The Third Absorption Bands of Co-ordination Compounds. IV. [Co dg_2' py Cl], [Co$(NH_3)_2(NO_2)_2ox$]$NH_4 \cdot H_2O$ and [Co ox_3]$K_3 \cdot 3.5H_2O$.

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According to Y. Shibata[1] and R. Tsuchida,[2] the third absorption bands of co-ordination compounds in aqueous solutions are due to a pair or pairs of negative radicals co-ordinated in trans positions, and a number of cobaltic complex compounds which have such third absorption bands have been illustrated by those[1][2][3] and the present[2][3][4] authors. The couples of negative radicals hitherto proved to give rise to the third bands may be classified according to their nature: (a) two univalent

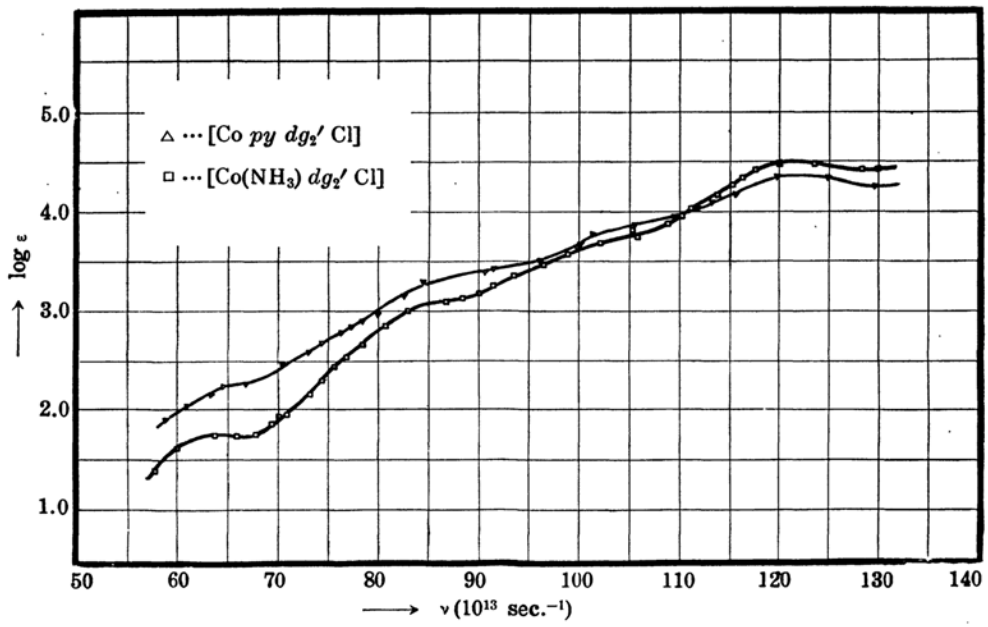

Fig. 1.

(1) Y. Shibata, *J. Chem. Soc. Japan*, **36** (1915), 1243.
(2) R. Tsuchida and S. Kashimoto, this Bulletin, **11** (1936), 785.
(3) R. Tsuchida and M. Kobayashi, this Bulletin, **12** (1937), 83.
(4) M. Kobayashi, A. Hagitani, and I. Mita, *J. Chem. Soc. Japan*, **58** (1937), 391.

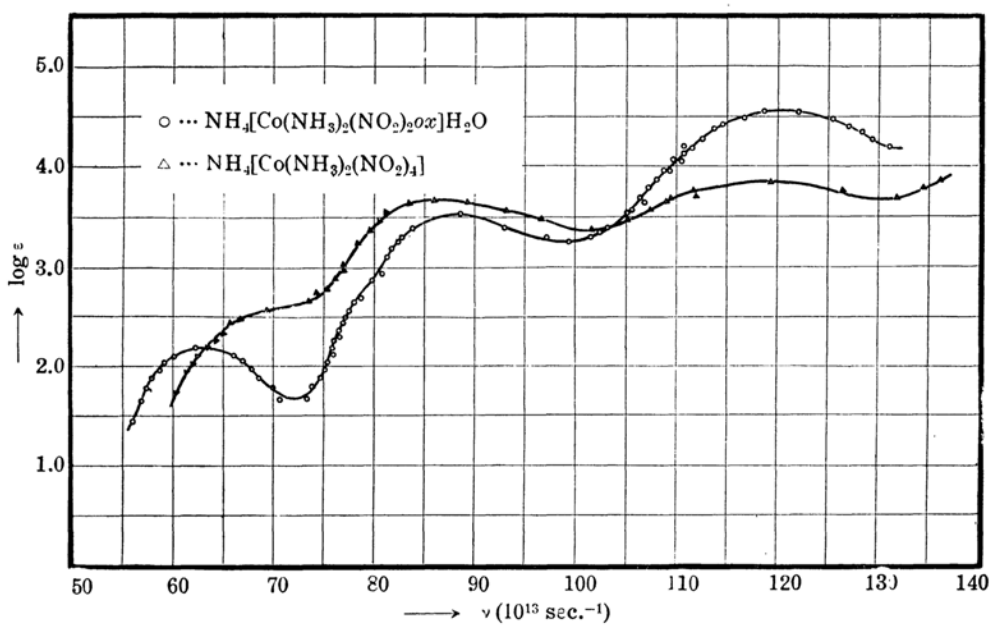
○ ··· $NH_4[Co(NH_3)_2(NO_2)_2ox]H_2O$
△ ··· $NH_4[Co(NH_3)_2(NO_2)_4]$
log ε
ν (10^{13} sec.$^{-1}$)

