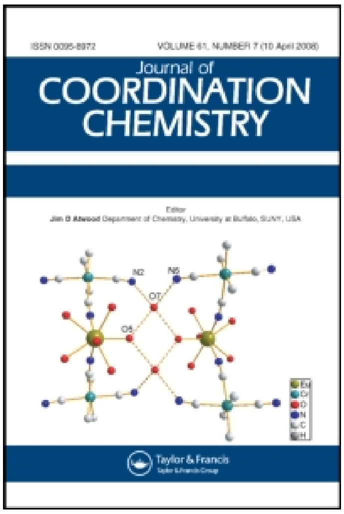

Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Stabilities of Monobridged Binuclear Cobalt Dioxygen Complexes: A Linear Free Energy Relationship

Wesley R. Harris[a]; James H. Timmons[a]; Arthur E. Martell[a]
[a] Department of Chemistry, Texas A&M University, College Station, Texas, USA

To cite this Article Harris, Wesley R. , Timmons, James H. and Martell, Arthur E.(1979) 'Stabilities of Monobridged Binuclear Cobalt Dioxygen Complexes: A Linear Free Energy Relationship', Journal of Coordination Chemistry, 8: 4, 251 — 253

To link to this Article: DOI: 10.1080/00958977908076506

URL: http://dx.doi.org/10.1080/00958977908076506

J. Coord. Chem.
1979, Vol. 8, pp. 251–253

SHORT COMMUNICATION
Stabilities of Monobridged Binuclear Cobalt Dioxygen Complexes: a Linear Free Energy Relationship

WESLEY R. HARRIS, JAMES H. TIMMONS and ARTHUR E. MARTELL†

Department of Chemistry, Texas A&M University, College Station, Texas 77843, USA

(Received April 18, 1978)

Equilibrium data for oxygenation of a number of cobalt(II) complexes of pentadentate ligands that form 5-membered chelate rings indicate that the logarithms of the stability constants of the oxygen adduct do not correlate with the stability constants of the cobalt (II)-ligand complexes, but correlate linearly with the sums of the pK's of the ligand donor groups coordinated to the cobalt.

It is now generally accepted that binuclear cobalt(II) dioxygen complexes may be considered formally as cobalt(III) coordinated to a bridging peroxide ion.[1] An important concept based on this formulation is that factors that tend to increase the strength of the ligand-metal bond should stabilize cobalt(III) relative to cobalt(II) and thus increase the stability of the dioxygen adduct. This prediction may be tested by varying the donor ligand so as to vary the stabilities of the cobalt complexes, and by observing the resulting effect on oxygen adduct equilibria. Recently, a linear relationship between the logarithms of the stability constant of oxygenation (Eq. 1) and the sums of the pK's of the ligand donor groups coordinated to cobalt (but not the stabilities of the cobalt(II) complexes) has been observed for the dibridging μ-peroxo-μ-hydroxo cobalt dioxygen complexes[2] and has been confirmed by others.[3] This correlation is based on the ligand pK's alone, and is therefore restricted to σ-bonding effects. The question of π-bonding on dioxygen complex stability remains open, since none of the ligands employed contained aromatic nitrogen atoms capable of π-bonding to the metal ion.

$$\text{Dibridged} \quad : \quad K_{O_2} = \frac{[\mathrm{MLO_2OHML}][\mathrm{H^+}]}{[\mathrm{ML}]^2[\mathrm{O_2}]} \qquad (1)$$

$$\text{Monobridged:} \quad K_{O_2} = \frac{[\mathrm{MLO_2ML}]}{[\mathrm{ML}]^2[\mathrm{O_2}]} \qquad (2)$$

It had not been possible previously to determine if an analogous correlation exists for the monobridged μ-peroxo-cobalt dioxygen adducts because of the lack of equilibrium data involving suitable ligands. Pentadentate ligands are generally necessary to prevent formation of a hydroxo bridge in addition to the peroxo bridge, although some monobridged complexes have been obtained with mixed-ligand complexes.[3–5] Equilibrium constants for reaction (2) are reported in Table I involving pentadentate polyamines containing both aliphatic and aromatic nitrogens that form 5- and 6-membered rings, along with the stability constants of the cobalt(II) complexes. The equilibrium constants for oxygenation were determined by potentiometric measurement of hydrogen ion concentration and, in some cases, by oxygen uptake measurements with an oxygen-sensing electrode. The ligand protonation constants were determined potentiometrically. Synthesis of the ligands[6] and complete experimental details[7] will be described elsewhere.

The data in Table I show that the stability constants of the cobalt(II) complexes are dependent on both basicities of the ligands (as measured by Σ pK) and on back-bonding from cobalt(II) to the aromatic nitrogen atoms (i.e., there is no correlation with ligand basicities alone). On the other hand, aromaticity of the nitrogen donors seem to have little affect on dioxygen affinities, and a linear correlation of log K_{O_2} with Σ pK is observed (Figure) for all pentadentate ligands that form 5-membered chelate rings with the metal ion. Thus the primary factors governing the stability of the cobalt(II)-dioxygen coordinate bond are those that increase σ-donation

TABLE I
Correlation of stabilities of monobridged dioxygen complexes with basicities of ligands[a]

Ligand	Σ pK$_a$[b]	Log K_{ML}	Log K_{O_2}	Reference
With 5-membered chelate rings				
TETREN[c]	35.8	13.66	15.8	7,8
EPYDEN[c]	30.6	13.99	14.7	7
4-IMDIEN[c]	29.1	13.84	12.6	present work
PYDIEN[c]	21.6	14.73	11.4	7
TRPY(PHEN)[c]	∿13	6.53[d]	6.3	2,5
TRPY(BIPY)[c]	∿12	5.38[d]	5.4	2,5
With 5- and 6-membered chelate rings				
4-IMDPT[c]	34.4	11.36	9.5	present work
2-IMDPT[c]	30.7	11.55	8.6	present work
PYDPT[c]	27.1	11.47	7.7	7

[a] All measuremnets made at 25 ± 0.1°C; μ = 1.0 (KNO$_3$).

