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Cobalt(II, III), Nickel(II) and Copper(II) Complexes with Tetra- and Hexamethylenediaminetetraacetate

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Synthesis of new complexes of cobalt(II), cobalt(III), nickel(II) and copper(II), $[Co_2hdta]\cdot 6.5H_2O$, $K[Co\,tdta]\cdot 3H_2O$, $[Ni_2\,hdta]\cdot 6.5H_2O$, $Na_2[Cu\,tdta]\cdot 6H_2O$, $[Cu_2\,tdta]\cdot 1.5H_2O$ and $[Cu_2\,hdta]\cdot 6.5H_2O$, has been carried out, where tdta and hdta represent $(OOCCH_2)_2N(CH_2)_4N(CH_2COO)_2{}^{4-}$ and $(OOCCH_2)_2N(CH_2)_6N(CH_2COO)_2{}^{4-}$, respectively. The infrared, nuclear magnetic resonance and visible and ultraviolet absorption spectra were measured. The infrared and the NMR spectra of the Co(III) complex with tdta indicate that a quadrivalent tdta anion behaves as a hexadentate in this complex.

The preparation and properties of the cobalt(II), cobalt(III), nickel(II) and copper(II) complexes with ethylenediaminetetraacetate (edta) have been extensively investigated. The stability constants of complexes with higher homologues of EDTA have also been reported.[1-3] This paper presents the synthesis and properties of cobalt(II), cobalt(III), nickel(II) and copper(II) complexes with tetramethylenediaminetetraacetate $((^-OOCCH_2)_2N(CH_2)_4N(CH_2COO^-)_2)$ and hexamethylenediaminetetraacetate $((^-OOCCH_2)_2N(CH_2)_6N(CH_2COO^-)_2)$.

Experimental

Preparation. H_4tdta[1] and H_4hdta[2] have been prepared by Schwarzenbach and Ackermann and by Müller and Bersin, respectively, where tdta and hdta represent quadrivalent anions of tetra- and hexamethylenediaminetetraacetate, respectively. In this study, however, these compounds were prepared with procedures similar to that applied to the synthesis of trimethylenediaminetetraacetic acid by Tanaka and Ogino.[4]

Tetramethylenediaminetetraacetic Acid: Monochloroacetic acid (170 g; 1.8 mol) was dissolved in 50 m*l* of water, to which 144 g (3.6 mol) of sodium hydroxide dissolved in 100 m*l* of water was added drop by drop with stirring at about 10°C, followed by the addition of 28 g (0.3 mol) of tetramethylenediamine. The resulting solution was heated at 100°C for 1 hr and was left standing overnight. The pH of the solution was adjusted to 2.3 with concentrated hydrochloric acid. The solution was evaporated on a water-bath, and the white powder containing sodium chloride was collected. This mixture was washed with water to remove as much sodium chloride as possible. The compound was recrystallized from hot water, when the hydrate was obtained. Recrystallization was repeated five times. Found: C, 40.22; H, 6.85; N, 7.76%. Calcd for $C_{12}H_{20}N_2O_8\cdot 2H_2O$: C, 40.45; H, 6.74; N, 7.87%.

Hexamethylenediaminetetraacetic Acid: Hexamethylenediaminetetraacetic acid was prepared with the same procedure as for tetramethylenediaminetetraacetic acid, except that 35 g (0.3 mol) of hexamethylenediamine was added instead of 28 g (0.3 mol) of tetramethylenediamine. The compound was recrystallized from hot water. Found: C, 47.98; H, 7.22; N, 7.89%. Calcd for $C_{14}H_{24}N_2O_8$: C, 48.28; H, 6.90; N, 8.05%.

$Na_2[Cu\,tdta]\cdot 6H_2O$: Copper(II) chloride dihydrate (3.4 g; 0.02 mol) was dissolved into 50 m*l* of water. Tetramethylenediaminetetraacetic acid (7.1 g; 0.02 mol) suspended in 50 m*l* of water was dissolved by adding 2.12 g (0.02 mol) of sodium carbonate. This solution was added to the copper(II) solution. The pH of the mixture was adjusted to about 7 with sodium bicarbonate. The resulting solution was evaporated on a water-bath to a volume of 20 m*l* and cooled in an ice-bath. A light blue crystalline compound appeared, which was collected and washed with water, alcohol and ether. The compound was recrystallized from hot water. Found: C, 26.83; H, 5.67; N, 5.31; H_2O, 21%. Calcd for $Na_2[CuC_{12}H_{16}N_2O_8]\cdot 6H_2O$: C, 26.99; H, 5.25; N, 5.25; H_2O, 20.2%.

