THE THIRD ABSORPTION BANDS OF CO-ORDINATION COMPOUNDS. I. $[Co(NH_3)_4Cl\ NO_2]Cl$ AND $[Co(NO_2)_6]Na_3$.

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Most of the complex salts show in aqueous solutions two selective absorption bands(1) in the visible and the near-ultraviolet regions, but some of them give the third absorption bands. For instance, Y. Shibata(2) has shown that nitro-ammine cobaltic compounds such as $[Co(NH_3)_4(NO_2)_2{}^{(1)}_{(6)}]Cl$, $[Co(NH_3)_3(NO_2)_3]$, and $[Co(NH_3)_2(NO_2)_4]NH_4$ have three absorption bands and thereby concluded that the third band is due to the pair of nitro-radicals co-ordinated in trans-positions to each other. Whereas the first and the second bands, especially the former, have frequently been investigated(3), there have scarcely been any theoretical considerations as to the third band, except that of Y. Shibata(4).

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(1) Y. Shibata, *J. Chem. Soc. Japan*, **36** (1915), 118; etc.

(2) Y. Shibata, *J. Chem. Soc. Japan*, **36** (1915), 1246.

(3) Y. Shibata; *J. Faculty Sci., Imp. Univ. Tokyo*, (1915—); *J. Chem. Soc. Japan*, (1915—); J. P. Mathieu, *Bull. soc. chim.*, (5), **3** (1936), 463; A. Mead, *Trans. Faraday Soc.*, **30** (1934), 1052; J. Lifschitz, *Z. physik. Chem.*, **97** (1921), 1; etc.

(4) Y. Shibata, *J. Chem. Soc. Japan*, **36** (1915), 1243.

One of the authors⁽⁵⁾ has recently measured the absorption coefficients of trans-dichlorotetrammine cobaltic chloride $[Co(NH_3)_4Cl_2\{^{(1)}_{(6)}]Cl$ and showed that this salt has also the third absorption band. The author has thus been led to the conclusion that the theory of Shibata might possibly be extended to many other complex compounds besides the above mentioned nitro-ammines; in other words the theory might be applied not only to nitro-radicals but also to any other radicals which are co-ordinated by neutralizing the charge of the central metallic atom. The theory may, therefore, be extended to the effect that the third band is due to the pair of negative radicals co-ordinated in trans-positions to each other. The present investigation was undertaken to confirm the postulate. The extinction coefficients of $[Co(NH_3)_4(NO_2)_2\{^{(1)}_{(6)}]Cl$, $[Co(NH_3)_2(NO_2)_4]NH_4$, $[Co(NO_2)_6]Na_3$, and $[Co(NH_3)_4Cl\ NO_2]Cl$ were measured. The existence of the third bands is well established for the first two compounds, but not for $[Co(NO_2)_6]Na_3$. If the above mentioned postulate is right, the salt should have a third absorption band no matter what the configuration of NO_2 may be, and if Cl and NO_2 in $[Co(NH_3)_4Cl\ NO_2]Cl$ are co-ordinated in trans-positions to each other as is easily supposed from the process of its preparation, a third band should be expected also for this compound.

Experimental. (1) $[Co(NH_3)_4(NO_2)_2\{^{(1)}_{(6)}]Cl$ was prepared by the method of Jörgensen⁽⁶⁾. The extinction coefficients were measured for 0.001 mol/l. solution with varying thicknesses from 1 to 50 mm. The results are given in Fig. 1.

(2) $[Co(NH_3)_2(NO_2)_4]NH_4$ was prepared by the method of Jörgensen⁽⁷⁾ and the extinction coefficients were measured for 0.001 mol/l. solution with varying thicknesses from 1 to 50 mm. The absorption curve is shown in Fig. 2.

(3) $[Co(NO_2)_6]Na_3$ was prepared by the method of Biilmann⁽⁸⁾. The extinction coefficients were determined for concentrations between 0.0025 and 0.01 mol/l. and with varying thicknesses from 0.2 to 50 mm. The solutions were freshly prepared from time to time to avoid errors caused by considerably rapid decomposition of the salt. The results are shown in Fig. 2.

(4) $[Co(NH_3)_4Cl\ NO_2]Cl$ was obtained as an orange-red fibrous substance with silky lustre by the method of Jörgensen⁽⁹⁾. The measurements were done with concentrations between 0.0025 and 0.01 mol/l. and with varying thicknesses from 0.2 to 50 mm. The absorption curve is given in Fig. 1.

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(5) R. Tsuchida, this bulletin, **11** (1936), 721.

(6) *Z. anorg. Chem.*, **17** (1898), 468.

(7) *Ibid.*, **17** (1898), 477.

(8) *Z. analyt. Chem.*, **39** (1900), 286.

