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Studies on Dinuclear Histidinatocobalt(III) Complexes Containing Peroxo and Superoxo Bridges

SVEN BAGGER and KEITH GIBSON

Chemistry Department A, Building 207, The Technical University of Denmark, DK-2800 Lyngby, Denmark

A group of closely related dinuclear histidinatocobalt(III) complexes containing peroxo and superoxo bridges has been studied. Absorption, circular dichroism, and infrared solution spectra have been measured. An elucidation of structural features is attempted.

In a previous study of dioxygen uptake by the aqueous L-histidine/cobalt(II) system [1] it was found that in addition to the fairly well-characterized reversible dioxygen carrier μ-peroxo-bis{bis(L-histidinato)cobalt(III)} a second μ-peroxo-cobalt(III) complex was formed at high pH. These two species exemplify compounds which in the present paper have been termed "type I" and "type II", respectively. We have continued the investigation of these two complexes and have studied some related μ-peroxo species and all the corresponding μ-superoxo derivatives. Table 1 gives a summary of the complexes under study together with a description of the terminology used.

Two recent reviews [2,3] give a survey of literature pertinent to the present work.

EXPERIMENTAL

Materials. L- and DL-Histidine (*purissimum*, chromatographic purity) were obtained from Fluka. All other chemicals were of analytical grade.

Apparatus. Absorption spectra were measured with Cary 11 and 14 recording spectrophotometers. When necessary the sample compartment was thermostated by circulation of ice water. CD spectra were obtained using Roussel-Jouan Dichrographes; a model with extended longwave-length region was used * for the CD at 600 – 800 nm. IR spectra were measured with a Beckman IR 20 spectrometer using solution cells with CaF_2 windows and a pathlength of 45 μm. (AgCl windows were not suitable as they were blackened and became nontransparent on contact with solutions of the peroxo complexes.)

[*p-I*(L)] *and* [*p-I*(DL)]. These two peroxo compounds were formed by oxygenation of bis(L-histidinato)cobalt(II) and bis(DL-histidinato)cobalt(II) solutions prepared *in situ* by mixing histidine and cobalt(II) (chloride or nitrate) in mol ratio 2.1 : 1 at pH 9.

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* By courtesy of Dr. Erik Larsen, Chemistry Department I, University of Copenhagen.

Table 1. A survey of the dinuclear cobalt(III) complexes discussed in this paper. Abbreviations are given in the last column. This notation distinguishes type I and type II, denotes the $-O-O-$ bridge as peroxo (p-) or superoxo (s-), and specifies if L- or DL-histidine was used in the preparation. (his = histidinate).

Origin	Characterization			Abbreviation
	Ligating histidine	Dioxygen bridge	Type	
$[Co(L\text{-his})_2] + O_2$	L	Peroxo	I	[p-I(L)]
Oxidized [p-I(L)]	L	Superoxo	I	[s-I(L)]
$[Co(DL\text{-his})_2] + O_2$	rac	Peroxo	I	[p-I(DL)]
Oxidized [p-I(DL)]	rac	Superoxo	I	[s-I(DL)]
$[p\text{-I}(L)] + OH^-$	L	Peroxo	II	[p-II(L)]
Oxidized [p-II(L)]	L	Superoxo	II	[s-II(L)]
$[p\text{-I}(DL)] + OH^-$	rac	Peroxo	II	[p-II(DL)]
Oxidized [p-II(DL)]	rac	Superoxo	II	[s-II(DL)]

These solutions were cooled in an ice-water bath and oxygen was bubbled through for 30 min. The final accurately known concentrations of Co were about 5×10^{-3} M.

The oxygenation equilibrium is described by

$$2Co(his)_2 + O_2 \rightleftharpoons (his)_2CoO_2Co(his)_2$$

with equilibrium constant K. The fraction of total Co oxygenated, x, is given in terms of the total Co concentration, $[Co]_t$, and the O_2 concentration by

$$\frac{x}{2(1-x)^2} = [Co]_t[O_2]K$$

Using literature values [4] of K for [p-I(L)] and O_2 solubility coefficients in pure water [5] a value $x > 0.99$ is obtained under the conditions used ($[O_2] = 2.19 \times 10^{-3}$ M). The K-value for [p-I(DL)] is known to be higher [4] than that for [p-I(L)], so in both cases $x > 0.99$. In view of this discussion ε and $\Delta\varepsilon$ in the spectra were calculated on the basis of 100 % oxygenation and the resulting concentrations of dinuclear complexes.

