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STABILITY AND REACTIVITY OF A BINUCLEAR μ-PEROXO COBALT(III) CHELATE

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Cobalt(II), when coordinated to at least three N donor groups, will bind molecular oxygen in aqueous solution irrespective of other ligands present. This rule [1] has proved to be very useful in studying the oxygen carrier properties of hexacoordinated cobalt(II) complexes with polyamines, carboxylate groups, NH_3 and H_2O as ligands. In all cases studied so far, a binuclear O_2 bridged complex is formed (1). If CoL_6 contains less than 3 N donors, for example

$$2\,CoL_6 + O_2 \rightleftharpoons L_5CoO_2CoL_5 + 2\,L \qquad (1)$$

in Co(edda) [2], O_2 uptake is incomplete and observed only above pH 11. In the case of $Co(edta)^{2-}$ slow oxidation to Co^{III} takes place, but the chelate is non reactive in the sense of adding O_2 reversibly and forming the binuclear O_2 adduct in appreciable amounts [3].

The primarily formed complex may undergo various further reactions:

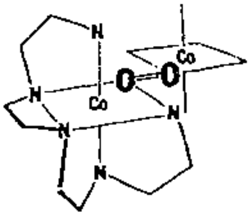
(i) If some of the coordinated groups L are labile, notably if L = H_2O, depending on pH an additional OH bridge will be formed (2).

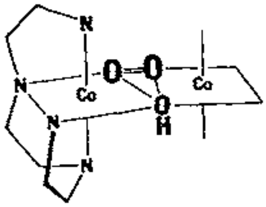
$$(H_2O)L_4CoO_2CoL_4(H_2O) \rightarrow L_4Co\genfrac{}{}{0pt}{}{O_2}{OH}CoL_4 + H_3O^+ \qquad (2)$$

(ii) Eventually every O_2 adduct will decompose to mononuclear Co^{III}. The mechanism of the latter reaction is not clear yet. There is not much evidence for a simple dissociation of the cobalt peroxide bond and formation of H_2O_2 [4]. A mechanism in which a homolytic dissociation of the peroxide is the first step must also be considered.

The stability of the binuclear O_2 adduct, as measured by equilibrium (1) and the rate of decomposition (ii), depends strongly on the coordination sphere of the metal. Roughly speaking, it parallels the number of N donors, for example, the uptake of O_2 by tetraethylene pentamine cobalt(II) according to (1) is complete even in strongly diluted neutral or slightly alkaline solution. The breakdown into mononuclear Co^{III} is slow, $t_{1/2}$ being in the range of 10^6 s (20°) [5]. From kinetic measurements we estimated the equilibrium constant (1) for the binuclear O_2 adduct formed by 1,7-bis-(2-pyridylmethyl)-diethylenetriamine cobalt(II): $K(O_2) = 10^{12}\ M^{-2}$ [6]. On the other hand the reaction of diethylenetriamine cobalt(II) with O_2 is incomplete and leads to adducts which decompose about a 100 times faster.

An additional OH bridge further stabilizes the adduct [7]. Cobalt(II) chelates of tetradentate amines, such as triethylenetetramine [8] or 1,6-bis-(4-imidazolyl)-2,5-diazahexane [9], form the most stable double bridged O_2 complexes known. The additionally OH bridged O_2 complex of the former decomposes with $t_{1/2} \approx 10^7$ s. Besides ligand field strength there are obviously steric effects which govern the kinetic stability of the complexes: In the case of tetraethylene pentamine cobalt(II) reacting with O_2, four different chelate configurations are possible, two of which have been found to exist. From these two the monobridged O_2 complex with α chelate configuration is markedly more stable [5] (I). In the case of triethylenetetramine cobalt(II), two of the possible isomers, in which the four N donors are non planar, have been isolated as perchlorates in pure form [10], the β configuration (II) being the more stable.



