Spectrochemical Study of Microscopic Crystals. XXI[1]. *The Structure and Absorption Spectra of the Red and the Black Form of Nitrosopentammine-cobalt Salts*[2]

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Two series of compounds with the same composition of $[Co(NH_3)_5NO]X_2$, have been known for a long time[3], one of them being colored black and the other red. The marked difference in the color and other properties between the two series of compounds has attracted a number of investigators[4-10], but rather conflicting conclusion have so far been drawn about the configuration and the electronic structure of the two compounds. It seems, therefore, to be of significance to examine the compounds using some new sorts of materials which have neither been much discussed nor obtained before. This paper presents ultraviolet absorption spectra of the black and the red salt in the crystalline state, and discusses their structure on the basis of the present measurement.

Experimental

Materials. — Red nitrosopentammine-cobalt(III) nitrate, $[Co(NH_3)_5NO](NO_3)_2$, was prepared in rectangular, thin plates by the method of Asmussen and others[9]. The compound is comparatively stable, and may be recrystallized from water.

Black nitrosopentammine-cobalt chloride, $[Co\cdot(NH_3)_5NO]Cl_2$ was prepared according to the direction of Asmussen and others[9]. The compound is unstable, undergoing decomposition by water, acid or alkali. On exposure to the air, the compound gradually changes into a red material. The decomposition, however, seemed to be so slow that no change of the crystal surface was observed under the microscope after the dichroism measurement. The compound is often contaminated with the $[Co(NH_3)_6]^{2+}$, which is very sensitive with respect to magnetic susceptibility, but not to ultraviolet spectra of the salt.

Measurements. — Visible and ultraviolet spectra of both the red and the black compound in the crystalline state have been quantitatively determined

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[1] Part XX of this series, S. Yamada and R. Tsuchida, This Bulletin, **33**, 98 (1960).

[2] Presented before the 12th Annual Meeting of Japan Chemical Society, Kyoto, April, 1959.

[3] J. Sand and O. Gennsler, *Ann.*, **123**, 43 (1862); ibid., **329**, 194 (1903); *Ber.*, **36**, 2083 (1903).

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[8] W. P. Griffith, J. Lewis and G. Wilkinson, *J. Inorg. Nuclear Chem.*, **7**, 38 (1958).

[9] R. W. Asmussen, O. Bostrup and J. P. Jensen, *Acta Chem. Scand.*, **12**, 24 (1958).

[10] E. P. Bertin, S. Mizushima, T. J. Lane and J. V. Quagliano, *J. Am. Chem. Soc.*, **81**, 3821 (1959).

at room temperature on well-developed planes by Tsuchida and Kobayashi's microscopic method[11] using linearly polarized light. The A- and the B-absorption refer to the direction shown in the figures.

Visible and ultraviolet absorption spectrum of the red salt in an aqueous solution was measured by a Beckman DU spectrophotometer.

The symbols used in the present paper are the same as those in the former reports of this series.

In the analysis of the absorption curve in Fig. 4, it is assumed that the second absorption band has a molar extinction coefficient almost equal to that of the first band, the distance between the maxima of the first and the second bands being almost equal for complexes of cobalt(III).

Results and Discussion

Structure of Black Nitrosopentammine-cobalt Salt. — Uninuclear and binuclear structures have been given to the black nitrosopentammine-cobalt salt. Contrary to the result by former investigators that the "black salts" were paramagnetic, Asmussen and others[9] found that the "black salts", when carefully purified, actually showed diamagnetism. The structures, as suggested formerly on the erroneous magnetic data, need not be given serious consideration. The black series of the salts were regarded by Asmussen and others as a co-ordination compound of cobalt(III), the lowest energy level being very close to the level of the bivalent cobalt.

Bertin and others[10] concluded on the basis of the infrared spectra of these compounds that the isomerism of the black and the red series is dependent upon the nature of the linkages of the co-ordinated NO-group and not upon difference in the oxidation state of the central metal. However, they did not discuss the structure of the salts in detail. Griffith and others[8] discussed the same problem on the basis of the chemical reactions, and finally favored the binuclear structure for the "black salt". Most of their discussion, however, seems to be rather speculative, and reexamination from materials of different kinds might be desirable.

