On the Relation between the Configuration of Metallic Complex Salts and their Absorption Spectra. II. *cis*-Trinitro-triammine-cobalt.[1]

By Hideo SUEDA.

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In a previous paper,[2] the assumption that the absorption band presented by complex salt solutions can be resolved into elements which are due to pairs of co-ordinated groups situated in trans-position and that these elements show an additive property in the same complex ion, was deduced from the comparison of absorption curves given by nitro-ammine cobaltic complex salts, and it was stated that it can be applied to $[Co(NH_3)_3(NO_2)_3]$ prepared by the ordinary method of S. M. Jörgensen.[3] That is, the author confirmed firmly the theory of Y. Shibata[4]

(1) Translated from the paper published in Japanese, *J. Chem. Soc. Japan*, **59** (1938), 47.

(2) This Bulletin, **12** (1937), 188.

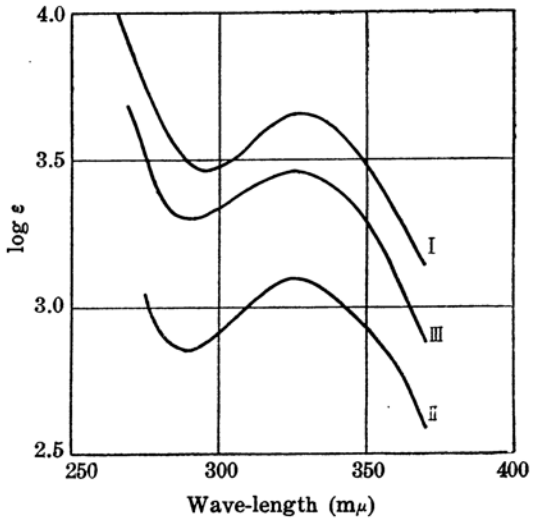
(3) H. Biltz and W. Biltz, "Übungsbeispiele aus der unorganischen Experimentalchemie," 3rd and 4th Ed. (1920).

(4) *J. Chem. Soc. Japan*, **30** (1915), 1243.

that the salt possesses trans-configuration. According to Werner's coordination theory, however, it is evident that cis-compound must also exist.

If *cis*-$[Co(NH_3)_3(NO_2)_3]$, of which nothing has ever been written, can be obtained, then such a salt must show, from the author's assumption, an absorption curve similar to that of $[Co(NH_3)_5(NO_2)]Cl_2$ and *cis*-$[Co(NH_3)_4(NO_2)_2]Cl$ and an absorption capacity three times that of the former and one and half times that of the latter. Since *cis*-$[Co(NH_3)_3(NO_2)_3]$ should show infallibly upon the author's assumption, it was prepared and tested.

$[Co(NH_3)_3(NO_3)_3]$ transforms into $[Co(NH_3)_3(H_2O)_3](NO_3)_3$ in water, and the latter has according to Y. Matsuno[5] a cis-configuration. Thus, if water molecules in $[Co(NH_3)_3(H_2O)_3](NO_3)_3$ can be replaced by nitro-radicals, then *cis*-$[Co(NH_3)_3(NO_2)_3]$ can be obtained. When the salt so prepared, it possessed a composition according to the above deduction and gave an absorption curve as indicated in Fig. 1, curve I. As the absorption curve differs from that of *trans*-$[Co(NH_3)_3(NO_2)_3]$, it can be considered as *cis*-$[Co(NH_3)_3(NO_2)_3]$. Curves II and III are absorption curves of $[Co(NH_3)_5(NO_2)]Cl_2$ and *cis*-$[Co(NH_3)_4(NO_2)_2]Cl$ respectively. As seen in Fig. 1, curves I, II and III are similar possessing maxima at wave-length 325 mμ. Extinction coefficient at the maximum of curve I is about 3.6 times that of curve II (the figure being slightly greater than expected) and about 1.6 times that of curve III.



I: *cis*-$[Co(NH_3)_3(NO_2)_3]$
II: $[Co(NH_3)_5(NO_2)]Cl_2$
III: *cis*-$[Co(NH_3)_4(NO_2)_2]Cl$

Fig. 1.

The results obtained above established the correctness of the prediction made from the author's assumption in his first paper. Moreover, according to Y. Shibata[4] and R. Tsuchida[6] *cis*-$[Co(NH_3)_3(NO_2)_3]$

(5) *J. Coll. Sci., Imp. Univ. Tokyo*, **41** (1921), Art 10, 14.
(6) This Bulletin, **11** (1936), 785.

should not possess the third absorption band, and, when measured down to nearly 250 mμ, no sign of such a band appeared.

Experimental.

To 5 g. of $[Co(NH_3)_3(NO_3)_3]$, prepared by the method of Jörgensen,[7] was added 50 c.c. water and on leaving the mixture to stand for 5 hours at about 10°C., a dark red solution was obtained. A small quantity remaining undissolved was removed by filtration, and to the filtrate was added 10 c.c. glacial acetic acid with cooling with ice. To the acidified solution 7 g. sodium nitrite was gradually added with constant stirring, the solution was left to stand for some time and filtered, and the filtrate left to stand for 24 hours in an ice box. Obtained crystals were washed thoroughly with cold water and recrystallized quickly from water, at a temperature not exceeding 50°C.

The recrystallized substance was analyzed for its hydrogen and nitrogen, the result being as follows. Found: H, 3.71; N, 32.7. Calculated for $[Co(NH_3)_3(NO_2)_3]$: H, 3.66; N, 33.9%.

Summary.

cis-$[Co(NH_3)_3(NO_2)_3]$ was prepared and its absorption band proved as being identical with that expected from author's assumption given in the first paper.

In conclusion, the author wishes to express his sincere thanks to Prof. Y. Shibata of the Imperial University of Tokyo, and to Assist. Prof. T. Uemura of the Tokyo University of Engineering for their kind encouragements.

Laboratory of Inorganic Chemistry,
Tokyo University of Engineering
(Tokyo Kôgyô-Daigaku).

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(7) *Z. anorg. Chem.*, **5** (1894), 185.