

PREPARATION OF $\text{Ca}[\text{CrNCS}(\text{edta})]$ BY THE USE OF SOLID-PHASE
THERMAL REACTION OF $[\text{CrNCS}(\text{NH}_3)_5][\text{Ca}(\text{edta})] \cdot 5\text{H}_2\text{O}$

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$[\text{CrNCS}(\text{NH}_3)_5][\text{Ca}(\text{edta})] \cdot 5\text{H}_2\text{O}$ was prepared by the reaction of $[\text{CrNCS}(\text{NH}_3)_5]\text{Cl}_2$ with $\text{Na}_2[\text{Ca}(\text{edta})] \cdot 3.5\text{H}_2\text{O}$. The thermal reaction of the complex in the solid-phase was investigated both non-isothermally and isothermally. It was found that the complex was finally converted into $\text{Ca}[\text{CrNCS}(\text{edta})]$ upon heating in the solid-phase, which was purified from water as the hexahydrate.

The following chromium(III)-ethylenediaminetetraacetato complexes are well known: $\text{Na}[\text{Cr}(\text{edta})] \cdot 2\text{H}_2\text{O}$ ¹⁾ and $[\text{Cr}(\text{Hedta})(\text{H}_2\text{O})]$ ²⁾. On the other hand, the complexes having a general formula $[\text{CrX}(\text{edta})]^{2-}$ or $[\text{CrX}(\text{Hedta})]^-$ have not yet been isolated, where X is one of univalent anions such as Cl, Br, NCS and so on. Ogino et al. studied the equilibrium and kinetics of the reactions of $[\text{CrY}(\text{H}_2\text{O})]^- + \text{X} \rightleftharpoons [\text{CrXY}]^{2-} + \text{H}_2\text{O}$ (X: an anion such as acetate³⁾ and azide ions⁴⁾; Y: edta and its analogues) and they found that the anation proceeds quite rapidly and the equilibrium constant is considerably large because the free carboxymethyl group assists to expel the water molecule from the coordination sphere, but in the case of X = NCS the equilibrium constant is very small.⁵⁾ The attempts to prepare $[\text{CrX}(\text{Hedta})]^-$ (X: Cl or Br) by treating $[\text{Cr}(\text{Hedta})(\text{H}_2\text{O})]$ with concentrated hydrochloric acid or hydrobromic acid resulted in the formation of other species such as $[\text{CrCl}_2(\text{H}_3\text{edta})(\text{H}_2\text{O})]$ or $[\text{CrBr}_2(\text{H}_3\text{edta})(\text{H}_2\text{O})]$.⁶⁾ Special regard should be taken to isolate the complexes $[\text{CrX}(\text{Hedta})]^-$ or $[\text{CrX}(\text{edta})]^{2-}$.

Previously, we reported that the complexes $[\text{Cr}(\text{NH}_3)_6][\text{Al}(\text{ox})_3]$ (yellow) and $[\text{Cr}(\text{NH}_3)_6][\text{Al}(\text{nta})_2] \cdot 4\text{H}_2\text{O}$ (yellow), upon heating, evolve six moles of ammonia to be converted into $\text{Al}[\text{Cr}(\text{ox})_3]$ (green) and $\text{Al}[\text{Cr}(\text{nta})_2]$ (pink) in the solid-phase, where nta denotes nitrilotriacetate ion.⁷⁾ It is of interest that the oxalate and nta ions in the respective anion moieties easily transfer from Al(III) to Cr(III) ions even in the solid-phase. The facts imply that the complexes $[\text{CrX}(\text{NH}_3)_5][\text{M}(\text{edta})]$ (X: one of non-volatile ligands such as Cl, Br, F, NCS and the like; M: an alkaline earth metal ion), when heated, evolve five moles of ammonia in the cationic moiety and the edta ion in the anionic moiety migrates to Cr(III) ion, and consequently $\text{M}[\text{CrX}(\text{edta})]$ can be obtained which have not yet been isolated from solution.