Dichroism in the visible and ultraviolet region of the "black salt" is shown in Fig. 1. It seems fortunate that the impurity, $[Co(NH_3)_6]^{2+}$, often appearing in the "black salt" is not important in the UV-absorption spectra of the compound, in contrast to magnetic susceptibility which is affected seriously by a small amount of the impurity. The absorption spectra, as shown in Fig. 1, seem to be so complicated that they would not be understandable on the assumption of the uninuclear model of the "black salt". Thus the "black salt" exhibits an absorption band at about 46×10^{13} sec^{-1}, the wavelength region which is much longer than would be expected for the uninuclear nitrosopentammine-cobalt(III) complex. There might be a possibility that the band at about 46×10^{13} sec^{-1} would originate from a nitroso-group. In fact, a number of nitroso-derivatives, such as nitroso-benzene and its derivatives, are known to show a rather special type of an absorption band characteristic of a nitroso-group in the long wavelength region. It may be difficult, however, to assume that the NO-group in the "black salt" should be isolated electronically from the cobalt ion to such an extent that the band of this sort may appear in this wavelength region. The band at about 46×10^{13} sec^{-1} of the "black salt", therefore, may not be regarded as due to a nitroso-group which is rather isolated in the cobalt-complex. Moreover, the absorption curve of the "black salt" appears to be too complicated for a uninuclear complex of cobalt(III).

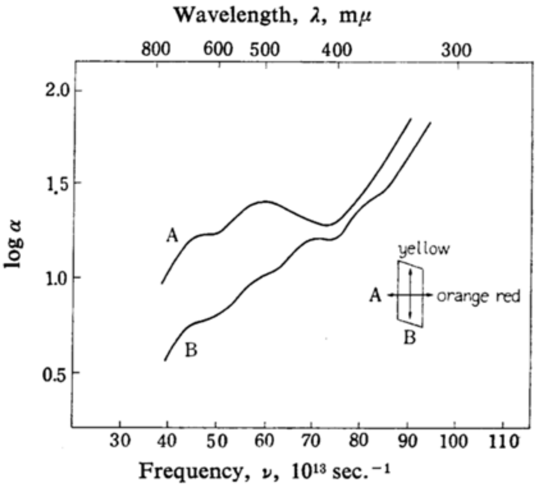

Fig. 1. Absorption spectra of black nitrosopentammine-cobalt chloride, $[Co(NH_3)_5NO]Cl_2$, in the crystalline state.

On the contrary, the absorption curve of the "black salt" may be understood much more readily as that of a binuclear complex than as that of a uninuclear complex. Possible structures for a binuclear form are shown in Fig. 2, the π-bonding between the metal and the NO^- ion being neglected for the present. It is to be noted that the dichroism of the "black salt" is markedly similar to that of μ-peroxo-dicobalt complexes with an O^{2-} group which connects two cobalt ions together[12]. Moreover, just as the peroxo-dicobalt compound

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[11] R. Tsuchida and M. Kobayashi, "The Color and the Structure of Metallic Compounds", Zoshindo, Osaka (1944), p. 180 (in Japanese), This Bulletin, 13, 619 (1938).

[12] S. Yamada, Y. Shimura and R. Tsuchida, This Bulletin, 26, 72 (1953).

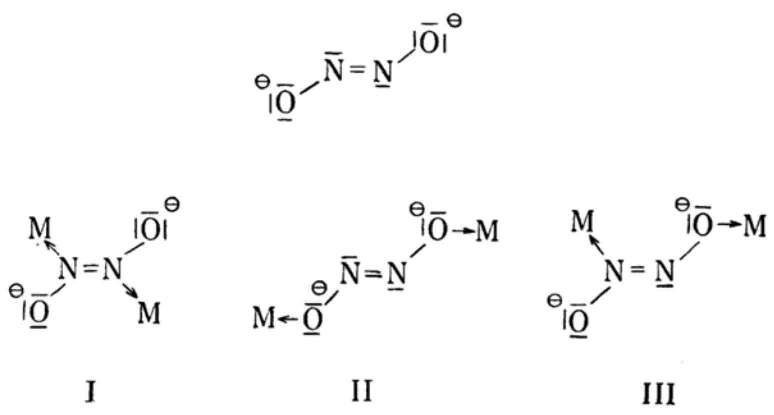

Fig. 2.