$[Cu_2tdta]\cdot 1.5H_2O$: Copper(II) chloride dihydrate (6.8 g; 0.04 mol) was dissolved in 50 m*l* of water. Tetramethylenediaminetetraacetic acid (7.1 g; 0.02 mol) suspended in 50 m*l* of water was dissolved by adding 2.12 g (0.02 mol) of sodium carbonate. This solution was added to the copper(II) solution. The pH of the mixture was adjusted to about 6 with sodium bicarbonate. A dark blue crystalline compound was crystallized immediately. The compound was collected and washed with water, alcohol and ether. Since it was not sufficiently soluble in water, it was purified in the following way: The compound was dissolved into dilute nitric acid solution and filtered. The pH of the solution was

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

[2] A. Müller and T. Bersin, *ibid.*, **38**, 1708 (1955).

[3] G. Anderegg, *ibid.*, **47**, 1801 (1964).

[4] N. Tanaka and H. Ogino, This Bulletin, **37**, 877 (1964).

adjusted to 6 with sodium carbonate, and the compound deposited was collected. Found: C, 30.52; H, 4.57; N, 6.13; H_2O, 6%. Calcd for $[Cu_2C_{12}H_{16}N_2O_8]\cdot 1.5H_2O$: C, 30.64; H, 4.04; N, 5.96; H_2O, 5.7%.

$[Co_2hdta]\cdot 6.5H_2O$: Cobalt(II) chloride hexahydrate (9.5 g; 0.04 mol) was dissolved in 50 m*l* of water. Hexamethylenediaminetetraacetic acid (7.0 g; 0.02 mol) suspended in 50 m*l* of water was dissolved by adding 2.12 g (0.02 mol) of sodium carbonate. The solution was added to cobalt(II) solution. The resulting solution was left standing overnight. Pink powder was collected and washed with water, alcohol and ether. Since the compound was not sufficiently soluble in water, it was purified in the same way as for $[Cu_2tdta]\cdot 1.5H_2O$. Found: C, 29.22; H, 6.03; N, 5.06; H_2O, 19%. Calcd for $[Co_2C_{14}H_{20}N_2O_8]\cdot 6.5H_2O$: C, 29.03; H, 5.70; N, 4.84; H_2O, 20.2%.

$[Ni_2hdta]\cdot 6.5H_2O$: This compound was prepared in the same way as for $[Co_2hdta]\cdot 6.5H_2O$. Found: C, 28.88; H, 5.99; N, 5.08; H_2O, 19.5%. Calcd for $[Ni_2C_{14}H_{20}N_2O_8]6.5H_2O$: C, 29.05; H, 5.71; N, 4.84; H_2O, 20.2%.

$[Cu_2hdta]\cdot 6.5H_2O$: This compound was prepared in the same way as for $[Co_2hdta]\cdot 6.5H_2O$. Found: C, 28.38; H, 5.89; N, 4.65; H_2O, 20%. Calcd for $[Cu_2C_{14}H_{20}N_2O_8]\cdot 6.5H_2O$: C, 28.57; H, 5.61; N, 4.76; H_2O, 19.9%.

$K[Co\,tdta]\cdot 3H_2O$: H_4tdta (7.1 g; 0.02 mol), potassium acetate (12.0 g; 0.12 mol) and cobalt(II) acetate tetrahydrate (5.0 g; 0.02 mol) were dissolved into 100 m*l* of water, to which 2.85 g of lead dioxide was added. The pink solution turned to dark blue immediately. The solution was filtered and the filtrate was evaporated under reduced pressure to 50 m*l* at about 50°C. After the solution was cooled to 0°C, alcohol was added drop by drop, when dark blue crystals were deposited, which were collected and washed with cold water, alcohol and ether. The compound was recrystallized from water of about 50°C by the addition of alcohol. The crystals decompose at about 100°C. Found: C, 31.05; H, 4.93; N, 5.97; H_2O, 11%. Calcd for $K[CoC_{12}H_{16}N_2O_8]\cdot 3H_2O$: C, 30.77; H, 4.70; N, 5.98; H_2O, 11.5%. It should be noted that the preparation of cobalt(III)-HDTA complexes was not successful because no suitable oxidizing agent was found to oxidize cobalt(II)-HDTA complexes to the cobalt(III) state.

