Spectrochemical Study of Microscopic Crystals. III. The Dichroisms of μ-Peroxo-Dicobalt Compounds

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It has been known since long ago that compounds containing the atoms of the same element in different valency states often show extraordinarily deep colors. Although the phenomena have attracted the attention of many investigators, and speculative views were also proposed on the phenomena,(1), (2) no direct research, based upon the absorption spectra of those compounds in the crystalline state, has ever been reported.

This work was initiated to clarify the above phenomena with the aid of their absorption spectra and further to investigate the nature of the chemical linkages in these compounds. For this purpose decammine-μ-peroxo-dicobalt compounds were selected. These compounds, which have two metal atoms of the same element combined through a peroxy radical, present an adequate model for those more complicated compounds in which would exist the above supposed mutual interaction between two metal atoms through a negative ion.

In the present work the dichroisms of decammine-μ-peroxo-cobalt (III)-cobalt (IV) nitrate and of decammine-μ-peroxo-dicobalt (III) nitrate dihydrate have been measured, and the results obtained from the above measurements have been discussed.

Experimental

Materials. (1) **Decammine-μ-peroxo-cobalt (III)-cobalt (IV) nitrate, $[(NH_3)_5Co\text{-}O_2\text{-}Co(NH_3)_5](NO_3)_5$.**—This compound was prepared as dark green acicular crystals according to the direction of Werner and Mylius.(3) The crystals exhibit a

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(1) See, for examples, E. H. Riesenfeld, "Lehrbuch der anorganischen Chemie," Rascher Verlag, Zürich, Switzerland, 1943, p. 573; H. J. Emeléus and J. S. Anderson, "Modern Aspects of Inorganic Chemistry," George Routledge and Sons, Ltd., London, England, 1940, p. 139.

(2) J. Whitney and N. Davidson, *J. Am. Chem. Soc.*, **69**, 2076 (1947); H. McConnell and N. Davidson, ibid., **72**, 3168 (1950), etc.

(3) A. Werner and A. Mylius, *Z. anorg. Chem.*, **16**, 245 (1898).

remarkable dichroism, i. e., they appear pale brownish yellow by polarized light with electric vector parallel to the direction of elongation and indigo blue by that perpendicular to the above. Acidic aqueous solutions of the compound, which appear dark blue, are comparatively stable, while neutral or alkaline solutions spontaneously decompose. The dichroism measurement of the crystal was made in the prism face.

(2) **Decammine-μ-peroxo-dicobalt (III) nitrate dihydrate, $[(NH_3)_5Co\text{-}O_2\text{-}Co(NH_3)_5](NO_3)_4 \cdot 2H_2O$.**—Dark greenish brown crystals were prepared by the method of Werner and Mylius.(3) These show a marked dichroism, i. e., brown by polarized light with electric vector parallel to the direction of elongation of the crystal, and bluish green by that perpendicular to the above. This compound is so unstable in aqueous solutions, acidic,(4) neutral or alkaline, that the absorption spectrum in solution could not be measured.

Measurements.—Quantitative dichroism measurements of the crystals were performed by the microscopic method(5) in the region covering 7500 to 2300 A. The //- or ⊥-absorption in the figures denotes, respectively, absorption with electric vector perpendicular or parallel to the direction of elongation of the crystals.(6) α represents absorption coefficient per mm. of the crystal.

The absorption spectrum of the aqueous solution, slightly acidified with dil. sulfuric acid, was determined with a Beckman model DU quartz spectrophotometer in silica cells having a 1 cm. light path. Extinction coefficients were calculated from the equation

$$\varepsilon = 1/cd. \log(I_0/I).$$

Measurements were made at room temperature. The complete spectrum was obtained from 8000 to 2200 A. Aqueous solutions of the complex salt were used at concentrations of 5.82×10^{-4} and 5.82×10^{-5} F.