(9) *Z. anorg. Chem.*, **5** (1894), 194; **7** (1894), 290; **17** (1898), 468.

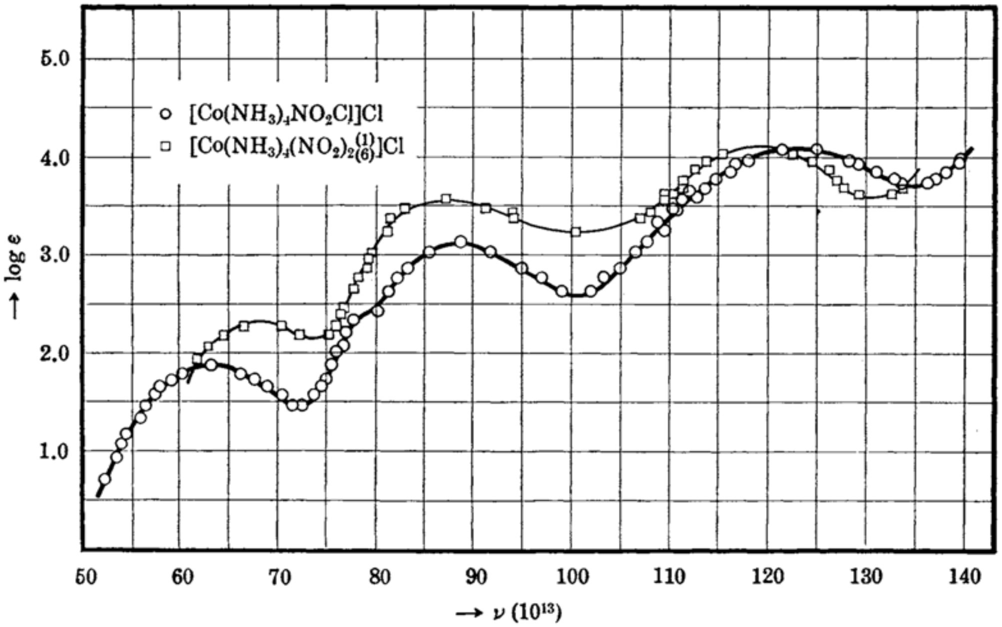
○ $[Co(NH_3)_4NO_2Cl]Cl$
□ $[Co(NH_3)_4(NO_2)_{2(6)}^{(1)}]Cl$
5.0
4.0
3.0
2.0
1.0
→ log ε
50
60
70
80
90
100
110
120
130
140
→ ν (10¹³)

Fig. 1.

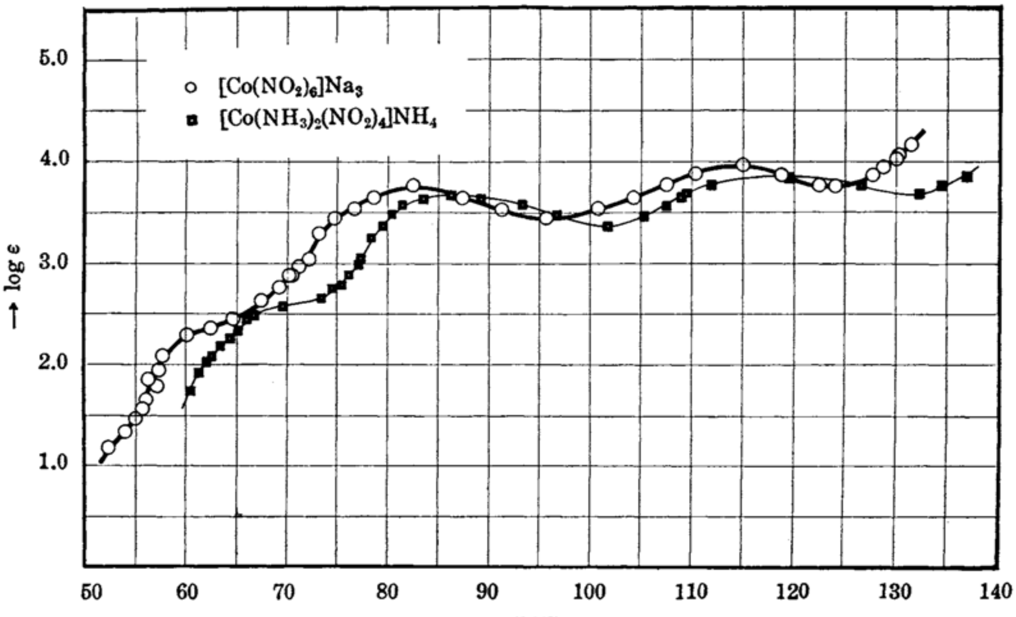
○ $[Co(NO_2)_6]Na_3$
■ $[Co(NH_3)_2(NO_2)_4]NH_4$
5.0
4.0
3.0
2.0
1.0
→ log ε
50
60
70
80
90
100
110
120
130
140
→ ν (10¹³)

Fig. 2.

