tographically homogeneous olefin XIII, b.p. 56–60° (0.1 mm.), $n^{24}\text{D}$ 1.4834, $[\alpha]^{20}\text{D}$ −75° (EtOH). Oxidation of XIII with osmium tetroxide afforded two diastereomeric diols. Diol XIV (80%), b.p. 120–125° (0.15 mm.), $[\alpha]^{26}\text{D}$ +7° ($CHCl_3$), and diol XV (20%), b.p. 110–115° (0.15 mm.), $[\alpha]^{26}\text{D}$ −31° ($CHCl_3$) with lead tetraacetate, were both cleaved to the same diketone (XVI), b.p. 140–145° (0.85 mm.), $[\alpha]^{19}\text{D}$ −80° ($CHCl_3$), $\nu_{\text{max}}^{\text{CCl}_4}$ 1707, 1715, 1360 cm.$^{-1}$ (cyclohexanone, methyl ketone). The formation of a cyclohexenone (XVII), b.p. 80–83° (0.15 mm.), $[\alpha]^{24}\text{D}$ −50° ($CHCl_3$), $\lambda_{\text{max}}^{\text{EtOH}}$ 241, 289 mμ, ϵ 14100, 1440, $\nu_{\text{max}}^{\text{CCl}_4}$ 1670, 1618 cm.$^{-1}$; 2,4-DNP, m.p. 151–152°, by acid catalyzed cyclization of XVI is only possible if the nuclear double bond of valerenic acid is located as shown in I. In agreement with our proposal, the 56.4 mc./sec. n.m.r. spectrum of II in $CDCl_3$ exhibited these peaks: doublet (3H) centered at τ 9.22 (J 8 c./s.); singlet (3H) at τ 8.34; doublet (3H) at τ 8.09 (J ~1 c./s.); singlet (3H) at τ 6.28; doublet centered at τ 2.95 (J 9 c./s.) with additional fine splitting.[7] The spectrum of methyl valerenolate prepared by hydrolysis and esterification of naturally occurring acetylvalerenolic acid[2] had a strikingly similar spectrum: doublet (3H) centered at τ 9.29 (J 7 c./s.); singlet (3H) at τ 8.36; doublet (3H) at τ 8.09 (J ~1 c./s.); singlet (1H) at τ 7.22; singlet (3H) τ 6.26; quadruplet centered at τ 5.85; doublet (1H) centered at τ 2.97 (J 9 c./s.) with further splitting. This situation *tentatively* suggests that valerenolic acid may be a hydroxyvalerenic acid. We are indebted to the National Institutes of Health for a predoctoral fellowship to T.L.P. and to Dr. W. D. Phillips, E. I. du Pont de Nemours and Company, Inc., for the n.m.r. spectra.

[7] *Cf.* the spectra of methyl angelate and methyl tiglate, L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, Ltd., London, 1959, p. 119; R. R. Fraser, *Can. J. Chem.*, **38**, 549 (1960).

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EFFECTS OF NUCLEAR RECOIL IN THE CHROMIUM (III)-THIOCYANATE SYSTEM OF COMPLEXES

Sir:

A dilute solution of the $Cr(NCS)_6^{-3}$ ion has been irradiated with neutrons in order to study the chemical effects of the recoil following the $Cr^{50}(n,\gamma)Cr^{51}$ reaction. This system was chosen because all of the complexes in the series, $Cr(NCS)_n(H_2O)_{6-n}^{-n+3}$, where $n = 1, 2, \ldots, 6$, have been isolated, and at room temperature in neutral or acidic solution the rates of interconversion of the different species are slow.[1] Ion exchange recently has been applied[2,3] for the separation of the cations in the series, including the geometrical isomers of $Cr(NCS)_2(H_2O)_4^+$. The Cr^{51} nucleus formed in the above reaction may have an energy up to a maximum of 880 ev., depending on the number and energies of the γ rays emitted. Each vacant coördination site left by rupture of a Cr–NCS bond is expected to be filled by H_2O, provided the solution is sufficiently dilute and there is a low concentration of free NCS^-. Thus, measurement of the amount of 27-day Cr^{51} in each species after irradiation will give information about the probability of bond rupture.

