

## Formation of Tris (ethylenediamine)cobalt(III) Coordination Complex in Dimethyl Sulfoxide

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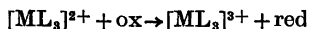
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Under anaerobic conditions at room temperature,  $[\text{Co en}_3]^{2+}$  in DMSO solution is not oxidized to  $[\text{Co en}_3]^{3+}$ , neither in solutions containing excess free ligand, nor in solutions with excess hydrogen chloride.

On admission of molecular oxygen, oxidation of the complex proceeds rapidly under development of  $(\text{CH}_3)_2\text{S}$ , which shows that DMSO takes part in the oxidation.

Dimethyl sulfoxide (DMSO) is often used as a reaction medium for the preparation of transition metal complexes. In view of its extensive use as a combined solvent and oxidant in organic chemistry<sup>1</sup> it would be interesting to study a complex forming reaction involving an oxidation, and to investigate whether DMSO itself could act as an oxidant.

Much work has been reported on the role of DMSO as a solvent and as a ligand.<sup>2</sup> However, to our knowledge its oxidation properties in coordination chemistry have not attracted attention, except for a note in the experimental section of a paper by Berney and Weber.<sup>3</sup> Thermodynamically it would be possible for DMSO to act as the oxidant in a number of reactions of preparative importance such as



where, *e.g.*, M = Co, Cr and L = ethylenediamine or similar ligands. DMSO is gaining increasing application as a medium for such reactions and it is obvious to ask whether in fact DMSO does participate in the reaction. Such a conjecture could be inspired by the obnoxious smell attributable to dimethylsulfide which manifests itself during such reactions.

Looking at standard potentials of redox pairs in aqueous solution at room temperature, we

find that as  $E^0(\text{Co}^{2+}/\text{Co}^{3+}) = 1.83$  V, it seems improbable that DMSO can oxidize  $\text{Co}^{2+}$  directly to  $\text{Co}^{3+}$ . (The potential is found in 1 N nitric acid by extrapolation from the measurements of Noyes and Deahl<sup>4</sup>). For ethylenediamine complexes, however, we find<sup>5</sup>  $E^0(\text{Co en}_3^{2+}/\text{Co en}_3^{3+}) = -0.26$  V, and, as DMSO oxidizes hydrogen iodide,<sup>6</sup> and  $E^0(2\text{I}^-/\text{I}_2) = 0.56$  V, it should thermodynamically be possible that DMSO would oxidize  $[\text{Co en}_3]^{2+}$ .

In the present work, the formation of  $[\text{Co en}_3]^{3+}$  from  $\text{Co}^{2+}$  and ethylenediamine in DMSO solution was studied. Anhydrous  $\text{CoCl}_2$  is easily dissolved in DMSO, and visible spectra of the resulting complexes are well known,<sup>7-10</sup> as are the spectra of  $[\text{Co en}_3]^{2+11}$  and  $[\text{Co en}_3]^{3+12}$ . Therefore the reaction was followed spectrophotometrically.

### EXPERIMENTAL

*Preparations.* All distillation and handling of solutions took place under nitrogen purified through conc.  $\text{H}_2\text{SO}_4$ , KOH pellets, and a column of reduced copper-chromium-oxide (BASF) kept at 100 °C.

Dimethyl sulfoxide (Th. Schuchardt) was dried over Linde 4A sieves and distilled in a stream of nitrogen at reduced pressure through a 50 mm column<sup>13</sup> packed with Dixon gauze rings. B.p. at 1.0–1.5 Torr 36–38 °C; according to Douglas<sup>14</sup> the vapour pressure at 37 °C is 1.35 Torr.

Ethylenediamine (Riedel-de-Haën) was dried over sodium hydroxide<sup>15</sup> and distilled under nitrogen at 1 atm. B.p. at 760 Torr 116.5 °C; accepted value<sup>16</sup> 116.5 °C. A stock solution of ethylenediamine in DMSO was prepared by dilution of 1.46 ml en to 25 ml with DMSO. Potentiometric titration in aqueous solution

showed a concentration of 0.052 g ethylenediamine per ml solution.

A stock solution of hydrochloric acid in DMSO was prepared by slowly bubbling nitrogen through an aqueous solution of conc. HCl, conc.  $H_2SO_4$ , and pure DMSO. Titration in aqueous solution with NaOH gave 0.019 g HCl per ml solution. All solutions were prepared in a glove box flushed with nitrogen.

$CoCl_2 \cdot 6H_2O$  (E. Merck) was dehydrated at 160 °C.