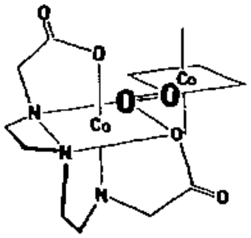


Since we know little yet about the reactivity of μ-peroxo-dicobalt(III) chelates, we began some studies with O_2 adducts which led us to expect high reactivity. From previous experiments [1] low stability can be expected when the coordination sphere contains only 3 N donors, e.g. with diethylenetriamine. However, cobalt(II) chelates of the latter ligand react with O_2 in a complex manner. Depending on pH and concentrations several different O_2 adducts are formed [11], which makes it difficult to relate structure and reactivity. We therefore synthesized a quinquedentate derivative of diethylenetriamine: diethylenetriamine-1,7-diacetic acid (dtda) [12]. The quinquedentate ligand can be isolated as its trihydrobromide. Its pK_a values are: < 1, 2.60, 4.45, 8.60, 9.55 (25°, 0.1 M KNO_3).

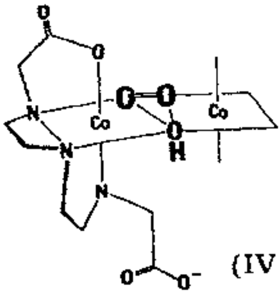
In dilute solutions of dtda and Co^{2+} below pH 10, Co(dtda) is found to be the only chelate species formed. From titration experiments we determined $\log K = 13.4$. The reaction of Co(dtda) with O_2 in aqueous solution has been studied at concentrations between 10^{-4} M and 10^{-3} M. In the pH range 6—9 Co(dtda) will add O_2 in a fast reaction [13], replacing H_2O in the hexacoordinated complex (3). The primary spectrophotometrically determinable species

$$2[Co(dtda)(H_2O)] + O_2 \rightleftharpoons [(dtda)CoO_2Co(dtda)] + 2\,H_2O \qquad (3)$$

is a binuclear O_2 bridged complex [14] with zero charge: $[(dtda)CoO_2Co(dtda)]$. The schematic drawing (Struture III) shows the chelate configuration believed to be the most stable. Complex (III) has a strong charge transfer band at 405 nm ($\epsilon = 1.1 \cdot 10^4$). In air saturated solutions ($[O_2] = 2.85 \cdot 10^{-4}$ at 20°) (3) is incomplete and from measurements of the decreasing $[O_2]$ during forma-



(III)



(IV)

tion of (III) an equilibrium constant $K(O_2) = 4.1(\pm\ 0.3)\cdot 10^6\ M^{-2}$ (20°) can be determined (4). Comparing this constant with the figure of

$$K(O_2) = \frac{[(\mathrm{dtda})\mathrm{CoO_2Co}(\mathrm{dtda})]}{[\mathrm{Co}(\mathrm{dtda})]^2\cdot[O_2]} \tag{4}$$

$10^{12}\ M^{-2}$ given in the introduction for an O_2 adduct of the same type but with a quinquedentate amine, (III) must be considered as being of relatively low stability. Table 1 gives further data for comparison cited from the literature. Among the many O_2 complexes now known our system is outstanding in that, at high pH it also forms a double bridged species. Oxygenation at pH > 8 leads to the same absorption spectrum with a maximum at 405 nm first. Subsequently (III) transforms

$$(\mathrm{dtda})\mathrm{CoO_2Co}(\mathrm{dtda}) + H_2O \rightarrow (\mathrm{dtda})\mathrm{Co}_{\mathrm{OH}}^{\mathrm{O_2}}\mathrm{Co}(\mathrm{dtda})^- + H^+ \tag{5}$$

to (IV). The reaction can be followed either spectrophotometrically (a band at 365 nm appears) or using a pH stat which shows release of protons according to (5). The reason why, in this case, both types of complexes can exist, lies undoubtably in the labile nature of the carboxylate–cobalt bond, which leads to an equilibrium with a partially dissociated chelate.

The oxygenation reaction is reversible in the sense that redissociation into cobalt(II) and molecular oxygen can be brought about either by bubbling N_2 through the solution, by acidification to about pH 2, or by adding edta to a neutral solution. However the two complexes, (III) and (IV), differ in reversibility.

