

## The Synthesis and Spectrum of *trans*-Isothiocyanatoaquobisethylenediaminechromium(III)

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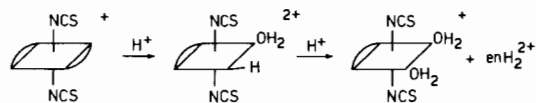
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The synthesis of *trans*-Cr(en)<sub>2</sub>NCS(H<sub>2</sub>O)<sup>2+</sup> is reported. This material results from reaction of *trans*-Cr(en)<sub>2</sub>NCSBr<sup>+</sup> with Hg<sup>2+</sup> in aqueous perchlorate solution; the complex is isolated in solution by ion-exchange chromatography. The spectrum of *trans*-Cr(en)<sub>2</sub>NCS(H<sub>2</sub>O)<sup>2+</sup> has peaks at 5010 Å (52.4 M<sup>-1</sup> cm<sup>-1</sup>), asymmetrical to the high energy side, and at 3650 (49.6). It is also proven that the molecule previously assigned the structure *trans*-Cr(en)<sub>2</sub>NCS(H<sub>2</sub>O)<sup>2+</sup> is in reality one of the two isomers of Cr(en)(H<sub>2</sub>O)<sub>3</sub>NCS<sup>2+</sup>.

### Introduction

The investigation of the photolysis of Cr(III) complexes has led to a need for accurate spectral data on a number of complexes hitherto not investigated, or examined only within the context of other studies. This need is especially critical for those who use differential spectroscopy to identify the isomeric composition of the products of photolytic aquation of Cr(III) complexes. The case relevant to this note is *trans*-Cr(en)<sub>2</sub>NCS(H<sub>2</sub>O)<sup>2+</sup>. There is recorded in the literature<sup>1</sup> a spectrum claimed to be that of *trans*-Cr(en)<sub>2</sub>NCS(H<sub>2</sub>O)<sup>2+</sup> and several authors have used this spectrum to determine<sup>2,3</sup> or to imply<sup>4</sup> a geometrical course for a photoaquation.

*trans*-Isothiocyanatoaquobisethylenediaminechromium(III) became of interest to us during studies on the photolysis of Cr(III) complexes containing the -NCS grouping. The procedure in the literature for the synthesis of *trans*-Cr(en)<sub>2</sub>NCS(H<sub>2</sub>O)<sup>2+</sup> starting from *trans*-Cr(en)<sub>2</sub>(NCS)<sub>2</sub><sup>+</sup>,<sup>1</sup> however, did not seem compatible with our earlier observations,<sup>6</sup> or those of Holba<sup>7,8</sup> on the aquation path of *trans*-Cr(en)<sub>2</sub>(NCS)<sub>2</sub><sup>+</sup>:



Because of the aforementioned need to have the correct spectrum of *trans*-Cr(en)<sub>2</sub>NCS(H<sub>2</sub>O)<sup>2+</sup> in the dif-

ferential spectroscopic technique, we felt it was necessary to re-examine the structural and stoichiometric properties of the molecule that Veigel and Garner<sup>1</sup> assigned to *trans*-Cr(en)<sub>2</sub>NCS(H<sub>2</sub>O)<sup>2+</sup>. In this paper we report that that original assignment is in error, identify the substance synthesized by Veigel and Garner, and give a correct synthesis and spectrum of *trans*-Cr(en)<sub>2</sub>NCS(H<sub>2</sub>O)<sup>2+</sup>.

### Experimental

#### Materials

The preparation and purification of *trans*-[Cr(en)<sub>2</sub>(NCS)<sub>2</sub>]ClO<sub>4</sub> has been reported previously.<sup>6</sup> *trans*-[Cr(en)<sub>2</sub>NCSBr]ClO<sub>4</sub> was prepared from *trans*-[Cr(en)<sub>2</sub>H<sub>2</sub>OBr]Br<sub>2</sub> with minor modifications of the procedure of Fee, Harrowfield and Jackson.<sup>9</sup> The complex was twice recrystallized from warm water by addition of NaClO<sub>4</sub>. *Anal.* Calcd. for *trans*-[Cr(en)<sub>2</sub>NCSBr]ClO<sub>4</sub>: Cr, 12.70; NCS, 14.20. Found: Cr, 12.93; NCS, 14.17.

