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A Convenient Method for the Preparation of Aminoethyliminodiacetatocobalt(III) Complexes

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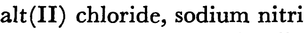
Synopsis. Sodium dinitro(aminoethyliminodiacetato)-cobaltate(III) has been obtained by the oxidation of an aqueous mixture of cobalt(II) chloride, sodium nitrite, and a reaction product between ethylenediamine and sodium monochloroacetate. Several other complexes with the tetradentate ligand have also been derived from the dinitro complex.

Schwarzenbach *et al.*[1] prepared β-aminoethyliminodiacetic acid,  $NH_2\text{-}CH_2\text{-}CH_2\text{-}N\langle{}^{CH_2\text{-}COOH}_{CH_2\text{-}COOH}$ (abbreviated as aeidaH$_2$ in this report), and measured the formation constants with various metal ions in aqueous solutions. Chu *et al.*[2] prepared the tetradentate ligand by Schwarzenbach's method and synthesized *cis*(*O*)- and *trans*(*O*)-isomers of [Co(aeida)(en)]X (X=Cl, ClO$_4$). Their preparation route for the ligand requires several reaction steps, however, and so is not very convenient. It has been reported that the main product of the reaction between 1 mol of ethylenediamine and 2 mol of the monochloroacetate ion is not the aeida or the ethylenediamine-*N,N'*-diacetate ion (EDDA), but the ethylenediaminetetraacetate ion (EDTA) with the unreacted diamine.[3] However, we supposed that there might be some aeida in the reaction mixture and that there might be a possibility for a cobalt(III) complex with the tetradentate ligand to be separable, together with the coordination of a unidentate or a bidentate ligand. Thus, the reaction mixture was combined with cobalt(II) chloride and sodium nitrite, and the mixture was oxidized by air bubbling. As a result, sodium dinitro(aminoethyliminodiacetato)cobaltate(III) was obtained. This substance and a few complexes derived from it were identified, as will be described below.

Experimental

Sodium Dinitro(aminoethyliminodiacetato)cobaltate(III), Na[Co(aeida)(NO$_2$)$_2$]. Ethylenediamine (6.0 g) was placed in a 150 ml flask furnished with a reflux condenser and a dropping funnel, and the flask was set in an oil bath at 110 °C. A sodium monochloroacetate solution, which had been prepared by mixing monochloroacetic acid (18.9 g in 25 ml) with sodium hydroxide (8.0 g in 25 ml) below 20 °C, was added, drop by drop, from the funnel into the flask, taking about 2 hr. A sodium hydroxide solution (8.0 g in 25 ml) was then added, taking about 30 min. After this addition, the heating was continued for a further 2 hr. The product solution was then adjusted to be slightly alkaline by the addition of hydrochloric acid, and was combined with a solution of cobalt(II) chloride hexahydrate (24 g in 50 ml). While vigorous air bubbling into the mixture was started, a sodium nitrite solution (14 g in 25 ml) was added, drop by drop, from the inlet of the air stream. The solution, dark violet at the early period of the oxidation, gradually turned dark brown; at the same time, bright brown crystals began to come out. The air bubbling was continued for 5 hr. After the product had been placed in a refrigerator overnight, the crystals were collected and then recrystallized from 50 ml of warm water. The purified crystals were washed with methanol and ether. Yield, 7.5 g. Found: C, 20.76; H, 2.95; N, 15.99%. Calcd for Na[Co(aeida)(NO$_2$)$_2$]=$CoC_6H_{10}O_8N_4Na$ (348.09): C, 20.70; H, 2.90; N, 16.10%.

trans(O)-*Aminoethyliminodiacetato(ethylenediamine)cobalt (III) Perchlorate,* trans(O)-[*Co(aeida)(en)*]*ClO$_4$*. In an evaporating dish, 1.0 g of the dinitro complex was mixed with 10 ml of acetic acid and 2 ml of water. The dish was covered with a watch-glass and was heated on a boiling-water bath until the solid had been completely dissolved. Nitric oxides were evolved during the dissolution, and a red-violet solution was formed. Then the solution was concentrated with the aid of an air stream to obtain a tarry residue. After it had then been dissolved in 5 ml of water, the solution was concentrated again to the tarry state; the odor of acetic acid thereupon vanished. The product was dissolved in 5 ml of water again, and 1.0 g of 20%-ethylenediamine solution was added. The heating of the mixture on the bath for 30 min, followed by cooling and the addition of 1 ml of 6 M HClO$_4$, produced a red precipitate. The precipitate was recrystallized from 20 ml of warm water with the addition of a few drops of 6 M HClO$_4$. Yield, 0.4 g. Found: C, 24.32; H, 4.65; N, 14.10%. Calcd for [Co(aeida)(en)]ClO$_4$=$CoC_8H_{18}O_8N_4Cl$ (392.64): C, 24.47; H, 4.62; N, 14.27%.

