The Third Absorption Bands of Co-ordination Compounds. III. The Configuration of [Co dg'_2 NH_3 Cl]. A New Type of Optically Active Complex Radicals.

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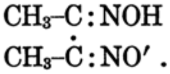
By the method of asymmetric adsorption⁽¹⁾ on quartz powder, the authors have proved that chloro-bisdimethylglyoximo-ammine-cobalt⁽²⁾ has an asymmetric structure and conventionally assigned to this non-electrolyte a cis-configuration as (a) in Fig. 1, i.e., [Co dg'_2 NH_3 $Cl^{(1)}_{(2)}$], where dg' denotes a dimethylglyoxime radical,



$$\begin{matrix} CH_3\text{–}C:NOH \\ CH_3\text{–}\dot{C}:NO' \end{matrix}.$$

On the other hand, however, it has been concluded by Nakatsuka⁽³⁾ that, in hexa-coordinated cobaltic complex salts which have a general formula [Co dg'_2 a_2]X, the two dimethylglyoxime radicals are strongly combined to the central cobalt atom in a common plane; viz., two a's are co-ordinated in trans position to each other. Also in hexa-coordinated cobaltous complex compounds of general formulæ [Co dg_2 X_2] and [Co dg_2 X Y], the two dimethylglyoxime molecules have been shown to form a plane, co-ordinating simply by auxiliary valences.⁽⁴⁾ Moreover, tetra-coordinated metallic complexes, which contain two glyoxime radicals, such as nickel-dimethylglyoxime, nickel-benzoyl-methyl-

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(1) R. Tsuchida, M. Kobayashi, and A. Nakamura, *J. Chem. Soc. Japan*, **56** (1935), 1339.

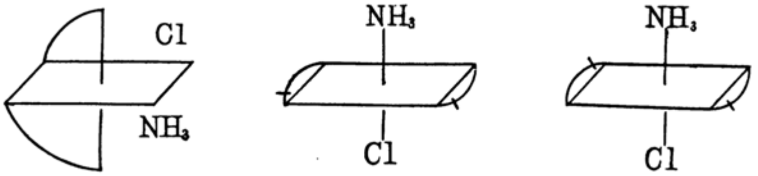
(2) R. Tsuchida, M. Kobayashi, and A. Nakamura, this Bulletin, **11** (1936), 38.

(3) Y. Nakatsuka, this Bulletin, **11** (1936), 48.

(4) Thilo and Heilborn, *Ber.*, **64** (1931), 1441.

glyoxime(5) and palladium-benzoyl-methyl-glyoxime(6), have also been proved to have all alike planar configuration.

The authors, therefore, are now inclined to the planar disposition and should like to assign to the optically active complex in question a trans-configuration, $[\mathrm{Co}\ dg'_2\ \mathrm{NH_3}\ \mathrm{Cl}{}^{(1)}_{(6)}]$. The types of uni-nuclear complex radicals, which have hitherto been shown to be resoluble into optical antimers, are $[\mathrm{M}\ ch_3]$, $[\mathrm{M}\ ch_2\ a_2{}^{(1)}_{(2)}]$, $[\mathrm{M}\ ch_2\ a\ b{}^{(1)}_{(2)}]$ and $[\mathrm{M}\ ch\ a_2{}^{(1)}_{(2)}\ b_2{}^{(5)}_{(6)}]$(7), where *ch* represents a chelate group. None of these types has trans-configuration. This apparent discrepancy may easily be overcome by reflecting upon the nature of dimethylglyoxime radical, which is co-ordinated to a central metallic atom by one auxiliary valence on one hand and by one principal valence on the other. Though $\mathrm{NH_3}$ and Cl are co-ordinated in trans-position and the two dimethylglyoxime radicals form a plane, the complex molecule remains asymmetric so long as the amphi-chelate radicals keep their two principal valences in trans-position to each other as (c) in Fig. 1.



(a) *cis*-Form active (b) *trans-cis*-Form inactive (c) *trans-trans*-Form active

Fig. 1.

If this be the case, the complex compound should have a third absorption band as will be predicted from the results given in the previous paper(8) of this series, in which it has been concluded that a pair of negative radicals co-ordinated in trans-position to each other gives rise to a third band. For the purpose of detecting the third band in order to verify the trans-configuration, the complex compound was prepared according to the method of Tschugaeff(9) and the molar extinction coefficients ε's were measured with aqueous solutions of concentrations between 0.010 and 0.002 mol/l. As had been expected, the third band was found at $\nu = 121 \times 10^{13}$ as in Fig. 2.

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(5) Sugden, *J. Chem. Soc.*, **1932**, 246.

(6) Dweyer and Mellor, *J. Am. Chem. Soc.*, **57** (1935), 605.

(7) This type has first been illustrated by Y. Shibata and T. Maruki, *J. Coll. Sci., Imp. Univ. Tokyo*, Sect. I, **41** (1917), Art. 2.

(8) R. Tsuchida and S. Kashimoto, this Bulletin, **11** (1936), 785.

(9) Tschugaeff, *Ber.*, **39** (1906), 2695.

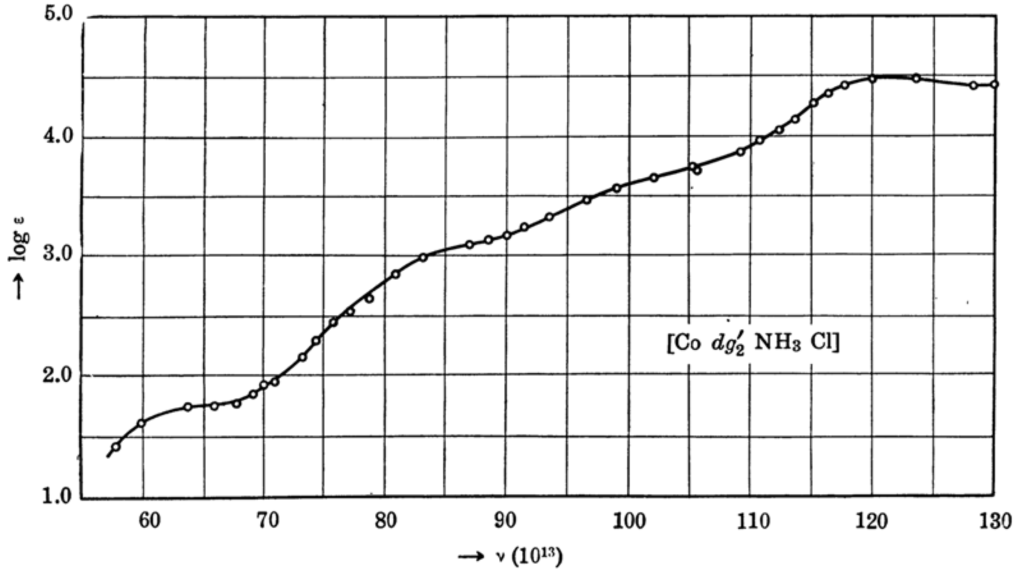

Fig. 2.

Thus the new types of active complex compound, [M ch_2 a $b^{(1)}_{(6)}$], has been introduced, and similar compounds of this type are now under investigation from the viewpoint of asymmetric resolution.

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