Recently, we succeeded in finding the first example that shows the above unique reaction. The present paper, therefore, deals with the preparation of $\text{Ca}[\text{CrNCS}(\text{edta})]$ through the thermal reaction of $[\text{CrNCS}(\text{NH}_3)_5][\text{Ca}(\text{edta})] \cdot 5\text{H}_2\text{O}$ in the solid-phase.

Preparation of Isothiocyanatopentaamminechromium(III) Ethylenediaminetetraacetatocalcate(II) Pentahydrate, $[\text{CrNCS}(\text{NH}_3)_5][\text{Ca}(\text{edta})] \cdot 5\text{H}_2\text{O}$ (orange-yellow). $[\text{CrNCS}(\text{NH}_3)_5]\text{Cl}_2$ ⁸⁾ and $\text{Na}_2[\text{Ca}(\text{edta})] \cdot 3.5\text{H}_2\text{O}$ ⁹⁾ were prepared according to the known methods. A solution of $\text{Na}_2[\text{Ca}(\text{edta})] \cdot 3.5\text{H}_2\text{O}$ (2 g, 5 mmol) in 40 ml of water was added to a solution of $[\text{CrNCS}(\text{NH}_3)_5]\text{Cl}_2$ (1.3 g, 5 mmol) in 100 ml of water. Eighty milliliters of ethanol was then gradually (preferably each 10 ml every 3 hr) added to the mixture. Rapid addition of the ethanol frequently gave the starting materials. The resulting solution was allowed to stand in a refrigerator for a few days; during this period it is preferred to scrub occasionally the wall of the container with glass rods in order to induce the formation of well-defined crystals. Orange-yellow needle-like crystals were obtained, which were recrystallized from water. Yield 2 g.

Found: C, 21.35; H, 5.85; N, 18.20%. Calcd for $\text{C}_{11}\text{H}_{37}\text{N}_8\text{O}_{13}\text{SCaCr}$: C, 21.53; H, 6.08; N, 18.26%.

Thermal Reaction of $[\text{CrNCS}(\text{NH}_3)_5][\text{Ca}(\text{edta})] \cdot 5\text{H}_2\text{O}$ in the Solid-phase. Figure 1 shows the derivatogram of the complex measured in a nitrogen stream at the heating rate of 1°C min^{-1} . As seen from the TG curve, the mass losses start moderately at $50\text{--}150^\circ\text{C}$, smoothly at $150\text{--}260^\circ\text{C}$ and rapidly above 290°C . One sharp endothermic peak appears at $50\text{--}150^\circ\text{C}$ and then the DTA curve is tailing up to 260°C . The mass losses up to 260°C correspond to the evolution of $5\text{NH}_3 + 5\text{H}_2\text{O}$. The complex turned to purple from orange-yellow in color at the end of the evolution of $5\text{NH}_3 + 5\text{H}_2\text{O}$. This result suggests the possibility of preparing $\text{Ca}[\text{CrNCS}(\text{edta})]$ by the use of the thermal reaction of $[\text{CrNCS}(\text{NH}_3)_5][\text{Ca}(\text{edta})] \cdot 5\text{H}_2\text{O}$. Then preliminary experiments were carried out to determine the heating condition (250°C for 200 min) for obtaining $\text{Ca}[\text{CrNCS}(\text{edta})]$. From the products obtained by the heating, $\text{Ca}[\text{CrNCS}(\text{edta})] \cdot 6\text{H}_2\text{O}$ was isolated as noted in the following section.

