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A MONOCYANO-EDTA COBALTATE(III) COMPLEX: $Na_2[Co(CN)edta]\cdot 4H_2O$

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The preparation of a novel cyano-EDTA cobalt(III) complex, in which the $edta^{4-}$ ion acts as a pentadentate ligand, has successfully been accomplished by treating the monocyanoiodotetramminecobalt(III) iodide with tetrasodium ethylenediaminetetraacetate dihydrate, $Na_4edta\cdot 2H_2O$.

Of EDTA complexes, some of the $[Co^{III}X\ edta]$-type with one unbound carboxylate group have so far been known (X = OH, Cl, Br, or NO_2),$^{1-3)}$ but the monocyano-EDTA complex has not yet been reported. The present communication deals with the synthesis and characterization of the disodium monocyanoethylenediaminetetraacetatocobaltate(III) tetrahydrate.

The $Na_2[Co(CN)edta]\cdot 4H_2O$ complex was synthesized according to the following scheme:

$$\text{trans-}[Co(CN)(OH_2)(NH_3)_4]Cl_2 \xrightarrow{KI} \text{trans-}[Co(CN)I(NH_3)_4]I \xrightarrow{Na_4edta\cdot 2H_2O} Na_2[Co(CN)edta]\cdot 4H_2O.$$

Thirty grams of trans-$[Co(CN)(OH_2)(NH_3)_4]Cl_2$$^{4)}$ were dissolved completely in 500 ml of water at 80°C. There were added 100 ml of water containing 80 g of potassium iodide to this solution, drop by drop, with stirring. Immediately brown crystals precipitated, which were filtered and washed with water, ethanol and ether. The precipitate was treated twice with a fresh KI solution at 80° so as to introduce the iodide ligand sufficiently into the trans-position to that of the cyanide. The complex is not stable, especially on exposure to light, even in the solid phase, from which the vapor of iodine was recognized to be released not only in vacuo but also under 1 atm. at room temperatures. Found: Co, 15.02; C, 2.55; N, 18.05; H, 3.33; I, 63.21%. Calcd for $[Co(CN)I(NH_3)_4]I$: Co, 14.49; C, 2.95; N, 17.21; H, 2.97; I, 62.38%.

Fifty grams of the cyanoiodotetramminecobalt(III) iodide obtained above, 51 g of $Na_4edta\cdot 2H_2O$, and 4 g of active charcoal were suspended in 120 ml of water and heated on a water bath at 80-85° for 2.5 hr with mechanical stirring. The reaction proceeded, evolving ammonia, and its progress was monitored by observing the disappearance of the solid complex into solution. Special care was taken to avoid an overrun of the reaction beyond the end-point, often yielding the $Na[Co\ edta]\cdot 4H_2O$ complex (violet). After removal of the unreacted complex and charcoal, and very slow addition of 400 ml of methanol, the desired complex appeared as red crystals from the magenta filtrate. The rapid addition of methanol and the use of ethanol cause the deposition of a viscous oil-like complex. The scarlet crude complex (23 g) was dissolved again in the requisite small amount of water (30 ml). There were added 5 ml of methanol and then 5 ml of ethanol successively. Red crystals deposited with cooling by ice. This procedure of purification was repeated several times. Finally, 3 g of pure red crystals were obtained and identified. Found: Co, 12.10; C, 27.32; N, 8.38; H, 3.97; Na, 10.12%. Calcd for $Na_2[Co(CN)(C_{10}H_{12}O_8N_2)]\cdot 4H_2O$: Co, 12.00; C, 26.90; N, 8.55; H, 4.10; Na, 9.36%. The possibility of obtaining the ammonium salt from the ammoniacal solution was denied by determining the content of sodium with atomic absorption spectroscopy. Instead of the cyano-iodo complex, the trans-$[Co(CN)(OH_2)(NH_3)_4]Cl_2$ salt[4] is certainly available directly for synthesis as a starting material, but not recommended when this purification procedure is used, since the separation of the aimed-at complex from sodium chloride is fairly difficult. The trans-configuration of the $[Co(CN)I(NH_3)_4]I$ complex was arrived at from the spectrochemical series for the complexes of the $[Co^{III}(CN)X(NH_3)_4]$ type which had been newly prepared from trans-$[Co(CN)(OH_2)(NH_3)_4]Cl_2$[4] ($X = P\equiv\phi_3$(triphenylphosphine), CN^-, NO_2^-, SO_3^{2-}, NO^-, NH_3, NH_2CH_3, pyridine, $NH_2C_2H_5$, OH_2, CO_3^{2-}, or N_3^-).

Figure 1 shows the absorption spectra of the cyano-EDTA cobalt(III) complex and of its related complexes in water. The positions of the absorption maxima obey the sequence of the spectrochemical series: Br^-, Cl^-, OH^-, NO_2^-, and CN^-. The absorption data are summarized in Table 1.

