

have earlier been reported to be tetragonal¹².

The compound was prepared according to Mayer and Kubasch¹¹, but was purified over the mercuric chloride adduct instead of by sublimation.

*3-Acetylrimino-5-acetamido-1,2-dithiole*⁵ crystallizes from butanol as light brownish-yellow needles elongated along *b*. Orthorhombic, $a = 17.41 \text{ \AA}$, $b = 10.54 \text{ \AA}$, $c = 15.64 \text{ \AA}$. Twelve molecules per unit cell; density, calc. 1.50, found 1.51 g/cm³. The systematic absences are those of the space groups $Pnma$ or $Pn2_1a$. The intensities of the $h0l$ reflections are normal for $l = 3$, but are very weak for the remainder. This implies that a pattern of four molecules is repeated three times in the *c*-axis direction as seen along the *b* axis, and may indicate that the asymmetric unit consists of three molecules, one from each pattern of four; this would correspond to the space group $Pn2_1a$.

Further work on the crystal structures of some of the compounds will be made.

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An Isoselenocyanate Complex of Chromium(III)

Preparation and Absorption Spectrum

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The selenocyanate- like the thiocyanate ion has, when acting as a ligand, the special characteristic of being able to bind through either end of the group. It looks as if there is a correlation between the division of metals into class (a) and class (b) acceptors proposed by Ahrlund, Chatt and Davies¹ and the type of binding, the class (a) metals tending to form isothiocyanate complexes, the class (b) metals to form thiocyanate complexes^{2,3}.

In the last years great interest has been taken in thiocyanate complexes, whereas little work has been done on the corresponding seleno-cyanate compounds. This work has mainly been concerned with complexes of the class (b) metals as platinum and mercury^{4,5}. Recently, however, Cotton *et al.*⁶ and Turco *et al.*⁷ have investigated some selenocyanate complexes of cobalt(II) and by means of spectral and magnetic data concluded that the selenocyanate groups are co-ordinated to cobalt through the nitrogen atoms in the $[\text{Co}(\text{NCSe})_6]^{3+}$ ion.

The intention of this work has been to investigate a selenocyanate complex of chromium(III) of the type $[\text{Cr}(\text{NCSe})_6]^{3+}$ and from spectral data to find out which end of the selenocyanate group is bound to the metal.

Chromium(III) is a class (a) acceptor, and in analogy with a thiocyanate complex,³ $[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^{3+}$, co-ordination through the nitrogen atoms should be expected. The spectral data obtained here seem to confirm this.

Experimental. Anhydrous CrCl_3 and KSeCN were prepared by methods described in the literature^{8,10}. All other chemicals were reagent grade and used without further purification.

Preparation of $((\text{CH}_3)_4\text{N})_3[\text{Cr}(\text{NCSe})_6]$. To the boiling solution of 43 g of KSeCN (0.3 mole) in 175 ml of 99.9% ethanol 5 g of CrCl_3 (0.03 mole) is added. The mixture is heated to reflux with constant stirring for 4 h. During

this operation contact with humid air is avoided. The liquid which has by now adopted a cherry-red colour is separated from unreacted products by filtering. After cooling to room temperature 30 ml of a 50 % aqueous solution of $(\text{CH}_3)_4\text{NCl}$ (0.15 mole) is dropped to the solution mentioned above, and a pink, fine crystalline precipitate consisting of $((\text{CH}_3)_4\text{N})_3[\text{Cr}(\text{NCSe})_6]$ separates out. The material is immediately filtered off, washed with water, 96 % ethanol, 99.9 % ethanol and extracted with acetone (400 ml). From now on all contact with humid air is once more avoided. The acetone solution is evaporated *in vacuo* leaving 20 g of a crude product, which is purified further by fractionated crystallization from acetone (analytical grade). Yield: 5.5 g of pure, well developed, purple coloured crystals (20 %). (Found: C 24.10; H 3.99; N 14.01; Cr 5.70. Calc. for

$((\text{CH}_3)_4\text{N})_3[\text{Cr}(\text{NCSe})_6]$: C 23.90; H 4.02; N 13.94; Cr 5.75). As a by-product a violet material arises, possibly impure

$((\text{CH}_3)_4\text{N})_2[\text{Cr}(\text{NCSe})_5(\text{H}_2\text{O})]$. Found: C 21.10; H 3.97; N 13.32; Cr 7.26. Calc. for $((\text{CH}_3)_4\text{N})_2[\text{Cr}(\text{NCSe})_5(\text{H}_2\text{O})]$: C 21.01; H 3.26; N 13.19; Cr 7.00).