Results and Discussion

Absorption Spectrum of the Aqueous Solution.—Results of the measurements with the aqueous solution are shown in Fig. 1 and Table 1. There have been published a few reports concerning absorption spectra of cobaltic polynuclear complexes in solutions. Shibata and Ohyagi reported the qualitative absorption curves of polynuclear complexes in aqueous solution(7) and in phosphoric acid.(8) One of the present authors and Kuroya(9) reported absorption spectra of $[Co\{(OH)_2Co\ en_2\}_3](NO_3)_6$, $[Co\{(OH)_2Co(NH_3)_4\}_3]Cl_6$ and $[(NH_3)_4Co(OH)_2Co(NH_3)_4]Cl_4$, and found that polynuclear complexes of such a type generally display a "third band,"(10) caused by ligandolysis,(11) the dissociation of NH_3 in coordination into NH_2^- and H^+, at $\nu = 100$ to 110×10^{13}/sec. and $\log \varepsilon = 3$ to 4, besides two absorption bands corresponding to the first and the second absorption band.(10) Consequently, the absorption band at $\nu = 101$ in the absorption spectrum of $[(NH_3)_5Co\text{-}O_2\text{-}Co(NH_3)_5](NO_3)_5$ is considered to be a "third band."

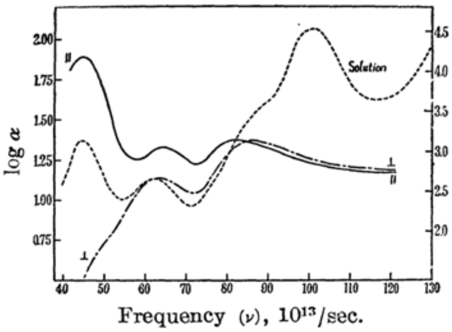

Fig. 1.—Dichroism of the crystal of $[(NH_3)_5Co\text{-}O_2\text{-}Co(NH_3)_5](NO_3)_5$ and absorption spectrum of the aqueous solution (dotted curve).

According to the previous report, monoaquo- and monohydroxy-pentammine cobaltic complexes show the first band at $\nu =$ about 60 and hexammine cobaltic salt at $\nu = 64-65$. Since binuclear complexes should show the corresponding absorption band at longer wave length than related uninuclear complexes,(12) it is supposed that the absorption band at $\nu = 62.6$ is the second absorption band and the band at $\nu = 44.6$ corresponds to the first absorption band. Besides those absorption bands as discussed above, there can be found an inflexion at $\nu = 88$. This inflexion should be attributed to the peroxy group and may well be named the "peroxy-specific band," since the solutions of binuclear complexes with a peroxy radical as a bridge(8) exhibit a similar inflexion or a separated band at $\nu =$ about 90 and $\log \varepsilon =$ about 3.

It is seen that the ε_{max} of the first absorption band is considerably larger than that of the

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(4) Decomposition of the compound was observed even in phosphoric acid solution.

(5) R. Tsuchida and M. Kobayashi, "The Colours and the Structures of Metallic Compounds," Zoshindo Co., Osaka, Japan, 1944, p. 180. See also the previous reports of this series (R. Tsuchida and M. Kobayashi, This Bulletin, **13**, 619 (1938); S. Yamada and R. Tsuchida, ibid., **25**, 127 (1952)).

(6) As will be shown in the later part of the present paper, the //-or ⊥-absorption corresponds to the absorption with the electric vector vibrating parallel or perpendicular to the Co-O-O-Co direction.

(7) Y. Shibata, *J. Coll. Sci., Imp. Univ. Tokyo*, **37**, Art. 8, 19 (1916); *J. Chem. Soc. Japan*, **38**, 99 (1917).

(8) Y. Ohyagi, This Bulletin, **15**, 186 (1940).

(9) R. Tsuchida and H. Kuroya, ibid., **15**, 427 (1940).

(10) As to the first, the second and the third absorption band, see for example, R. Tsuchida, This Bulletin, **13**, 388 and 436 (1938).

