters (standard deviations in parentheses) have been rounded off for complexes for which more detailed data are given in the original reports. <sup>c</sup> Average value if there is more than one O<sub>2</sub> per metal in the molecular unit (see Table I); in these cases (O<sub>2</sub>:M ≥ 2) there are no significant differences (O-O, Å) within the same complex. <sup>d</sup> Average value (except for Ia complexes which have only one M-O bond) of two or more M-O distances. The vast majority of studies report no significant differences between individual M-O bond lengths in the same complex. <sup>e</sup> Sum of "nonpolar covalent radii," ref 41. <sup>f</sup> See eq 3. <sup>g</sup> Not strictly a type IIb complex: includes multiple M(O<sub>2</sub>)M bridging and the coordination number of oxygen is higher than two.

and mono- and polydentate ligands, and both inorganic (e.g., H<sub>2</sub>O) and organic (e.g., C<sub>2</sub>H<sub>4</sub>) groups. Numerous complexes contain various combinations of these ligand types, while some have none of them, e.g., [Cr(O<sub>2</sub>)<sub>4</sub>]<sup>3-</sup>. (9) The formation of these species is not restricted to one kind of dioxygen source. (10)

The distribution of the modes of O<sub>2</sub> binding (Figure 1) among the metals is, at this writing, as follows: Ia: Fe(III),<sup>10</sup> Co(III), Rh(III); Ib: Co(III); IIa: all (Table

(10) Iron-dioxygen complexes, both synthetic and biological, are usually not expressed as containing Fe(III)-(O<sub>2</sub><sup>-</sup>); in fact, most authors write Fe(II)-(O<sub>2</sub>); see ref 7a and references quoted therein.

Table III  
 Dioxygen Vibrational Frequencies in Metal Complexes<sup>a</sup>

Type	Metal			No. <sup>b</sup>	$\nu_{O_2}$ , cm <sup>-1</sup>			
					Range	Average		
Ia	Fe			9	1103–1195	1134		
Ib	Co			5	1075–1122	1110		
	Total, superoxo complexes:			14	1075–1195	1125		
IIa	Ti	V	Cr	Co	Ni	33	818–932	881
	Zr	Nb	Mo	Ru	Rh	66	800–929	872
		Ta	W	Os	Ir	75	807–911	850
IIb	Fe			Co		7	790–844	807
	Total, peroxo complexes:			181	790–932		~860	

<sup>a</sup> The data for IIa complexes have been compiled from ref 2b,f,g, 19d, (a few dozen Co, Rh, and Ir compounds), and 24 and those in Table II which report such data. For other types, see these references: Ia: 13a,b (Fe); 2g, 11b,c, and references quoted (Co); Ib: 43 (Co); IIb: 44 (Fe); 43b (Co). <sup>b</sup> Number of different complexes.

I) except Mn, Fe, Cu; IIb: Mn(III), Fe(III), Co(III), Cu(II) (?), Rh(III), Mo(VI) (see footnote *g* to Table II). Thus, type IIa is the most widespread one, and cobalt appears to be unique in that all four dioxygen binding modes are represented. (11) While all these types of O<sub>2</sub> coordination are known among synthetic complexes, the natural metal-dioxygen compounds appear to include only two of them [Ia (Fe); IIb (Fe, Cu ?)].

**Historical Overview of Interpretations.** All currently established types of dioxygen-metal complexes (Figure 1) have undergone more than one interpretation regarding the state of coordinated O<sub>2</sub> and/or the bonding in the M(O<sub>2</sub>) unit. The following remarks briefly cite these developments, but they chiefly pertain to IIa peroxo compounds which illustrate the problems involved in the unfolding of interpretations of the coordination of small molecules to metal complexes at large.

The dimeric  $\mu$ -dioxygen cobalt compounds (Ib, IIb) were the first to undergo extensive scrutiny because of their early and numerous existence, and, particularly, the puzzling observation that some were paramagnetic and others, diamagnetic. The solution to this problem, however, developed relatively shortly when ESR and x-ray structural studies (Table II) provided unambiguous evidence that the first class represent superoxo and the second, peroxo complexes (eq 9).<sup>2d</sup> This interpretation has since found general acceptance (references in Table II).

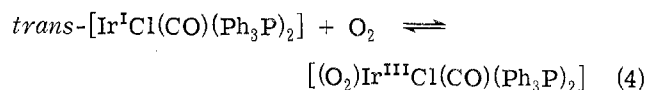
The monomeric superoxo species (Ia) of cobalt(III) have been formulated as such only lately, although their existence apparently goes back to the origin of synthetic dioxygen complexes. When the first direct experimental information (ESR, ir, x-ray) recently became available (references to Tables II, III), the type Ia interpretation was quickly recognized.<sup>11</sup>

In terms of speculations, the history of the end-on dioxygen-metal bonding (Ia) dates from the 1930's when it was first proposed by Pauling for dioxygen-hemoglobin [oxyhemoglobin, (O<sub>2</sub>)Fe(Hb)].<sup>12</sup> Subsequently, the suggestion found disputants as well as proponents (not reviewed here since the subject has

repeatedly been covered elsewhere), but currently available data on (O<sub>2</sub>)Fe(Hb) and (O<sub>2</sub>)Fe(Mb) (Mb = myoglobin), direct (Table III)<sup>13</sup> and indirect,<sup>14</sup> agree with the formulation of these compounds as containing formally iron(III) superoxo units.

