THE CONFIGURATION OF CHLOROBISDIMETHYL-GLYOXIMOAMMINE-COBALT.

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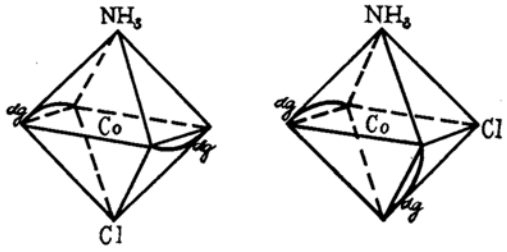
The authors have recently published a paper[1] on asymmetric adsorption of quartz and proposed a convenient method for detecting molecular asymmetry. It affords the means of revealing optical activity of racemic substances even when the traditional methods for resolution are unavailable. In the present paper is given one of the conspicuous examples of this method.

The steric configuration of chlorobisdimethylglyoximoammine-cobalt [Codg_2(NH_3)Cl] has not yet been determined. For this non-electrolytic ammine may be assumed two possible configurations, i.e., cis- and trans-forms (Fig.). If we could prove optical activity in the ammine, the configuration should consequently be of the cis-form, i.e. [Codg_2(NH_3)Cl$\{^{(1)}_{(2)}\}$]. The ammine, how-

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

ever, would not combine with active acids or bases to form resoluble diastereomers and the crystals have so far failed to give any enantiomorphic faces. In order to determine the configuration the authors applied the new metod making use of well-developed enantiomorphic crystals of quartz of various localities, Brazil, Kimbusen (Yamanashi Prefecture) and Naegi (Gifu Prefecture). The rock-crystals from Kimbusen were transparent quartz with large trapezohedral faces and the crystals from Naegi were smoky quartz with well-defined form and beautiful lustre. The latter species occurs often as twins of the Dauphiné type and it has been supposed to have irregular internal structure in spite of its well-defined external form. One of the purposes of using this species was to have some information about the internal structure of this interesting mineral. The authors, therefore, chose a left-handed single crystal and a right-handed twin of the Dauphiné type.



Trans-form $[Co\,dg_2(NH_3)Cl^{(1)}_{(6)}]$ Cis-form $[Co\,dg_2(NH_3)Cl^{(1)}_{(2)}]$

The ammine prepared from chloropentammine cobaltic chloride by the method of Tschugaeff[2], was dissolved in water at 50°C. and 10 c.c. of the warm saturated solution was shaken with g g. of quartz powder. When cold the supernatant solution was syphoned out for polarimetry. It rotated the plane of polarized light by α_c degrees for the C-line in a 4 cm. tube.

Locality	Crystal	g	α_c
Brazil	right-handed	1.03	−0.03
	left-handed	3.94	+0.00
Kimbusen	right-handed	2.43	−0.05
	left-handed	1.42	+0.02
Naegi	right-handed	5.55	−0.02
	left-handed	2.93	+0.03

The solution over left-handed quartz is dextrorotatory for the C-line and lævorotatory over right-handed species. The explanation of the effect is that the ammine is a racemic mixture of d- and l-isomers and the powder of quartz which has asymmetric structure in itself adsorbs molecules of one of the antipodes of the ammine more strongly than the other. In other words, the phenomenon of asymmetric adsorption takes place. The configuration of the ammine has thus been determined as $[Co dg_2(NH_3)Cl^{(1)}_{(2)}]$ instead of $[Co dg_2(NH_3)Cl^{(1)}_{(6)}]$.

(2) L. Tschugaeff, *Ber.*, **39** (1906), 2695.

It is noteworthy that, so far as the sign of rotation is concerned, $[Codg_2(NH_3)Cl\{^{1}_{2}\}]$ shows the same effect as similarly configurated cobalt ammines, e.g., $[Coen_2(NH_3)Cl\{^{1}_{2}\}]^{++}$, in spite of their different electrical charges. We may, therefore, assume that similar configurations give rise to similar asymmetric adsorption[3].

It is also interesting to note that the smoky quartz from Naegi shows the same specificity as other rock-crystals, though the effect produced by the right-handed twin crystal was observed a little less than that of the corresponding left-handed single crystal. It may, therefore, be concluded that the mineral species retains, at least locally, the same asymmetric structure as shown by the external form. As the left-handed quartz from Brazil had scarcely shown the effect, the experiment was repeated with greater quantities of the quartz, but the results were always negative, while the smallest quantity of the corresponding right-handed quartz was sufficiently effective. This fact may be explained by assuming that the crystal was racemic, as in the case of the twin of the Brazil law, in spite of its external asymmetric form. The utmost caution should, therefore, be paid to the choice of crystals.

The authors have tried similar experiments with quartz powder covered with monoatomic layer of nickel, as was used in the researches by Schwab, Rost and Rudolph[4] on asymmetric catalysis. The results, however, were negative.

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(3) *J. Chem. Soc. Japan*, **56** (1935), 1342.
(4) *Kolloid-Z.*, **68** (1934), 157.