Figure 2 shows the infrared spectra of $Na_2[Co(CN)edta]\cdot 4H_2O$ and $Na_4edta\cdot 2H_2O$ in KBr pellets. The carbonyl region of the infrared spectrum for the complex

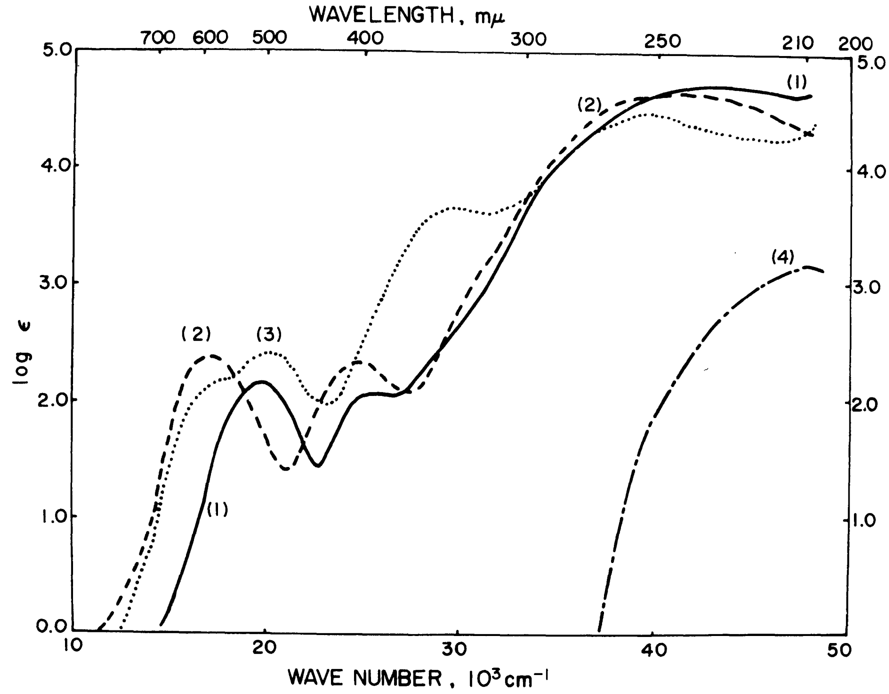

Fig. 1. Absorption spectra in the visible and ultraviolet region: (1) ——— $Na_2[Co(CN)edta]\cdot 4H_2O$; (2) – – – – – $K_2[Co(Cl)edta]\cdot 3H_2O$ in 0.5 M HCl; (3) ·············· $Na_2[Co(NO_2)edta]\cdot 3H_2O$; (4) —·—·— $Na_4edta\cdot 2H_2O$; water was used except in (2).

Table 1. The absorption data for EDTA Co(III) complexes

Complex	I-Band	II-Band	III-Band	Ref.
	$\nu_{max}^{a)}(\log \varepsilon_{max})$	$\nu_{max}(\log \varepsilon_{max})$	$\nu_{max}(\log \varepsilon_{max})$	
$Na_2[Co(CN)edta]\cdot 4H_2O$	19.6(1.89)	ca 26 (1.90)	42.3(4.45)	
$Na_2[Co(NO_2)edta]\cdot 3H_2O$	17.4(2.11)			5)
	20.4(2.39)			
$K_2[Co(Cl)edta]\cdot 3H_2O$	17.2(2.38)	25.0(2.28)		2)
$Na_2[Co(Br)edta]\cdot 4H_2O$	17.0(2.39)			5)
$Na_2[Co(OH)edta]\cdot 3H_2O$	17.5(2.30)	26.0(2.21)		6)
$K[Co\ edta]\cdot 2H_2O$	18.7(2.60)	26.3(2.45)		5)

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a) In units of 10^3/cm

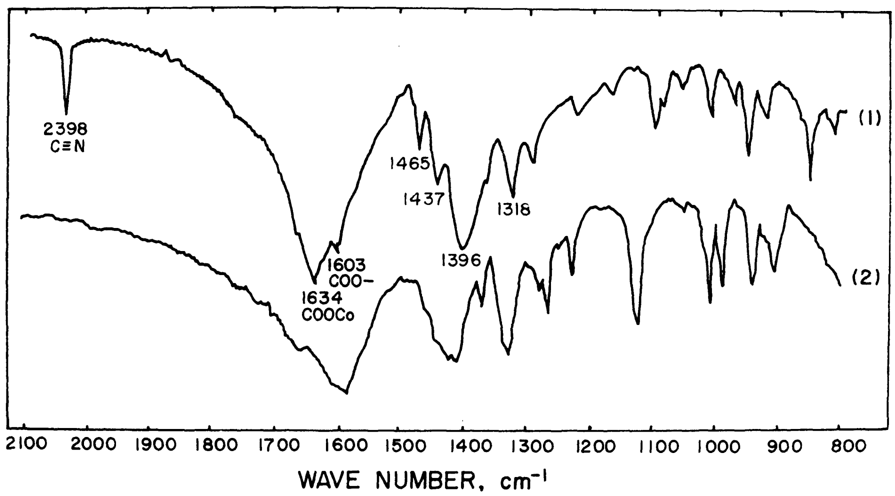

Fig. 2. Infrared spectra of $Na_2[Co(CN)edta]\cdot 4H_2O$ (1) and $Na_4edta\cdot 2H_2O$ (2) in KBr pellets.

exhibits stretching vibration modes at 1634, 1603, 1465, and 1437 cm^{-1}. The peak at 1603 cm^{-1} is evidence for the free carboxylate group. The cyanide stretching vibration is observable at 2398 cm^{-1}. The close similarity of this pattern to those of the quinquedentate EDTA cobalt(III) complexes[7] shows that the complex obtained may be formulated as $Na_2[Co(CN)edta]\cdot 4H_2O$ with great confidence.

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