The interpretation of side-on O<sub>2</sub> coordination in IIa species has occupied much thought and theoretical analyses over the past dozen years. These compounds were first named peroxo complexes on the reasonable ground that their unusually high oxygen content appeared to originate from hydrogen peroxide (eq 5). Early infrared spectral and x-ray diffraction studies confirmed this formulation in general terms.<sup>2b</sup> However, the metal-O<sub>2</sub> association turned out to be unusual: the triangular M(O<sub>2</sub>) unit had no direct precedents in transition-metal chemistry. Accordingly, discussions of "strain", "bent bonds", and " $\pi$  bonding" and the consequent problems of assigning oxidation and coordination numbers of the central atom ensued.

The first report of the preparation of a IIa complex by reaction with molecular oxygen (eq 4)<sup>15</sup> marked



the beginning of detailed inquiries into the nature of coordinated dioxygen in 1:1 O<sub>2</sub>-M complexes, largely because this system was unprecedentedly simple and involved stable species readily susceptible to comprehensive studies, and, in particular, the oxygenation was *reversible* under ambient conditions. Based on chemical and physical properties, it was concluded that the "oxygenation reaction [eq 4] thus emerges as an oxidation of the univalent (spin-paired d<sup>8</sup>) and four-coordinate iridium compound to a trivalent (spin-paired d<sup>6</sup>) and six-coordinate iridium peroxo complex".<sup>15</sup> This interpretation was also intuitively guided by the preceding discovery of generalized "oxidative addition reactions" that involved the same Ir(I) species.<sup>16</sup>

The crystal-structure determination of [(O<sub>2</sub>)Ir-

(11) (a) B. M. Hoffman and D. H. Petering, *Proc. Natl. Acad. Sci. U.S.A.*, **67**, 637 (1970); (b) G. A. Rodley and W. T. Robinson, *Nature (London)*, **235**, 438 (1972); (c) M. J. Carter, D. P. Rillema, and F. Basolo, *J. Am. Chem. Soc.*, **96**, 392 (1974); (d) D. L. Anderson, C. J. Weschler, and F. Basolo, *ibid.*, **96**, 5599 (1974).

(12) L. Pauling and C. D. Coryell, *Proc. Natl. Acad. Sci. U.S.A.*, **22**, 210 (1936).

(13) (a) C. H. Barlow, J. C. Maxwell, W. J. Wallace, and W. S. Caughey, *Biochem. Biophys. Res. Commun.*, **55**, 91 (1973); (b) J. C. Maxwell, J. A. Volpe, C. H. Barlow, and W. S. Caughey, *ibid.*, **58**, 166 (1974); (c) W. J. Wallace, J. C. Maxwell, and W. S. Caughey, *ibid.*, **57**, 1104 (1974); (d) W. S. Caughey, C. H. Barlow, J. C. Maxwell, J. A. Volpe, and W. J. Wallace, *Ann. N.Y. Acad. Sci.*, **244**, 1 (1975).

(14) T. Spiro, *Acc. Chem. Res.*, **7**, 339 (1974).

(15) L. Vaska, *Science*, **140**, 809 (1963).

(16) L. Vaska and J. W. DiLuzio, *J. Am. Chem. Soc.*, **84**, 679 (1962).

Cl(CO)(Ph<sub>3</sub>P)<sub>2</sub>]<sup>17a</sup> confirmed the side-on O<sub>2</sub> coordination, but the O-O distance, 1.30 Å, differed significantly from that found in classical peroxo complexes and suggested the presence of a superoxo ligand (Table II). Subsequently, the structures of three related Ir and Rh compounds were reported with these results: O-O, Å: 1.42 (Rh),<sup>17b</sup> 1.51 (Ir),<sup>17c</sup> and 1.62 (Ir).<sup>17b</sup> Since the formation (eq 1) of the two complexes with shorter O-O bond lengths (1.30, 1.42) was readily reversible, but that of species with longer distances (1.51, 1.62) essentially irreversible, it appeared that this structural parameter varies with the reversibility of oxygenation. These observations were swiftly publicized in reviews and other articles since they offered a simple and straightforward interpretation.<sup>18</sup> Ensuing dynamic<sup>19</sup> and structural<sup>20</sup> studies on closely related compounds, however, gave contrary evidence: the formation and stability constants of some complexes of the same type were found to differ by orders of magnitude, but the O-O distances in these O<sub>2</sub>ML<sub>i</sub> showed a relatively constant value (ca. 1.45 Å).

