A Cobalt(III) Complex with Trimethylenediaminetetraacetate

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The preparation and the properties of the cobalt(III) complexes with ethylenediaminetetraacetate (edta) have been extensively investigated. The cobalt(III) complexes with propylenediaminetetraacetate (pdta) and *trans*-1, 2-cyclohexanediaminetetraacetate (cydta) have also been reported on.[1,2] In these complexes, the chelate rings around the central cobalt(III) ions are all five-membered.

This paper will present the synthesis of a cobalt(III) complex with trimethylenediaminetetraacetate (trdta, $(^-OOCH_2C)_2N(CH_2)_3N(CH_2COO^-)_2$) in which a six-membered chelate ring involving two nitrogen atoms is formed. The infrared, visible and ultraviolet absorption spectra of the complex, as well as those of edta-, pdta- and cydta-cobalt(III) complexes, are also presented and discussed.

Experimental

Preparation.—H_4pdta,[1] H_4hdta[3] (hexamethylenediaminetetraacetic acid, $(HOOCH_2C)_2N(CH_2)_6N(CH_2COOH)_2$), Na[Coedta]·$4H_2O$,[4] K[Copdta]·$H_2O$[1] and K[Cocydta]·$3H_2O$[2] were preparaed in essentially the same way as has been reported in the literature. The H_4edta and H_4cydta used were purchased from Dojindo & Co., Ltd.

Trimethylenediaminetetraacetic acid: Twenty-eight grams of monochloroacetic acid in 25 ml. of water was cooled in an ice-bath and then 16.5 g. of potassium hydroxide dissolved in 30 ml. of water was added drop by drop with stirring, followed by the addition of 5 g. of trimethylenediamine. The resulting solution was heated for 1 hr. After cooling, the pH of the solution was adjusted to 2.3 with concentrated hydrochloric acid. The solution was filtered and evaporated on a water-bath to a volume of 40 ml. Then, the deposited potassium chloride was removed and the solution kept in a refrigerator until white powder appeared. This powder was collected and washed with water, alcohol and ether. The filtrate was concentrated on a water-bath, and the same procedure was repeated to recover the compound from the solution; yield, 6 g. The compound was recrystallized from aqueous alcohol and dried at 110°C.

Found: C, 43.24; H, 6.06; N, 9.23. Calcd. for $C_{11}H_{18}N_2O_8$: C, 43.14; H, 5.92; N, 9.15%.

Schwarzenbach and Ackermann[5] reported that H_4trdta did not precipitate upon the acidification of the condensation-mixture of monochloroacetic acid, sodium hydroxide and trimethylenediamine. In this study, however, H_4trdta was successfully crystallized by the careful adjustment of the pH of the condensation-mixture (pH 2.3).

K[Cotrdta]·$2H_2O$: 6.1 g. of H_4trdta, 12 g. of potassium acetate and 5.0 g. of cobalt(II) acetate tetrahydrate were dissolved into 100 ml. of water, to which 2 g. of active charcoal and 4 ml. of 30% hydrogen peroxide were then added. Air was passed through the mixture for 50 hr. at room temperature. Then the solution was filtered and the filtrate evaporated to 25 ml. on a water-bath. During the evaporation the solution was bubbled with a current of air. After the solution had been cooled to 0°C, the reddish violet crystals deposited were collected and washed with alcohol and ether. The compound was recrystallized from water by the addition of alcohol and dried over a silica gel desiccator.

Found: C, 30.27; H, 3.93; N, 6.26; H_2O, 8.13. Calcd. for $K[Co(C_{11}H_{14}N_2O_8)]\cdot 2H_2O$: C, 30.28; H, 4.16; N, 6.42; H_2O, 8.26%.

Apparatus.—The crystalline water of the complexes was determined by a Shimadzu RT-2 recording thermobalance. The infrared spectra were measured with a Hitachi EPI-2G recording infrared spectrophotometer by the potassium bromide disk method. The visible and ultraviolet spectra were obtained by using a Hitachi EPU-2 spectrophotometer at room temperature.