Spectral measurements in the ultraviolet, visible and red region. These spectra were obtained on a Cary Model 14 recording spectrophotometer. From 230 to 400 $m\mu$ the complex was held in a dimethylsulfoxide solution; from 400 to 940 $m\mu$ an acetone solution was used. The accuracy of the ϵ values in the region 700–940 $m\mu$ is about 5 %, because the concentration of the complex ion in these solutions was determined spectrophotometrically after dilution.

Infrared spectrum. This was recorded on a Beckman Model IR-8 spectrometer, the complex being held in a Nujol suspension.

$((\text{CH}_3)_4\text{N})_3[\text{Cr}(\text{NCSe})_6]$ is rapidly decomposed under the combined influence of either oxygen and water or carbon dioxide and water. Exposure to the atmosphere for 5–10 min causes destruction on the surface. On the other hand experiments showed that the compound did not change when exposed to dry oxygen or dry carbon dioxide alone.

$((\text{CH}_3)_4\text{N})_3[\text{Cr}(\text{NCSe})_6]$ is soluble in acetone and dimethylsulfoxide, slightly soluble in ethanol and nearly insoluble in water, benzene and ether.

Discussion. The electronic spectrum. The absorption spectrum of $((\text{CH}_3)_4\text{N})_3[\text{Cr}(\text{NCSe})_6]$ (Fig. 1) shows three distinct absorption bands situated at 18 000 cm^{-1} (${}^4A_{2g} \rightarrow {}^4T_{2g}$), at 29 200 cm^{-1} (possibly due

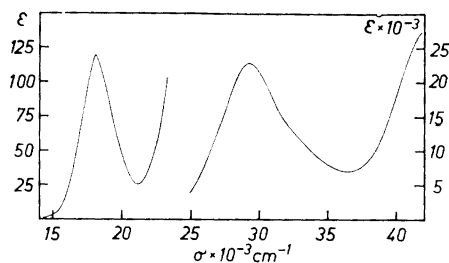


Fig. 1. Absorption spectrum of $((\text{CH}_3)_4\text{N})_3[\text{Cr}(\text{NCSe})_6]$ in the visible and ultraviolet region. ϵ = the molar extinction coefficient. σ = wave number.

to an internal transition in the NCSe-group) and at about 43 500 cm^{-1} . This last band (presumably a redox band) could not be determined with a satisfactory accuracy with the technique used. The ${}^4A_{2g} \rightarrow {}^4T_{1g}$ transition must be situated at a wave number higher than 23 000 cm^{-1} and is covered by the steep rise of the band at 29 200 cm^{-1} . The first band has got an unusual shape, possibly caused by an interaction between ${}^4T_{2g}$ and ${}^2T_{2g}$ giving rise to a superposition of bands with unequal widths.

The Δ value of 18 000 cm^{-1} places the isoselenocyanate ion between water (17 400 cm^{-1}) and ammonia (21 550 cm^{-1}) in the spectrochemical series, indicating

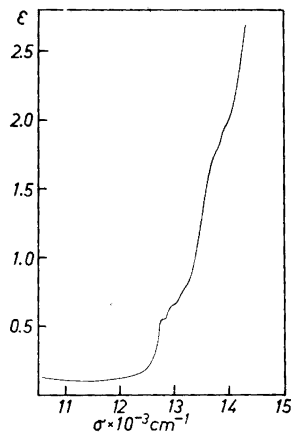


Fig. 2. Absorption spectrum of $((\text{CH}_3)_4\text{N})_3[\text{Cr}(\text{NCSe})_6]$ in the red region. ϵ = the molar extinction coefficient. σ = wave number.