has an absorption band in the very long wavelength region, so the "black salt" shows an absorption band at about $46\times10^{13}\,\mathrm{sec}^{-1}$. The band of the peroxo-dicobalt compound in the longer wavelength region, with maximum at about $46\times10^{13}\,\mathrm{sec}^{-1}$, was ascribed to a group of Co–O_2–Co with a special electronic structure which gives rise to a special absorption band due to the interaction between the two cobalt ions through the peroxide group[12]. The band in question of the "black salt", therefore, may be a special type of the interaction band due to a group of atoms having an electronic structure of Co–X–Co somewhat similar to that of Co–O_2–Co, originating from the interaction between the two cobalt ions through N_2 group. A-absorption in Fig. 1 may be regarded as representing the main features of the component absorption which is richer with the interaction absorption due to the Co–N_2–Co group than is the other component absorption.

Since it is difficult to expect the interaction band with structure II and structure III, structure I having a group of Co–N–N–Co may be favored best as a model of the "black salt" by the ultraviolet absorption spectra with the interaction band. The conclusion obtained here by the present authors about the structure of the "black salt" is found to be in agreement with the view of Griffith and others[8], who regarded it as most likely that the "black salt" has a binuclear structure with a hyponitrite-group as a bridge, on the ground that the "black salt" undergoes decomposition by acid or carbon dioxide to give nitrous oxide and that the salt can be prepared, though in a low yield, from sodium hyponitrite and a cobalt salt.

It may also be noteworthy that an infrared absorption band at 1620 to 1640 cm^{-1} due to the NO part of the "black salt"[10] is very close to the frequency of the –N=N– group in ordinary azo-compounds. This to beseems consistent with structure I, having a kind of interaction between the two cobalt ions through the N_2 group, as has been concluded to be most probable in the present work. The order of the N–N bond may be almost equal to the bond order in ordinary azo-groups of organic azo-compounds.

In summary, it may be concluded that *the "black salt" has structure I with the Co–N=N–Co group, displaying the special band due to the interaction between the two cobalt ions through the –N=N– group.*

Polarized Absorption Spectra of Red Nitrosopentammine-cobalt(III) Nitrate. — Ultraviolet absorption spectra of the "red salt" in the crystalline state are shown in Fig. 3 and Table I. The crystal structure analysis has not been

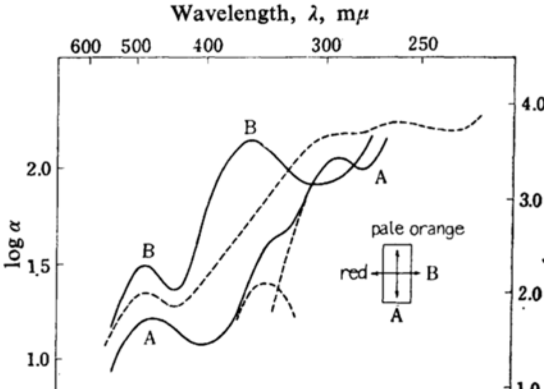

Fig. 3. Absorption spectra of red nitrosopentammine-cobalt nitrate, $[Co(NH_3)_5ON]\cdot(NO_3)_2$, in the crystalline state (——) and in aqueous solution (----).

TABLE I. UV ABSORPTION SPECTRA OF RED NITROSOPENTAMMINE-COBALT(III) NITRATE $[Co(NH_3)_5NO](NO_3)_2$ IN THE CRYSTALLINE STATE AND IN SOLUTION

Absorption band	Spin-forbidden	I ν, log α	NO-spec. ν, log α	II ν, log α	III ν, log α	IV
In crystalline state						
B-abs.		62, 1.5	84, 2.3	(covered)	— —	
A-abs.		1.15	1.2	87, 1.5	102, 2.1	
Stronger component[a]		Z	Z	(X, Y)	X, Y	
In aqueous solution						
	ν, log ε	ν, log ε	ν, log ε		ν, log ε	ν, log ε
	38.5, $\bar{1}$.85	62.1, 1.98	83.5, 2.6	(covered)	100, 3.6	114.5, 3.83

ν: 10^{13} sec^{-1}

a) Z refers to the direction combining the cobalt ion with the ON-group in the complex-ion.

reported with the compound as yet. However, the dichroism, as has been determined in the present work, may be regarded to represent the main characteristics of the component absorptions of the complex-ion itself under slight perturbation from the surrounding ions.