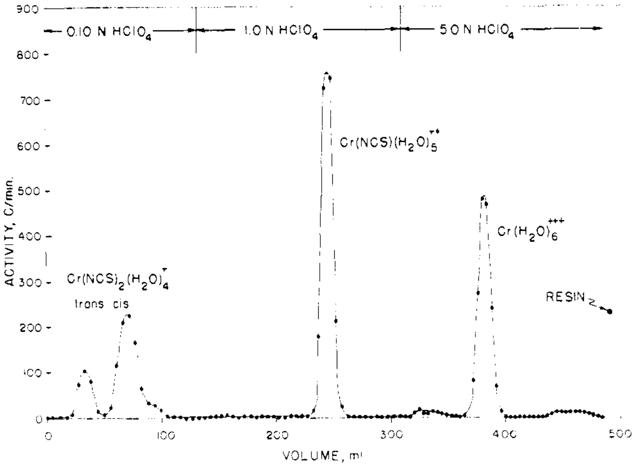

Fig. 1.

An aqueous solution, 1.69 × 10^{-3} mole fraction in $(NH_4)_3Cr(NCS)_6$, and containing no free NCS^-, was irradiated for 1 min. at a neutron flux of *ca.* 10^{13} neutrons cm.$^{-2}$ sec.$^{-1}$. The solution was passed through a Dowex-50 cation-exchange resin column, and then through a chromatographic alumina column. $Cr(NCS)_3(H_2O)_3$ was extracted into ether. The elution curve of Cr^{51} activity from the cation-exchange column is shown in Fig. 1, and the elution curve of total Cr from the alumina column in Fig. 2. The results are summarized in Table I, which gives the distribution of Cr^{51} radioactivity and total Cr found in each species.

TABLE I

DISTRIBUTION OF Cr^{51} RADIOACTIVITY AND TOTAL Cr IN DIFFERENT SPECIES

Species	Radioactivity, %	Total Cr, %
$Cr(NCS)_6^{-3}$	<0.1	31
$Cr(NCS)_5^{-2}$	0.1	57
$Cr(NCS)_4^-$	3.9	4.0
$Cr(NCS)_3$	1.9	0.3
cis-$Cr(NCS)_2^+$	15.5	1.9
trans-$Cr(NCS)_2^+$	4.8	0.6
$Cr(NCS)^{+2}$	33.6	3.7
Cr^{+3}	29.1	1.5
Others[a]	7.2	..
Resin[b]	4.0	..

[a] Total activity outside of main peaks. [b] Activity remaining on cation-exchange resin.

There is no retention of radioactivity in the parent species, and very little retention in any species with more than two NCS^- groups. In view of the large recoil energy available compared to chemical bond energies, it is surprising that any NCS^- groups could remain bound to the Cr. However, there may be mechanisms which would

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[1] N. Bjerrum, *Z. anorg. Chem.*, **118**, 131 (1921); **119**, 39, 54, 179 (1921).

[2] E. L. King and E. B. Dismukes, THIS JOURNAL, **74**, 1674 (1952).

[3] J. T. Hougen, K. Schug and E. L. King, *ibid.*, **79**, 519 (1957).

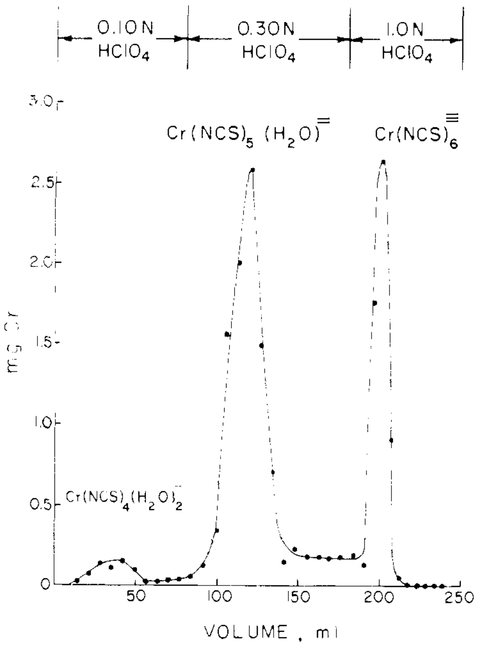

Fig. 2.

favor recombination of the "hot" Cr with radicals produced by radiation damage, in spite of their low concentration relative to water molecules. The extent of the radiation-induced decomposition can be seen from the distribution of the total Cr, initially present as $Cr(NCS)_6^{-3}$. Extensive conversion to $Cr(NCS)_5(H_2O)^{-2}$ occurred, but the amount of lower complexes formed is relatively small.