Measurement. The crystalline water of the complexes was determined by a Shimadzu RT-2 recording thermobalance. The infrared spectra were obtained with a Hitachi EPI-2G recording infrared spectrophotometer by the potassium bromide disk method. The proton NMR spectra were obtained with a Varian A-60 high resolution nuclear magnetic resonance spectrometer, and the visible and ultraviolet absorption spectra, with a Hitachi EPS-3 spectrophotometer.

Result and Discussion

Infrared Absorption Spectra. In Table 1 are given the frequencies of the absorption bands of H_4edta, $H_4tdta\cdot 2H_2O$, H_4hdta, $Na_2[Cu\,tdta]\cdot 6H_2O$, $[Cu_2tdta]\cdot 1.5H_2O$, $[Co_2hdta]\cdot 6.5H_2O$, $[Ni_2hdta]\cdot 6.5H_2O$, $[Cu_2hdta]\cdot 6.5H_2O$, $Na[Co\,edta]\cdot 4H_2O$ and $K[Co\,tdta]\cdot 3H_2O$. The values obtained for H_4hdta almost agree with those in literature.[4]

TABLE 1. INFRARED ABSORPTION OF H_4edta, $H_4tdta\cdot 2H_2O$ AND H_4hdta AND THEIR COMPLEXES (cm^{-1})

Compound	COOH	COO^- or $COO^-\cdots M$	$COO^-\cdots M$
H_4 edta[4]	1634, 1704		
$H_4\,tdta\cdot 2H_2O$	1682		
H_4 hdta	1682, 1709		
H_4 hdta[4]	1686, 1709		
$Na_2[Cu\,tdta]\cdot 6H_2O$		1597	
$[Cu_2\,tdta]\cdot 1.5H_2O$		1577, 1613	
$[Co_2\,hdta]\cdot 6.5H_2O$		1595, 1626	
$[Ni_2\,hdta]\cdot 6.5H_2O$		1582, 1600	
$[Cu_2\,hdta]\cdot 6.5H_2O$		1585, 1634	
$Na[Co\,edta]\cdot 4H_2O$			1639
$K[Co\,tdta]\cdot 3H_2O$			1619, 1639

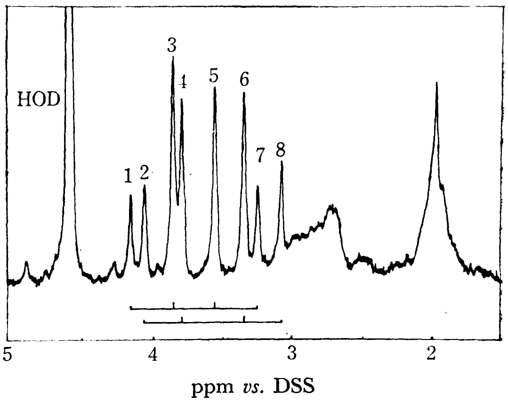
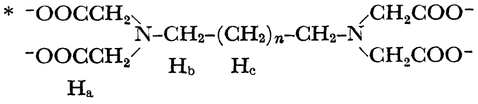


Fig. 1. Proton NMR spectra of $K[Co\,tdta]\cdot 3H_2O$ in D_2O. (DSS: Sodium 3-(trimethylsilyl)-1-propanesulfonate)

TABLE 2. CHEMICAL SHIFT (ppm *vs.* DSS) AND COUPLING CONSTANTS (cps) OF tdta AND hdta ANION AND $K[Co\,tdta]\cdot 3H_2O$

Compound	Chemical shift*			Coupling constant
	H_c	H_b	H_a**	
edta[5]	—	2.70	3.22	
tdta	1.38	2.44	3.06	
hdta	1.28	2.48	3.10	
Co^{III}edta[6]			3.75 (0.33)	16.5
			3.92 (0.15)	18.5
Co^{III}tdta	1.97	2.71	3.57 (0.66)	16.2
			3.71 (0.51)	18.4

*


$$\begin{matrix} {}^-OOC\underset{H_a}{C}H_2 \\ {}^-OOCCH_2 \end{matrix}\!\!>N\text{-}\underset{H_b}{CH_2}\text{-}(\underset{H_c}{CH_2})_n\text{-}CH_2\text{-}N\!<\!\!\begin{matrix} CH_2COO^- \\ CH_2COO^- \end{matrix}$$

$n = 0$ (edta), 2 (tdta) and 4 (hdta)

** Relative chemical shifts of two AB protons are given in parentheses.

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[5] J. L. Sudmeier and C. N. Reilley, *Anal. Chem.*, **36**, 1698 (1964).

