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Studies of Ethylenediamine-*N*,*N*′-diacetatocobalt(III) Complexes. II. The Preparation and Identification of Ethylenediamine-*N*,*N*′-diacetatocobalt(III) Complexes, with Some Anions as the Additional Ligand

Kashiro KURODA and Kiyokatsu WATANABE

Department of Chemistry, Faculty of Science, Ehime University, Matsuyama, Ehime

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Several authors[1–8] have reported cobalt(III) complexes which contain the tetradentate ethylenediamine-*N*,*N*′-diacetate (EDDA). However, the number of such complexes is still small in comparison with those of such other series as the triethylenetetraminecobalt(III) series, and only a few anionic species have been isolated. The reason for this situation has been discussed in the preceding report.[1] It has also been discussed there how chloro(ethylenediamine-*N*,*N*′-diacetato)aquocobalt(III) or ethylenediamine-*N*,*N*′-diacetato(diaquo)cobalt(III) perchlorate has a character suitable as a starting material for the preparation of the series, and the preparations of some cationic species from these complexes have been illustrated. In this report, two new anionic species as well as the known oxalato complex, which have been derived from the chloroaquo or the diaquo complex, will be dealt with. The geometrical configuration of the complexes obtained was identified by means of their electronic absorption spectra and NMR spectra.

Experimental

Materials, Analysis, Apparatus, and Measurements. Ethylenediamine-*N*,*N*′-diacetic acid (Dotite Reagents), cesium chloride and acetate (Wako Pure Chemicals), and all the other reagent-grade chemicals were used without further purification. The apparatus used and the procedures for the analysis and the measurements have been described in the preceding report.[1]

Preparations. *(1) Cesium Dinitro(ethylenediamine-*N,N′*-diacetato)cobaltate(III) Monohydrate,* $Cs[Co(EDDA)(NO_2)_2]\cdot H_2O$: In 30 m*l* of water, 0.4 g of the chloroaquo complex $[Co(EDDA)(Cl)(H_2O)]\cdot H_2O$,[1] was suspended and heated until the complex dissolved completely. After the subsequent addition of 0.2 g of sodium nitrite, the mixture was evaporated to dryness at ~70°C; during the evaporation the color changed to a deep orange-red. The residue was extracted with ~2 m*l* of water, and after the addition of 0.4 g of cesium chloride to the extract, it was kept at 0°C for one day. The orange-red precipitate thus formed was recrystallized from a small amount of water by the addition of cesium chloride, and washed with ethanol and ether. Yield, 0.3 g.

Found: C, 14.87; H, 2.56; N, 11.61%. Calcd for $Cs[Co(EDDA)(NO_2)_2]\cdot H_2O = CoC_6H_{12}O_9N_4Cs$ (476.02): C, 15.14. H, 2.54; N, 11.77%.

*(2) Cesium Diazido(ethylenediamine-*N,N′*-diacetato)cobaltate(III),* $Cs[Co(EDDA)(N_3)_2]$: In 30 m*l* of water, 0.4 g of the chloroaquo complex was dissolved as in the case of (1). After the addition of 0.18 g of sodium azide, the solution was evaporated to dryness at ~70°C. The residue was dissolved in 2 m*l* of water, and then 0.2 g of cesium chloride was added;

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[1] Part I of this series, K. Kuroda and K. Watanabe, This Bulletin, **44**, 1034 (1971).

[2] M. Mori, M. Shibata, E. Kyuno, and F. Maruyama, *ibid.*, **35**, 75 (1962).

[3] J. I. Legg and D. W. Cooke, *Inorg. Chem.*, **4**, 1576 (1965).

[4] J. I. Legg, D. W. Cooke, and B. E. Douglas, *ibid.*, **6**, 700 (1967).

[5] J. I. Legg and B. E. Douglas, *ibid.*, **7**, 1452 (1968).

[6] C. W. Van Saun and B. E. Douglas, *ibid.*, **8**, 115 (1969).

[7] P. J. Garnett, D. W. Watts, and J. I. Legg, *ibid.*, **8**, 2534 (1969).

[8] P. F. Coleman, J. I. Legg, and J. Steele, *ibid.*, **9**, 937 (1970).

A dark green precipitate appeared upon cooling. It was recrystallized from a small amount of water by the addition of cesium chloride, and then washed with methanol and ether. Yield, 0.3 g.

Found: Co, 12.92; C, 15.76; H, 2.36; N, 24.75%. Calcd for $Cs[Co(EDDA)(N_3)_2]=CoC_6H_{10}O_4N_8Cs$ (450.04): Co, 13.10; C, 16.01; H, 2.24; N, 24.90%.

*(3) Cesium α-*cis*-Oxalato(ethylenediamine-*N,N′*-diacetato)cobaltate(III) Dihydrate, α-cis-Cs[Co(EDDA)(ox)]·2H₂O:*

*(4) Sodium β-*cis*-Oxalato(ethylenediamine-*N,N′*-diacetato)cobaltate(III) Monohydrate, β-cis-Na[Co(EDDA)(ox)]·H₂O:* These two isomers were separated from a reaction product. The *β-cis* isomer was also prepared independently from the diaquo complex.

