Stabilities of Binuclear Cobalt Oxygen Adducts: A Linear Free Energy Relationship

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Summary Equilibrium data for a number of dibridged μ-peroxo-μ-hydroxo-cobalt oxygen carriers are reported; the logarithm of the stability constant of the oxygen adduct bears a linear relationship to the sum of the p*K*'s of the ligand(s) co-ordinated to the cobalt(II) ion.

Recently there has been considerable interest in the structure and properties of transition-metal complexes containing co-ordinated dioxygen.[1–10] The simplest model compounds of biological relevance are the binuclear cobalt complexes.[2,3] While considerable work has been done using these complexes, particularly in determining equilibrium,[3–7] and kinetic[1,7,10] parameters there has not been any systematic treatment of the factors governing these properties.

We now report a linear free energy relationship which offers a quantitative correlation between ligand basicity of the cobalt(II) polyamines, and their affinity for oxygen.

Equilibrium constants were determined by potentiometric titrations and are reported for the oxygenation reaction involving cobaltous chelates of the following ligands: *NN*-bis(2-aminoethyl)glycine (S-DTMA), diethylenetriamine-*N*-acetic acid (U-DTMA), tris(2-aminoethyl)amine (TREN), ethylenediamine-*NN'*-diacetic acid (S-EDDA), and ethylenediamine-*NN*-diacetic acid (U-EDDA) (Table). The correlation between ligand basicity and oxygen affinity is shown in the Figure.

$K_{O_2} = [MLO_2ML]/[ML]^2[O_2]$ for the μ-peroxo monobridged species

$K_{O_2} = [MLO_2OHML][H^+]/[ML]^2[O_2]$ for the μ-peroxo-μ-hydroxo dibridged species

Previous attempts have been made,[7,12] to correlate properties of cobalt dioxygen complexes with the number of nitrogen donor groups in the co-ordination sphere, without significant success. Stynes *et al.*[13] have attempted to correlate oxygen affinity with basicity of the axial ligand for some mononuclear cobalt dioxygen complexes (holding the equatorial ligands constant). These attempts seem more successful, but are still controversial.[14]

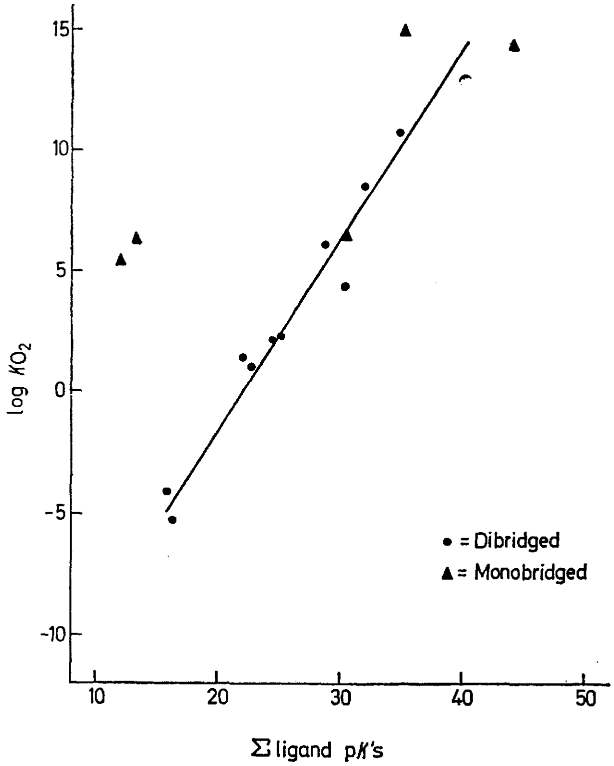

FIGURE. Correlation of log K_{O_2} with the sum of the log protonation constants of the ligands. K_{O_2} is the equilibrium constant for the combination of oxygen with the completely formed cobalt(II) single ligand or mixed ligand complex.