[6] J. B. Terill and C. N. Reilley, *Inorg. Chem.*, **5**, 1988 (1966).

It has been reported that in the case of such divalent metal complexes as dealt with in this study, coordinated and free carboxyl ions cannot be distiguished from each other by their infrared absorption spectra.[7] The cobalt(III) complex with tdta gave a strong carboxylate band at higher frequencies than those of the absorption band due to free COO^-. Although the carboxylate band of K[Co tdta]·$3H_2O$ splits into two absorption peaks at 1639 cm^{-1} and 1619 (sh) cm^{-1}, both peaks are considered to be associated with the coordinated carboxyl groups. This suggests that a quadrivalent tdta anion in the cobalt(III) complex behaves as a hexadentate.

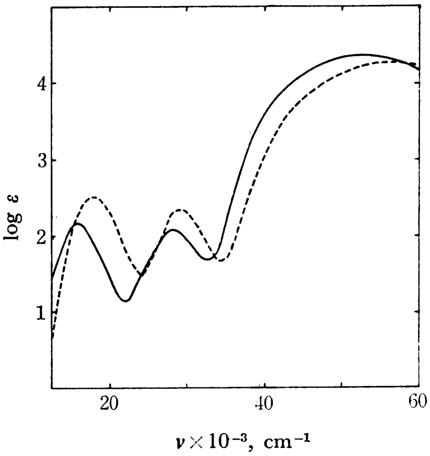

Fig. 2. Visible and ultraviolet absorption spectra of K[Co tdta]·$3H_2O$ (full line) and Na[Co edta]·$4H_2O$ (broken line).

Nuclear Magnetic Resonance Spectra. Proton NMR spectra of tdta and hdta anions were measured in 0.2M aqueous sodium hydroxide solution and those of cobalt(III) complex with tdta, in D_2O. The latter is shown in Fig. 1. In Table 2 are given the chemical shifts of proton NMR spectra of these compounds.

TABLE 3. FREQUENCIES AND log ε OF VISIBLE AND ULTRAVIOLET ABSORPTION MAXIMA FOR Co(III) COMPLEXES WITH edta AND tdta

Compound	I band		II band		Specific band	
	$\tilde{\nu} \times 10^{-3}$ cm^{-1}	log ε	$\tilde{\nu} \times 10^{-3}$ cm^{-1}	log ε	$\tilde{\nu} \times 10^{-3}$ cm^{-1}	log ε
Na[Co edta]·$4H_2O$[8]	18.6	2.51	26.0	2.36	44.3	4.33
K[Co tdta]·$3H_2O$	17.2	2.13	25.4	2.08	42.0	4.37

K[Co tdta]·$3H_2O$: Spectrum of the acetate protons splits into eight peaks in a region from 3.0 ppm to 4.2 ppm, indicating two AB patterns. The coupling constants are also given in Table 2. The two AB patterns show that four acetates are divided into two groups; the acetates of one group are of the out-of-plane type while those of the other group are of the in-plane type, when the plane involving two nitrogen atoms and a central metal ion is considered.

Visible and Ultraviolet Absorption Spectra. The visible and ultraviolet absorption spectra of cobalt(III) complexes with edta and tdta are shown in Fig. 2, and wave numbers and log ε of absorption maxima for cobalt(III) complexes with edta and tdta are given in Table 3. The first and the second absorption bands of the cobalt(III) complex with tdta give a red shift as compared with edta, indicating that the spectrochemical series is in the order of edta $>$ tdta.

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[7] Y. Shimura, *Kagaku*, **15**, 331 (1959).

[8] J. Hidaka, Y. Shimura and R. Tsuchida, This Bulletin, **33**, 847 (1960).