Apart from the question of the O-O bond length vs. reversibility, the widely varying oxygen-oxygen distances in the first four structurally studied O<sub>2</sub> complexes were intriguing since the data could not all be readily related to those of the dioxygen ions. At first, a suggestion was made that the observed bond lengths could be explained by a nonintegral (cf. eq 3) electron transfer from filled nonbonding metal d orbitals to antibonding orbitals of O<sub>2</sub> (eq 2).<sup>17b</sup> Thus, the O-O distance would gradually increase with increasing electron donation and hence the basicity or charge density of the metal center, and qualitative evidence for the extent of metal basicity in these four cases bore out this view. It indeed appeared at one time that the O-O bond lengthening in various dioxygen complexes may represent a continuum, i.e., is unrelated to discrete states.<sup>21</sup>

A different interpretation was announced about the same time. It was proposed that the activation and coordination of small molecules by metal complexes result in the promotion of these molecules to one of their electronically excited states.<sup>3a</sup> This view was based on the observation that the geometries of some unsaturated organic ligands resemble those of their excited-state configurations.<sup>3a-c</sup> The suggestion included the explanation for the varied O-O distances under discussion. For example, the unusually long O-O bond in one of the iridium complexes, 1.62

(17) (a) S. J. La Placa and J. A. Ibers, *J. Am. Chem. Soc.*, **87**, 2581 (1965); (b) J. A. McGinnety, N. C. Payne, and J. A. Ibers, *ibid.*, **91**, 6301 (1969); (c) J. A. McGinnety, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 2243 (1967).

(18) (a) This writer even went as far as publishing a graph depicting a smooth curve relating the increase in enthalpy change (-ΔH) of oxygenation to the lengthening of O-O bond in the resulting dioxygen complexes;<sup>18b</sup> (b) L. Vaska, L. S. Chen, and C. V. Senoff, *Science*, **174**, 587 (1971).

(19) (a) L. Vaska and L. S. Chen, *Chem. Commun.*, 1080 (1971); (b) L. Vaska, L. S. Chen, and W. V. Miller, *J. Am. Chem. Soc.*, **93**, 6671 (1971); (c) L. S. Chen, Ph.D. Dissertation, Clarkson College of Technology, 1973; (d) L. Vaska and co-workers, unpublished results.

(20) (a) N. W. Terry, III, E. L. Amma, and L. Vaska, *J. Am. Chem. Soc.*, **94**, 653 (1972); (b) N. W. Terry, III, E. L. Amma, and L. Vaska, unpublished results; (c) M. S. Weininger, B. L. Kindley, E. L. Amma, L. S. Chen, and L. Vaska, unpublished results; (d) W. A. Spofford, III, and E. L. Amma, private communication from E. L. Amma; (e) N. W. Terry, III, A. G. Gasl, L. Vaska, and E. L. Amma, unpublished results; (f) M. S. Weininger, I. F. Taylor, Jr., and E. L. Amma, *Chem. Commun.*, 1172 (1971).

(21) L. Vaska, *Acc. Chem. Res.*, **1**, 335 (1968).

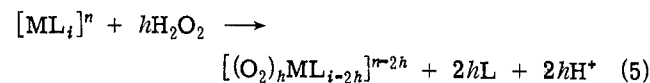
Å, could be related to an excited state of dioxygen, <sup>3</sup>Σ<sub>u</sub><sup>-</sup> (O-O, 1.60 Å),<sup>4a</sup> and thus account for the observed data.

The excited-state theory for coordinated small molecules continues to be applied in current chemical literature, but an objection to this view lies in the definition and nomenclature. An electronically excited state refers to an isolated or free species which is unaffected by its environment. As ligands, however, these "former molecules" have lost their original identity: at least for the type IIa complexes, there is unambiguous evidence for strong metal-dioxygen *covalent* bonds.<sup>22</sup>

At present, it seems that a full cycle has occurred in the interpretation of type IIa dioxygen complexes; that is, the original and simple "peroxo views"<sup>2b,15,23,24</sup> appear still largely valid. Nonetheless, one should hasten to add that all of the theories cited and other theoretical treatments which have appeared recently<sup>25</sup> are not necessarily mutually exclusive, as is often the case in viewing the same phenomenon from different standpoints. The premise here is to suggest that the simple valence bond formalism is quite adequate and sufficient to account for the properties of most of the presently known dioxygen-metal complexes, and it is thus satisfying to note that this observation contributes to restoring respectability to the old-fashioned and simple concept of valence.

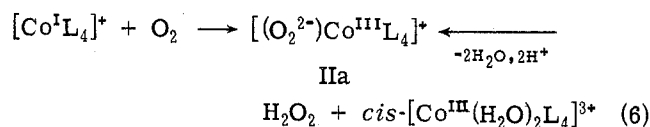
## Experimental Evidence

**Preparation and Chemical Properties.** It has been customary to divide the largest class of dioxygen complexes, type IIa or the "π-bonded" O<sub>2</sub> species, into two kinds of chemical compounds, based on the route to their synthesis: "peroxo" complexes, formed by reaction with hydrogen peroxide (eq 5, L



= monodentate neutral ligand in the general case shown), and "molecular oxygen adducts", prepared by addition of O<sub>2</sub> (eq 1, Table I). This distinction has continued to persist in spite of no other significant difference between these supposedly disparate groups of complexes (Tables II, III).

A recent report is likely to put to rest this rather artificial view. A cobalt(III)-dioxygen complex of type IIa has been synthesized by reactions of Co(I) with molecular oxygen *and* of Co(III) with hydrogen peroxide (eq 6, L<sub>4</sub> = 2 chelating diarsines).<sup>26</sup>



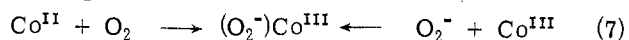
(22) Metal-dioxygen bond energies in some IIa complexes, estimated from structural and dynamic data, are in the 90-100-kcal/mol range<sup>18d</sup> (see also ref 18b).