[b] Σ pK is summation of pK's of all donor groups of ligands coordinated to cobalt(II) ion.

[c] TETREN = 1,4,7,10,13-pentaazatridecane; EPYDEN = 2,6-bis(5-(1,4-diazahexyl)) pyridine; 4-IMDIEN = 1,9-bis(4-imidazolyl)-2,5,8-triazanonane; PYDIEN = 1,9-bis(2-pyridyl)-2,5,8-triazanonane; TRPY = terpyridyl; PHEN = o-phenanthroline; BIPY = bipyridyl; 4-IMDPT = 1,11-bis(4-imidazolyl)-2,6,10-triazaundecane; 2-IMDPT = 1,11-bis(2-imidazolyl)-2,6,10-triazaundecane; PYDPT = 1,11-bis(2-pyridyl)-2,6,10-triazaundecane.

[d] For reaction of Co(TRPY)$^{2+}$ with second ligand.

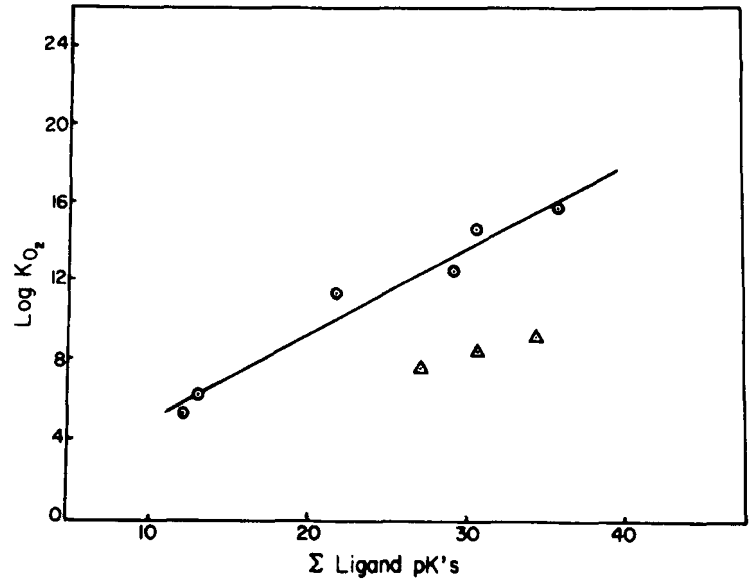

FIGURE 1 Correlation of log K_{O_2} with the sum of the log protonation constant of the ligands. K_{O_2} is the equilibrium constant for the combination of oxygen with the completely formed cobalt(II) single ligand or mixed ligand complex. Equilibrium constants for oxygenation of complexes which contain 6-membered chelate rings (lower right) do not correlate.

by the ligands to the cobalt, and π-bonding effects seem to have little or no influence.

The only significant deviation from the linear correlation of the figure was observed for those ligands that also form two 6-membered chelate rings. This would at first seem difficult to understand since the size of the ring is generally recognized as an entropy effect, and should have no influence on charge transfer in σ-coordinate bonding between the ligand and cobalt(II). On the other hand, it is noted that the increase in the formal charge on the cobalt atom that occurs on oxygenation reduces the size of the metal center. It is now suggested that the donor groups of ligands that form the larger chelate rings cannot as readily adapt to inward movement of the donor groups as the metal center shrinks; thus, these groups are not as suitably oriented for binding and the coordinate bond energy is reduced. A recent x-ray crystal structure determination of the PYDPT cobalt dioxygen complex[8] is in agreement with this interpretation. Another indication that factors involving chelate ring structure affect oxygenation equilibrium constants may be seen in the oxygenation constant of the 2:1 complex of 2,3-diaminopropanoic acid and cobalt(II),[3,4] which is well below the value predicted by the correlation presented in this paper. Thus it seems that branched-chain ligands may also have steric barriers to effective coordination, and should be treated separately. Therefore, in applying the correlation given in this paper to the prediction of log K_{O_2} it is essential that the ligand structures not vary substantially in type from the linear multidentate ligands employed in establishing the correlation.

Financial support of The Robert A. Welch Foundation under Grant No. A-259 is gratefully acknowledged.

REFERENCES

1. G. McLendon and A. E. Martell, *Coord. Chem. Rev.*, **19**, 1 (1976).
2. G. McLendon and A. E. Martell, *J. Chem. Soc., Chem. Commun.*, 223 (1975).
3. T. S. Kee and H. K. J. Powell, *J. Chem. Soc., Dalton*, 2023 (1975).
4. M. Gold and H. K. J. Powell, *J. Chem. Soc., Dalton*, 1418 (1976).
5. D. H. Huchital and A. E. Martell, *Inorg. Chem.*, **13**, 2966 (1974).
6. W. R. Harris, I. Murase, J. H. Timmons and A. E. Martell, *Inorg. Chem.*, in press.
7. J. H. Timmons, A. E. Martell, W. R. Harris, and I. Murase, *Inorg. Chem.*, **17**, 889 (1978).
8. J. H. Timmons, A. E. Martell, R. H. Niswander and A. Clearfield, *Inorg. Chem.*, in press.