Stable *trans*-Isomers of Bis(acetato)-triethylenetetramine-cobalt(III) and Bis(propionato)-triethylenetetramine-cobalt(III) Complexes

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Although a diacido-triethylenetetramine-cobalt(III) complex may exist in three stereoisomeric forms, two *cis*- and one *trans*-isomers, all of the complexes prepared so far have been *cis*-isomers except for *trans*-[$CoBr_2$trien]X.[1] Concerning the complex, however, the absorption spectrum has not been measured because of its instability in solution. In our previous studies of [Co(halac)$_2$-$(NH_3)_4$]X and [Co(halac)$_2$(en)$_2$]X,[2] where halac= acetato and halogenoacetato ligands, we have noticed that *trans*-isomers occur when the reaction mixture of a carbonato-complex and a halogenoacetic acid is evaporated at a high temperature and that they are apt to arise in the cases of halac ligands with low halogen contents. In the light of this knowledge, two compounds, [Co(CH_3CO_2)$_2$-trien]ClO_4·$HClO_4$ and [Co($C_2H_5CO_2$)$_2$]trienClO_4·$HClO_4$, have been obtained which must be *trans*-isomers judging from their preparation procedures[3] and absorption spectra.

Figure 1 and Table I show the absorption spectra of the complexes prepared, together with those of some related complexes. It has been well-established that, in a [Coa_4b_2]-type complex, the first band of the *trans*-isomer splits much more significantly than that of the *cis*-isomer.[4,5] As may be seen in Fig. 1, the absorption curves of the prepared complexes obviously exhibit the features of a *trans*-isomer. In addition, the absorption maxima are in good correspondence with those of *trans*-[Co(CH_3CO_2)$_2$-(en)$_2$]ClO_4. The identification is also reasonable in view of the preparation procedures. Much as in the procedures for some *trans*-[Co(halac)$_2$(en)$_2$]-ClO_4,[2] the reaction mixture of [$CoCO_3$ trien]ClO_4 and CH_3CO_2H (or $C_2H_5CO_2H$) was boiled for a few minutes at the final period of the evaporation. Moreover, just as *trans*-[Co(halac)$_2$(en)$_2$]$^+$ precipitate as acidic salts upon the addition of perchloric acid,[2] so do the present complexes.

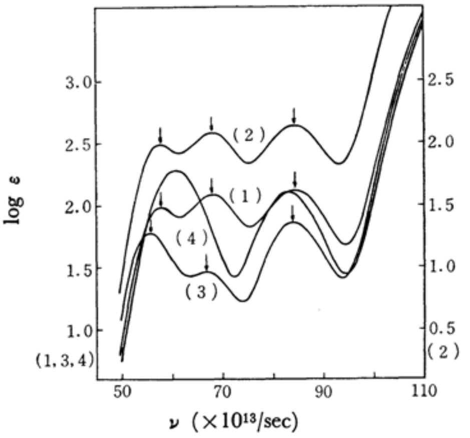

Fig. 1. Absorption spectra of *trans*-[Co(CH_3CO_2)$_2$-trien]ClO_4 and some related complexes.

1 : *trans*-[Co(CH_3CO_2)$_2$ trien]ClO_4
2 : *trans*-[Co($C_2H_5CO_2$)$_2$ trien]ClO_4
3 : *trans*-[Co(CH_3CO_2)$_2$ (en)$_2$]ClO_4
4 : *cis*-[Co($CHCl_2CO_2$)$_2$ trien]ClO_4

The intensity is the most significant difference between the spectra of *trans*-[Co(CH_3CO_2)$_2$(en)$_2$]$^+$ and of *trans*-[Co(CH_3CO_2)$_2$ trien]$^+$. The high intensity of the latter is probably due to the low symmetry of the complex. Because the trien molecule is constrained by the square planar coordination and because there is no chelation at one side of the square, the square is necessalily distorted to some extent. That is, the symmetry of the complex is much lower than those of the $(NH_3)_4$- and (en)$_2$- analogues. This may effect the increase in the transition moment and, hence, the high extinction coefficients.

TABLE I. ABSORPTION SPECTRA OF *trans*-[Co(CH_3CO_2)$_2$ trien]ClO_4

	ν_{1a} (10¹³/sec.)	log ε_{1a}	ν_{1b} (10¹³/sec.)	log ε_{1b}	ν_2 (10¹³/sec.)	log ε_2
trans-[Co(CH_3CO_2)$_2$trien]$^+$	57.7	1.981	67.8	2.083	84.3	2.122
trans-[Co($C_2H_5CO_2$)$_2$trien]$^+$	57.7	1.989	67.8	2.082	84.2	2.139
trans-[Co(CH_3CO_2)$_2$(en)$_2$]$^+$	55.8	1.778	66.7	1.462	84.0	1.863

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[3] To be published in detail shortly.

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