Comments on the Synthesis and Aquation of *cis*- and *trans*-$Co(en)_2(NO_2)Cl^+$ in Aqueous Solution

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An earlier study from this laboratory reported volumes of activation for the linkage isomerization (O-bonded to N-bonded) reactions of complexes of the type $M(NH_3)_5ONO^{2+}$ (M = Co(III), Rh(III) and Ir(III)) [1]. We are at present expanding this investigation to include the linkage isomerization reactions of *cis*- and *trans*-$Co(en)_2(ONO)_2^+$. Such reactions are expected [2] to occur in two consecutive steps, each involving one nitrito ligand. The preparation of the intermediate $Co(en)_2(NO_2)(ONO)^+$ species should significantly simplify the kinetic analysis of the isomerization reactions of the dinitrito complexes, since they allow a direct measurement of the second isomerization step. We were unsuccessful in isolating the pure nitro–nitrito species as intermediates during the isomerization reactions of the dinitrito complexes [3], but prepared these in solution via NO^+ uptake [4] by the $Co(en)_2(NO_2)OH_2^{2+}$ species. The latter can be synthesized *via* aquation of *cis*- and *trans*-$Co(en)_2(NO_2)Cl^+$. Although various papers mention the preparation of these species, they mostly refer to the original work by Werner [5, 6]. We encountered various difficulties with the synthetic work, and report our experiences in this communication.

trans-$[Co(en)_2Cl_2]Cl$ is used as starting material in these preparations. Numerous papers [5, 7–13] report different synthetic procedures, indicating that the preparation may indeed be problematic. As a consequence of various attempts, the following method was employed as a combination of other procedures. 160 g $CoCl_2 \cdot 6H_2O$ dissolved in 500 ml H_2O was added to 83 g fuming ethylenediamine in 550 ml H_2O, after which 60 ml 30% H_2O_2 was added slowly under constant stirring over a period of one hour. This was followed by the addition of 300 ml HCl(c) and slow evaporation on a water bath until a crust was formed. The solution was cooled and allowed to stand overnight. (It is important to add the concentrated HCl immediately after the completion of the oxidation step in order to prevent the formation of $[Co(en)_3]Cl_3$). The green crystals of *trans*-$[Co(en)_2Cl_2]Cl \cdot HCl$ were filtered and washed with alcohol and ether. The complex was then recrystallized from a water–HCl mixture and dried at 110 °C according to published procedures [8]. During the drying stage the hydrogen chloride of crystallisation is released and a dull green powder of *trans*-$[Co(en)_2Cl_2]Cl$ is obtained, yielding 116 g. The chloride salt was converted into the perchlorate salt by recrystallisation from a $NaClO_4$ solution.

Anal. *Trans*-$[Co(en)_2Cl_2]ClO_4$. Calcd.: C, 13.7; H, 4.6; N, 16.0; Cl, 30.5. Found: C, 13.8; H, 4.5; N, 16.0; Cl, 30.7%.

The preparation of *trans*-$[Co(en)_2(NO_2)Cl]X$ (X = NO_3^-, ClO_4^-) was performed as described by Werner [5, 6]. The method for the *cis* analogue resulted in very poor yields, in most cases strongly impurified with *cis*/*trans*-$Co(en)_2(NO_2)_2^+$, *cis*/*trans*- $Co(en)_2Cl_2^+$ and/or *cis*/*trans*-$Co(en)_2(NO_2)OH_2^{2+}$, depending on the reaction conditions employed. The following modified method however gave good results: 34 g *trans*-$[Co(en)_2Cl_2]Cl$ was dissolved in 70 ml H_2O, and 10 ml of a saturated $NaNO_2$ solution (82 g/100 ml) was added slowly under constant stirring. The mixture was allowed to stand at room temperature for 1 hour, after which the orange–red precipitate was filtered off, washed with alcohol and ether, and dried in air. 2 g of the raw product was dissolved in 20 ml H_2O, 3 to 4 drops HCl(c) added, and immediately cooled in an ice bath with thorough stirring. After 20 minutes the precipitate was filtered, washed with alcohol and ether, and dried in vacuo. Yield: 1.4 g.

Anal. *Cis*-$[Co(en)_2(NO_2)Cl]Cl$. Calcd.: C, 16.2; H, 5.4; N, 23.6; Cl, 23.9. Found: C, 15.9; H, 5.4; N, 23.1; Cl, 23.1%.