[p-II(L)] and [p-II(DL)]. These were prepared by making solutions of the corresponding peroxo type I compounds 1 M with respect to NaOH at *ca.* 2°C. The solutions were then warmed to room temperature and the transformation was complete after *ca.* 1 h. To obtain solutions of [p-II(L)] and [p-II(DL)] at pH 9 the basic solutions were cooled in an ice-water bath and 4 M HCl or 4 M HNO_3 was added from a piston buret very slowly and with stirring.

[s-I(L)], [s-I(DL)], [s-II(L)], and [s-II(DL)]. To prepare these superoxo species, solutions of the corresponding peroxo compounds (*ca.* 2.5×10^{-3} M, pH 9) were added slowly and with stirring to equal volumes of solutions of $(NH_4)_2Ce(NO_3)_6$ in 2 M HNO_3. The temperature was kept as near to 0°C as possible. The oxidation yielded green solutions of type I and pink-brown solutions of type II complexes.

From a series of oxidation experiments of this type with [p-I(L)] and [p-II(L)], in which only the concentration of Ce(IV) was varied, the optical density of the 680 nm band maximum of the superoxo complex was found to be linearly dependent on the mol ratio Ce(IV) : peroxo complex when this was < 1 but independent when > 1. The "equiv-

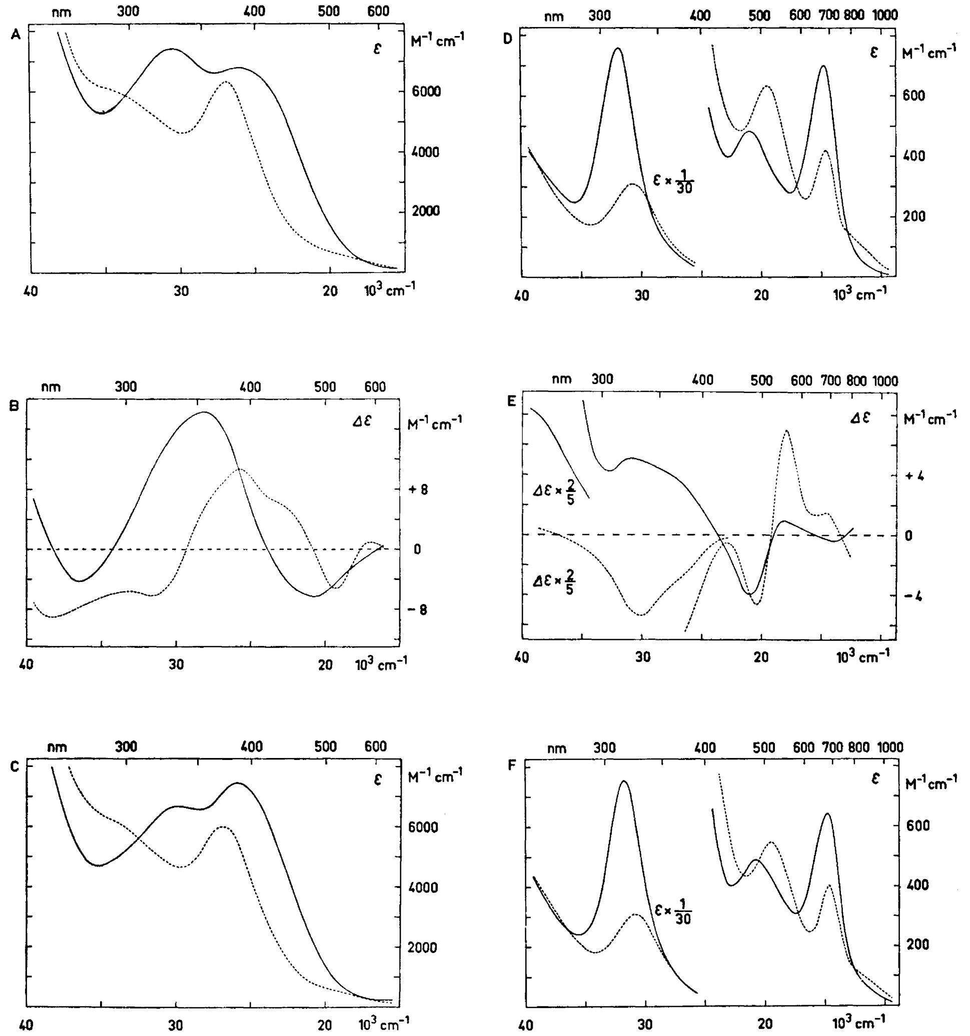


Fig. 1. Absorption and circular dichroism spectra. A and B: ——[p-I(L)], – – –[p-II(L)]. C: ——[p-I(DL)], – – –[p-II(DL)]. D and E: —— [s-I(L)], – – –[s-II(L)]. F: ——[s-I(DL)], – – –[s-II(DL)]. The spectra in A, B, and C were measured at pH 9. For the spectra in D, E, and F, the medium was 1 M HNO_3.

alence point" determined graphically agreed with that expected for a quantitative one-electron reaction within 2 % for the oxidation of [p-I(L)] and within 4 % for the oxidation of [p-II(L)].

The absorption spectra of all four superoxo complexes and the CD spectra of [s-I(L)] and [s-II(L)] were obtained with 10 % excess of Ce(IV). Because Ce(IV) in 1 M HNO_3 absorbs significantly below 450 nm the absorption spectra have been corrected for the excess Ce(IV) present. This correction was never more than 5 % of the total optical

