

CCCLXII.—*Attempted Resolution of Triethylenedi-
aminenickel Chloride.*

By WILLIAM RALPH BUCKNALL and WILLIAM WARDLAW.

By the resolution of the triethylenediamines of cobalt, chromium, rhodium, and iridium into their optically active antipodes, Werner (*Ber.*, 1912, **45**, 121, 865, 1228; *Helv. Chim. Acta*, 1920, **3**, 472)

advanced a brilliant proof of his theory that in these salts the associated ethylenediamine molecules are octahedrally distributed round the central metallic atom. Nevertheless, it is a matter of interest that the similarly constituted derivatives of bivalent metals such as copper, zinc, and nickel have so far remained unresolved. The idea that in these salts the units are distributed otherwise than octahedrally seems to be disproved by the *X*-ray evidence (Wyckoff, *J. Amer. Chem. Soc.*, 1922, **44**, 1239) that in salts such as $[\text{Ni}_6\text{NH}_3]\text{Cl}_2$ the units have the customary octahedral distribution. In view of this conclusion, and especially because there was no recorded attempt at the resolution of the complex salt $[\text{Ni}(\text{en})_3]\text{Cl}_2$, the present research was undertaken, but with negative results.

For the resolution of triethylenediaminecobaltic chloride, Werner (*loc. cit.*) used the chloride- or bromide-tartrate, $[\text{Co}(\text{en})_3]_X\text{C}_4\text{H}_4\text{O}_6$, since he had found the normal tartrate unsuitable; and we therefore attempted to prepare the chloride-tartrate from $[\text{Ni}(\text{en})_3]\text{Cl}_2$ by a similar method, *viz.*, the use of one equivalent of silver tartrate. It was found, however, that on crystallisation the solution gave rise to a mixture of the normal tartrate and the original chloride. Consequently, it was decided to attempt the fractional crystallisation of the normal *tartrate*, a solution of which was obtained by triturating a solution of the chloride with the theoretical amount of silver tartrate and repeatedly extracting the residue with hot water. On evaporation, the liquid became syrupy and the crystals which separated were difficult to filter. After several recrystallisations, no difference in rotatory power could be detected, although there seemed to be two tartrates present, one crystalline and the other a gel—the deep violet colour of the solution rendered accurate reading of small rotations difficult.

Although warm hydrobromic acid converts the tartrates of triethylenediaminecobalt into the bromides (Werner, *loc. cit.*), yet in the case of the nickel salt this acid effects a complete disruption of the complex ion, even in the cold, with the formation of nickel bromide and ethylenediamine hydrobromide; hence it appears that the nickel complex ion is less stable than its cobalt analogue. This disruption of the nickel salt was avoided by the addition of barium chloride solution in excess to a solution of the complex tartrate; the filtrate was then treated with alcohol to complete the precipitation of barium tartrate and examined in the polarimeter, but all fractions of the complex tartrate treated in this way were found to yield inactive solutions.

Since it was possible that tartaric acid was too weak an acid to

effect a good resolution (see Pope, J., 1899, **75**, 1105), the stronger acid, *d*-camphorsulphonic acid, was used. On crystallisation, the *triethylenediaminenickel d-camphorsulphonate* showed no tendency to form a gel, but after several recrystallisations, the difference in rotatory power between the first and last fractions was still too small to warrant the assumption that a resolution had been effected.

Thus it seems either that the rotatory power of the active nickel triethylenediamine is very small or that racemisation in solution is extremely rapid.

EXPERIMENTAL.

Preparation of Triethylenediaminenickel Chloride.—The method used was that of Werner and others (*Z. anorg. Chem.*, 1899, **21**, 201). Ethylenediamine hydrate (3 mols.) was added to a concentrated solution of pure crystallised nickel chloride (1 mol.), the solution evaporated and crystallised, and the crystals twice recrystallised from water (Found: Ni, 16.85. Calc. for $[\text{Ni}(\text{en})_3]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$: Ni, 16.95%).

Attempted Preparation of the Chloride-Tartrate.—A concentrated solution of the complex chloride (5 g.) was triturated with silver tartrate (2.5 g.), prepared from a concentrated solution of Rochelle salt by precipitation with concentrated silver nitrate solution, washing with water, and drying in a desiccator covered with black paper. The residue of silver chloride was repeatedly extracted with hot water and the extracts were filtered and evaporated. Different fractions of the deep violet crystals had nickel contents varying from 14.1 to 16.5%. Thus it is probable that the chloride-tartrate cannot be isolated and that the crystals obtained were mixtures of the tartrate and the chloride (Calc. for $[\text{Ni}(\text{en})_3](\text{C}_4\text{H}_4\text{O}_6) \cdot 2\text{H}_2\text{O}$: Ni, 13.8; for $[\text{Ni}(\text{en})_3]_2(\text{C}_4\text{H}_4\text{O}_6) \cdot \text{Cl}_2$: Ni, 16.8%).

Preparation of Triethylenediaminenickel Tartrate.—A concentrated solution of triethylenediaminenickel chloride (4 g.) was triturated with silver tartrate (4 g.), and worked up as in the preceding case. The filtrate was very gel-like, rendering filtration difficult. Various fractions of crystals were dried on a porous plate, and all gave a constant nickel content (Found: Ni, 13.2; N, 19.3.

$[\text{Ni}(\text{en})_3](\text{C}_4\text{H}_4\text{O}_6) \cdot 3\text{H}_2\text{O}$
requires Ni, 13.3; N, 19.1%). Rotations of this substance were measured in a 0.5-dm. tube; after four recrystallisations the values of $[\alpha]_D$ for the first and last fractions were 17° and 21° respectively (α_D 0.11° and 0.15°). This difference is not greater than the probable experimental error. The tartrate was converted into the corresponding chloride by the method described above, but in each case the resulting solution was inactive.

Preparation of Triethylenediaminenickel d-Camphorsulphonate.—To 200 c.c. of a solution of silver nitrate (15 g.), just sufficient sodium hydroxide was added to precipitate all the silver as oxide; this was washed with distilled water until free from alkali salts, filtered, and the moist precipitate (11 g.) warmed with 150 c.c. of a solution of *d*-camphorsulphonic acid (20·5 g.). When dissolution of the oxide was complete, the filtered solution was neutral to litmus and contained 10 g. of the silver salt in 40 c.c. To 20 c.c. of a solution of recrystallised triethylenediaminenickel chloride (5 g.), 40 c.c. of the silver *d*-camphorsulphonate solution were added in small portions until the addition of one drop caused no more silver chloride to be precipitated; the solution was filtered, evaporated, and crystallised (Found : Ni, 8·15.

$[\text{Ni}(\text{en})_3](\text{C}_{10}\text{H}_{15}\text{O}_4\text{S})_2, \text{H}_2\text{O}$

requires Ni, 8·16%). The substance contained no chlorine. It was recrystallised several times from water, and rotations were measured for the mercury yellow line in a 0·5-dm. tube. No difference in rotation could be detected even after four recrystallisations, and $[\alpha]$ was constant at 17°.

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UNIVERSITY OF BIRMINGHAM,
EDGBASTON.

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