(23) (a) R. Stomberg, *Ark. Kemi*, **22**, 29 (1964); (b) R. Stomberg and I. B. Ainalem, *Acta Chem. Scand.*, **22**, 1439 (1968); (c) R. Stomberg, *Ark. Kemi*, **24**, 283 (1965), and references given to previous papers by R. Stomberg.

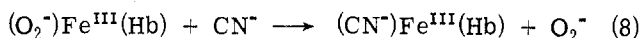
(24) (a) W. P. Griffith, *J. Chem. Soc.*, 3948 (1962); 5345 (1963); 5248 (1964); (b) W. P. Griffith and T. D. Wickins, *J. Chem. Soc. A*, 397 (1968).

(25) See, for example: (a) P. D. Dacre and M. Elder, *J. Chem. Soc., Dalton Trans.*, 1426 (1972); (b) R. D. Harcourt, *Inorg. Nucl. Chem. Lett.*, **9**, 475 (1973), and references given; (c) J. G. Norman, Jr., *J. Am. Chem. Soc.*, **96**, 3327 (1974).

Furthermore, a superoxo species of type Ia tervalent cobalt has been cited to result by two analogous reactions (eq 7).<sup>27</sup>

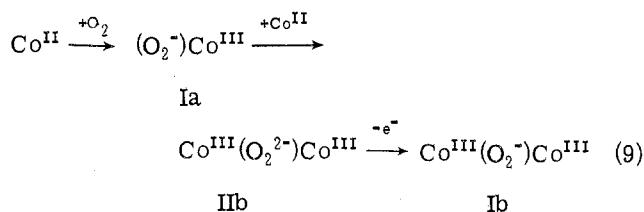


The left-hand halves of eq 6 and 7 represent oxidations of the metal by two and one units, respectively, while the right-hand sides depict substitution reactions. Pertinent to this subject is also the recent observation that dioxygen in oxyhemoglobin can be displaced by univalent anionic ligands to yield authenticated ferric derivatives (eq 8).<sup>13c</sup>



Although these isolated instances (eq 6–8) may appear unrepresentative, they probably point to a general phenomenon.

The preparation of O<sub>2</sub>-bridged complexes of types Ib and IIb is best illustrated by citing the extensively studied cobalt species as examples (eq 9).<sup>2d,e</sup>



The initial intermediate apparently is a type Ia compound which reacts further with a second Co(II) and is oxidized to the tervalent state by the superoxo ligand, yielding a peroxo dimer, IIb. The only presently known route to superoxo-bridged complexes, Ib, appears to be the oxidation of the peroxo group in IIb (eq 9).

Although direct *chemical* evidence for the nature of coordinated dioxygen in the two principal types (I, II) is not extensive, the available reports conform with the given interpretation.<sup>2b</sup> The reactions of metal-bound dioxygen with various molecules are numerous.<sup>2g</sup> They involve cleavage of the O–O bond and oxygen transfer to the reactant used. These interactions, including those of catalytic oxidations,<sup>28</sup> are beyond the scope of this article.

**Molecular Structures in Crystals.** Probably the most voluminously discussed aspect of dioxygen complexes has been their stereochemistry, particularly the oxygen–oxygen bond lengths which have formed the principal basis for various interpretations. This necessitates a presentation of what I believe to be a reasonably representative, but probably not complete, list of available bond length data in Table II (see ref 5–7, 9, 11b, 17, 20, 23, 29–41). Space limita-

tion allows only a very condensed summary essential to the theme of this Account.

Most of the complexes display an essentially constant oxygen–oxygen distance in each of the two principal types (I, II). Iridium, a large third-row transition metal, stands out as a notable exception. The O–O bond length is not significantly affected by whether the dioxygen is bound to one [M(O<sub>2</sub>), a] or two [M(O<sub>2</sub>)M, b] metal atoms.

It is customary to compare the O–O bond lengths in metal complexes with those of dioxygen ions, and the distance in peroxide, 1.49 Å, is usually cited when metal–O<sub>2</sub> bonding is discussed. The data in Table II show that in type II compounds the O–O distance tends to be shorter than in O<sub>2</sub><sup>2-</sup>, and this is indeed expected since the repulsion between the lone electron pairs on each oxygen in the ion, [:(O:O):]<sup>2-</sup>, should diminish when two of these nonbonding pairs engage in M(O<sub>2</sub>) and M(O<sub>2</sub>)M covalent bonds. A more reasonable value for comparison is the sum of –O– single bond *covalent* radii, 1.46 Å, which excellently agrees with most of the experimental data. For type I species, the difference between the O–O distances in complexes and the superoxide ion, 1.33 Å, should be less pronounced since the nonbonding charge density in the latter is lower than in O<sub>2</sub><sup>2-</sup>. The significance of the metal–oxygen bond lengths, especially in the oxygenated (eq 1) IIa compounds, has been discussed only cursorily, although these data furnish information as valuable as the O–O parameter. In addition to the observation that the M–O linkages in all of the dioxygen complexes approximate those of single covalent bonds (sum of M–O radii),<sup>42</sup> we note that the variation of these distances for each metal is small, and in most cases negligible, even for iridium (cf. above). For IIa species, the two identical M–O single bonds strongly favor, as does other evidence,<sup>15,22,23c,24,26</sup> a formulation of the coordinated dioxygen as a *bidentate* or chelating ligand,<sup>2f</sup> rather than

(31) (a) D. Schwarzenbach, *Inorg. Chem.*, **9**, 2391 (1970); (b) *Helv. Chim. Acta*, **55**, 2490 (1972).