TABLE 1

$\mathrm{CoL_5}$	$K(O_2)$	Notes
Co(dtda)	$4.1\ \cdot 10^6$	By O_2 uptake measurements
$\mathrm{Co(bpdt)^{2+}}$ [15]	10^{12}	By kinetic measurements
$\mathrm{Co(dien)_2^{2+}}$	$3.0\ \cdot 10^8$	Wilkins et al. [17]
$\mathrm{Co(L\text{-}histidine)_2}$	$7.2\ \cdot 10^6$	Wilkins et al. [18]
$\mathrm{Co(tpy)(phen)^{2+}}$ [16]	$7.06\cdot 10^6$	By pH measurements, Martell et al. [19]

Acidifying a solution of the monobridged complex (III) to pH 2 only yields about 70% of the oxygen bonded to cobalt. Astonishingly the double bridged complex (IV), formed at high pH, is a "better" oxygen carrier. Shifting the pH to 2, deoxygenation is practically complete, as precisely as it can be measured by the oxygen electrode. The sequence of reaction steps taking place after adding acid to a neutral solution of (III) has not been completely analysed yet. Stopped flow experiments reveal an initial fast step with $t_{1/2}$ smaller than 10 ms. Quantitative evaluation of the spectral changes observed, makes it clear that a protonation reaction with $pK_a \approx 4$ takes place.

The rate of O_2 release, as measured by the O_2 electrode, is first order in complex (III) and varies only slightly with pH. $k = 3 \cdot 10^{-3}\ s^{-1}$ (6°) [20]. k approaches a limiting value of $9 \cdot 10^{-3}\ s^{-1}$ above pH 5, which is in good agreement with the results of edta experiments. Since the spectral changes, observed after the fast protonation step, are about 10 times faster than $d[O_2]/dt$ it must be concluded that dissociation of the complex proceeds in at least two steps. The site of protonation of the fully chelated complex must necessarily be the peroxide group (6). Under the influence of the positive charge,

$$(\mathrm{dtda})\mathrm{CoO_2Co}(\mathrm{dtda}) + \mathrm{H^+} \rightleftharpoons (\mathrm{dtda})\mathrm{Co}(\mathrm{O_2H})\mathrm{Co}(\mathrm{dtda})^+ \qquad (6)$$

rearrangement of the peroxide group takes place, which in turn may lead to dissociation of an acetate and an amino group. By then the bond between metal and oxygen is sufficiently weakened and the whole complex falls apart.

In neutral solution complex (III) decomposes into mononuclear $\mathrm{Co}(\mathrm{dtda})^+$. From spectrophotometric measurements a half life time of $2.5 \cdot 10^3$ s (20°) can be estimated. The resulting spectrum is characteristic of a mononuclear cobalt(III) chelate. Its identity has been proved by isolation of a crystalline solid which analyses for $[\mathrm{Co}(\mathrm{dtda})(\mathrm{H_2O})]\mathrm{ClO_4}$. The chelate configuration is not certain yet. From the IR spectrum we suspect that the configuration is α, (III). Since the reaction is carried out under mild conditions, one might also assume predominately α configuration for the oxygen adduct III.

The reaction mechanism is not yet clear. Simple decomposition into cobalt(III) fragments by uptake of H^+ and production of H_2O_2 (7)

$$(\mathrm{dtda})\mathrm{CoO_2Co}(\mathrm{dtda}) + 2\,\mathrm{H^+} \rightarrow 2\,\mathrm{Co}(\mathrm{dtda})^+ + \mathrm{H_2O_2} \qquad (7)$$

has not been demonstrated clearly. Other mechanisms, e.g. homonuclear dissociation of the peroxide bond and intermediate formation of radicals (dtda)CoO must also be considered. A comparison of the above half life time of (III) with data of other systems again reveals a relatively low kinetic stability. $\alpha(\mathrm{tetren})\mathrm{CoO_2Co}(\mathrm{tetren})^{4+}$ [5] decomposes with $t_{1/2} \approx 10^5$ s (25°) and $\beta(\mathrm{trien})\mathrm{Co}^{\mathrm{O_2}}_{\mathrm{OH}}\mathrm{Co}(\mathrm{trien})^{3+}$ [10] is even more stable with $t_{1/2} > 2 \cdot 10^6$ s (25°). As found in previous studies [7], the OH bridge greatly stabilizes the O_2 complex against irreversible decomposition into $\mathrm{Co^{III}}$ fragments. Consequently complex (IV) is much more stable than (III). At pH 10.5 (IV) has a half life time of ca. 10^6 s (25°). From the pH dependence it can be deduced that the rate determining step is the opening of the OH bridge (8). However, (III) does not appear as intermediate because above pH 7 its decomposition is faster than (8).

