

Dioxygen Uptake by the L-Histidine-Cobalt(II) System

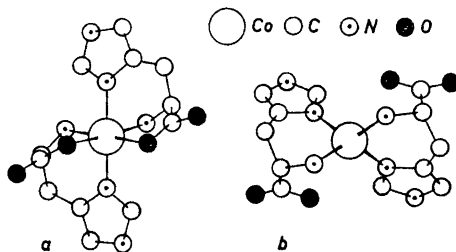
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The dioxygen uptake of aqueous solutions of cobalt(II) and L-histidine has been examined at a pH of 9.3 and in 1 M KOH. The existence of two different dioxygen carrying species at pH=9.3 has been proved. Both of these have a Co:O₂ ratio of 2:1.

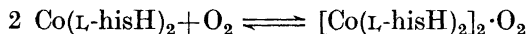
It is known that cobalt(II) and L-histidine form two 1:2 complexes in aqueous solution, the pink Co(L-hisH)₂* in the pH interval 7-10,^{1,2} and the blue Co(L-his)₂²⁻ at pH >12.² The interconversion of the two complexes on variation of pH is reversible. The probable² structures are shown in Fig. 1.

Fig. 1. a: The pink, hexacoordinated Co(L-hisH)₂; the carboxyl groups are deprotonated. b: The blue, tetracoordinated Co(L-his)₂²⁻; the carboxyl groups and the nitrogen atoms in the imidazole rings are deprotonated.



Both of these complexes react with dioxygen yielding species with an intense, amber colour originating in strong charge-transfer-like absorption bands in the near UV.

The octahedral Co(L-hisH)₂ was one of the synthetic dioxygen carriers first discovered;¹ it is found to take up and release dioxygen according to



The detailed structure of [Co(L-hisH)₂]₂·O₂ is not known but it almost certainly³ contains a Co-O-O-Co linkage.

* L-hisH₂ ≡ L-histidine.

McDonald and Phillips² observed that also the blue complex Co(L-his)_3^{2-} turned amber in air, and the question was brought up, if the two oxygenated species were identical or not. The aim of this work was to settle this point.

EXPERIMENTAL

In general. 1 M KOH has been used as the solvent medium for the examinations of Co(L-his)_3^{2-} and 10 % in excess of the stoichiometric amount of Co(OH)_2 added to prevent precipitation of Co(OH)_2 .

All titration experiments cited were performed in a thermostated room at $20.0 \pm 0.5^\circ\text{C}$.

Apparatus. To enable one to control the dioxygen activity the experiments were performed by means of the apparatus diagrammatically drawn in Fig. 2. It consists of glass burets with PTFE pistons ("Metrohm", Switzerland) in a number and of sizes adequate for the experiment in question. In the set up shown four burets, A, B, C, and R, are interconnected by capillaries with spherical joints; each buret has a three-way stopcock with a V-bore key. It is possible to flush the equipment or part of it with O_2 -free N_2 . Known volumes from either buret may be transferred to the reaction chamber, R, or from R to a spectrophotometric cell ("Cary", variable path length, UV, flow cell)

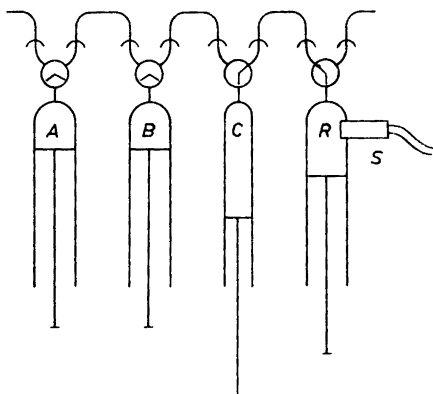


Fig. 2. Schematic drawing of the burets A, B, C, and R. S is the Clark sensor.

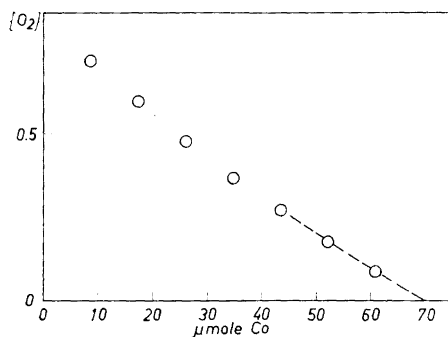


Fig. 3. Titration of $34.0 \mu\text{mole O}_2$ in 1 M KOH by Co(L-hisH)_2 . \circ : Experimental points.

without disturbance from the atmosphere. The pistons are operated by turning dial drums, and the graduation of the drums are such, that one division corresponds to one thousandth of the buret capacity. R is provided with a magnetic stirrer.

The dioxygen activity, $\{O_2\}$, in R is measured amperometrically by a Clark dioxygen sensor ("Radiometer", Copenhagen);⁴ after amplification the current signal from the sensor is read on a potentiometric recorder. The sensitivity of the sensor used is 1.9×10^{-7} A per unit of $\{O_2\}$ and in the range used for the titrations this corresponds to 15 cm pen deflection per unit of $\{O_2\}$.

It is emphasized that the membrane-covered sensor measures $\{O_2\}$ and not directly the dioxygen concentration. This is to have in mind when the solubility of O_2 changes, e.g. during a titration. We define $\{O_2\}$ to equal unity in a liquid, which is in equilibrium with pure O_2 -gas of 1 atm pressure.