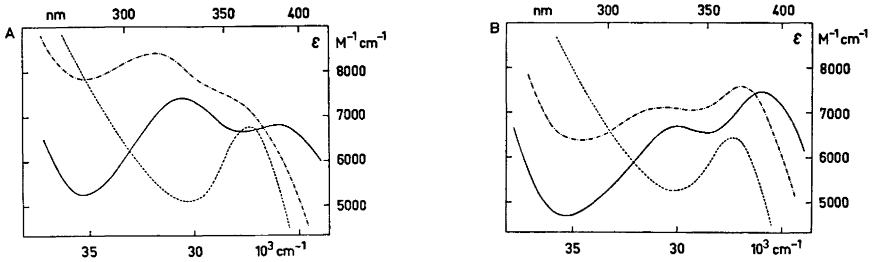


Fig. 2. Changes in absorption spectra on formation of [p-II(L)] from [p-I(L)], and of [p-II(DL)] from [p-I(DL)]. A: ——— [p-I(L)] at pH 9, —·—·—· intermediate species, — — — final [p-II(L)] solution in 1 M NaOH. B: ——— [p-I(DL)] at pH 9, ·—·— intermediate species, — — — final [p-II(DL)] solution in 1 M NaOH. The spectra of the intermediates were recorded within 5 min of addition of base.

density. Since chloride is oxidized by Ce(IV), Co(II) nitrate and HNO_3 were used in the steps preceeding the Ce(IV) oxidation.

Solutions for IR spectra. For the IR studies preparation and handling of solutions had to be modified in some details. D_2O was used as solvent throughout. All operations were carried out at room temperature. The total Co concentration was always *ca.* 7×10^{-2} M. $[Co(his)_2]$ was prepared at pD 9 under N_2 using the stoichiometric ratio of Co and histidine; oxygenation and readjustment of pD to 9 yielded the solutions of [p-I(L)] and [p-I(DL)]. In order to get [p-II(L)] and [p-II(DL)] the latter solutions were made 1 M with respect to OD^- by addition of 40 % NaOD. The spectra were recorded by the double beam technique with D_2O in the reference cell.

RESULTS

The absorption and circular dichroism spectra which were obtained are shown in Fig. 1.

The course of transformation of the peroxo compounds from type I to type II was followed spectrophotometrically at *ca.* 2°C (see Fig. 2). On addition of NaOH to solutions of [p-I(L)] or [p-I(DL)] an intermediate was rapidly formed during the time of mixing. In both cases the final type II spectrum slowly developed from the intermediate during a period of several hours with preservation of an isosbestic point.

$$\text{type I} \xrightleftharpoons{\text{OH}^-} \text{intermediate} \rightarrow \text{type II}$$

The first step was reversible with pH whereas neutralisation of the final type II solutions caused only minor changes in the absorption spectrum as is seen by comparison of Fig. 1 and Fig. 2.