Fig. 2.

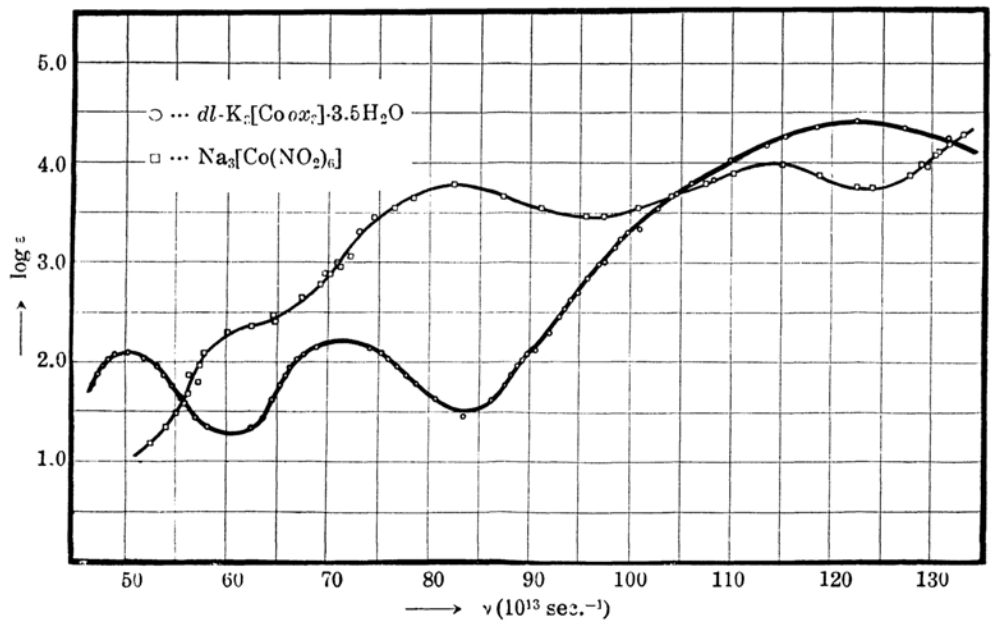
○ ··· *dl*-$K_3[Co\,ox_3]\cdot 3.5H_2O$
□ ··· $Na_3[Co(NO_2)_6]$
log ε
ν (10^{13} sec.$^{-1}$)

Fig. 3.

radicals, e.g., NO_2–NO_2, NO_2–Cl and Cl–Cl; and (b) two chelate univalent groups, e.g., dimethylglyoxime–dimethylglyoxime.

In the present paper another example of the class (b) is reported and moreover two other classes have been introduced: (c) one univalent and one bivalent radicals, i.e., NO_2–C_2O_4; and (d) two chelate bivalent radicals coupled with one valence each, i.e., C_2O_4–C_2O_4. In other words, it has been shown that a chelate bivalent radical such as oxalate can also give rise to the third band when it is coupled with a negative radical coordinated in trans position.

$[Co(NH_3)_2(NO_2)_2ox]NH_4 \cdot H_2O$[5] and $[Co\ ox_3]K_3 \cdot 3.5H_2O$[6] were prepared by the methods of Jörgensen and $[Co\ dg'_2\ py\ Cl]$[7], by that of Tschugaeff. The extinction coefficients of these compounds in aqueous solutions were determined for concentrations between 0.01 and 0.002 mol/l. and with varying thicknesses from 0.2 to 50 mm. The absorption curves are given in Fig. 1, 2, and 3.

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(5) S. M. Jörgensen, *Z. anorg. Chem.*, **11** (1896), 416. The symbol *ox* denotes an oxalate radical.

(6) *Ibid.*, **11** (1896), 440.

(7) L. Tschugaeff, *Ber.*, **40** (1907), 3503, 3505. The symbols *dg'* and *py* represent a dimethylglyoxime radical and a pyridine molecule respectively.