Perchloric acid solutions, ion-exchange resin, and solutions of mercuric perchlorate were prepared and analyzed as previously described.<sup>6,10</sup>

#### Techniques

All operations were performed in dim light. Spectrophotometric observations were made on a Cary Model 14 Recording Spectrophotometer. Ion-exchange separations were conducted on Dowex 50W-X2 at 0–5°C. Analytical techniques for Cr and NCS<sup>-</sup> have previously been described.<sup>6</sup> Nitrogen was analyzed by a micro-Kjeldahl technique using HgO–K<sub>2</sub>SO<sub>4</sub> as a catalyst for decomposition to NH<sub>3</sub>. Blank experiments on KNCS solutions indicated extensive heating was necessary to cause the decomposition of NCS<sup>-</sup> to NH<sub>3</sub>.

### Results and Discussion

Our previous experiments on the aquation of *trans*-Cr(en)<sub>2</sub>(NCS)<sub>2</sub><sup>+</sup> indicated that this species initially aquates with loss of ethylenediamine, through a one-ended complex.<sup>6</sup> On the other hand, the reported pre-

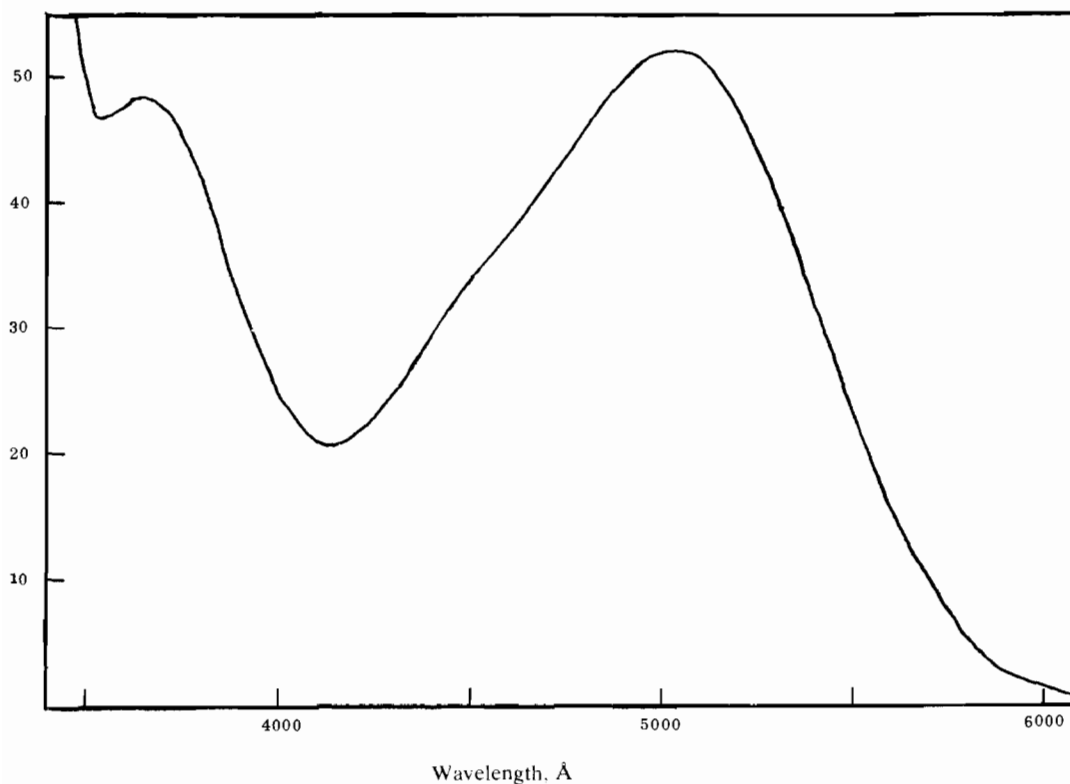


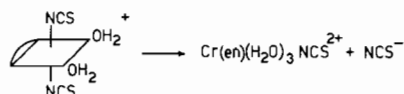
Figure 1. The visible absorption spectrum of  $trans\text{-Cr(en)}_2\text{NCS(H}_2\text{O)}^{2+}$ .