The infrared spectra in Fig. 3 exhibit the region of the antisymmetric stretching frequency of the carboxyl groups in the peroxo bridged complexes. No separate spectrum of the intermediate species described above was observed using our technique at room temperature.

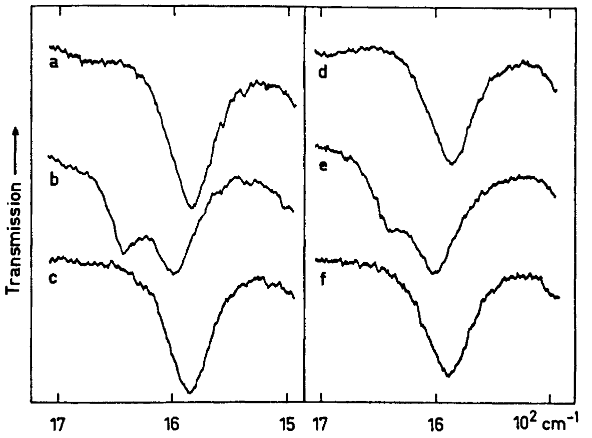


Fig. 3. Infrared spectra in D_2O solution. a: [Co(L-his)$_2$], pD 9. b: [p-I(L)], pD 9. c: [p-II(L)] in 1 M NaOD. d: [Co(DL-his)$_2$], pD 9. e: [p-I(DL)], pD 9. f: [p-II(DL)] in 1 M NaOD.

The type I and type II peroxo complexes at pH 9 responded differently to addition of excess EDTA: [p-I(L)] and [p-I(DL)] decompose rapidly with release of oxygen,[4] whereas [p-II(L)] and [p-II(DL)] loose the brown colour only slowly.

On acidification all the peroxo compounds release oxygen gas with decolourisation.

DISCUSSION

Of the compounds listed in Table 1, [p-I(L)], or μ-peroxo-bis{bis(L-histidinato)cobalt(III)}, is the only one that has been obtained in crystalline form and subjected to elemental analysis.[6] The others, which hitherto have resisted proper isolation, are at present identified mainly by their solution spectra, and some of their properties are deduced from their mode of preparation and by analogy from the chemistry of similar compounds.[2,3] The 1 : 2 O_2 : Co ratio in [p-II(L)], however, has been experimentally verified.[1]

Isomerism of the type I species. Our model for the structure of [p-I(L)], [p-I(DL)], [s-I(L)], and [s-I(DL)] is sketched in Fig. 4b. The $-O-O-$ unit links two cobalt(III) coordination octahedra together and the remaining

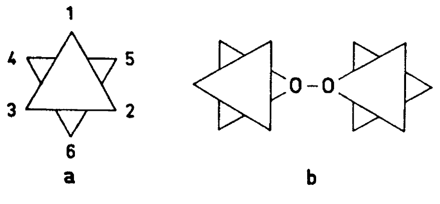


Fig. 4. a: Numbering of the octahedron sites. b: Simplified model for the structure of the monobridged complexes.

Table 2. The nine possible stereomers[7] (I – IX) of $[\mathrm{Co[his)_2}]^+$ are outlined. a, i, and c indicate the amino, the imidazole, and the carboxylate groups of L-histidinate, whereas a′, i′, and c′ are the corresponding groups of D-histidinate. One ligand is always attached to the octahedron sites Nos. 1, 2, and 3, and the other to Nos. 4, 5, and 6. The last row of the table gives the possible stereomeric five-coordinated entities that can be formed by detaching one ligating group in the $[\mathrm{Co(his)_2}]^+$ isomers; the number of the empty octahedron site is given as a subscript to the roman number of the "parent" isomer.