Experiments. The experimental facts, which form the immediate basis of the present report are the following:

a. Titrations. In order to determine the stoichiometry of the oxygenation of the blue complex 45 ml 1 M KOH of a known O_2 content was titrated with 8 ml 10^{-2} M $Co(L-hisH)_2$. The titrand was made up in R by mixing 25 ml O_2 -saturated (1 atm, $20.0^\circ C$) H_2O from A and 20 ml O_2 -free KOH solution from B. The O_2 -free titrator was prepared from $CoCl_2 \cdot 6H_2O$, L-histidine, and H_2O , and drawn into the 10 ml buret, C. The intercepts of the extrapolated curves on the horizontal axis for three separate runs gave $Co:O_2$ values of 1.97, 2.05, and 2.06. Each titration was performed within 20 min; see Fig. 3.

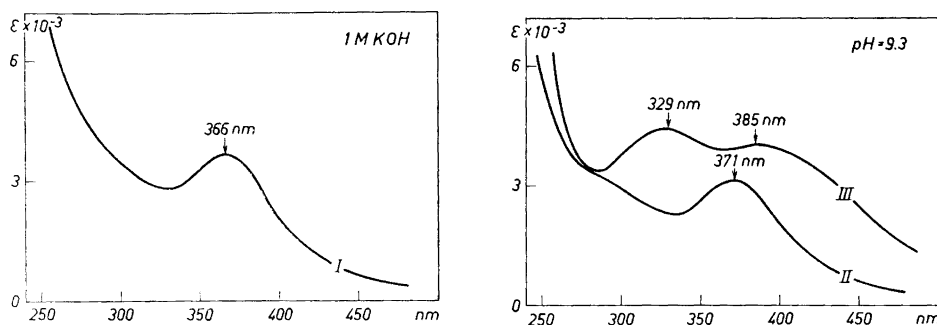


Fig. 4. Absorption spectra. I: X in 1 M KOH. II: X in the $KOH-H_3BO_3$ buffer solution at $pH=9.3$ but formed in 1 M KOH. III: $[Co(L-hisH)_2]_2 \cdot O_2$ in the $KOH-H_3BO_3$ buffer at $pH=9.3$ and formed in that medium. ϵ is given in $\text{mole}^{-1} \cdot \text{liter} \cdot \text{cm}^{-1}$ on the basis of Co formality.

b. Absorption spectrum of oxygenated $Co(L-his)_2^{2-}$ in 1 M KOH, *i.e.* of the final solution from a titration as under a. Spectrum I, Fig. 4. The same spectrum is found, when an O_2 -free, blue solution of $Co(L-his)_2^{2-}$ in 1 M KOH is brought in equilibrium with the air.

c. Spectrum of the final solution of a titration as under a with solid H_3BO_3 added after oxygenation so that pH is lowered to 9.3. II, Fig. 4.

d. Spectrum of a solution of $Co(L-hisH)_2$ in the $KOH-H_3BO_3$ buffer, oxygenated at $pH=9.3$. This is the known^{1,5} spectrum of $[Co(L-hisH)_2]_2 \cdot O_2$. III, Fig. 4.

e. Spectrum of a solution of $[Co(L-hisH)_2]_2 \cdot O_2$ with KOH added after oxygenation so that the medium became 1 M with respect to KOH. The result was a spectrum identical with I, Fig. 4.

f. On addition of O_2 -free hydrochloric acid to the final solution of a titration as under a a decolorization accompanied by a rapid increase in $\{O_2\}$ was observed when pH reached ~ 5 . Qualitatively it is estimated that essentially all the coordinated dioxygen is released on acidification.

Additional observations. The spectrum I in 1 M KOH is remarkably stable in time. Repeated records after several hours showed no change. Contrary to this the peaks of II and III at $pH=9.3$ slowly decrease on standing.

$Co(L-his)_2^{2-}$ has a higher affinity to O_2 than $Co(L-hisH)_2$. As a consequence the equivalence point could be obtained by the simple extrapolation of the titration curve to zero $\{O_2\}$, as in Fig. 3.

Materials. L-Histidine from Fluka AG ("puriss. CHR") was used. Other chemicals were reagent grade.

DISCUSSION

It is concluded that two different oxygenated species can be formed on oxygenation of the Cobalt(II)-L-histidine system in aqueous solution.

One of these dioxygen carriers is the already known¹ $[\text{Co}(\text{L-hisH})_2]_2 \cdot \text{O}_2$ with the spectrum III; and the experiments support the hypothesis, that the other form, X, showing the spectrum II, has the same stoichiometric composition, and that the difference between the two dioxygen carriers stems from the orientation of the O—O unit. The shift of peak maximum between spectrum I and II is provisionally thought to be an effect of protonization.

X is formed either by direct oxygenation of the blue $\text{Co}(\text{L-his})_2^{2-}$ in strongly alkaline medium (*e.g.* 1 M KOH) or by adding strong base (*e.g.* KOH) to an oxygenated solution of the pink $\text{Co}(\text{L-hisH})_2$.

Judged by the absorption spectrum, X is stable for days in 1 M KOH, whereas it slowly decomposes in neutral solution, probably due to irreversible oxidation.

Isolation of the two dioxygen carriers in crystalline form is to be attempted.

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