A striking dichroism is observed with the first absorption band. It may be assumed that A-absorption in Fig. 3, having the stronger absorption band at about 62×10^{13} sec^{-1} represents characteristics of the component absorption of the complex-ion with electric vector along the direction connecting the cobalt(III) ion and the nitroso-group.

The specific band due to the NO-group in co-ordination is observed as a distinct maximum at about 84×10^{13} sec^{-1} in Fig. 3, whereas the band is obscured by neighboring stronger absorption in the absorption curve of the compound in solution. The present measurement shows that the specific band is greatly polarized along the Co-ON direction. This is readily understandable if it is assumed that the band is due to electron transfer, possibly from the ON-group to the central metal-ion.

The band at about 102×10^{13} sec^{-1} is seen to be polarized in the direction perpendicular to the Co-ON direction. The absorption band due to nitrate ions is expected to appear at about 100×10^{13} sec^{-1}, but the band of the nitrate ion is so low that the band at about 102×10^{13} sec^{-1}, as observed with the "red salt" in the present work, may be due to another origin. This band may be a sort of charge transfer band, but its origin is not quite clear for the present.

The second ligand field band is covered under greater specific band in A-absorption, but appears as inflation at about 87×10^{13} sec^{-1} in B-absorption. This may be consistent with the frequency difference of about 25×10^{13} sec^{-1} between the first and the second band, which was reported with numerous cobalt(III)-complexes.

Structure of Red Nitrosopentammine-cobalt Salts.—Both the uni- and the bi-nuclear structure have been proposed for the "red salt". Very recently Asmussen et al.[9] regarded, mostly from magnetic measurements, that the "red salt" may be either a uninuclear or a binuclear complex of cobalt(III). Griffith et al.[8] concluded from examination of its chemical property that the "red salt" may be uninuclear. Bertin et al.[10] concluded, from its infrared spectrum, the oxidation state of the cobalt to be tervalent, but presented no detailed discussion about the structure of the "red salt". Thus the "red salt" may be a uninuclear or a binuclear complex of cobalt(III). In the following, we shall discuss about the structure of the "red salt" on the basis of the present measurements with consideration to the former results.

Possible structures of the binuclear ions for the "red salt" are shown in Fig. 2. Structure I is assigned to the "black salt", as discussed above. Structure II and structure III may be rejected on the ground of the chemical reactions of the "red salt", since the compound with structure II or structure III would be expected to give nitrous oxide in acidic solution, just like the hyponitrite ion. In fact, the "red salt" is stable in water, whereas the "black salt" is readily decomposed to give nitrous oxide. Moreover, the fact that the "red salt" in solution or in the crystalline state shows a definite maximum for the first absorption band seems to be inconsistent with structure III, which would show two "first ligand field absorption bands" originating from the two kinds of cobalt ions. Therefore, the "red salt" can not be assigned to a binuclear form. Thus the present authors are inclined to assume that the "red salt" be uninuclear.

