AN ADDUCT OF THIOUREA WITH *trans*-DICHLOROBIS(ETHYLENE-DIAMINE)COBALT(III) CHLORIDE

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The first-order rate constant at 25° for the aquation of the chlorothioureabis-(ethylenediamine)cobalt(III) cation has been reported by Baker and Gaesser,[1] and found to be virtually identical $(2 \cdot 9 \times 10^{-5} \text{ sec}^{-1})$ with the corresponding value for the *trans*-dichlorobis(ethylenediamine)cobalt(III) cation $(3 \cdot 2 \times 10^{-5} \text{ sec}^{-1})$,[2] but information on base hydrolysis is apparently not yet available. The chloro thiourea complex was obtained as green crystals, and was assigned[1] the formula $[\text{Co(en)}_2\text{tuCl}]\text{Cl}_2$ based on elementary analyses of C, H, S, and *total* Cl (en = ethylenediamine, tu = thiourea), no distinction being made between *ionic* and *coordinated* chloride in the sample. A *trans* configuration was assigned[1] on the basis of spectral similarity between this complex $(\lambda_{\max} 615, 455, \text{ and } 408 \text{ m}\mu)$ and the *trans*-dichloro cation $(\lambda_{\max} 612, 450, \text{ and } 400 \text{ m}\mu)$, but the corresponding extinction coefficients were not reported.

In view of our interest in base hydrolysis of complexes of the type $[\text{Co(en)}_2\text{ACl}]^{n+}$ (where A is a variable ligand), we have repeated Baker and Gaesser's preparation and obtained a product with essentially the same analytical results. In our attempts to characterize the product further, as well as to establish the isomeric purity of the complex cation, we converted the chloride salt into perchlorate and nitrate salts, and determined the percentages of ionic and coordinated chloride in all the samples

TABLE 1

ANALYSES OF THE SUPPOSED $[\text{Co(en)}_2\text{tuCl}]X_2$ COMPLEXES

X	Co (%)		Ionic Cl (%)		Coord. Cl (%)	
	Found	Theor.	Found	Theor.	Found	Theor.
Cl	16·5	16·3	—	19·7	—	9·8
ClO$_4$	16·5	12·1	0·0	0·0	19·7	7·3
NO$_3$	18·4	14·3	0·0	0·0	22·0	8·6

by the Volhard method, after removing the complex cations from the solutions by ion exchange. However, in the case of the chloride salt, we found that the effluent from the ion-exchange resin column did not give rise to a precipitate of silver chloride. For both the perchlorate and nitrate salts, the Volhard analysis was free from such complications, but here there was disagreement between theoretical and found values as shown in Table 1.

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[1] Baker, W. A., and Gaesser, F. M., *J. inorg. nucl. Chem.*, 1963, **25**, 1161.

[2] Ingold, C. K., Nyholm, R. S., and Tobe, M. L., *Nature*, 1960, **187**, 477.

These observations suggest that the compositions of the chloride, perchlorate, and nitrate salts are respectively trans-[Co(en)$_2$Cl$_2$]Cl,tu, trans-[Co(en)$_2$Cl$_2$]ClO$_4$, (Calc.: Co, 16·9; coord. Cl, 20·3%), and trans-[Co(en)$_2$Cl$_2$]NO$_3$ (Calc.: Co, 18·9; coord. Cl, 22·7%). Measurements of extinction coefficients in the visible absorption spectra of these complexes provided further support to such a suggestion. For the adduct of thiourea with trans-dichlorobis(ethylenediamine)cobalt(III) chloride, the alternative possibility of a simple 1 : 1 mixture is excluded since Soxhlet extraction with anhydrous acetone failed to remove the thiourea from the complex. It is worth mentioning that trans-dichlorobis(ethylenediamine)cobalt(III) chloride is known to form adducts with a variety of compounds, e.g., with two molecules of HCl; this additive can be removed by conversion of the chloride salt into the perchlorate salt.

The formulation as an adduct can account for the observed interferences in the Volhard determinations, since on passing a solution of the adduct through an ion-exchange resin column, the thiourea remains unabsorbed, and subsequently forms complex species with the added silver ion. It also explains why the rate constant reported by Baker and Gaesser[1] is so similar to the value determined independently for the aquation of the trans-dichloro cation,[2] as in both cases the same cation is involved in slightly different environments only. On the other hand, a chloro thiourea complex would be expected to aquate at a considerably higher rate in view of the powerful $+E$ effect whereby the lone-pair of electrons on the donating sulphur atom can conjugate with the vacating orbital of cobalt and facilitate the dissociation of the outgoing chloro ligand (I).

(I)   (II)
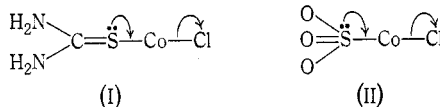
This labilizing effect of the sulphur lone-pair finds its counterpart in the chloro sulphito complex (II), whose aquation is known to be virtually complete on mixing.[3] Since the field strength of the thiourea is significantly different from that of the chloro ligand, the observed identity in the d–d spectra (both in wavelength and in extinction coefficient) is also inconsistent with the presence of coordinated thiourea in the complex.

Experimental

Preparations

trans-Dichlorobis(ethylenediamine)cobalt(III) chloride–thiourea adduct was prepared as described by Baker and Gaesser[1] for their trans-chlorothioureabis(ethylenediamine)cobalt(III) chloride. The corresponding perchlorate and nitrate salts were obtained by adding the appropriate acid to a cooled solution of the chloride salt in water. The crystals formed were filtered off, and washed with alcohol and ether.

Analyses and Measurement

Elementary microanalyses were by the Australian Microanalytical Service, Melbourne. Cobalt was estimated on the macro scale iodometrically by the method of Laitinen and Burdett.[4] Ionic

[3] Baldwin, M. E., J. chem. Soc., 1961, 3123.

[4] Laitinen, H. A., and Burdett, L. W., Analyt. Chem., 1951, 23, 1268.

chloride was determined by passing a freshly prepared solution of the complex through a column of Amberlite IR-120 (H⁺ form), whereby the complex cation was replaced by hydrogen ion. The chloride content in the effluent was then analysed by the Volhard method. Coordinated chloride in the complexes was first converted into ionic chloride by alkali before analysis.

Visible absorption spectra were measured with a Unicam SP800 spectrophotometer and 4-cm silica cells.