Short Communications

Preparation of *cis*-Dinitrobis(trimethylenediamine)cobalt(III) Nitrite Using Dimethylsulfoxide as Solvent

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One of the authors has reported the preparation of several cobalt(III) complexes using dimethylsulfoxide (DMSO) as a solvent.^{1–3} It is of interest that there is some difference between ligand substitution reactions in water and in non-aqueous solvent and that even a complex difficult or troublesome to synthesize in water can be synthesized easily in non-aqueous solvent. In this paper we report that *cis*-isomer of dinitrobis(trimethylenediamine (= 1,3-diaminopropane))cobalt(III) nitrite is selectively synthesized using DMSO as a solvent.

The *trans*-[Co(NO₂)₂(tn)₂]⁺ (tn: trimethylenediamine = 1,3-diaminopropane) was first synthesized by Werner and Lindenberg,⁴ whereas two studies were recently reported on the *cis*-form, one by Kawaguchi and Kawaguchi⁵ and the other by Celap *et al.*⁶ In the former⁵ the complex was obtained from *trans*-[CoCl₂(tn)₂]Cl and sodium nitrite in water, while in the latter⁶ from [CoCO₃(tn)₂]·Cl·H₂O and sodium nitrite in 12% acetic acid aqueous solution. However, the data reported in the two investigations differ, particularly the UV absorption spectra.

Previous investigators have found that the *cis*-isomer has a much higher solubility in water than the *trans*-form. Moreover evidence was presented that in an aqueous solution the *cis-trans* equilibrium is rapidly established at room temperature. Because water and non hydrogen-bonded solvents often

show mutually exclusive solubilities, we attempted to synthesize the *cis*-isomer by precipitating it from a DMSO solution. These experiments, resulting in a convenient method of preparation for the *cis*-complex, form the subject of the present communication.

Experimental. Preparation. To 3 g (7.4 mmol) powdered Na₃[Co(NO₂)₆] suspended in 10 ml of DMSO 1.1 g (14.8 mmol) trimethylenediamine was added. The mixture was heated on a water bath, whereby the suspended complex reacted gradually with the amine and after a while, an orange yellow crystalline precipitate was formed. The reaction was completed within 15–20 min. The precipitate was filtered off, washed several times with ethanol and then with ether, finally, dried *in vacuo*. Yield was ca. 1.4 g.

Found: C, 21.04; H, 5.95; N, 27.18%. Calc. for [Co(NO₂)₂(tn)₂]NO₂: C, 20.88; H, 5.84; N, 27.40%.

The *trans*-isomer was synthesized in the usual way.⁴

Thin-layer chromatography. As an adsorbent, cation-exchange cellulose P-41 pretreated with 5 M sodium chloride solution was used. The development was carried out at room temperature using a 0.5 M sodium chloride solution.

Spectral measurement. The visible and UV spectra were recorded with a Hitachi 124 spectrophotometer, and the IR spectra with a Hitachi EPI-L spectrophotometer.

The ¹H NMR spectra were obtained with a Japan Electrooptics JNM-60 spectrometer.

Results and discussion. Preparation of complex. In this study DMSO was used as a solvent. With dimethylformamide, instead of DMSO, a mixture of *cis*- and *trans*-form was found to be precipitated.

Thin-layer chromatography. The solution of our complex yields only spot at an R_f value of 0.5, and the filtrate shows a spot at 0.7 accompanied by a very faint spot at 0.5. On the other hand, the *trans* complex synthesized in the usual way⁴ shows a spot at 0.7. The *cis*-isomer being the more polar of the two would be expected to have a lower R_f value than the *trans*-isomer. This suggests that the main product of the synthesis is, in fact, the *cis*-isomer.

Visible and UV spectra. The absorption curve of our complex is similar to that of the *cis*-isomer in Ref. 6. The IR spectrum of the proposed *cis*-isomer of Ref. 5 corresponds closely to that of the *trans*-

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Fig. 1. Infrared absorption spectra in the 400–650 cm^{-1} region. (1) *cis*-[Co(NO₂)₂(tn)₂]NO₂ and *trans*-[Co(NO₂)₂(tn)₂]NO₂.

isomer. The first absorption band of the *trans*-isomer seems to split into two (21.2 and 22.3 kK), but the *cis*-isomer has a single maximum at 22.1 kK. A difference of the same kind arises with the *cis*-isomer and *trans*-isomer of [Co(NO₂)₂(en)₂]NO₂.⁷

IR spectra. As shown in Fig. 1, the spectrum of *trans*-isomer shows a slightly split Co–N(NH₂) stretching at about 530 cm^{-1} , whereas in that of our complex two bands are observed. The *trans*-isomer further exhibits two bands attributable to NO₂ wagging (610 cm^{-1}) and Co–N(NO₂) stretching

Fig. 2. Proton nuclear magnetic resonance spectra in dimethylsulfoxide-*d*₆. (1) *cis*-[Co(NO₂)₂(tn)₂]NO₂ and (2) *trans*-[Co(NO₂)₂(tn)₂]NO₂.

(450 cm^{-1}) each of which is clearly split into two bands in the spectrum of our complex.

¹H NMR spectra. The ¹H NMR spectra were assigned by comparing with [Co(tn)₃]³⁺. The spectrum of our complex is shown in Fig. 2 together with *trans*-isomer. The *trans*-isomer gives two singlets which correspond respectively to the single species of β -methylene proton at 1.50 ppm and α,α' -methylene proton at 2.22 ppm, the ratio of their areas being 1:2, which show the symmetrical configuration of the *trans*-form. In the corresponding parts of the spectrum of our complex complicated patterns are observed as would be expected for the *cis*-isomer.

The results described support strongly our conclusion that the complex prepared by us – as well as that described in Ref. 6, but not the complex presented in Ref. 5 – consists mainly of the *cis*-dinitrobis(trimethylenediamine)cobalt(III) nitrite.

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