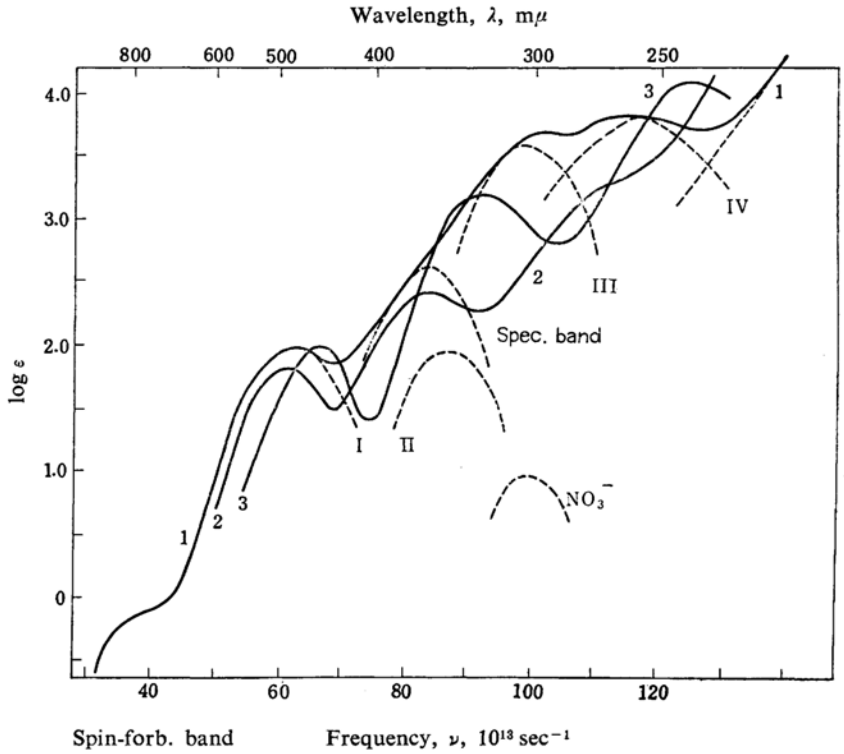

Fig. 4. Absorption spectra of $[Co(NH_3)_5X]^{2+}$ in aqueous solution: 1, X=NO⁻; 2, X=ONO⁻ (nitrito); 3, $X=NO_2^-$ (nitro-). Dotted curves represent absorption bands obtained by analysis of the absorption curve 1. The curves 1 and 2 are taken from Ref. 13 in the text.

In addition, the absorption spectra of the "red salt" may be consistent with the assumption of the uninuclear model of the "red salt", as shown in the succeeding paragraph of the present discussion.

Ultraviolet absorption spectra of the "red salt" in solution and in the crystalline state have been determined in the present work, and are shown in Figs. 3 and 4 and Table I. The absorption curve of the compound in solution, as determined in the present work, shows absorption maxima which generally agree with those reported by the former investigators with the compound in solution[9]. Asmussen and others[9] pointed out vague similarity of its absorption spectrum to spectra of most cobaltic compounds, but gave no further discussion about the spectrum. After all, they seemed to conclude that the "red salt" may be either uninuclear or binuclear. It is seen in Fig. 3 and Table I that the "red salt" shows a well-defined maximum for the first band at about 61 to $62\times10^{13}\,sec^{-1}$. The second band, which is characteristic of most complexes of cobalt(III), is covered under strong neighboring absorption bands in the curve of the salt in aqueous solution. Analysis of the absorption curve reveals that there appears a band at about $84\times10^{13}\,sec^{-1}$ which may be regarded as a specific band due mainly to an NO-group in combination with the cobalt(III)-ion. The intensity of the specific band is found to be much smaller than the intensity of the specific band due to a nitro-, an isothiocyanato- or an azide group in the pentammine-cobalt(III) complex. As is evident from inspection of the data in Table II, it is difficult to assume that the band at about $100\times10^{13}\,sec^{-1}$ in the curve of the "red salt"

TABLE II. ABSORPTION MAXIMA OF COMPLEXES OF A TYPE, $[Co(NH_3)_5X]^{2+}$, IN SOLUTION

X	1st band		Specific band		Ref.
	ν	log ε	ν	log ε	
NO_2^-	65.8	2.00	92.4	3.22	a
NH_3	63.2	1.78	—	—	b
ONO⁻	61.2	1.86	82.9	2.44	a
ON⁻	62.1	1.98	84	2.5	c

ν: $10^{13}\,sec^{-1}$.

a) M. Linhard, H. Siebert and M. Weigel, *Z. anorg. allgem. Chem.*, **278**, 287 (1955).

b) M. Linhard, *Z. Elektrochem.*, **50**, 224 (1944).

c) Present measurement.

may correspond to the specific band due to the NO-group in the complex-ion. On the contrary, it is noteworthy that the band at about $84\times10^{13}\,\mathrm{sec}^{-1}$ of the " red salt " is almost as intense as the specific band of a nitrite-group in the pentammine-cobalt(III) in which a nitrite group is co-ordinated to the cobalt(III) ion through its oxygen atom.

It also is to be noted that the absorption curve of the " red salt ", $[Co(NH_3)_5ON](NO_3)_2$ in solution bears a resemblance to the curve[13] of the $[Co(NH_3)_5ONO]^{2+}$ ion in which a nitrite ion is co-ordinated to the cobalt(III) ion through its oxygen atom. This seems to indicate that the NO-group in the " red salt " is co-ordinated to the cobalt(III) ion through its oxygen atom, as will be described in more detail in the later part of the present discussion.