(11) R. Tsuchida and M. Kobayashi, *J. Chem. Soc. Japan*, **64**, 1268 (1943); L. Tschugaev, *Z. anorg. Chem.*, **137**, 1401 (1924); G. Urbain, *Bull. soc. chim.*, **51**, 853 (1932); G. Okamoto, *J. Chem. Soc. Japan*, **57**, 1175 (1936); T. Uemura and H. Sueda, This Bulletin, **10**, 50 and 85 (1935), etc.

(12) See, for example, ref. (5), p. 159.

Table 1

Absorption Maxima of $[(NH_3)_5Co\text{-}O\text{-}O\text{-}Co(NH_3)_5](NO_3)_5$

	1st Band		2nd Band		O_2-Band		3rd Band	
Crystal	ν	$\log \alpha$	ν	$\log \alpha$	ν	$\log \alpha$		
//-abs.	45	1.88	64.6	1.32	82.6	1.38		
⊥-abs.			63.0	1.13	86.8	1.38		
Solution	ν	$\log \varepsilon$	ν	$\log \varepsilon$	ν	$\log \varepsilon$	ν	$\log \varepsilon$
	44.6	3.14	62.6	2.66	(88)	(3.5)	100.8	4.54

second band, which seems unusual as compared with previous data. This will be discussed in the later part of the present report along with the dichroisms of the crystals.

It is found that the compound is greatly bathochromic to the hexol and the diol complexes which contain bridging OH^- radicals. This shows that bathochromic effect of a peroxy radical is larger than that of OH^-.

The Dichroisms of the Crystals. (1) $\mathbf{[(NH_3)_5Co\text{-}O_2\text{-}Co(NH_3)_5](NO_3)_5}$.—The dichroism of the crystal of the compound is shown in Fig. 1 and the data are tabulated in Table 1. The crystal exhibits the first, the second and the "peroxy-specific" absorption band, but lacks the third band, which is found in the absorption spectrum of the solution and observed to be considerably large as compared with the other bands. Comparing the absorption in the crystalline state with that of the aqueous solution, it is found that in the //-absorption the band at $\nu=45$ corresponds to the first band, the one at $\nu=64.6$ to the second band, and the one at $\nu=82.6$ to the peroxy-specific absorption band. Similarly, in the ⊥-absorption the band at $\nu=63$ represents the second absorption band and the one at $\nu=86.8$ the peroxy-specific absorption band, the first band being so weak that it could be assumed that the band has no component in that direction.

The dichroic nature is found in any of the first, the second and the peroxy-specific band. Above all, exceedingly large dichroism is recognized in the first absorption band. Comparing the two characteristic directions, the Co-O-O-Co direction and that perpendicular to the above, a larger electric moment is expected in the former than in the latter. In consequence, the dichroism measurement shows that the direction, Co-O-O-Co, in the complex should be perpendicular to the direction of elongation of this crystal. The remarkable dichroism in the first band shows the far more frequent transition of *d*-electrons in the direction of the linkage, Co-O-O-Co, than in the direction perpendicular to the linkage. And the different features of the first and the second absorption band suggest the different origins of these bands.

(2) $\mathbf{[(NH_3)_5Co\text{-}O_2\text{-}Co(NH_3)_5](NO_3)_4.2H_2O}$. — The dichroism of the crystal is shown Fig. 2 and Table 2. Similarly as in the cobalt (III)-cobalt (IV) complex, the crystal shows the first, the second and the peroxy-specific band, but the third band, which should be exhibited by the aqueous solutions, was not observed. From a similar consideration as in the case of the cobalt (III)-cobalt (IV) complex, it is found that the band at $\nu=46$ in the //-absorption is the first absorption band. The broad and flat band at $\nu=60$ to 80 may be considered to be superposition of the second and the peroxy-specific band. Similarly, the band at $\nu=48$ in the ⊥-absorption is the first absorption band, the one at $\nu=63$ the second absorption band, and the one at $\nu=83$ the peroxy-specific absorption band.