paration<sup>1</sup> of  $trans\text{-Cr(en)}_2\text{NCS(H}_2\text{O)}^{2+}$  called for heating  $trans\text{-Cr(en)}_2(\text{NCS})_2^+$  at  $50^\circ\text{C}$  in dilute acid for 2.5 days. Under these acidic conditions, it seems unlikely that ethylenediamine would re-coordinate to form the desired  $trans\text{-Cr(en)}_2\text{NCS(H}_2\text{O)}^{2+}$ . In order to test this argument we repeated Veigel and Garner's preparation and isolated by ion-exchange a violet complex that agrees in spectral characteristics with the one they report. We find values for  $\lambda(\epsilon)$ : 5250 (72.5), 3890 (40.0); they report<sup>1</sup> 5250 (73.6), 3890 (46.1). In addition we find a  $\text{NCS}^-$  to Cr ratio in the violet complex of 1.01, again in agreement with Veigel and Garner. But we have carried out one further experiment that unequivocally establishes that the violet complex is not  $trans\text{-Cr(en)}_2\text{NCS(H}_2\text{O)}^{2+}$ . We have analyzed the N:Cr ratio in the violet complex (in  $\text{Cl}^-$  media)<sup>11</sup> and find a value of  $3.35 \pm 0.05$ . Although this value is about 10% too high, it is clearly far too low to be compatible with the calculated value of 5 for the N:Cr ratio of  $trans\text{-Cr(en)}_2\text{NCS(H}_2\text{O)}^{2+}$ . It should be noted that any  $\text{enH}_2^{2+}$  ion in the solution from which the violet complex is prepared might be eluted at nearly the same rate as the violet complex is, thereby raising the N concentration somewhat.

A second experiment also establishes that the violet complex is not  $trans\text{-Cr(en)}_2\text{NCS(H}_2\text{O)}^{2+}$ . We have

treated a solution of the violet complex in  $\text{ClO}_4^-$  media with mercuric ion. A change in color consistent with rapid establishment of the equilibrium<sup>12</sup> (or equilibria)<sup>10</sup> between  $\text{Hg}^{2+}$  and coordinated thiocyanate takes place followed by a slower change in absorptivity. Unfortunately, these absorbance changes occur with no crossing of spectral traces and hence use of isosbestic behavior to indicate only two components (reactant and product(s)) is not possible. However, kinetic analysis can be accomplished. Plots of  $\ln(A_t - A_\infty)$  versus time, where  $A_t$  and  $A_\infty$  are the absorbancies at time  $t$  and at the end of reaction, are linear at several wavelengths indicating one reactant producing product(s) without further complications. The spectral scan at the conclusion of reaction was characteristic of  $\text{Cr(en)(H}_2\text{O)}_4^{3+}$ :  $\lambda(\epsilon)$  5125 (41), 3860 (24.2); literature values are 5120 (41.7), 3850 (24.3).<sup>13</sup>

The experiments discussed above prove that the violet complex is not  $trans\text{-Cr(en)}_2\text{NCS(H}_2\text{O)}^{2+}$ , but is  $\text{Cr(en)NCS(H}_2\text{O)}_3^{2+}$ . This conclusion is consistent with the N/Cr analysis, the  $\text{Hg}^{2+}$  induced aquation product, and the established path for aquation of  $trans\text{-Cr(en)}_2(\text{NCS})_2^+$ . Since the only other complex isolated after preparation of the violet complex was  $\text{Cr(en)(H}_2\text{O)}_2(\text{NCS})_2^+$ ,<sup>5</sup> the aquation path given in equation (1) can be expanded to include a final step,