The following preparation of complexes in solution was representative: 13.00 mg  $CoCl_2$  was weighed into a 10 ml measuring flask. This was placed in the glove box, opened, and flushed with nitrogen applied through a small tube. The salt was dissolved in 5 ml DMSO, and 0.36 ml ethylenediamine solution added. The measuring flask was then filled to the mark with DMSO, the contents mixed, and a 1 cm cell for spectral measurements was filled. After measurement, the cell was emptied into the measuring flask, and 0.20 ml HCl solution was added. After mixing, a cell was filled and the spectrum measured. In this experiment, the molar ratios  $CoCl_2:en:HCl$  were 1:3.33:1.04, and the formality with respect to  $CoCl_2$  was 0.010 F.

Compositions investigated were:  $CoCl_2$  (mg), en (ml), HCl (ml): 3.93, 0.11, 0.10; 13.00, 0.36, 0.20; 23.66, 0.63, 0; 15.37, 0.41, 0; 16.63, 0.45, 0.25; 26.94, 0.72, 0.80; 14.07, 1.00, 0.21. Molar ratios  $CoCl_2:en:HCl$  were 1:3.37:0.52; 1:3.33:1.04; 1:3.20:0; 1:3.21:0; 1:3.25:1.02; 1:3.22:2.01; 1:8.60:1.01.

Absorption spectra in the range 325–800 nm were recorded with a Cary model 11 spectrophotometer.

**Qualitative observations.**  $CoCl_2$  dissolved in DMSO to give an intensely blue complex. On addition of ethylenediamine only, the colour changed to slightly reddish, which colour persisted if air was rigorously excluded. Diffusion of air through ground glass joints produced an intense reddish brown colour. This happened whenever measuring flasks were left in the room, though no changes were seen in solutions stored in spectrophotometer cells for periods of up to one month. Deliberate air oxidation of the reddish brown solutions produced no further changes, and oxidation of the contents of a cell by air applied through a capillary produced the same reddish brown colour. Concurrent with this oxidation, an intense smell of sulfide was detected. Dimethyl sulfide, which boils at 37 °C, was driven off by a stream of air and absorbed in a 1 M solution of mercury(II) chloride in abs. ethanol. The derivative was filtered off and washed with abs. ethanol. M.p. 155–157 °C (uncorr.), lit. value 158 °C.<sup>17</sup> An estimate of the amount of sulfide formed in relation to the amount of cobalt oxidized was not attempted.

HCl added to the solution of  $CoCl_2$  and ethylenediamine produced a slightly green colour, changing to blue with larger amounts of HCl. Oxidation of such solutions produced a

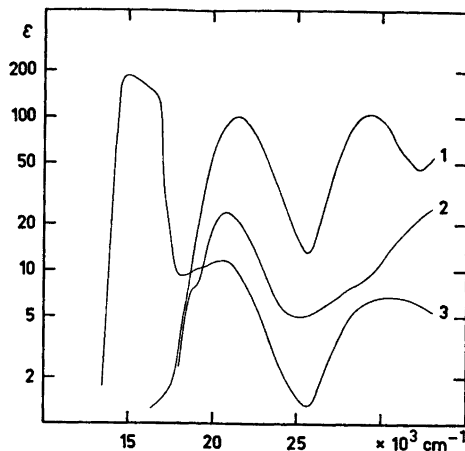


Fig. 1. Absorption spectra of  $[Co en_3]^{3+}$  (1) and  $[Co en_3]^{2+}$  (2) in DMSO compared with a solution of  $CoCl_2:en:HCl$  (1:3.2:2) (3).

yellow or brownish yellow colour, identical with the colour of  $[Co en_3]Cl_2$  dissolved in DMSO, and released dimethyl sulfide.

HCl added to an oxidized solution as mentioned above produced no visible change in the reddish brown colour.

## RESULTS

Spectra of  $[Co en_3]^{3+}$  and  $[Co en_3]^{2+}$  in DMSO are shown in Fig. 1. The spectral data ( $\lambda$ , nm;  $\sigma$ ,  $cm^{-1}$ ;  $\epsilon$ ,  $l mol^{-1} cm^{-1}$ ) are for  $[Co en_3]^{2+}$ : (535; 18 700; 5) and (482; 20 700; 24), and for  $[Co en_3]^{3+}$ : (467; 21 400; 102) and (342; 29 200; 105). The positions of the visible bands are thus close to values reported for aqueous solutions,<sup>8,9</sup>  $[Co en_3]^{2+}$ : (535; 18 700; 2) and (461; 21 700; 14), and  $[Co en_3]^{3+}$ : (467; 21 400; 86) and (338; 29 600; 80). The larger extinction coefficients in DMSO are probably due to either the higher index of refraction or to the formation of outer-sphere complexes modifying the conformation to slightly larger deviation from octahedral microsymmetry.