(32) (a) I. B. Svensson and R. Stomberg, *Acta Chem. Scand.*, **25**, 898 (1971); (b) R. E. Drew and F. W. B. Einstein, *Inorg. Chem.*, **12**, 829 (1973); (c) *ibid.*, **11**, 1079 (1972).

(33) (a) B. Mathern and R. Weiss, *Acta Crystallogr., Sect. B*, **27**, 1572 (1971); (b) *ibid.*, 1598 (1971); (c) *ibid.*, 1582 (1971).

(34) (a) R. Stomberg, *Acta Chem. Scand.*, **23**, 2755 (1969); (b) *ibid.*, **22**, 1076 (1968); (c) *ibid.*, **24**, 2024 (1970); (d) D. Grandjean and R. Weiss, *Bull. Soc. Chim. Fr.*, **8**, 3044 (1967); (e) J.-M. Le Carpentier, A. Mitscher, and R. Weiss, *Acta Crystallogr., Sect. B*, **28**, 1288 (1972); (f) J.-M. Le Carpentier, R. Schlupp, and R. Weiss, *ibid.*, 1278 (1972).

(35) F. W. B. Einstein and P. R. Penfold, *Acta Crystallogr.*, **17**, 1127 (1964).

(36) N. W. Alcock, *J. Chem. Soc. A*, 1588 (1968).

(37) (a) N. C. Payne, private communication; (b) J. Halpern, B. L. Goodall, G. P. Khare, H. S. Lim, and J. J. Pluth, *J. Am. Chem. Soc.*, **97**, 2301 (1975).

(38) (a) T. Kashiwagi, N. Yasuoka, N. Kasai, M. Kakudo, S. Takahashi, and N. Hagihara, *Chem. Commun.*, 743 (1969); (b) P. T. Cheng, C. D. Cook, S. C. Nyburg, and K. Y. Wan, *Can. J. Chem.*, **49**, 3772 (1971).

(26) B. Bosnich, W. G. Jackson, S. T. D. Lo, and J. W. McLaren, *Inorg. Chem.*, **13**, 2605 (1974).

(27) J. Ellis and J. N. Pratt, *J. Chem. Soc., Chem. Commun.*, 781 (1973).

(28) J. E. Lyons, *Adv. Chem. Ser.*, **No. 132**, 64 (1974).

(29) (a) M. Galligaris, G. Nardin, L. Randaccio, and G. Tauzher, *Inorg. Nucl. Chem. Lett.*, **9**, 419 (1973); (b) J. P. Collman, H. Takaya, B. Winkler, L. Libit, S. S. Koon, G. A. Rodley, and W. T. Robinson, *J. Am. Chem. Soc.*, **95**, 1656 (1973); this paper gives structural evidence for a type Ia Co complex, but no bond lengths are reported.

(30) (a) R. E. Marsh and W. P. Schaefer, *Acta Crystallogr., Sect. B*, **24**, 246 (1968); (b) W. P. Schaefer and R. E. Marsh, *ibid.*, **21**, 735 (1966); (c) B. C. Wang and W. P. Schaefer, *Science*, **166**, 1404 (1969); (d) G. G. Christoph, R. E. Marsh, and W. P. Schaefer, *Inorg. Chem.*, **8**, 291 (1969); (e) U. Thewalt and R. Marsh, *J. Am. Chem. Soc.*, **89**, 6364 (1967); (f) F. R. Fronczek, W. P. Schaefer, and R. E. Marsh, *Inorg. Chem.*, **14**, 611 (1975).

(39) (a) M. Galligaris, G. Nardin, L. Randaccio, and A. Ripamonti, *J. Chem. Soc. A*, 1069 (1970); (b) L. A. Lindblom, W. P. Schaefer, and R. Marsh, *Acta Crystallogr., Sect. B*, **27**, 1461 (1971); (c) W. P. Schaefer, *Inorg. Chem.*, **7**, 725 (1968); (d) F. R. Fronczek and W. P. Schaefer, *Inorg. Chim. Acta*, **9**, 143 (1974).

(40) (a) M. J. Bennett and P. B. Donaldson, *J. Am. Chem. Soc.*, **93**, 3307 (1971); (b) R. Stomberg, L. Trysberg, and I. Larking, *Acta Chem. Scand.*, **24**, 2678 (1970).

(41) R. T. Sanderson, "Inorganic Chemistry", Reinhold, New York, N.Y., 1967, p 74.