Results and Discussion. The frequencies for maximum absorption of these complex salts are summarized in Table 1 together with those of $[\mathrm{Co(NH_3)_4Cl_2}{}_{\left\{\substack{(1)\\(6)}\right\}}]\mathrm{Cl}$⁽¹⁰⁾ and $[\mathrm{Co(NH_3)_3(NO_2)_3}]$⁽¹¹⁾. The frequencies are shown as ν_1, ν_2, and ν_3, the suffixes denoting the first, the second, and the third band respectively.

Table 1. Three Band Series.

	1st band		2nd band		3rd band		$\nu_2-\nu_1$ (10^{13})	$\nu_3-\nu_2$ (10^{13})	$\nu_3-\nu_1$ (10^{13})
	ν_1 (10^{13})	log ε	ν_2 (10^{13})	log ε	ν_3 (10^{13})	log ε			
$[\mathrm{Co(NH_3)_4Cl_2}{}_{\left\{\substack{(1)\\(6)}\right\}}]\mathrm{Cl}$	45	1.2	63	1.37	96	3.16	18	33	51
$[\mathrm{Co(NH_3)_4ClNO_2}]\mathrm{Cl}$	63	1.87	89	3.13	123	4.10	26	34	60
$[\mathrm{Co(NH_3)_4(NO_2)_2}{}_{\left\{\substack{(1)\\(6)}\right\}}]\mathrm{Cl}$	68	2.32	87	3.54	120	4.11	19	33	52
$[\mathrm{Co(NH_3)_3(NO_2)_3}]$	69	2.21	87	3.45	120	3.81	18	33	51
$[\mathrm{Co(NH_3)_2(NO_2)_4}]\mathrm{NH_4}$	68	2.56	86	3.67	119	3.85	18	33	51
$[\mathrm{Co(NO_2)_6}]\mathrm{Na_3}$	63	2.35	82	3.77	114	3.95	19	32	51

$[\mathrm{Co(NH_3)_4Cl\ NO_2}]\mathrm{Cl}$ and $[\mathrm{Co(NO_2)_6}]\mathrm{Na_3}$ have thus been proved to have three bands each in the visible and the near-ultraviolet regions as had been expected. The third band of $[\mathrm{Co(NO_2)_6}]\mathrm{Na_3}$ may be explained as due to the pairs of either nitro-radicals or nitrito-radicals in trans-positions, but the colour of the salt favours the former view and accordingly the nitro-radicals are responsible for the third band as will be expected from the original theory of Shibata.

Whereas $[\mathrm{Co(NH_3)_4(NO_2)_2}{}_{\left\{\substack{(1)\\(6)}\right\}}]\mathrm{Cl}$ and $[\mathrm{Co(NH_3)_3(NO_2)_3}]$ give their third bands at 120×10^{13}, nevertheless $[\mathrm{Co(NH_3)_2(NO_2)_4}]\mathrm{NH_4}$ shows its own at 119×10^{13}. The frequency 120×10^{13} may be assumed to be characteristic of the pair of nitro-radicals in trans-position to each other and the shift of the frequency towards longer wave-lengths may be explained as due to a disturbing effect on the pair of nitro-radicals by others which do not belong to the pair. In $[\mathrm{Co(NH_3)_3(NO_2)_3}]$, however, the disturbing effect is small and the shift is almost imperceptible. As for $[\mathrm{Co(NH_3)_2(NO_2)_4}]\mathrm{NH_4}$, the shift is perceptible, indicating that the accumulation of negative charges in the complex radical gives rise to more or less instabilization. In $[\mathrm{Co(NO_2)_6}]\mathrm{Na_3}$, the disturbing effect is still greater than in $[\mathrm{Co(NH_3)_2(NO_2)_4}]\mathrm{NH_4}$, causing the shift

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(10) *Loc. cit.*

(11) M. Kobayashi, unpublished.

to 114×10^{13}, and the higher instability may thereby be indicated. In $[Co(NH_3)_4Cl_2\{{}^{(1)}_{(6)}\}]Cl$ and $[Co(NH_3)_4Cl\ NO_2]Cl$, however, there will not exist such disturbing effect, and accordingly the frequencies 96×10^{13} and 123×10^{13} may be regarded as characteristic of the pair of two chlorine ions and that of a chlorine ion and a nitro-radical respectively.