Table 1. The C—N, C—S and C—Se stretching frequencies in some inorganic thiocyanate- and selenocyanate compounds (cm⁻¹).

Compound	ν_3 C—N	ν_1 C—S	ν_1 C—Se	Ref.
KSCN	2053 s	748 w		11
KSeCN	2070 s		558 w	12
K ₂ [Hg(SCN) ₄]	2115 s	716 w		7
K ₂ [Hg(SeCN) ₄]	2098 s		543 w	7
K ₂ [Pt(SCN) ₆]	2125 s	694 w		13
K ₂ [Pt(SeCN) ₆]	2124 s		520 w	7
((CH ₃) ₄ N) ₂ [Co(NCS) ₄]	2075			6
((CH ₃) ₄ N) ₂ [Co(NCSe) ₄]	2075			6
((C ₂ H ₅) ₄ N) ₂ [Co(NCS) ₄]	2053 s	840 w		7
((C ₂ H ₅) ₄ N) ₂ [Co(NCSe) ₄]	2053 s		672 m	7
K ₃ [Cr(NCS) ₆].4 aq	2105 s	820 vw		2
(NH ₄) ₃ [Cr(NH ₃) ₂ (NCS) ₄]	2110 s	825 w		
	2042 sh			
((CH ₃) ₄ N) ₃ [Cr(NCS) ₆]	2075 s			
	2042 sh			
((CH ₃) ₄ N) ₃ [Cr(NCSe) ₆]	2067 s		663 m	
	2041 sh		668 m	

that the bonding takes place through the nitrogen atom. At the same time the isoselenocyanate is recognized to create a stronger field than the isothiocyanate ion (17 800 cm⁻¹). In the red region (Fig. 2) two series of lines near 13 000 cm⁻¹ and 13 800 cm⁻¹ are observed. They are possibly representing the spin-forbidden transitions ${}^4A_{2g} \rightarrow {}^2E_g$ and ${}^2A_{2g} \rightarrow {}^2T_{1g}$.

Infrared spectrum. The thiocyanate complexes^{3,2} exhibit C—N and C—S stretching and N—C—S bending vibrations at 2150—2050, 820—690 and 500—460 cm⁻¹, respectively. Mitchell and Williams³ have studied the correlations between the frequency of the C—N bond and the binding of the ligand in inorganic thiocyanate complexes (a) through nitrogen, (b) through sulphur or (c) through both. They suggest that the order of the C—N stretching frequency is M—NCS < M—SCN < M—NCS—M, when all other factors are constant. Lewis, Nyholm and Smith² have found that the C—S stretching is higher in isothiocyanate than in thiocyanate complexes (around 820 cm⁻¹ (760—880) compared to 700 cm⁻¹ (690—720)).

Only Turco *et al.*⁷ and Cotton *et al.*⁶ have till now used infrared spectroscopy in the diagnosis of the type of binding in selenocyanate complexes. They found a parallel behaviour of corresponding thiocyanate- and selenocyanate compounds with respect to the variation of the C—N stretch (ν_3) and the C—Se stretch (ν_1) with the type of binding. Furthermore ν_3

for sulphur and selenium compounds appeared to have nearly the same values (<2080 cm⁻¹ for NCS⁻, > 2080 cm⁻¹ for SeCN⁻) while the values for ν_1 were considerably smaller for the selenium compounds (around 650 cm⁻¹ (600—700) for NCS⁻, around 550 cm⁻¹ (500—600) for SeCN⁻).

From the spectral data of ((CH₃)₄N)₃[Cr(NCSe)₆] (Table 1) it seems reasonable to conclude that the selenocyanate group is co-ordinated through nitrogen in the chromium(III) complex.