Using the relationship given in the Figure, the tendencies of cobalt complexes to combine with molecular oxygen can be predicted. Using $\log K_{O_2} = 0{\cdot}85,\ \Sigma\ \mathrm{p}K - 19$, it is possible to calculate the approximate stabilities of the dioxygen complexes for those cobalt(II) complexes not previously investigated provided that they meet the requirements of the complexes for which the relationship holds, *i.e.* that the basic donor groups of the ligands satisfy no more than four co-ordination positions of the cobalt(II) atom. The use of the formation constants of the cobalt(II) complexes in the absence of oxygen (Table) makes possible the calculation of the degree of oxygenation over any reasonable range of concentration and pH. It is especially interesting that the Figure correlates stabilities of cobalt dioxygen complexes for two ligands which on the basis of previously stated principles would not have been predicted to form dioxygen complexes. Thus the symmetrical and unsymmetrical ethylenediaminediacetic acids form quite stable dioxygen complexes in an appropriate pH range, even though they contain two basic nitrogen atoms, rather than the three that have previously been claimed as necessary.

The present work, together with the recent availability of additional new equilibrium data for the binuclear cobalt dioxygen systems, makes possible a more quantitative treatment for these systems.

TABLE

Correlation of stabilities of dioxygen complexes of cobalt with basicities of ligands[a]

Ligand	Σ pK_a[b]	Log K_{MLx}	Log K_{O_2}	Reference
Dibridged (monohydroxo) species				
SEDDA	16·2	11·2	−4·1	present work
UEDDA	16·7	11·6	−5·3	,,
SDTMA	25·3	12·3	2·3	,,
UDTMA	24·6	12·1	2·4	,,
DIEN[c]	23·2	8·2	1·1	5, 7
TRIEN[c]	28·7	10·4	6·1	3, 14a
TREN	30·5	12·3	4·4	present work
EN[c,d]	35	10·7	10·8	5, 6
Histamine[d]	32	9·0	8·5	7, 6
HEDIEN[c,d]	22·5	7·9	1·5	present work
Monobridged species				
TEP[c]	34·6	13·2	15	5
DGENTA[c]	44	8·5[e]	14·5	4
TRPY(PHEN)[c]	~13	6·53[f]	6·3	11
TRPY(BIPY)[c]	~12	5·38[f]	5·4	11
Histidine[d]	30·4	13·9	6·6	6, 6

[a] *All measurements made at* 25 ± 0·1 °C *and ionic strength of* 0·10 adjusted with KNO_3. [b] Σ pK_a is summation of pK's of all donor groups of ligands coordinated to cobalt(II) ion [c] DIEN = diethylenetriamine, TRIEN = triethylenetetramine, EN = ethylenediamine, HEDIEN = *N*-2(hydroxyethyl)ethylenediamine, TEP = tetraethylenepentamine, DGENTA = diglycylethylenediaminetetraacetic acid, TRPY = terpyridyl, BIPY = bipyridyl, PHEN = *o*-phenanthroline, other abbreviations defined in the text. [d] Data given are for 2:1 complexes. [e] Recalculated from Ref. 13 for $K_{O_2} = [MLH_{-2}O_2MLH_{-2}]/[MLH_{-2}]^2[O_2]$, assuming stepwise amide deprotonation, pK_1 *ca.* 12, pK_2 *ca.* 14. [f] For reaction for $Co(TRPY)^{2+}$ with second ligand.

In the oxygenation reaction, the dioxygen portion donates an electron into the appropriate Co *d* orbitals while the metal centre is thought to π-donate an electron from the d_{O_2} orbital[1,15] into the π^* orbital of electrophilic molecular oxygen, thus forming a complex. The ease of this electron transfer should depend on the available electron density at the central metal. But this density is greatly affected by the electron donor properties of the ligands in the co-ordination sphere; as the ligand basicity increases, its electron donating ability also increases, facilitating such a transfer.

It may also be that the nature of the ligand field on increasing the basicity narrows the energy between the metal donor orbital and the π^* orbital of O_2. Because of the low symmetry of the complexes treated here, ligand field calculations designed to test this hypothesis are not readily carried out.

For the monobridged (μ-peroxo) species, insufficient data is available to permit an analysis of the effect of ligand basicity on oxygen adduct stability, although such a correlation would be of interest, since any effects due to the olation reaction found in the dibridged oxygen carriers would be absent.

It may be noted that the stability of the mixed ligand pyridyl systems appears much higher than the ligand basicity might warrant. Such anomalous behaviour would be expected on the basis of the above arguments, since the strong π character of these ligands is absent from the other ligands considered, and might be expected to interact with and strongly influence the ordering of electronic energy levels, thus enhancing the stability of the complex.

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