$[\mathrm{Co(his)_2}]^+$ structures		I	II	III	IV	V	VI	VII	VIII	IX
Allocation of groups on octahedron sites	1	a	i	c	c′	i′	a′	c′	i′	a′
	2	c	a	i	a′	c′	i′	a′	c′	i′
	3	i	c	a	i′	a′	c′	i′	a′	c′
	4	a	a	a	a	a	a	i′	i′	i′
	5	i	i	i	i	i	i	a′	a′	a′
	6	c	c	c	c	c	c	c′	c′	c′
5-Coordinate entities		$\mathrm{I_1\ I_2\ I_3}$	$\mathrm{II_1\ II_2}$ $\mathrm{II_3}$	$\mathrm{III_1\ III_2}$ $\mathrm{III_3}$	$\mathrm{IV_1\ IV_2}$ $\mathrm{IV_3}$	$\mathrm{V_1\ V_2\ V_3}$ $\mathrm{V_4\ V_5\ V_6}$	$\mathrm{VI_1\ VI_2}$ $\mathrm{VI_3\ VI_4}$ $\mathrm{VI_5\ VI_6}$	$\mathrm{VII_1\ VII_2}$ $\mathrm{VII_3}$	$\mathrm{VIII_1}$ $\mathrm{VIII_2}$ $\mathrm{VIII_3}$	$\mathrm{IX_1\ IX_2}$ $\mathrm{IX_3}$

five sites on each octahedron are occupied by two tridentate histidinate ligands. One of the six potentially ligating groups must therefore be unbound.

As previously discussed[7] there are nine possible isomers of $[\mathrm{Co(his)_2}]^+$. These are defined in Table 2 together with the various five-coordinated entities that can be derived from each isomer by detachment of one coordinated group. Possible isomers of the type I complexes are obtained by linking pairs of these five-coordinated entities together. An enumeration shows that this procedure yields 45 stereomers of [p-I(L)] and 561 of [p-I(DL)]; counting only diastereomeric five-coordinated entities the result is 45 and 171 dinuclear stereomers, respectively.

Infrared spectroscopic studies (*vide infra*) of [p-I(L)] give evidence for two coordinated and two free carboxylate groups. Taking this into account leaves only 3 LL-entities ($\mathrm{I_2}$, $\mathrm{II_3}$, and $\mathrm{III_1}$ in Table 2) to be considered, yielding 6 possible diastereomers of [p-I(L)].

In the investigation[7] of $[\mathrm{Co(DL\text{-}his)_2}]^+$, formed by air oxidation of the cobalt(II)/*rac*-histidine system,

$$[\mathrm{Co(DL\text{-}his)_2}] \xrightleftharpoons{\mathrm{O_2}} [\mathrm{p\text{-}I(DL)}] \rightarrow [\mathrm{Co(DL\text{-}his)_2}]^+$$

it was shown that the racemic all-*cis*-[Co(D-his)(L-his)]$^+$ complex (enantiomeric structures V and VI, Table 2) accounted for more than 90 % of the isomers present. It is not improbable that the *all-cis* configuration is also predominant in the bridged complex. Assuming *all-cis* configuration and a non-coordinated carboxylate one is left with only two pairs of enantiomeric five-coordinated entities ($\mathrm{V_2}$ and $\mathrm{V_6}$, $\mathrm{VI_3}$ and $\mathrm{VI_6}$) giving rise to 10 stereomers of [p-I(DL)].

The differences between the spectra of [p-I(L)] and [p-I(DL)] must be due to the presence of different mixtures of stereomers in the two cases. Because of the labile equilibrium with cobalt(II) complexes interconversion of the possible stereomers would be expected to be fairly rapid and their separation may not be feasible.

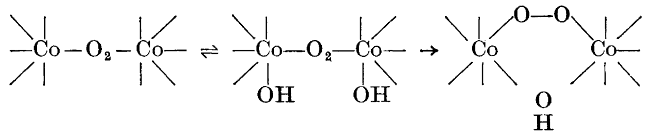
The above discussion on isomerism is equally valid for [s-I(L)] and [s-I(DL)] which are thought to differ from the corresponding peroxo complexes only in the bridging ligand. Moreover the labile pathway for interconversion of isomers is lost, and so separation may be practicable, for instance by chromatography of the acid solutions in the cold.