Results and Discussion

Infrared Absorption Spectra.—The carboxyl stretching bands of H_4edta and the related compounds are shown in Fig. 1. In Table I are summarized the frequencies of the absorption bands of these compounds. The values obtained for H_4edta and H_4pdta almost agree with those reported in the literature.[6,7] It has been known that the ionized COO^- stretching band occurs at 1610~1550 cm^{-1} and the unionized COOH stretching band at 1725~1700 cm^{-1}.[8] The compounds investigated in

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[1] F. P. Dwyer and F. L. Garvan, *J. Am. Chem. Soc.*, **81**, 2955 (1959).

[2] F. P. Dwyer and F. L. Garvan, ibid., **83**, 2610 (1961).

[3] A. Müller and T. Bersin, *Helv. Chim. Acta*, **38**, 1708 (1955).

[4] S. Kirschner, *Inorg. Syntheses*, **5**, 186 (1957).

[5] G. Schwarzenbach and H. Ackermann, *Helv. Chim. Acta*, **31**, 1029 (1948).

[6] D. T. Sawyer and P. J. Paulsen, *J. Am. Chem. Soc.*, **80**, 1597 (1958).

[7] K. Nakamoto, Y. Morimoto and A. E. Martell, ibid., **85**, 309 (1963).

[8] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y. (1954).

TABLE I. INFRARED ABSORPTION OF H_4trdta AND THE RELATED COMPOUNDS (cm^{-1})

Compound	COOH	COO^-
H_4trdta	1724, 1656	—
H_4edta	1704, 1634	—
H_4cydta	1751 1730 1706, 1656	1587
H_4pdta	1704, 1626	—
H_4hdta	1709(sh), 1686	—

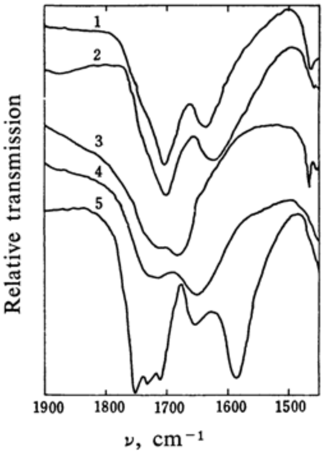

Fig. 1. Infrared absorption spectra of H_4edta (1), H_4pdta (2), H_4hdta (3), H_4trdta (4) and H_4cydta (5).

this study show similar absorption spectra, except that H_4cydta gives an additional strong and sharp absorption band at 1587 cm^{-1}, a band which can be assigned as ionized COO^-. This may be the evidence for the fact that H_4cydta forms a so-called "zwitter ion" in the solid state.

The coordinated $COO^- \cdots M$ stretching bands of the cobalt(III)-trdta and the related complexes are listed in Table II. The values obtained for the cobalt(III)-edta and the cobalt(III)-pdta complexes agree with that reported by Busch and Bailar[9] and those by Gillard[10] and Swaminathan and Busch[11] respectively. Busch et al. found that the cobalt(III)-edta complex gave a single and strong carboxylate band at higher frequencies than those of the free COO^- band, and they considered this to be the indication of the covalent character of the metal-carboxylate bond.[9,12] The results given in Table II indicate that the character of the metal-carboxylate bond in the cobalt(III) complexes with trdta, pdta and cydta closely resembles that in the cobalt(III)-edta complex. Although the carboxylate band of K[Cotrdta]$\cdot 2H_2O$ split into two absorption peaks at 1661 cm^{-1} and 1639 cm^{-1} (Fig. 2), both peaks are considered to be associated with the coordinated carboxyl groups. This strongly suggests that a quadrivalent trdta anion in the cobalt(III) complex is hexadentate.

TABLE II. INFRARED ABSORPTION OF Co(III)-trdta AND THE RELATED COMPLEXES (cm^{-1})

Compound	$COO^- \cdots M$
K[Cotrdta]$\cdot 2H_2O$	1661(sh), 1639
Na[Coedta]$\cdot 4H_2O$	1639
K[Cocydta]$\cdot 3H_2O$	1645
K[Copdta]$\cdot H_2O$	1653

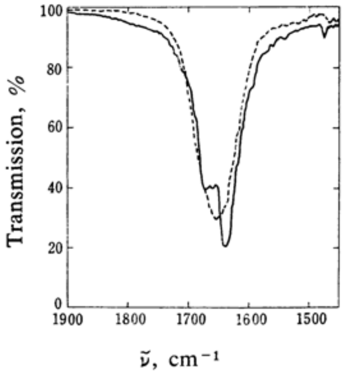

Fig. 2. Infrared absorption spectra of K[Copdta] $\cdot H_2O$ (dotted line) and K[Cotrdta] $\cdot 2H_2O$ (full line).