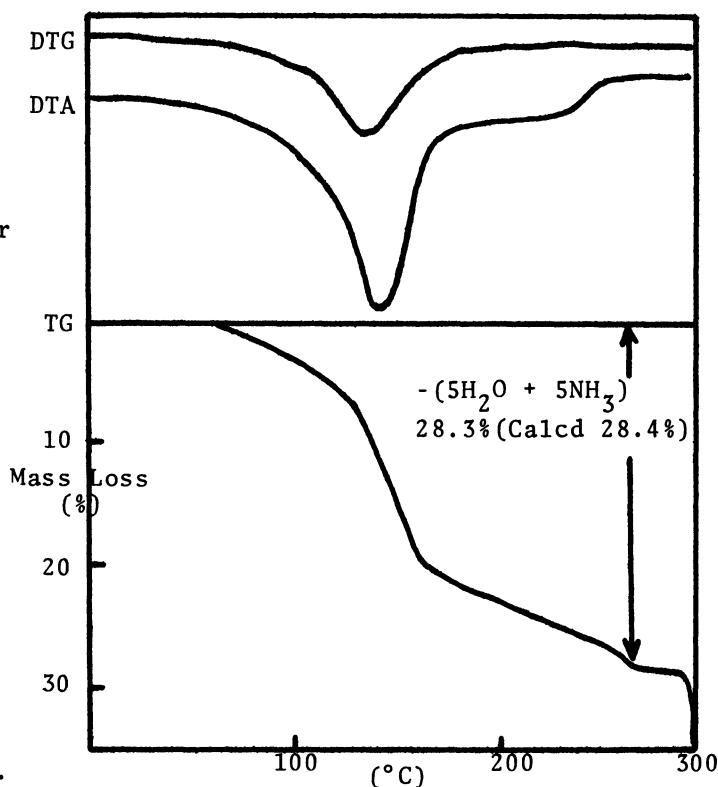


Fig. 1 Derivatogram of $[\text{CrNCS}(\text{NH}_3)_5][\text{Ca}(\text{edta})] \cdot 5\text{H}_2\text{O}$.

Preparation of Calcium Isothiocyanatoethylenediaminetetraacetatochromate(III) Hexahydrate, $\text{Ca}[\text{CrNCS}(\text{edta})]\cdot 6\text{H}_2\text{O}$ (purple). The starting complex $[\text{CrNCS}(\text{NH}_3)_5][\text{Ca}(\text{edta})]\cdot 5\text{H}_2\text{O}$ was triturated thoroughly in an agate mortar, spread thinly on a watch glass and heated at 250°C for 200 min. The heating condition (250°C for 200 min) were predetermined non-isothermally (derivatographically) and isothermally as specified in the foregoing section. The products obtained were dissolved in warm water as quickly as possible. Then, the solution was rapidly filtered and the filtrate was stored in an ice-salt bath. Purple microcrystalline powders were soon obtained. Two grams of the compound was yielded from 7 g of the starting complex.

Found: C, 23.64; H, 4.42; N, 7.54%. Calcd for $\text{C}_{11}\text{H}_{24}\text{N}_3\text{O}_{14}\text{SCaCr}$: C, 24.18; H, 4.43; N, 7.69%.

The complex had to be stored in a container completely dried because the complex gradually decomposed with moisture in the air. Being exposed to moisture or dissolved in water, the complex gave off an unpleasant odor peculiar to the decomposition of NCS^- released. This suggests that the complex reacted with H_2O to undergo some complicated reactions other than simple substitution of NCS^- by H_2O . The fact may have a connection with the results by Ogino⁵⁾ that the equilibrium constant for the reaction of $[\text{CrY}(\text{H}_2\text{O})]^-$ with X is exceptionally small only in the case of $\text{X} = \text{NCS}$.

IR Spectra. Table 1 summarizes the bands due to the $\text{C}\equiv\text{N}$ and $\text{C}=\text{O}$ stretching vibrations, which are diagnostic for determining the coordination modes of $-\text{COO}^-$ and NCS^- groups.

Table 1 IR data due to the $\text{C}\equiv\text{N}$ and $\text{C}=\text{O}$ stretching vibrations (cm^{-1}).