The UV-visible spectra of the prepared complexes are summarized, along with literature values, in Table I. The spectra of aqueous solution of *cis*- and *trans*-$Co(en)_2(NO_2)Cl^+$ change rapidly with time, ascribed to the aquation reactions [14, 15] during which *cis*- and *trans*-$Co(en)_2(NO_2)OH_2^{2+}$ are formed. Repetitive scan spectra of the latter aquation reactions (Fig. 1) show clean isosbestic points at 488 and 406, and 468 and 410 nm respectively for the *cis* and *trans* species. These also show that the nitro–chloro complexes partially aquate during the dissolution process, such that solutions of the nitro–chloro complexes always contain some nitro–aquo species. This is especially true for the *trans* species. Furthermore, the aquation equilibrium is essentially shifted to the nitro–aquo side, since it is impossible to stabilize the nitro–chloro species by even working in 2 to 3 *M* chloride medium. The spectral properties of the aquation products are also included in Table I. Pure stock solutions of the nitro–aquo complexes were obtained as follows: The nitro–chloro complexes were dissolved and allowed to aquate overnight at room temperature. The solutions were then passed through an

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TABLE I. UV-Visible Absorption Spectra.

Species	λ_{max}, nm	ϵ_{max}, M^{-1} cm^{-1}	Reference
trans-$[Co(en)_2Cl_2]ClO_4$	618; 455; 400	37.2; 28.2; 37.8	16
	618; 457 (sh); 402 (sh)	39.5; 29.6; 38.9	This work
cis-$[Co(en)_2(NO_2)Cl]Cl$	~510; [a]	~90; [a]	17
	504; 336	85.3; 1672	This work
trans-$[Co(en)_2(NO_2)Cl]NO_3$	489; 335	[a]; 965	18
	484; 335	87.8; 1404	This work
cis-$Co(en)_2(NO_2)OH_2^{2+}$	460; 329	94; ~ 2100	14, 18, 19
	458; 328	92.9; 2021	This work
trans-$Co(en)_2(NO_2)OH_2^{2+}$	464; 335	[a]; 952	14, 18
	464; 336	81; 1033	This work

[a] Not quoted in the reference.

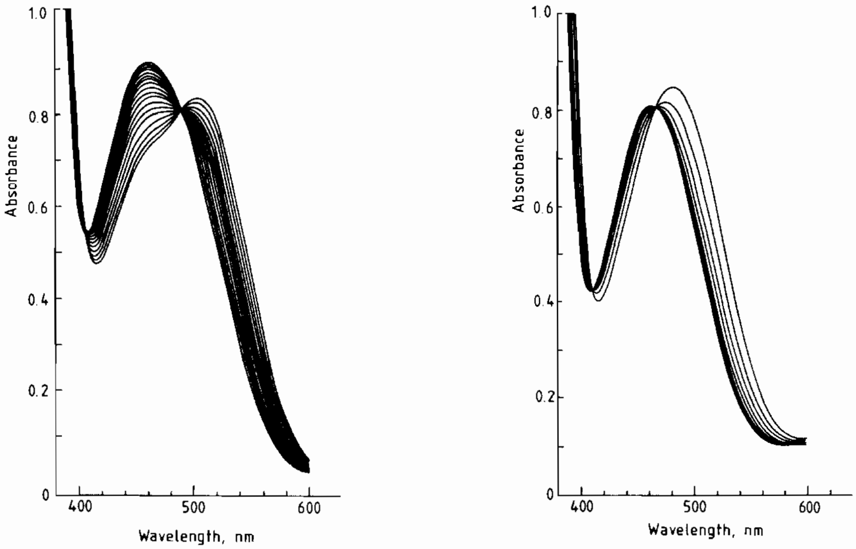

Fig. 1. Repetitive scan spectra of the aquation of $Co(en)_2(NO_2)Cl^+$ to $Co(en)_2(NO_2)OH_2^{2+}$ at 25 °C. a) *cis* complex: [Co(III)] = 1.02×10^{-2} *M*, Δt = 15 min. b) *trans* complex: [Co(III)] = 1.01×10^{-2} *M*, Δt = 7 min. Optical pathlength = 1 cm.

anion exchange column (Lewasit 5080) in its OH^- form, after which the final pH of the solution was adjusted to 3 by dropwise addition of $HClO_4$.

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