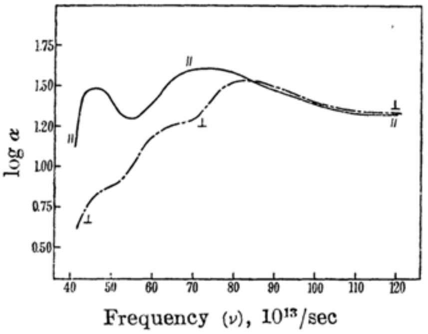

Fig. 2.—Dichroism of the crystal of $[(NH_3)_5Co\text{-}O_2\text{-}Co(NH_3)_5](NO_3)_4\cdot 2H_2O$.

Table 2

Absorption Maxima of $[(NH_3)_5Co\text{-}O\text{-}O\text{-}Co(NH_3)_5](NO_3)_4.2H_2O$

	1st Band		2nd Band		O_2-Band	
	ν	$\log \alpha$	ν	$\log \alpha$	ν	$\log \alpha$
//-abs.	46.0	1.48	flat (superposed)			
⊥-abs.	(48)	0.85	(63)	(1.2)	83.0	1.53

The dichroism is observed in any of those bands. The dichroism as to the first band appears especially marked. Electric moment responsible for the first absorption band, which is supposed by the present authors to originate from transitions in an incomplete transition shell of the central cobaltic ions, would be larger in the Co-O-O-Co direction than in the direction perpendicular to the above. Therefore, it may be presumed that in the crystal the complex ions are arranged so that the Co-O-O-Co direction is almost perpendicular to the direction of elongation.

General Features of the Dichroisms.—Both the complexes in the crystalline state as well as in solution are bathochromic to the diol, the hexol and related complexes which have two OH^- radicals as bridges. This indicates that the peroxy radical usually exerts larger bathochromic effect than the hydroxy radical.

The crystals of both compounds lack the third band which should usually be observed in solution at ν = about 100 and $\log \varepsilon = 3 \sim 4$. This shows that the said band may be attributed to such a ligandolysis, as is greatly favoured by interaction of solvent molecules with ligands of the complex ions. It is possible to suppose that ammonia molecules in the complex ion, which may be rather labilized under the influence of the peroxy radical in the complex, would be much more easily dissociated when the solvent molecules approach the ions, and that the band would disappear in the crystalline state where there exists no interaction of solvent molecules.

The two complex ions, μ-peroxo-dicobalt (III) and μ-peroxo-cobalt (III)-cobalt (IV) ions, have a similar configuration having two metal atoms connected through a peroxy radical. From the results of their dichroism measurements the following rules may be obtained for the dichroism of complexes of the above type:

(1) The first absorption band. The //-absorption, the absorption with the electric vector vibrating along the Co-O-O-Co direction, is remarkably hyperchromic to the ⊥-absorption, the absorption with the electric vector vibrating perpendicularly to the above.

(2) The second absorption band. The //-absorption is hyperchromic and hypsochromic to the ⊥-absorption.

(3) The peroxy-specific absorption band. The //-absorption is bathochromic to the ⊥-absorption,(13) extinction coefficients of both absorptions being almost equal.

Interaction between Central Metallic Ions through a Bridging Peroxy Group.—Examining the absorption curves as presented in this report, it is found that the first absorption band of peroxy-cobalt (III)-cobalt (IV) nitrate is different from what the so-called first band should be, since (1) the first band in aqueous solution is about three times as strong as the second absorption band, which differs from the empirically derived tendency(14) that the first band of a cobalt (III) complex in solution is almost as strong as the second band, (2) in the //-absorption of the crystal, too, the first band is about three times as strong as the second band, which represents a quite unusual case with the absorption spectra of crystals, and (3) the first band of the //-absorption is extraordinarily hyperchromic to that of the ⊥-absorption, the latter having a negligibly small extinction coefficient.