Infrared studies. An important piece of information about the structure of [p-I(L)] stems from an IR study by Sano and Tanabe,[6] who found that there are two bands to be attributed to the antisymmetric COO stretching vibration in [p-I(L)] whereas only one corresponding band is present in $[Co(his)_2]$. These features are seen in Fig. 3, which gives spectra of both L- and DL-complexes. The interpretation is [6] that the O_2 group in the peroxo complexes has replaced two of the four carboxyl groups.

The spectrum of the mononuclear Co(III) complex, all-*cis*-[Co(D-his)(L-his)]$^+$, prepared as described in Ref. 7, has also been measured. In this case a single band with maximum at 1637 cm^{-1} is observed. This suggests that the higher frequency component in the spectra of [p-I(L)] and [p-I(DL)] can be assigned to carboxyl bound to Co(III) and the lower frequency must be due to the free carboxylate groups.

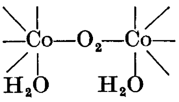
The spectra of [p-II(L)] and [p-II(DL)] show single bands indicating that the difference between the carboxyl groups in the type I complexes has now been removed. The frequencies observed are not compatible with carboxyl bound to Co(III). This is reflected in the structural model proposed below, where all the carboxyl groups are uncoordinated.

The type II compounds. The formation of [p-II(L)] and [p-II(DL)] is furthered by high hydroxyl ion activity.[1] The present experiments showed that the transformation from type I to type II took place in two steps. A suitable hypothesis for the reaction path is



where the two histidinate ligands on each Co are left out. In the first, reversible and rapid step two hydroxyl groups are thought to coordinate, replacing two carboxylate groups; in the second and slow step rearrangements take place and a condensation of the two hydroxyl groups is effected. The μ-peroxo-μ-hydroxo bridge system has been proposed before for [p-II(L)][8] and for the dinuclear cobalt(III) complexes with histamine,[9] ethylenediamine,[9] and triethylenetetramine [10,11] as ligands. In the latter case it was observed that addition of EDTA did not cause breakdown of the structure [11] and this is in accordance with our results for [p-II(L)] and [p-II(DL)]. In addition, preliminary experiments have shown that Ce(IV) oxidation of μ-hydroxo-μ-peroxo-bis{triethylenetetraminecobalt(III)} gives solutions with absorption spectra very similar to those of [s-II(L)] and [s-II(DL)].

A possible structure for the type II superoxo complexes, existing only in strongly acid solution, is



Concurrent with the oxidation of the peroxo complex by Ce(IV) in strong HNO_3 a cleavage of the hydroxo bridge is likely to occur by reaction with protons.[3]

Absorption and circular dichroism spectra. The absorption spectra of all the peroxo complexes are dominated by strong bands in the near ultraviolet which are probably due to charge transfer between the peroxo group and cobalt(III). Although the cobalt(III) *d-d* bands are masked in the absorption spectra they clearly manifest themselves in the visible circular dichroism.

The charge transfer bands in the superoxo complexes are less broad and thus in these cases the *d-d* transitions are observable at around 500 nm. The characteristic feature of these spectra is, however, the distinct band at around 680 nm. Various interpretations[12–15] of this long-wavelength band in other μ-superoxo cobalt(III) complexes have been put forward, of which the suggestion[15] that it arises from an ordinarily spin-forbidden *d-d* transition seems apt. This idea may be elaborated a little. Due to presence of an odd, delocalized electron on the $Co-O_2-Co$ unit[3] a singlet → triplet cobalt(III) transition may take place with conservation of total spin.[16] The transition

$$Co^{3+}\ (S=0) \rightarrow Co^{3+}\ (S=1)$$

is forbidden but

$$Co^{3+}\ (S=0)+\text{electron}\ (S=\tfrac{1}{2}) \rightarrow Co^{3+}(S=1)+\text{electron}\ (S=\tfrac{1}{2})$$

would be allowed because of spin-spin coupling. The presence of the unpaired, delocalized electron in [s-I(*L*)] has been ascertained by EPR spectroscopy.[17]

The hypothesis also explains why the long-wavelength band is not present in the diamagnetic peroxo complexes. The CD spectra of the band in [s-I(L)] and [s-II(L)] reveal a considerable rotational strength, which is consistent with a *d-d* transition.

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