Into a mixture of cobalt(II) chloride hexahydrate (2.3 g), ethylenediamine-*N,N′*-diacetic acid (1.8 g), and sodium oxalate (2.7 g) in 50 m*l* of water, we bubbled air at ~55°C for 2 hr, during which time 10 m*l* of hydrogen peroxide (30%) was added drop by drop. The resulting mixture was kept at 0°C overnight, and then the undissolved excess sodium oxalate was filtered off. The red-violet filtrate was concentrated on a steam bath to ~15 m*l*, and 30 m*l* of methanol was added. The precipitate thus formed was collected on a glass filter; then it was fractionally extracted with 5 m*l* of cold water and with 10 m*l* portions of warm (~35°C) water twice. The first extract was discarded. Two-gram portions of cesium acetate were added to the second and the third extracts. In the second extract a large amount of a precipitate formed immediately, while in the third a small amount of a precipitate appeared after a while. The precipitate was recrystallized from warm water upon the addition of cesium acetate. The filtrate from the third fraction was placed in a refrigerator overnight; a large amount of a precipitate which was apparently different from the above one thus appeared. This precipitate was recrystallized from warm water with the addition of sodium perchlorate; the appearance of crystals was also slow. The color of the former was violet, while that of the latter was deep red-violet.

Found: C, 19.50; N, 5.69% for the violet isomer. Calcd for $Cs[Co(EDDA)(ox)]\cdot 2H_2O=CoC_8H_{14}O_{10}N_2Cs$ (490.05): C, 19.61; N, 5.72%. Found: C, 26.04; N, 7.68% for the red-violet isomer. Calcd for $Na[Co(EDDA)(ox)]\cdot H_2O=CoC_8H_{12}O_9N_2Na$ (362.12): C, 26.54; N, 7.74%.

By the evaporation of the second extract *in vacuo* without cesium acetate (the temperature depressed during the process), sodium salt of the violet isomer appeared as deep violet needles. This crystal dissolved in its own water of crystallization as the temperature was raised. This indicates that the sodium salt of the violet isomer is more soluble than that of the red-violet isomer.

The same product as the red-violet isomer was also obtained from $[Co(EDDA)(H_2O)_2]ClO_4$.[1] A mixture of the diaquo complex (0.37 g) and sodium oxalate (0.13 g) in 5 m*l* of water was heated on a water bath; deep red-violet crystals appeared as the evaporation proceeded. The yield was nearly quantitative (0.33 g).

Results and Discussion

Preparative Procedures. Most of the Co(III)-EDDA complexes in the literature were synthesized directly from a cobalt(II) salt, EDDA, and the necessary ligand. The method of preparation used in this study, in contrast, utilized the substitution reaction of the starting chloroaquo or diaquo complex with the various anions. One advantage of this method is that we can mix equivalent amounts of the reactants; therefore, we can reduce the number of components in the reaction mixture as much as possible. Hence, the crystallization of the product becomes easier. It was found that the cesium ion made a good precipitate in aqueous media with most of the anionic species studied.

The potassium salt of the *α-cis* isomer of the oxalato complex was first obtained by Van Saun and Douglas,[6] and the sodium salt of the *β-cis* isomer (dihydrate), by Coleman *et al*[8]. The violet and the red-violet isomer in this study showed absorption spectra identical with those of their respective complexes, although the analyses indicated that our *β-cis* isomer was the monohydrate. Coleman *et al.* separated the *β-cis* isomer by means of ion-exchange chromatography; hence, their method took a long time. The preparation has been simplified in two ways. First, the *α-cis* and the *β-cis* isomers were separated from a reaction mixture by the use of fractional extraction and fractional precipitation with the cesium ion; hence, no special or time-consuming technique was needed. Second, the sodium salt of the *β-cis* isomer was easily obtained by evaporating a solution of $[Co(EDDA)\ (H_2O)_2]ClO_4$ and sodium oxalate. Despite the *α-cis* configuration of the diaquo complex,[1] the deposit was exclusively the *β-cis* isomer; this means that the *β-cis* isomer is supplied by the shift of the equilibrium between the two isomers:

$$\begin{tikzcd}\alpha\text{-}cis\text{ isomer} \arrow[r, shift left] & \beta\text{-}cis\text{ isomer} \arrow[l, shift left] \arrow[d] \\ & \text{deposit}\end{tikzcd}$$

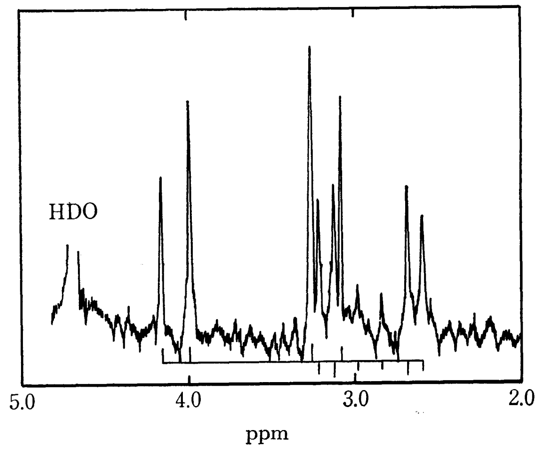

Fig. 1. PMR spectrum of $Cs[Co(EDDA)(N_3)_2]$ in D_2O.

