

and A to our modification which has the shortest *a*-axis of 27.60 Å.

In order to establish the water content of our modification we made an analysis of the amount of carbon present in our sample. The observed value was 21.15% \pm 0.15 and the calculated values for the anhydrous, monohydrate and dihydrate compounds are 21.80, 21.10, and 20.46, respectively.

We thus conclude that all four modifications belong to orthorhombic unit cells and that the modification studied by us corresponds to the monohydrate.

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trans-Dinitrotetrammine-cobalt(III) Acetate — Synthesis and Preliminary Crystal Data

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We here report a direct synthesis of *trans*-dinitrotetramminecobalt(III) acetate in a highly crystalline, analytically pure form and in better than 80% yield.

The ultra-violet-visible spectrum in aqueous solution shows the following maxima:

440 m μ (log ϵ = 4.20); 346 m μ (log ϵ = 3.61);
252 m μ (log ϵ = 4.20) and 193 m μ (log ϵ = 4.32).

This spectrum agrees well with that recorded by Carrassiti and Martelli.¹ The small deviations are attributable to the rapid aquation the compound undergoes in aqueous solution. Our spectrum was recorded within 10 min of commencing the dissolution, but a small amount of compound remained undissolved at that time.

The infra-red spectrum is useful to characterize the compound and the spectrum from 4000 to 400 cm⁻¹ is shown in Fig. 1. This spectrum differs considerably from that for the chloride or iodide. These latter salts are readily prepared by treatment of the acetate in aqueous solution with sodium chloride and iodide, respectively. The spectrum of the chloride is identical with that given by Le Postollec, Mathieu and Poulet² for the *trans*-chloride. We conclude that Beattie and Tyrell³ and also Blyholder and Kittila⁴ have confused the isomers of this compound in their infra-red studies.

Synthesis. Cobalt(II) acetate 4-hydrate (105 g, 0.42 mole) is dissolved in a solution of sodium nitrite (105 g) in 25% ammonia (500 ml), partly neutralised with 30 ml of 80% acetic acid. The mixture becomes slightly warm and to the warm solution is added 28 ml of 30% hydrogen peroxide as quickly as the effervescence will allow. The mixture is then heated on a hot plate just below its boiling point for 30 min. Much ammonia is given off and the product begins to separate from the hot solution. The heating is then stopped and the mixture cooled in ice and filtered under suction. When most of the mother liquid has been thus removed, the moist finely divided product is transferred to a beaker and stirred with 200 ml of acetone and again filtered. A second fraction which separates from the mother liquid is collected in the same way. These moist products are then transferred to a 4 l beaker and dissolved in 2.5–3 l 0.5% acetic acid by heating to near the boiling point. The solution is allowed to cool overnight and the thin golden-yellow plates are filtered under suction, washed with ethanol and acetone and dried under the heat lamp. The yield is 81 g, 80% based on the cobalt(II) acetate used. The compound requires no further purification.

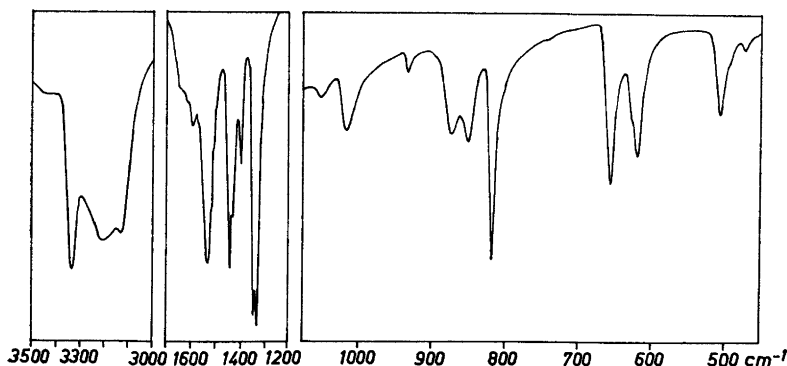


Fig. 1. Infra-red spectrum of *trans*-[Co(NO₂)₂(NH₃)₄]CH₃COO.

(Found: C 8.62; H 5.42; N 30.21; Co 21.07. Calc. for CoC₂H₁₅N₅O₆: C 8.63; H 5.40; N 30.22; Co 21.22). Cobalt was determined thermogravimetrically (Co₂O₄), the other elements by micro analyses.

Paper chromatography. Chromatography on Whatman 3 MM paper eluted with butanol, pyridine, water, acetic acid (40:30:20:10) causes this compound to move slowly ($R_F = 0.10$), as a single component. This procedure readily distinguishes our product from *trans*-trinitrotri-aminocobalt(III) which is a likely impurity⁵ ($R_F = 0.33$).

Spectra. The ultra-violet-visible spectrum was measured for a 10⁻⁴ M solution in 1 and 10 cm cells using a Carey 14 Spectrophotometer. The infra-red spectra were obtained using a Perkin-Elmer 337 Infra-red (Grating) Spectrophotometer with samples in vacuum-pressed potassium bromide discs.

Crystal studies. Crystallographic data were obtained from Weissenberg photographs of single crystal specimens using CuK α radiation. The crystals are orthorhombic with unit cell dimensions $a = 9.98 \text{ \AA}$, $b = 16.02 \text{ \AA}$, and $c = 6.71 \text{ \AA}$. This gives a cell volume of 1073.5 \AA^3 and a calculated density of 1.721 g/cm³ for four molecules per unit cell. Density of the

crystals measured by the flotation method is 1.722 g/cm³. Reflections hkl are missing for $h + k$ odd, and reflections $h0l$ are missing for l odd. The space group is therefore either $Cmc2_1$ or $Cmcm$.

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