From the above discussions, and considering the fact that the absorption with the electric vector vibrating along the Co-O-O-Co direction should be much larger than the absorption with the electric vector perpendicular to the above, it may be supposed that two cobalt atoms of different valency states exert an interaction upon each other through a peroxy-radical between them; one may think that electrons vibrate back and forth between the two cores through a peroxy-radical as a bridge, and that in the ground state two cobalt atoms may not be distinguishable.

The previous data on absorption spectra of coordination compounds indicate that, generally speaking, complexes of a metal of a higher oxidation number show their absorption bands at shorter wave length regions than the corresponding ones of the same metal of a lower oxidation number. The absorption curves of the compounds reported in the present paper are inconsistent with the above tendency derived with most compounds. Thus comparing the μ-peroxo-cobalt (III)-cobalt (IV) complex with the μ-peroxo-dicobalt (III) complex, the former is not hypsochromic but even slightly bathochromic to the latter. This discrepancy also suggests the unusualness of the former compound and the possibility of the strong interaction between the central metallic ion as described above.

In the case of the μ-peroxo-dicobalt (III) complexes, too, the difference in α of the first band between the //- and the ⊥-direction is so large that it may be possible to expect a sort of interaction between central metallic ions through a peroxy radical in the Co-O-O-Co direction. As is clear from the above descriptions, however, the interaction seems much large in the Co (III)-O-O-Co (IV) direction than in the Co (III)-O-O-Co (III) direction. This can also be understood from electronic configurations of cobalt ions. That is, since Co (III) has a $3d^6$ configuration and Co (IV) has a $3d^5$ configuration, it is probable that the said interaction in the μ-peroxo-Co (III)-Co (IV) complex is much stronger than in the Co (III)-Co (III) complex.

The same applies for similar Fe (II)-Fe (III)-polynuclear complexes, since Fe (II) and Fe (III) are isoelectronic, respectively, with Co (III) and Co (IV). Thus, in the magnetite, Fe_3O_4, and the prussian blue, K Fe Fe $(CN)_6$, mutual interactions between Fe (II) and Fe (III) are expected through an oxygen ion or a cyanide ion, which would cause anomalies in optical and magnetic properties of those compounds.

It is also suggested that a similar explanation holds for those compounds of a similar type which contain atoms of the same element in different valency states and exhibit unusual colours, and that the interaction of the above type between metallic ions through a bridging ion or radical represents a favourable and adequate model for processes in those more complicated compounds.

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(13) This tendency resembles the rule observed about the dichroism of the π band of the benzene ring (cf. R. Tsuchida, M. Kobayashi and K. Nakamoto, *J. Chem. Soc. Japan*, **70**, 12 (1949); K. Nakamoto, *J. Am. Chem. Soc.*, **74**, 390 (1952)), which may suggest that the electronic state of O-O- in those complexes is rather similar to that of the π-linkage in the benzene ring.

(14) H. Kuroya, *J. Inst. Polytech., Osaka City Univ.*, **1**, No. 1, Ser. C, 29 (1950); K. Sone, *J. Chem. Soc. Japan*, **71**, 270 (1950).

Summary

(1) The dichroisms of decammine-μ-peroxodicobalt (III) nitrate dihydrate, $[(NH_3)_5Co\text{-}O_2\text{-}Co(NH_3)_5](NO_3)_4\cdot 2H_2O$, and of decammine-$\mu$-peroxocobalt (III)-cobalt (IV) nitrate, $[(NH_3)_5Co\text{-}O_2\text{-}Co(NH_3)_5](NO_3)_5$, and the absorption spectrum of the latter in aqueous solution have been quantitatively measured.

(2) The empirical rules on the dichroisms of those crystals have been obtained.

(3) The considerations on the absorption spectra of the above compounds have led to the conclusions that there exists a kind of mutual interaction between metallic ions through a bridging peroxy-radical and that the interaction between Co (III) and Co (IV) is considerably larger than that between two Co (III) atoms. The interaction of the above type is supposed to be applicable to the explanation of unusually deep colors in the crystals containing the same atoms in different oxidation states.

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