What remains to be done is to establish the spectral properties of  $\text{trans-Cr(en)}_2\text{NCS(H}_2\text{O)}^{2+}$ . To do so, a synthetic path is needed. We utilized  $\text{Hg}^{2+}$  induced aquation of  $\text{trans-Cr(en)}_2\text{NCSBr}^+$  to accomplish this synthesis. A solution  $1.2 \times 10^{-2} M$  in this complex in  $10^{-3} M \text{ HClO}_4$  was treated with a 10 fold excess of  $\text{Hg}^{2+}$  and allowed to stand in the dark at room temperature for about 40 minutes. Addition of  $\text{HCl}$  in a 2 fold excess over  $[\text{Hg}^{2+}]$  and an ion-exchange separation of the resulting solution yielded as the almost exclusive product an orange-pink species. This species is eluted easily with 1.0 N  $\text{HClO}_4$ , has a  $\text{NCS}^-$  to Cr ratio of 1.04 and a N to Cr ratio of  $4.98 \pm 0.04$ . The only molecules derivable from  $\text{trans-Cr(en)}_2\text{NCSBr}^+$  with the correct  $\text{NCS}^-/\text{Cr}$  and  $\text{N}/\text{Cr}$  ratios are *cis* and  $\text{trans-Cr(en)}_2\text{NCS(H}_2\text{O)}^{2+}$ , the four isomers of composition  $\text{Cr(en)(enH)(H}_2\text{O)}_2\text{NCS}^{3+}$ , and the three isomers of composition  $\text{Cr(enH)}_2\text{(H}_2\text{O)}_3\text{NCS}^{4+}$ . All of these assignments except  $\text{trans-Cr(en)}_2\text{NCS(H}_2\text{O)}^{2+}$  may be eliminated by the ion exchange and chemical behavior. The orange-pink species elutes more rapidly than an authentic sample<sup>1</sup> of *cis-Cr(en)}\_2\text{NCS(H}\_2\text{O)}^{2+}; further, the mild conditions of the aquation (room temperature for only 40 minutes) are incompatible with Cr-en bond rupture. Thermal aquation studies of the orange-pink species are also compatible with the assignment of the structure,  $\text{trans-Cr(en)}_2\text{NCS(H}_2\text{O)}^{2+}$ , as is the fact that the orange-pink species is the dominant aquation product of  $\text{trans-Cr(en)}_2\text{NCSBr}^+$ <sup>14</sup>.*

Finally, the orange-pink species has spectral characteristics very similar to those reported for  $\text{trans-Cr(NH}_3)_4\text{NCS(H}_2\text{O)}^{2+}$ : the latter has  $\lambda(\epsilon)$ , 5100 (50.0), 3710 (45.7)<sup>5</sup>; we find for the orange-pink species,  $\lambda(\epsilon)$ , 5010 (52.4), 3650 (49.6). The complete visible spectrum is given in Figure 1.

We have, therefore, identified the Veigel and Garner complex<sup>1</sup> as  $\text{Cr(en)(H}_2\text{O)}_3\text{NCS}^{2+}$  (probably the 1.2.3-triaquo isomer) and have successfully synthesized  $\text{trans-Cr(en)}_2\text{NCS(H}_2\text{O)}^{2+}$ . The isomeric purity of this species is confirmed by ion-exchange separation from the corresponding *cis* isomer. Attempts to obtain a solid salt have, thus far, failed. Finally, it is to be

noted that preparation of  $\text{trans-Cr(en)}_2\text{NCS(H}_2\text{O)}^{2+}$  from  $\text{trans-Cr(en)}_2\text{NCSBr}^+$  by thermal aquation<sup>5</sup> is not a very efficient pathway because secondary aquation of  $\text{trans-Cr(en)}_2\text{NCS(H}_2\text{O)}^{2+}$  competes kinetically with the primary aquation of  $\text{trans-Cr(en)}_2\text{NCSBr}^+$ .<sup>14</sup>

It should be noted here that although several authors have used the incorrect spectrum of  $\text{trans-Cr(en)}_2\text{NCS(H}_2\text{O)}^{2+}$  to analyze photochemical products, the use of the correct spectrum does not change the conclusions in the study of  $\text{trans-Cr(en)}_2\text{NCSCl}^{2+}$ :<sup>3</sup> the  $\text{Cr(en)}_2\text{NCS(H}_2\text{O)}^{2+}$  product has *cis* geometry.<sup>15</sup>

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