Further we may point out some regularities among the frequencies for maximum absorption of those complex compounds in Table 1; viz., $\nu_3-\nu_1$, $\nu_2-\nu_1$, and $\nu_3-\nu_2$ are 51×10^{13}, 18×10^{13}, and 33×10^{13} respectively, with the only exception of $[Co(NH_3)_4Cl\ NO_2]Cl$ for which $\nu_2-\nu_1$ is 26×10^{13}.

Similar regularities may be found for other complex compounds. Absorption coefficients of a number of cobalt complex salts have recently(12) been measured in this laboratory and among them some of pentammine and tetrammine series are exemplified in Table 2 and 3.

Table 2. Pentammine Cobaltic Series.

	1st band		2nd band		$\nu_2-\nu_1$ (10^{13})
	ν_1 (10^{13})	log ε	ν_2 (10^{13})	log ε	
$[Co(NH_3)_5NO_3](NO_3)_2$	60	1.69	87	1.71	27
$[Co(NH_3)_5NO_2]Cl_2$	66	1.95	93	3.12	27
$[Co(NH_3)_5ONO]Cl_2$	64	1.74	91	2.79	27

Table 3. Tetrammine Cobaltic Series.

	1st band		2nd band		$\nu_2-\nu_1$ (10^{13})
	ν_1 (10^{13})	log ε	ν_2 (10^{13})	log ε	
$[Co(NH_3)_4(NO_2)_2\{{}^{(1)}_{(2)}\}]Cl$	65	1.98	91	3.11	26
$[Co(NH_3)_4CO_3]Br$	57	2.03	83	2.01	26
$[Co(NH_3)_4C_2O_4]Br$	59	1.78	84	1.88	25
$[Co(NH_3)_4Cl\ H_2O\{{}^{(1)}_{(6)}\}]Cl_2$	50	1.30	75	1.76	25
$[Co(NH_3)_4Cl\ H_2O\{{}^{(1)}_{(2)}\}]Cl_2$	59	1.67	83	1.57	24
$[Co(NH_3)_4(H_2O)_2\{{}^{(1)}_{(2)}\}]Cl_3$	60	1.40	84	1.48	24

For the pentammine series, $\nu_2-\nu_1$ is 27×10^{13} and for the tetrammine series, $24 \sim 26 \times 10^{13}$. It is noteworthy that the monacido-pentammine and

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(12) M. Kobayashi and others, unpublished.

the monacido-aquo-tetrammine salts form quite different series in regard to the value $\nu_2-\nu_1$, while all the tetrammine salts belong to the same series in spite of their different charges of complex radicals. This fact is somewhat significant from the viewpoint of the stability of linkages between the central ion and the co-ordinated ions and molecules. It is still more remarkable that for the trans-diacido-tetrammine salts $\nu_2-\nu_1$ is 18×10^{13}, whereas for the cis-diacido-tetrammine salts the value is 26×10^{13}.

Aqueous solutions of $[Co(NH_3)_4Cl\ NO_2]Cl$ behave as a compound of the tetrammine series so far as the first two bands are concerned. On the other hand the third band is observed for the same salt, as will be expected for a trans-diacido-tetrammine compound. This discrepancy may be explained as due to the following equilibrium⁽¹³⁾ which is set up immediately after dissolution in water.

$$[Co(NH_3)_4Cl\ NO_2]Cl + H_2O \rightleftarrows [Co(NH_3)_4NO_2\ H_2O]Cl_2\,.$$

The authors are preparing further investigation on this equilibrium.

Summary.

(1) In order to verify the postulate that the third band is due to a pair or pairs of negative radicals co-ordinated in trans-positions to each other, extinction coefficients of $[Co(NO_2)_6]Na_3$, $[Co(NH_3)_4Cl\ NO_2]Cl$, $[Co(NH_3)_4(NO_2)_2\genfrac{\{}{\}}{0pt}{}{1}{6}]Cl$, $[Co(NH_3)_2(NO_2)_4]NH_4$, etc. were measured.

(2) Aqueous solutions of $[Co(NO_2)_6]Na_3$ and $[Co(NH_3)_4Cl\ NO_2]Cl$ were proved to have the third bands as will be predicted from the postulate.

(3) Regularities among the frequencies of the first, the second, and the third band were pointed out, viz., for the cobalt complex salts, which show the third band, $\nu_3-\nu_2$ and $\nu_2-\nu_1$ are 33×10^{13} and 18×10^{13}, whereas for the pentammine and the tetrammine cobaltic salts, $\nu_2-\nu_1$ is 27×10^{13} and $24\sim26\times10^{13}$ respectively.

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(13) A. Werner, *Ber.*, **40** (1907), 4119; W. D. Harkins, R. E. Hall, and W. A. Roberts, *J. Am. Chem. Soc.*, **38** (1916), 2644.