It is known from existing data that substitution of a nitro-group for ammonia in the hexammine-cobalt(III) ion gives rise to a hypsochromic shift of the first absorption band, whereas the substitution of a nitrite group for ammonia yields a bathochromic shift of the first band. In the case of a nitrate-group, an even greater bathochromic shift is observed. It is found in Fig. 4 and Table II that the first absorption band of the " red salt " lies at a longer wavelength than the first band of the hexammine-cobalt(III) ion. Therefore, it may be concluded, from comparison of the wavelength of the first absorption band of the " red salt " with those of the relevant complexes, that *the NO-group in the " red salt " is co-ordinated to the cobalt(III) ion throuh its oxygen atom, and not through the nitrogen atom*, as is customarily assumed for this compound.

Inspection of existing data, summarized in Table II and Fig. 4, also reveals that the specific band due to a nitrite-group lies at about 83 to $84\times10^{13}\,\mathrm{sec}^{-1}$ and the band due to a nitro-group lies at about $92\times10^{13}\,\mathrm{sec}^{-1}$ in the pentammine-cobalt(III) complex. It is seen that the nitrite-group with its oxygen co-ordinated to the cobalt(III) ion shows its specific absorption band at a longer wavelength than does the nitro-group with its nitrogen co-ordinated to the cobalt(III) ion. The present measurement shows that the " red salt " has its specific band at about $84\times10^{13}\,\mathrm{sec}^{-1}$ with $\log\varepsilon$ of about 2.6. Thus it is concluded also from examination of the specific band that the NO-group in the " red salt " is co-ordinated to the cobalt(III) ion through its oxygen atom.

The intensity of the specific band due to the nitroso-group in the " red nitroso-pentammine complex " is found to be smaller than the intensity of the specific band due to a nitro-group in the metallic complex, but is almost equal to the intensity of the specific band due to the nitrite group in the pentammine-cobalt(III) complex. This fact also may be consistent with the conclusion that the nitroso-group is co-ordinated to the cobalt(III) ion through the oxygen atom in the " red salt ".

In this connection, the close similarity of the absorption curve of the " red salt " to the curve of the nitritopentammine-cobalt(III) complex is noteworthy. In the case of the " red salt ", band III and band IV are seen to be displaced to a little longer wavelength than the corresponding bands of the nitritopentammine-cobalt(III) complex, as is seen in Fig. 4, but the correspondence of the absorption bands between the " red salt " and the nitritopentammine-cobalt(III) complex may be evident. This fact also may be taken as indicating that the absorption spectrum of the " red salt " is understood on the assumption of the mononuclear model with the cobalt-to-oxygen bond.

It is interesting to find that a very weak absorption system appears at about $39\times10^{13}\,\mathrm{sec}^{-1}$ in the absorption curve of the " red salt " in solution, as shown in Fig. 4. This absorption band is regarded as being due to electronic transitions between levels with different multiplicities. This spin-forbidden band of the " red salt " is found to lie in the longer wavelength region than $[Co(NH_3)_6]Cl_3$ which shows the band at about $40\times10^{13}\,\mathrm{sec}^{-1}$. This fact is also compatible with the conclusion in the present article that the NO-group is bound to the cobalt ion through its oxygen atom, since the band of this kind would appear in the shorter wavelength region if the NO-group were bound to the cobalt(III) ion through its nitrogen atom.

Summarizing the above discussion, mainly on the basis of the absorption spectra, it is concluded that *the " red salt " is uninuclear, with the nitroso-group co-ordinated to the cobalt(III) ion through the oxygen atom.*

Summary

In order to examine the structure of the red and the black nitrosopentammine-cobalt salts, their dichroism in the visible and near-ultraviolet region has been quantitatively determined at room temperature by the microscopic method.

The absorption spectrum of the " black salt " is found to be understandable best on the assumption that the " black salt " has binuclear complexes of cobalt(III), showing a special kind of absorption band due to the interaction between the two cobalt(III) ions through the N_2 group.

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[13] M. Weigel, H. Siebert and M. Linhard, *Z. anorg. allgem. Chem.*, 278, 287 (1955).

The absorption spectrum of the "red salt" is concluded to be consistent with the model of the uninuclear complex of cobalt(III) with the NO-group co-ordinated to the cobalt(III) ion through its oxygen atom.

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