Complexes	$\tilde{\nu}^{\text{a)}}_{\text{C}\equiv\text{N}}$	$\tilde{\nu}^{\text{a)}}_{\text{C}=\text{O}}$		
		$-\text{COOH}$	$-\text{COO}-\text{M}^{\text{b)}}_1$	$-\text{COO}^-$
$[\text{CrNCS}(\text{NH}_3)_5][\text{Ca}(\text{edta})]\cdot 5\text{H}_2\text{O}$	2083(s)		1595(vs,br)	
$\text{Ca}[\text{CrNCS}(\text{edta})]\cdot 6\text{H}_2\text{O}$	2080(s)		1630(vs,br)	1580(s)
$\text{Na}_2[\text{Ca}(\text{edta})]\cdot 3.5\text{H}_2\text{O}$			1600(vs,br)	
$\text{Na}[\text{Cr}(\text{edta})]\cdot 2\text{H}_2\text{O}^{\text{c)}}_1$			1640(vs,br)	
$[\text{Cr}(\text{Hedta})(\text{H}_2\text{O})]^{\text{d)}}_1$		1728(s)	1635(vs,br)	

a) The terms s, vs and br denote strong, very strong and broad, respectively.

b) M means $\text{Cr}(\text{III})$ or $\text{Ca}(\text{II})$ ion. c) prepared according to Ref. 1.

d) prepared according to Ref. 2c.

Many IR spectral studies have already been carried out on the divalent¹⁰⁾ and trivalent^{1,11)} metal complexes containing ethylenediaminetetraacetic acid. The band assignable to $-\text{COO}-\text{Cr}(\text{III})$ ($\text{Na}[\text{Cr}(\text{edta})]\cdot 2\text{H}_2\text{O}$: 1640 cm^{-1}) appears in the higher wavenumber regions than that of $-\text{COO}-\text{Ca}(\text{II})$ ($\text{Na}_2[\text{Ca}(\text{edta})]\cdot 3.5\text{H}_2\text{O}$: 1600^{-1}).^{1,10,11)} The bands due to $-\text{COOH}$ and $-\text{COO}^-$ appear in the ranges of $1700\text{--}1740\text{ cm}^{-1}$ ($[\text{Cr}(\text{Hedta})(\text{H}_2\text{O})]$: 1728 cm^{-1}) and $1550\text{--}1600\text{ cm}^{-1}$. $[\text{CrNCS}(\text{NH}_3)_5][\text{Ca}(\text{edta})]\cdot 5\text{H}_2\text{O}$ gives one band at 1595 cm^{-1} attributable to $-\text{COO}-\text{Ca}$. On the other hand, $\text{Ca}[\text{CrNCS}(\text{edta})]\cdot 6\text{H}_2\text{O}$ has two bands at 1630 and 1580 cm^{-1} ; the former is due to $-\text{COO}-\text{Cr}$ and the latter may come from $-\text{COO}^-$. No substantial difference was detectable in the bands due to the $\text{C}\equiv\text{N}$ stretching vibration between $[\text{CrNCS}(\text{NH}_3)_5][\text{Ca}(\text{edta})]\cdot 5\text{H}_2\text{O}$ (2083 cm^{-1})¹²⁾ and $\text{Ca}[\text{CrNCS}(\text{edta})]\cdot 6\text{H}_2\text{O}$ (2080 cm^{-1})¹²⁾, suggesting that the $\text{Cr}(\text{III})\text{-NCS}$ bond is

maintained before and after the above treatment.

Electronic Spectra. Table 2 lists up the electronic spectral data due to d-d transition. $[\text{CrNCS}(\text{NH}_3)_5][\text{Ca}(\text{edta})] \cdot 5\text{H}_2\text{O}$ gives the bands at 20.6 and 27.4 $\times 10^3 \text{ cm}^{-1}$, which are essentially the same as those for $[\text{CrNCS}(\text{NH}_3)_5]\text{Cl}_2$ (not listed in the table). The first band of $\text{Ca}[\text{CrNCS}(\text{edta})] \cdot 6\text{H}_2\text{O}$ ($18.0 \times 10^3 \text{ cm}^{-1}$) lies in between those of $[\text{Cr}(\text{edta})(\text{H}_2\text{O})]^-$ ($18.4 \times 10^3 \text{ cm}^{-1}$) and $[\text{Cr}(\text{OAc})(\text{edta})]^{2-}$ (17.7 cm^{-1}), indicating that the NCS ion resides in one of the six coordination sites of octahedral environment of chromium(III) ion.