(42) Several dioxygen complexes contain also metal–oxo unit(s), M=O, and these provide a convenient comparison of metal–oxygen distances in the same molecular unit. For example, in [(O<sub>2</sub>)<sub>2</sub>Cr(O)(phen)] (IIa), Cr–O (peroxo), 1.83 (1), and Cr=O (oxo), 1.56 (2) Å.<sup>23c</sup>

a monodentate one. As can be verified from the references in Table II, the numerous variables indicated above exert little, if any, influence on the O-O and M-O distances. Throughout this Account we are interested in *molecular* properties, i.e., those of isolated or unperturbed species. Presently, however, the only direct structural data (with all of its potential limitations) are derived from condensed aggregates.

**Vibrational Spectra.** The most widely measured property of O<sub>2</sub>-metal complexes has been the vibrational spectrum of coordinated dioxygen (Table III; see ref 2b,f,g, 11b,c, 13a,b 19d, 24, 43, 44). While the nature of the infrared spectral frequency near 1100 cm<sup>-1</sup> in Ia compounds was immediately recognized as the oxygen-oxygen stretching vibration of the superoxo ligand, the assignment of the band in the 800-900-cm<sup>-1</sup> range of IIa peroxo complexes has caused considerable controversy owing chiefly to incongruity of spectral and structural data for some iridium complexes.<sup>45</sup> Lately, however, a consensus has developed that the frequency derives from the O-O stretching motion,<sup>46a,47</sup> originally interpreted for the classical IIa peroxo species<sup>24</sup> and supported by comparing the bulk of the oxygen-oxygen bond lengths (Table II) with the corresponding vibrational spectra (Table III).

The intent here is not to review the arguments over this spectral assignment, but to draw attention to the relative closeness of dioxygen vibrational energies in each class of compounds. Since the  $\nu_{O_2}$  is not derived from a "pure" O-O stretching vibration, the mass of the metal and the auxiliary ligands, as well as the overall symmetry of the complex, must play at least some role in determining the observed frequency (force constant calculations seem to have been made only in a few instances<sup>46a,47</sup>). In agreement with structural data, and for the same reasons as cited above, the O-O vibrational energies are somewhat higher than those of the respective ions, O<sub>2</sub><sup>-</sup> and O<sub>2</sub><sup>2-</sup> (eq 3). Although rather limited results are available for dioxygen-bridged species (b), their spectra are reasonably close to type a complexes (cf. analogous observations on O-O distances). The average  $\nu_{O_2}$  values for each type (I, II) give a considerably truer indication of the relative constancy of this property than their respective total ranges.<sup>48</sup>

A new subclass of metal-dioxygen associations has recently been reported. The species are formed by co-condensation reactions of metal atoms with molecular oxygen in low temperature (4.2-10 K) matrices.<sup>46</sup> These compounds represent the first binary nonionic dioxygen complexes. The evidence for their existence and type, IIa, rests on infrared spectral analyses, but

their O-O stretching frequencies (not included in the summaries of Table III) do not fall into the relatively narrow range:  $\nu_{O_2}$ , cm<sup>-1</sup>, in M(O<sub>2</sub>): M = Ni, 966; Pd, 1024; Pt, 927; in M(O<sub>2</sub>)<sub>2</sub>: Ni, 1062; Pd, 1111; Pt, 1050. There is one further notable exception.<sup>7c</sup> Also, the  $\nu_{O_2}$  in dioxygen-hemocyanin, 742 cm<sup>-1</sup>,<sup>49</sup> is not given in Table III because of the uncertainty of Cu<sub>2</sub>(O<sub>2</sub>) structural type.

**Other Physical Properties.** The electronic spectra of oxygenated complexes have not been extensively investigated, and the available data do not directly point to the nature of metal-bound dioxygen. These spectra do, however, corroborate the chemical, structural, and ir results which show that oxygenation (eq 1) is an oxidation (metal)-reduction (O<sub>2</sub>) process. On addition of O<sub>2</sub>, the visible spectrum of ML<sub>i</sub> changes, in many cases drastically, and, where other bands do not interfere, the change is similar to that accompanying "ordinary" oxidation of the metal.<sup>19b-d,50</sup> At least in one instance there is also direct visible spectral evidence that oxygenation of a Co(I) species yields a genuine Co(III) derivative (eq 6).<sup>26</sup>

The diamagnetism of most of the dioxygen complexes renders the magnetic criterion nondiagnostic of the formal oxidation states of the metal and dioxygen in these compounds. There are cases, however, which demonstrate that the magnetic properties do not influence the metal-dioxygen bond type. For example, the O-O and M-O distances are the same (within experimental error) in the following IIa chromium complexes: brown-red K<sub>3</sub>[(O<sub>2</sub>)<sub>2</sub>Cr<sup>IV</sup>(CN)<sub>3</sub>], paramagnetic (*S* = 1), d<sup>2</sup>, coordination number 7; red K<sub>3</sub>[(O<sub>2</sub>)<sub>4</sub>Cr<sup>V</sup>], paramagnetic (*S* = 1/2), d<sup>1</sup>, coordination number 8; dark blue [(O<sub>2</sub>)<sub>2</sub>Cr<sup>VI</sup>(O)(C<sub>5</sub>H<sub>5</sub>N)], diamagnetic (*S* = 0), d<sup>0</sup>, coordination number 6.<sup>23c</sup> This series also illustrates the earlier statements concerning the independence of the M(O<sub>2</sub>) bond parameters on the oxidation and coordination numbers, d<sup>n</sup> configuration, O<sub>2</sub>-M ratio, and the type of auxiliary ligands. The superoxo metal complexes display paramagnetism (*S* = 1/2) when the total number of electrons is odd (Ia, Ib) and diamagnetism when that number is even (Ia; but see ref 7d).