Table 1. Resonance frequencies in the PMR spectra of $Cs[Co(EDDA)(X)_2]$ in D_2O
(ppm downfield referred to TMS as zero)

X	Glycinate protons	Ethylene protons
N_3	3.08, 3.26, 3.98, 4.16	2.58, 2.68, 2.83
	$J_{AB}=18$ Hz	2.97, 3.12, 3.22
NO_2	3.13, 3.32, 4.18, 4.36	2.73, 2.82, 2.95
	$J_{AB}=18$ Hz	3.03, 3.16, 3.26

NMR Spectra. The pmr spectrum of the diazido complex is shown in Fig. 1. It has the characteristic feature of the *α-cis* isomer,[3,6] in which an AB quartet

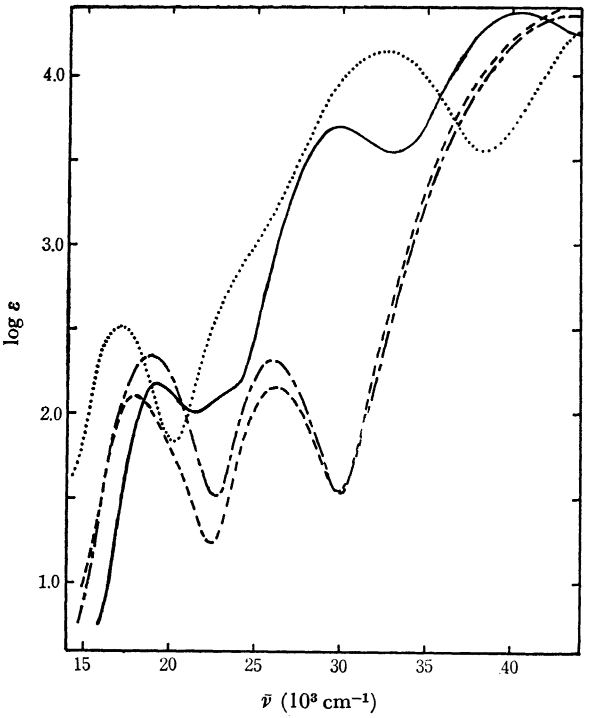

Fig. 2. Absorption spectra of some Co(III)-EDDA complexes.

———: Cs[Co(EDDA)$(NO_2)_2$]
·········: Cs[Co(EDDA)$(N_3)_2$]
- - - - - -: *α-cis*-Cs[Co(EDDA)(ox)]
— — — —: *β-cis*-Na[Co(EDDA)(ox)]

pattern originating from the two equivalent glycinate and symmetrical A_2B_2 absorptions from the ethylene protons are observable. The nitro and the violet oxalato complexes also showed analogous spectra. It is, therefore, certain that the nitro and the azido complexes are *α-cis* isomers. The numerical values are summarized in Table 1.

Electronic Absorption Spectra. The electronic absorption spectra are shown in Fig. 2, while the numerical values of the maxima are summarized in Table 2. In the spectrum of the nitro complex, it is clearly indicated that a band exists at ~23×10³ cm⁻¹. There is a slight but distinct shoulder around 24×10³ cm⁻¹ in that of the azido complex, too. The shoulder of the azido complex may be assigned to the second band covered by the strong ligand-specific band. On the other hand, the band of the nitro complex can not be the second band, since the position is in too low a wave-number region for the second band of this complex. As the nitro complex has the *α-cis* configuration (*trans* with respect to O), and hence belongs approximately to the *trans*-[Co-A_4B_2]-type, a large split of the first band can be expected; such a split has been observed in the spectra of a large number of *trans*-[CoA_4B_2]-type complexes. Therefore, it is reasonable to assign the band to the Ib band; in other word, the presence of this band is further evidence that the complex is an *α-cis* isomer. Mori *et al*[2] previously reported the preparation and absorption spectrum of the nitro complex, but their spectrum differs considerably from that of our complex; especially, the band mentioned above can not be clearly observed. We considered that their complex was a different kind of nitro complex or that it included impurities because it was precipitated by ethanol.

TABLE 2. ABSORPTION MAXIMA OF THE ELECTRONIC SPECTRA OF Co-EDDA COMPLEXES

	Ia $\bar{\nu}$(kK) (ε)	Ib $\bar{\nu}$(kK) (ε)	II $\bar{\nu}$(kK) (ε)	Sp $\bar{\nu}$(kK) (ε)
Cs[Co(EDDA)$(NO_2)_2$]	19.23 (150)	23 (100)		29.8 (5000)
Cs[Co(EDDA)$(N_3)_2$]	17.04 (323)		sh	32.6 (13800)
α-cis-Cs[Co(EDDA)(ox)]	17.83 (124)	sh	26.1 (143)	
β-cis-Na[Co(EDDA)(ox)]	18.85 (217)		25.9 (205)	