Table 2 Electronic spectral data due to d-d transition ($\times 10^3 \text{ cm}^{-1}$).

Complexes	$\tilde{\nu}_I (\log \epsilon)$	$\tilde{\nu}_{II} (\log \epsilon)$
$[\text{CrNCS}(\text{NH}_3)_5][\text{Ca}(\text{edta})] \cdot 5\text{H}_2\text{O}$	20.6 (1.86)	27.4 (1.70)
$\text{Ca}[\text{CrNCS}(\text{edta})] \cdot 6\text{H}_2\text{O}^{\text{a)}$	18.0 (1.97)	b)
$[\text{Cr}(\text{edta})(\text{H}_2\text{O})]^- \text{ c)}$	18.4 (2.33)	25.5 (2.06)
$[\text{Cr}(\text{OAc})(\text{edta})]^{2-} \text{ c)}$	17.7 (2.17)	25.4 (2.08)

a) measured in 60% HClO_4 . b) The second band could not clearly appear probably because of the overlap with the specific band due to the coordinated NCS^- in $[\text{CrNCS}(\text{edta})]^{2-}$. c) cited from Ref. 3b.

The complex $[\text{CrNCS}(\text{edta})]^{2-}$ had previously been thought to be hardly obtained, but we succeeded in preparing the complex by the use of the thermal reaction of $[\text{CrNCS}(\text{NH}_3)_5][\text{Ca}(\text{edta})] \cdot 5\text{H}_2\text{O}$. The preparative method based on the present idea will shortly lead to proliferous production of other new chromium(III) complexes of the series $[\text{CrX}(\text{edta or its analogue})]^{2-}$ (X is different unidentate anions).

References

- 1) D. T. Sawyer and J. M. McKinnie, J. Am. Chem. Soc., **82**, 4191 (1960).
- 2) a) H. Brintzinger, H. Thiele, and U. Müller, Z. Anorg. Allg. Chem., **251**, 285 (1943); b) G. Schwarzenbach and H. Ackermann, Helv. Chim. Acta, **31**, 1029 (1948); c) R. E. Hamm, J. Am. Chem. Soc., **75**, 5670 (1953).
- 3) a) H. Ogino, T. Watanabe, and N. Tanaka, Chem. Lett., **1974**, 91; b) Inorg. Chem., **14**, 2093 (1975).
- 4) H. Ogino, M. Shimura, and N. Tanaka, Chem. Lett., **1976**, 127.
- 5) H. Ogino, private communication.
- 6) R. N. Thornelly, B. Kipling, and A. G. Sykes, J. Chem. Soc. (A), **1968**, 2847.
- 7) R. Tsuchiya, A. Uehara, and E. Kyuno, Chem. Lett., **1974**, 21; 595.
- 8) T. Inoue, "Mukikagaku Seizō Jikken", Shokabō Pub. Co., 493 (1946).
- 9) P. Pfeiffer and H. Simmons, Ber., **76**, 847 (1943).
- 10) D. T. Sawyer and P. J. Paulsen, J. Am. Chem. Soc., **80**, 1597 (1958); **81**, 816 (1959).
- 11) a) D. H. Busch and J. C. Bailar, Jr., J. Am. Chem. Soc., **75**, 4574 (1953); b) M. L. Morris and D. H. Busch, J. Am. Chem. Soc., **78**, 5178 (1956).
- 12) The band is assignable to the Cr-NCS bond: see a) L. H. Jones, J. Chem. Phys., **25**, 1069 (1956); b) P. C. H. Mitchell, and R. J. P. Williams, J. Chem. Soc., **1960**, 1912; c) H. Oki, E. Kyuno, and R. Tsuchiya, Bull. Chem. Soc. Jpn., **41**, 2357 (1968).

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