### Concluding Remarks

The rigid picture of the metal-coordinated dioxygen presented in this Account may leave the impression that the main questions concerning the title compounds have been settled. Such a notion is, of course, far from the truth. We have already referred to some exceptions to the unified view,<sup>7c,d,17a,b,40,46</sup> and investigations on numerous important dioxygen complexes<sup>7,11,13,51,52</sup> are continuing at a rapid rate. These qualifying remarks notwithstanding, the vast majority of presently available experimental results support the main conclusions given in this Account.

(43) (a) T. Shibahara, *J. Chem. Soc., Chem. Commun.*, 864 (1973); (b) T. B. Freedman, C. M. Yoshida, and T. M. Loehr, *ibid.*, 1016 (1974).

(44) J. B. R. Dunn, D. F. Shriver, and I. M. Klotz, *Proc. Natl. Acad. Sci. U.S.A.*, 70, 2582 (1973).

(45) For example, the  $\nu_{O_2}$  (cm<sup>-1</sup>) and O-O (Å) for [IrA(CO)(Ph<sub>3</sub>P)<sub>2</sub>]<sub>2</sub> are: A = Cl: 858 (Nujol); 858, CHCl<sub>3</sub>, 1.30; Br: 860 (Nujol); 861, CHCl<sub>3</sub>, 1.36; I: 862 (Nujol); 862, CHCl<sub>3</sub>, 1.51, respectively.

(46) (a) H. Huber, W. Klotzbücher, G. A. Ozin, and A. Vander Voet, *Can. J. Chem.*, 51, 2722 (1973); (b) G. A. Ozin and A. Vander Voet, *Acc. Chem. Res.*, 6, 313 (1973).

(47) (a) A. Nakamura, Y. Tatsuno, M. Yamamoto, and S. Otsuka, *J. Am. Chem. Soc.*, 93, 6052 (1971); (b) T. C. Streckas and T. G. Spiro, unpublished results; private communication from T. G. Spiro.

(48) A distribution curve would show that the O-O stretching modes of IIa complexes are largely concentrated near 860 cm<sup>-1</sup>.

(49) J. S. Loehr, T. B. Freedman, and T. M. Loehr, *Biochem. Biophys. Res. Commun.*, 56, 510 (1974).

(50) Ph.D. Dissertations, Clarkson College of Technology: (a) M. F. Werneke, 1971; (b) J. Peone, Jr., 1971.

(51) (a) J. Almog, J. E. Baldwin, R. L. Dyer, J. Huff, and C. J. Wilkerson, *J. Am. Chem. Soc.*, 96, 5600 (1974); (b) W. S. Brinigar, C. K. Chang, J. Geibel, and T. G. Traylor, *ibid.*, 96, 5597 (1974); (c) R. Kellerman, P. J. Hutta, and K. Klier *ibid.*, 96, 5946 (1974); (d) W. D. Lemke and D. H. Busch, 168th National Meeting, American Chemical Society, Atlantic City, N.J., Sept 1974, Abstract INOR-155.

(52) F. Basolo, B. M. Hoffman, and J. A. Ibers, *Acc. Chem. Res.*, 8, 384 (1975).

Furthermore, I believe that it is more appropriate to begin by summarizing common properties of a group of chemical compounds, and then proceed to finer points and differences, rather than adopting the reverse procedure.

Finally, a central aspect of this Account seems to require a summarizing emphasis. Although there are claims for the isolation of metal complexes containing "neutral"  $O_2$ , there appears to be insufficient evidence for this type of formulation at present. Obviously, the valence of dioxygen and the central metal atom in several  $(O_2)ML_i$  cannot be unambiguously defined, especially in compounds of heavy transition metals in which the formal oxidation states of the component elements are often blurred. However, there is little doubt that in all of the metal- $O_2$  associations the dioxygen ligand acts as the negative component,<sup>53</sup> as expected from differences in electron affinity (M vs.  $O_2$ ) and according to chemical common sense. In other words, there seems to be no justification for formulating the state of the metal as remaining unaffected by oxygenation. All experimental data show that the formation of covalent M- $(O_2)$  bonds on  $O_2$  addition to  $ML_i$  (eq 1) is accompanied by an extensive redistribution of electrons, and the *direction* of electron transfer is clearly from the metal to dioxygen.<sup>53</sup> In summary, then, oxygenation = oxidation, even if it is reversible.<sup>54</sup>

#### Note Added in Proof

Since the manuscript was submitted, a number of important papers pertinent to the conclusions of this article have appeared.

(1) **Chemical Properties of Coordinated Dioxygen.** Oxyhemoglobin,  $(O_2)Fe(Hb)$ , reacts even with very weak nucleophiles ( $Cl^-$ ) to produce superoxide (or  $HO_2$ ) and metHb [ $Fe^{III}(Hb)$ ]<sup>55a</sup> (cf. eq 8, ref 13c); one-electron donation to  $(O_2)Fe(Hb)$  gives rise to peroxide and metHb as reaction products.<sup>55b</sup> Both of these observations support the presence of formally iron(III) superoxo units in oxyhemoglobin (see text).