The ratio of *trans-* to *cis*-$Cr(NCS)_2(H_2O)_4^+$ is 0.31 for both the radioactivity and the total Cr, as compared to the equilibrium value[3] of 0.5 at 370°K. About 11% of the radioactivity fell outside of the main peaks, and two small unidentified peaks can be seen in the cation elution curve. These may be due to complexes with fragments of the NCS^- group, such as $Cr(NC)(H_2O)_5^{+2}$ or $Cr(NH_3)(H_2O)_5^{+3}$.

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THE STATE OF IONIZATION OF CRYSTALLINE SODIUM DIHYDROGEN CITRATE[1]

Sir:

The structure of sodium dihydrogen citrate has been determined by three-dimensional X-ray diffraction methods. This substance crystallizes in the monoclinic space group $P2_1/a$ with 4 molecules of $NaH_2(C_6O_7H_5)$ in a cell of dimensions $a = 9.648$ Å., $b = 11.680$ Å., $c = 7.481$ Å., $\beta = 105°$-$15'$. The observed density was 1.747 g. cm.$^{-3}$ while that calculated was 1.749 g. cm.$^{-3}$. The standard error in axial lengths is less than $\pm 0.13\%$ and in angle less than $\pm 6'$. The observed density was reproducible to 1%.

The analysis was based on 1917 independent reflections photographed with CuKα and MoKα radiation. Of these 223 were too weak to be measured. The trial structure was found from a three-dimensional sharpened F^2-map and refined by two- and three-dimensional difference Fourier series and by three-dimensional least-squares methods with individual isotropic temperature factors.[2] At the present stage of refinement the reliability factor R is 13.2% for all reflections. All seven hydrogen atoms have been located on a difference synthesis.

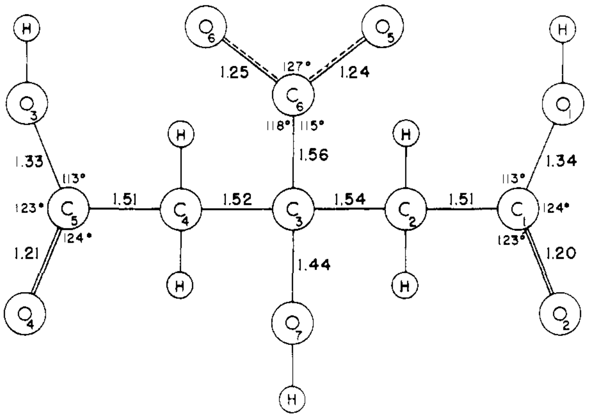

Fig. 1.

The covalent bond lengths and angles in the citrate ion are shown in the diagram. Of the three carboxyl groups, the two end carboxyls have C–O distances which are non-equivalent (1.20, 1.34 and 1.21, 1.33 Å.) whereas the central carboxyl has two equivalent C–O distances (1.24, 1.25 Å.). The bond angles confirm these relations. These findings together with the observed attachment of hydrogen atoms to O_1 and O_3 demonstrate that it is the central carboxyl group which is ionized in this crystal. It is interesting to note that nuclear magnetic resonance measurements[3] indicate that in solution the singly ionized citrate is predominately ionized in the end carboxyl groups.

Although full discussion of the structure will be reported elsewhere it is worth while noting that the sodium ion is octahedrally coördinated to oxygens. These octahedra occur in centrosymmetrically related pairs with one edge shared (O_7O_7'). Each molecule forms two bidentate chelate rings, one with each of the sodium ions of the above-mentioned pairs of octahedra. One of the chelate rings is five-membered ($NaO_6C_6C_3O_7$) and the other is six-membered ($Na'O_4C_5C_4C_3O_7$).

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[1] (1) Supported by a grant (C1253) from the National Cancer Institute, Public Health Service.

[2] (2) We are indebted to Princeton University and to Indiana University for the use of their computation facilities.

[3] (3) A. Loewenstein and J. D. Roberts, THIS JOURNAL, **82**, 2705 (1960).