Also shown in Fig. 1 is the spectrum of a solution of  $CoCl_2$ , en, and HCl (1:3.22:2.01). This spectrum is influenced by formation of tetrahedral chlorocomplexes. An analysis of the spectrum shows that 24 % of the cobalt is tetrahedral. This is close to the 20 % of the tetrahedral form found by Buffagni and Dunn<sup>10</sup> in a solution of  $[CoCl_4]^{2-}$  in DMSO not containing ethylenediamine.

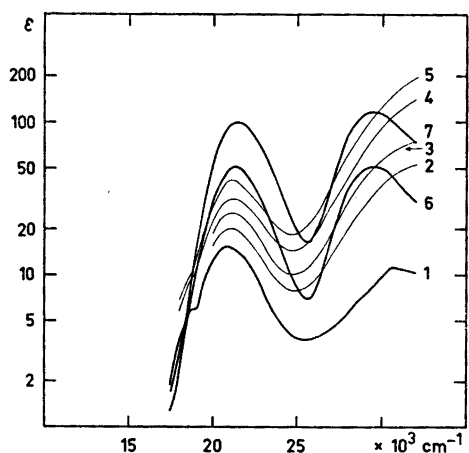


Fig. 2. Gradual oxidation over eight days of a DMSO-solution containing  $\text{CoCl}_2 \cdot \text{en} : \text{HCl}$  (1:8.6:1).

Fig. 2 shows spectra of a solution of  $\text{CoCl}_2 \cdot \text{en}$ , and  $\text{HCl}$  (1:8.60:1.01) for various degrees of oxidation. There is a lapse of five days between curves Nos. 1–5 and No. 6, and of three more days to No. 7. It is seen how the  $[\text{Co en}_3]^{2+}$  formed originally is gradually oxidized to  $[\text{Co en}_3]^{3+}$  through intermediates absorbing in the ultraviolet.

Fig. 3 shows spectra of a solution not containing  $\text{HCl}$  (1:3.21:0) for various degrees of

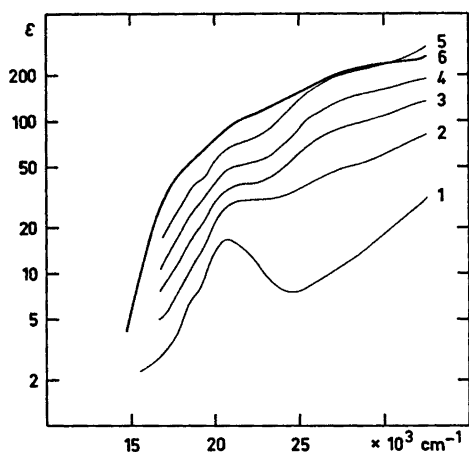


Fig. 3. Oxidation over five days of a DMSO-solution containing  $\text{CoCl}_2 \cdot \text{en} : \text{HCl}$  (1:3.2:0).

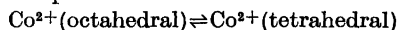
oxidation. Curves Nos. 1–5 were obtained on the same day; and No. 6 five days later. It is seen that  $[\text{Co en}_3]^{2+}$  does indeed react, but that very little or no  $[\text{Co en}_3]^{3+}$  is formed. Rather, reaction products are formed which seem to correspond to the intermediates seen in acidic solution.

## DISCUSSION

The following conclusions may be drawn:

(1)  $[\text{Co en}_3]^{2+}$  is not oxidized by DMSO under anaerobic conditions.

(2) Addition of  $\text{HCl}$  does not catalyse such a reaction, but changes the distribution of labile complexes:



(3) Admission of air causes oxidation to start.

(3a) When solutions do not contain  $\text{HCl}$ , di- or polynuclear complexes are formed. Such complexes may have the general formula  $[\text{en}_2\text{XCo}-\text{O}_2-\text{CoY en}_2]^{4+}$ , with most probably  $\text{X} = \text{Y} = \text{DMSO}$ .  $-\text{O}_2-$  may be a peroxo group, giving the  $\text{Co}$  atoms the formal oxidation number 2.5. When  $\text{HCl}$  is added to these solutions, the complexes are not degraded to simple mononuclear species.

(3b) Solutions containing  $\text{HCl}$  before oxidation give  $[\text{Co en}_3]^{3+}$  through di- or polynuclear intermediates, analogous to aqueous solutions.

(4) As a strong smell of sulfide (identified as dimethyl sulfide through its mercury(II) chloride derivative) was found over all oxidized solutions, basic and acidic alike, it seems likely that DMSO does act as an oxidant towards  $[\text{Co en}_3]^{2+}$ , though only when oxygen, maybe as a peroxo group, is present as a catalyst. This behaviour of DMSO would be analogous to that found in selective oxidation of benzyl alcohols.<sup>18</sup>

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