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On the Stability of the Acetate and Glycolate Complexes of Trivalent Curium

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In a previous communication¹ the stability constants of the acetate and glycolate complexes of trivalent europium and americium were reported. In this work the corresponding complexes of trivalent curium have been studied. No quantitative reports of the stability constants of these complexes have been delivered so far. Qualitative studies of the cation exchange behaviour of curium in glycolate solutions have been published by Stewart². In this investigation the curium acetate and glycolate complexes were studied by using the cation-exchange method developed by Fronaus¹, p. 1696. All stability constants refer to a 0.50 M sodium perchlorate medium and a temperature of 20.0°C.

Experimental. Chemicals used. A stock solution of trivalent curium was prepared by dissolving a curium sample obtained from A. E. R. E. Harwell in a solution of the composition: $C_{\text{NaClO}_4} = 500 \text{ mM}$, $C_{\text{HClO}_4} = 2.00 \text{ mM}$. The curium sample consisted of 92.3 % ²⁴⁴Cm, 7.6 % ²⁴²Cm and 0.14 % ²³⁸Pu. Dibutylphosphate, DBP, (Albright & Wilson Ltd) was purified according to Dyrssen *et al.*³ A 0.1 M stock solution in hexane was prepared from the purified product. All other chemicals were the same as used before.¹, p. 1697 Stock solutions of the various chemicals were prepared and analysed as described before.¹, p. 1697

Procedure. 0.100 ml of a curium(III)-stock solution was added to 5.00 ml of buffer solutions S of the composition: $C_A \text{ mM NaA}$, $C_{\text{HA}} = C_{\text{NaA}} \text{ mM HA}$, $I = 0.50 \text{ M}$. Each of these solutions was then equilibrated with 150 mg ion-exchanger (Dowex 50 W \times 8, 50–100 mesh, in the sodium form) in a thermostat at

20.0°C. After equilibrium had been attained, 4.00 ml of the aqueous phase was extracted with an equal volume of 0.1 M DBP in hexane. In all cases more than 99 % of the curium was extracted into the organic phase. The curium concentration was then determined by measuring the α -activity of the DBP-phase. The procedure for preparing solid samples for the activity determinations has been described before⁴, p. 1063. All activity measurements were made using an α -scintillation counter. From the activity of the solutions before and after addition of ion exchanger the distribution coefficients φ were calculated. The concentration free ligand was obtained in the same way as described before¹, p. 1697. For each ligand, series with varying C_A were performed at four different values of C_M (1.4, 2.7, 3.8, $7.4 \times 10^{-9} \text{ M}$) and each series was repeated several times. The average φ -values with their corresponding standard deviations have been tabulated in Table 1. The reproducibility of the measurements was much lower than for the corresponding americium systems. The low accuracy was most pronounced for low values of φ and the useful C_A -range was therefore smaller than for the corresponding americium systems. It was not possible to detect any variation in the measured φ -values with the value of C_M . The ion-exchanger is thus monofunctional for the loads used here.

Calculation of stability constants. From the corresponding values of the distribution coefficient φ and the concentration free ligand A, the stability constants were computed by using the least-square procedure "Letagrop"⁵. Two different weighing procedures were used. In the first procedure the individual weights were based on the measured σ_φ -values and in the second one on a constant percentual error in φ .

Approximately the same result was obtained by the two methods (*cf.* Table 2). In the first attempt five constants l_0 , l_1' , β_1 , β_2 and β_3 were determined. The result for the glycolate system is given in Table 2. Both l_1' and β_3 turned out to be negative and as negative values of l_1' and β_3 have no physical meaning, only three parameters were used to describe the experimental material. These three constants (l_0 , β_1 and β_2) obtained by using weighing procedure 1 and 2 are also given in Table 2. The final constants are for the acetate system:

$$l_0 = 2.37 \pm 0.07 \text{ l.g}^{-1}; \beta_1 = 114 \pm 9 \text{ M}^{-1}; \beta_2 = 1240 \pm 240 \text{ M}^{-2};$$

and for the glycolate system:

$$l_0 = 2.39 \pm 0.07 \text{ l.g}^{-1}; \beta_1 = 700 \pm 60 \text{ M}^{-1}; \beta_2 = (5.6 \pm 0.6) \times 10^4 \text{ M}^{-2}.$$