trans(O)-*Aminoethyliminodiacetato(trimethylenediamine)cobalt(III) Perchlorate,* trans(O)-[*Co(aeida)(tn)*]*ClO$_4$*. This complex was isolated by the use of trimethylenediamine instead of ethylenediamine in the above preparation. Yield, 0.4 g. Found: C, 26.50; H, 5.02; N, 13.60%. Calcd for [Co(aeida)(tn)]ClO$_4$=$CoC_9H_{20}O_8N_4Cl$ (406.67): C, 26.58; H, 4.96; N, 13.78%.

trans(O)-*Aminoethyliminodiacetato(diammine)cobalt(III) Perchlorate,* trans(O)-[*Co(aeida)(NH$_3$)$_2$*]*ClO$_4$*. One gram of the dinitro complex was treated with acetic acid and then with water, such as in the preparation of the ethylenediamine complex. Then, 5 ml of aqueous ammonia (6M) and 0.1g of active charcoal were added. After the mixture had been concentrated to dryness at ~60 °C, the residue was extracted with 20 ml of warm water. The addition of 1 ml of 6M HClO$_4$ to the extract, followed by cooling, produced a red-violet precipitate. It was recrystallized from 15 ml of warm water with the addition of a few drops of 6M HClO$_4$. Yield, 0.3 g. Found: C, 19.67; H, 4.51; N, 15.11%. Calcd for [Co(aeida)(NH$_3$)$_2$]ClO$_4$=$CoC_6H_{16}O_8N_4Cl$ (366.60): C, 19.66; H, 4.40; N, 15.28%.

Discussion

Identification. Figure 1 shows the absorption spectra of the diammine- and the diamine-complexes, in which a splitting is observable in each first band. Thus, the spectra clearly indicate that their configurations are *trans*-[CoN$_4$O$_2$]. The numerical values of the

Table 1. Absorption maxima of the electronic spectra of some Co(III)-aeida complexes

	I $\tilde{\nu}$ (kK) (ε)		II or Sp
	Ia	Ib	$\tilde{\nu}$ (kK) (ε)
Na[Co(aeida)$(NO_2)_2$]	21.28(224.0)		29.80(5640)[a]
trans(*O*)-[Co(aeida)(en)]ClO_4	18.97(142.4)	sh	28.20(172.0)
trans(*O*)-[Co(aeida)(tn)]ClO_4	18.62(146.0)	sh	27.86(186.2)
trans(*O*)-[Co(aeida)$(NH_3)_2$]ClO_4	18.73(145.0)	sh	27.93(178.2)

a) Ligand specific band.

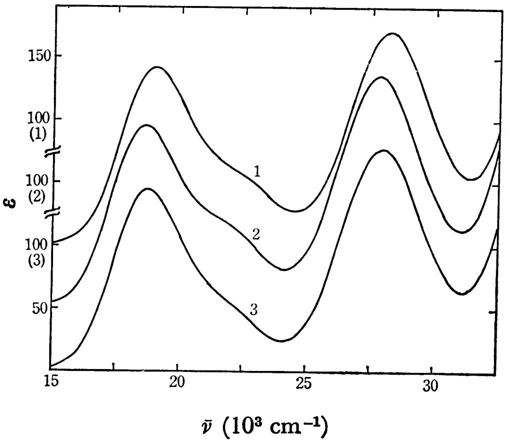


Fig. 1. Absorption spectra of some Co(III)-aeida complexes.
1: *trans*(O)-[Co(aeida)(en)]ClO_4
2: *trans*(O)-[Co(aeida)(tn)]ClO_4
3: *trans*(O)-[Co(aeida)$(NH_3)_2$]ClO_4

absorption maxima (Table 1) of our ethylenediamine complex agree satisfactorily with those of the *trans*(*O*)-isomer prepared by Chu *et al.*[2)] Each of the spectra is definitely different from the spectrum of the Co(III)-EDDA complex with the corresponding ligand.[4)] (An aeida-complex has the same elemental composition as the EDDA-complex with the same additional ligand.) Thus, on the basis of the absorption spectra as well as the elemental analyses, there remains no question as to the identification of the complexes.

Notes on the Preparations. Following are some notes on things observed qualitatively during the preparations:

(1) The solubility of the dinitro complex varies greatly with the temperature. The growth of the crystals from the reacting mixture is relatively slow. Thus, cooling the mixture during the later half of the air oxidation makes the preparation time shorter.

(2) In the preparations of cobalt(III) complexes with another multidentate ligand, such as trien or DTMA, a nitro complex is usually treated with hydrochloric acid to convert it into the chloro complex.[5)] A similar treatment was attempted here. However, it appeared to decompose the complex itself. A large excess of acetic acid, as has been described above, is useful in expelling the nitro groups. Perchloric acid is not useful, since there is no proper means to remove the excess of the acid after the reaction.

(3) For the preparation of the diammine complex, it is necessary to add charcoal to the reacting mixture; otherwise, an aquoammine complex arises. Many other unidentate and bidentate ligands, such as SCN^-, N_3^-, phen, and dipy, also react with the product from the dinitro complex treated with acetic acid. The aquoammine complex as well as the other species in this series will be reported on elsewhere.

References

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