$$\mathrm{(dtda)Co{}^{O_2}_{OH}Co(dtda)^- + H^+ \rightarrow (dtda)CoO_2Co(dtda) + H_2O} \tag{8}$$

EXPERIMENTAL NOTES

Diethylenetriamine-1,7-diacetic acid (dtda) has been synthesized by tosylating diethylenetriamine and condensing the tritosylate with ethyl bromoacetate [21]. The trihydrobromide of the acid can be crystallized from ethyl ether.

Analysis

Calculated for $C_8H_{20}O_4N_3Br_3$: C, 20.80; H, 4.37; N, 9.12; Br, 52.50. Found: C, 20.79; H, 4.37; N, 9.18; Br, 53.03.

Spectrophotometric measurements were carried out with a Varian Techtron 625. Working solutions were prepared by mixing buffer (borate or 2,6-lutidine 0.1 *M*) and ligand at the desirable pH. After saturation with oxygen (or air) a stock solution of $CoSO_4.7H_2O$ was added. The total $[Co^{2+}]$ was maintained at $2.22 \cdot 10^{-4}$ and the ligand kept 2.5 times in excess. Unless otherwise stated, solutions and cuvettes were thermoregulated at 20°C.

The O_2 uptake was followed by a Beckman Field Lab Oxygen Analyzer, mixing buffer and ligand first in a 15 ml vessel, fitted with a Clark oxygen electrode and a glass electrode. The $CoSO_4$ solution was added through a capillary tube by means of a micrometer syringe. $[Co(dtda)(H_2O)]ClO_4$ has been prepared [22] by dissolving 3.5 g diethylenetriamine-1,7-diacetic acid trihydrobromide in 20 ml H_2O and slowly adding a saturated solution of 1.8 g $Co(ClO_4)_2.6H_2O$, the pH being kept at 6. O_2 was then bubbled through the ice cold solution for 10 min. After allowing it to stand at room temperature for 24 h 1 *N* $HClO_4$ was added slowly until the pH reached 2, followed by 1 g $NaClO_4.H_2O$ and a few drops of glacial acetic acid. Within a few hours red crystals formed which were filtered off and washed with methanol and ethanol. For analysis the strongly hydroscopic product was dried at 0.4 torr for 3 days.

Analysis

Calculated for $CoC_8H_{17}O_9N_3Cl$: C, 24.41; H, 4.40; N, 10.67; Cl, 9.10. Found: C, 25.25; H, 5.20; N, 10.62; Cl, 9.90.

The IR spectrum (Perkin Elmer 125, KBr, disc) shows the typical bands of a coordinated amino acid. The two CO stretching vibrations are at 1635 and 1435 cm^{-1} [23]. The only stretching NH band at low frequency points to α configuration of the diethylenetriamine portion of the molecule. We find 4 CH_2 rocking frequencies [24] at 920, 910, 860 and 830 cm^{-1}. The former two may be assigned to the acetate and the latter to the ethylene groups. The acetate groups can therefore be assumed to be in *cis* position which again implies α configuration as seen in structure (III).

CONCLUSIONS

The reaction of diethylenetriamine-1,7-diacetate cobalt(II) with O_2 in neutral aqueous solution leads to a binuclear adduct: (dtda)CoO_2Co(dtda). Its solution stability has been determined by $[O_2]$ measurements: $K(O_2) = 4.1 \cdot 10^6$ (20°). At pH > 9 a more stable double bridged species is formed: (dtda)$CO^{O_2}_{OH}Co(dtda)^-$. Both complexes slowly decompose into mononuclear cobalt(III) chelates. The former with $t_{1/2} = 2.5 \cdot 10^3$ s (25°) at pH 7 and the latter with $t_{1/2} = 10^6$ s (25°) at pH 10.5. On acidifying its solutions to pH 2, dissociation into Co^{2+} and O_2 takes place.

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