Visible and Ultraviolet Absorption Spectra.—The characteristic numerical data of the visible and ultraviolet spectra for the cobalt(III) complexes with trdta and the related complexes are presented in Table III, from which it can be seen that the absorption spectra of Na[Coedta]$\cdot 4H_2O$, K[Copdta]$\cdot H_2O$ and K[Cocydta]$\cdot 3H_2O$ are essentially identical, while those of K[Cotrdta]$\cdot 2H_2O$ are somewhat different. The intensities of the first and the second absorption bands of K[Cotrdta]$\cdot 2H_2O$ are smaller than, and the wavelength of the first band of K[Cotrdta]$\cdot 2H_2O$ is longer than, those of the other three complexes. Furthermore, as may be seen in Fig. 3, the broadening of the first band is observed with K[Cotrdta]$\cdot 2H_2O$. Yamatera predicted from the molecular orbital calculations that the first band of a complex of the [CoA_4B_2] type splits into two components.[13] The broadening of the first band of K[Cotrdta]$\cdot 2H_2O$ seems to support Yamatera's prediction. Although the broadening or splitting of the first band was not

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[9] D. H. Busch and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **75**, 4574 (1953).

[10] R. D. Gillard, Nature, **188**, 487 (1960).

[11] K. Swaminathan and D. H. Busch, *J. Inorg. Nucl. Chem.*, **20**, 159 (1961).

[12] M. L. Morris and D. H. Busch, *J. Am. Chem. Soc.*, **78**, 5178 (1956).

[13] H. Yamatera, This Bulletin, **31**, 95 (1958).

TABLE III. VISIBLE AND ULTRAVIOLET ABSORPTION MAXIMA (10^{13} sec^{-1}) AND log ε FOR Co(III) COMPLEXES WITH trdta AND THE RELATED COMPLEXES

Compound	B band		I band		II band		Specific band	
	max.	log ε	max.	log ε	max.	log ε	max.	log ε
K[Cotrdta]·$2H_2O$	ca. 43	ca. 0.3	54.3	2.12	79.1	2.05	133	4.40
Na[Coedta]·$4H_2O$[14]	ca. 43	ca. 0.4	55.9	2.51	78.1	2.36	133	4.33
K[Cocydta]·$3H_2O$	ca. 43	ca. 0.5	55.8	2.50	78.6	2.34	134	4.43
K[Copdta]·H_2O	ca. 43	ca. 0.5	56.1	2.50	78.8	2.34	133	4.34

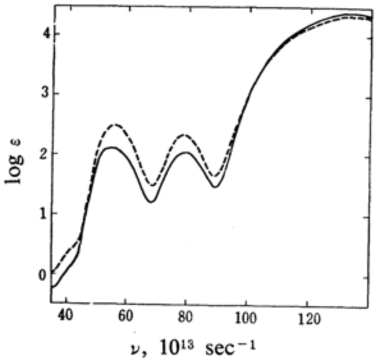

Fig. 3. Visible and ultraviolet absorption spectra of K[Cotrdta]·$2H_2O$ (full line) and K[Copdta]·H_2O(dotted line).

observed with the Na[Coedta]·$4H_2O$, K[Copdta]·H_2O and K[Cocydta]·$3H_2O$, Hidaka et al.[14] concluded from their analysis of the optical rotatory dispersion curve that the first absorption band of $[Coedta]^-$ may have two component absorptions.

Summary

The synthesis of a new cobalt(III) complex, K[Cotrdta]·$2H_2O$ (trdta, $(^-OOCH_2C)_2N(CH_2)_3N(CH_2COO^-)_2$), has been carried out. The infrared, visible and ultraviolet absorption spectra indicate that a quadrivalent trdta anion in this complex is hexadentate. The infrared, visible and ultraviolet absorption spectra of the cobalt(III) complexes with ethylenediaminetetraacetate, propylenediaminetetraacetate and *trans*-1, 2-cyclohexanediaminetetraacetate have also been observed and discussed.

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[14] J. Hidaka, Y. Shimura and R. Tsuchida, ibid., 33, 847 (1960).