(2) **Molecular Structures.** The data for five new rhodium and iridium complexes of type IIa have been reported; O-O ( $\sigma$ , 0.01–0.03) and M-O ( $\sigma$ , 0.01–0.02) Å, respectively: 1.43, 2.03 (Rh); 1.46, 2.03 (Rh); 1.45, 2.01 (Ir); 1.49, 2.05 (Ir); 1.49, 2.05 (Ir).<sup>56a</sup> More significantly, a redetermination of the structure of  $[O_2Ir(Ph_2PCH_2CH_2PPh_2)_2]PF_6$ , previously reported to exhibit an unusually long O-O distance (1.62 Å),<sup>17b</sup> has shown the O-O bond length to be 1.52 (1) Å (Ir-O, 2.06 Å).<sup>56b</sup> Thus, altogether, these new data remove iridium as an exception to the unified view, and further suggest that it is not necessary or appropriate to evoke the excited-state theory for coordinated dioxygen (see text and Table II).

(53) (a) These statements do not refer to dioxygenyl salts ( $O_2^+MX_n^-$ ); these interesting compounds, some of which are formed reversibly with molecular oxygen,<sup>53b</sup> are not discussed in this paper since they do not seem to contain metal-dioxygen covalent bonds.<sup>1b</sup> (b) M. J. Vasile and E. Falconer, *J. Chem. Soc., Dalton Trans.*, 316 (1975).

(54) The question of reversibility of oxygenation will be discussed in another article.

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The structure of a cobalt superoxo complex of type Ia, reported to show an essentially linear  $CoOO$  group,<sup>6</sup> has been reformulated as a disordered bent species,  $\angle CoOO = 153(2)^\circ$ .<sup>57</sup>

(3) **Vibrational Spectra.** The O-O stretching frequency in cobalt oxyhemoglobin,  $(O_2)Co(Hb)$  (type Ia), appears at  $1105\text{ cm}^{-1}$  in ir spectrum; the corresponding iron derivative,  $(O_2)Fe(Hb)$ , shows  $\nu_{O_2} = 1106\text{ cm}^{-1}$ .<sup>58a</sup> These data provide direct evidence of strikingly similar end-on dioxygen coordination for the two metals, and thus again support the formulation of  $(O_2)Fe(Hb)$  as containing formally trivalent iron-superoxo groups (Ia) (see text and Table III). Resonance Raman studies have provided additional  $\nu_{O_2}$  data for  $\mu$ -superoxo (Ib) cobalt complexes ( $1104, 1108\text{ cm}^{-1}$ ; cf. Table III).<sup>58b</sup>

The previously reported unusual  $\nu_{O_2}$  at  $1385\text{ cm}^{-1}$  in a dioxygen-porphyrin complex<sup>7c</sup> has been found to be an artifact.<sup>59</sup>

(4) **Electronic Spectra.** A recent paper<sup>60a</sup> corroborates previous evidence<sup>26</sup> that oxygenation of  $Co(I)$  yields peroxy complexes of trivalent cobalt,  $(O_2^{2-})Co^{III}$  (type IIa, eq 6). Another spectral study<sup>60b</sup> of  $\mu$ -superoxo species,  $Co^{III}(O_2^-)Co^{III}$  (Ib, eq 9), conclusively establishes the presence of low-spin  $d^6$   $Co(III)$  centers in these compounds.

(5) **X-Ray Photoelectron Spectra (XPS).** This technique has been applied to investigate the electronic charge distribution in a series of four- and five-coordinate cobalt(II) complexes and their oxygenation products,  $\mu$ -peroxy (IIb) and superoxo (Ia) compounds. The results present unambiguous evidence that cobalt(II) is oxidized in the oxygenation process, i.e., that the dioxygen complexes should *not* be formulated as containing bivalent cobalt bound to singlet oxygen.<sup>61</sup>

(6) **New Modes of Dioxygen Binding.** A manganese(II) porphyrin complex reacts reversibly with  $O_2$  forming an adduct which is tentatively formulated as a monomeric Mn(IV) species of type IIa (cf. Table I).<sup>62</sup> This dioxygen complex would represent the first side-on peroxy coordination to a metal- $N_4$  macrocycle.

A novel heme- $O_2$  association has been reported.<sup>63</sup> Solid hemes (without axial ligands) take up oxygen reversibly, one  $O_2$  per heme. The oxygenated species shows ir bands near  $1660$  and  $1590\text{ cm}^{-1}$  which are assigned to  $\nu_{O_2}$ . The product is a dimeric ferric complex suggested to result from electron transfer from iron(II) into the porphyrin forming a  $\pi$  anion. It is considered that two dioxygen molecules are held sandwich fashion between two hemes via donor-acceptor interactions.<sup>63</sup> This new type of complex does not seem to involve a metal- $O_2$  covalent bond, and is thus unrelated to the compounds reviewed here. The observation is, however, relevant to the currently very active area of dioxygen-

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