TABLE I

THE RATE OF EXCHANGE OF CHROMIUM(II) ION AND AZIDOCHROMIUM(III) ION

$I \cong [H^+] = 0.5\ M$ (except as noted)

Temp., °C.	$[Cr^{2+}]$ × 10^3 l. mole^{-1}	$[Cr(N_3)^{2+}]$ × 10^3 l. mole^{-1}	k_2 × mole l.$^{-1}$ sec.
0	1.2	1.60	1.23
	1.4	1.60	1.24
	2.20	2.57	1.34
	3.45	1.25	1.32[a]
	4.2	1.60	1.39[a]
	1.4	1.50	1.48[b]
11.1	3.7	2.08	2.46
	3.8	1.40	2.40
	4.4	2.10	2.63
	6.5	2.10	2.56
20	1.1	2.12	4.94
	1.1	2.65	4.40
	2.6	1.40	4.70
28.9	1.15	2.65	7.7
	1.8	1.18	7.5[c]
	1.8	1.01	7.2
	2.8	1.35	6.0
36.4	1.55	1.40	12.9

[a] $I \cong [H^+] = 0.4\ M$. [b] $I \cong [H^+] = 0.9\ M$. [c] $[Zn^{2+}] = 0.02\ M$.

with fluorochromium(III) ion and with *cis*-difluorochromium(III) ion, each *via* a single-bridged transition state, have comparable rates, the reaction of fluorochromium(III) ion being ~2.5-fold faster.[4,8]

Comparison of the efficiently bridging azide ion and the more poorly bridging fluoride ion can be made through the activation parameters given below.

	ΔH^* × mole kcal.$^{-1}$	ΔS^* × mole deg. cal.$^{-1}$
$Cr^{2+} + CrN_3^{2+}$	9.6	−22.8
$Cr^{2+} + CrF^{2+}$	13.7[4]	−20.[4]

The above results indicate the enthalpy of activation to be primarily responsible for the difference.

The entropy of activation for exchange of chromium(II) and azidochromium(III) ions is very different from the value obtained by Bunn, Dainton, and Duckworth[9] for the exchange of iron(II) and iron(III) by a pathway involving azide ion. For the process

$$Fe^{2+} + \overset{\otimes}{Fe}N_3^{2+} = FeN_3^{2+} + \overset{\otimes}{Fe}{}^{2+}$$

they obtain a value of $\Delta S^* = +7.0$ cal. mole^{-1} deg.$^{-1}$ (the value of ΔH^* is 13.9 kcal. mole^{-1}) in the temperature range below 13°. At higher temperatures, the Arrhenius plot shows curvature giving rise to a lower activation energy and more negative entropy of activation. (Their reported values of the second-order rate coefficient at the highest two temperatures studied (15 and 27°) give $\Delta S^* \sim -24$ e.u.) However, it seems unwarranted to conclude that analogous mechanisms are responsible for the chromium reaction at 0–36° and the iron reaction at the high temperature extreme of the studies by Bunn, Dainton, and Duckworth.[9,10]

[8] Y. T. Chia and E. L. King, *Discussions Faraday Soc.*, **29**, 109 (1960).

[9] D. Bunn, F. S. Dainton, and S. Duckworth, *Trans. Faraday Soc.*, **57**, 1131 (1961).

[10] The apparent curvature in log *k vs.* 1/*T* plots at high temperatures observed in unreported experiments on the exchange of chromium(II) and azidochromium(III) ion (footnote 6) has the opposite sign to that observed in the iron system.

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Anhydrous Lithium Thiocyanate[1]

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Lithium thiocyanate is the least stable of the alkali metal thiocyanates due to the large electrostatic deforming field of the lithium ion. It is extremely hygroscopic and there is good evidence that the solvent, tenaciously attached to the lithium ion, enhances LiSCN decomposition upon heating. Hydrated lithium thiocyanate has been prepared by several methods.[2] However, methods for dehydration have been unsuccessful, and no measurements have been recorded for the physical properties of anhydrous LiSCN. An obvious procedure for the preparation of anhydrous LiSCN would be to use anhydrous reactants; however, when this was attempted, using methanol solutions of KSCN and $LiNO_3$, the product included a double salt $LiK(SCN)_2$. Ether solutions, however, gave an etherate which could be desolvated by heating under reduced pressure.

Experimental

Hydrated LiSCN was prepared by mixing equal molar quantities of the solids $LiOH \cdot H_2O$ and NH_4SCN. When warmed, the mixture dissolved completely in the water of hydration of the $LiOH \cdot H_2O$. This solution was filtered, and the H_2O and NH_3 were removed by exposure to the vacuum pump and liquid N_2 trap at ~60°. When no more water distilled, the residue, which may still be liquid, was dissolved in about an equal volume of diethyl ether. This solution was filtered. To the filtrate was added 1.5–2 volumes of petroleum ether. (If sufficient water remains, two immiscible liquid phases will form.) A precipitate, corresponding in weight to $LiSCN \cdot (C_2H_5)_2O$, crystallized upon cooling and stirring. The etherate crystals were filtered with a minimum exposure to moist air, using a Büchner funnel. The ether in the crystals was removed under vacuum at 25°; the LiSCN was heated overnight to about 110° under vacuum. The product was redissolved in diethyl ether, crystallized with petroleum ether, and reprocessed by the procedure described above. The yield was usually about 90%. LiSCN was further purified by crystallization from diethyl ether. The product contained 9.9% Li, 88.5% SCN, and 0.09% H_2O by Karl Fischer determination. The m.p. was 281°.

The heat of fusion of LiSCN was determined by the method of mixtures using a calorimeter and furnace similar to that described by Goodkin, *et al.*,[3]; it was 5.0 ± 1.0 kcal./mole; the entropy of fusion was 9 ± 2 e.u./mole.

The change in volume on melting was determined by the dilatometric method similar to that of Plester, *et al.*[4] The volume change at the melting point corresponded to 2.58 ± 0.02 ml./mole. The density of LiSCN was 1.43 g./ml. at 26°.

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[1] This paper is based on work performed for the U. S. Atomic Energy Commission by Union Carbide Corporation.

[2] (a) F. A. Schimmel, *J. Chem. Eng. Data*, **5**, 519 (1960); (b) Gmelins Handbuch der Anorganischen Chemie, Lithium No. 20, Verlag Chemie, GMBH, Weinheim/Bergstrasse, 1960, p. 503.

[3] J. Goodkin, C. Solomons, and G. J. Janz, *Rev. Sci. Instr.*, **29**, 105 (1958).

[4] D. W. Plester, S. E. Rogers, and A. R. Ubbelohde, *Proc. Roy. Soc.* (London), **A235**, 469 (1956).

A thermogravimetric analysis of LiSCN was also performed. During a 3-hr. period, LiSCN was heated in air to 1000°. The weight change of the sample remained within 1% until a temperature of 400° was reached. At that point decomposition began and proceeded rapidly until oxidation occurred.

The solubility of LiSCN in several common organic solvents was determined qualitatively. A solubility in excess of 10 mg./ml. at 26° was observed using as solvents: *n*-propylamine, *sec*-butylamine, ethylenediamine, pyridine, 2-aminoethanol, acetonitrile, phenylacetonitrile, formamide, N-methylformamide, N-methylacetamide, N,N-dimethylacetamide, *p*-dioxane, tetrahydrofuran, ethylene glycol monomethyl ether, diethyl carbitol, *o*-nitrophenetole, glycol, methanol to octanol, benzyl alcohol, 1,3-propanediol, acetone, 2,4-pentanedione, propiophenone, diisobutyl ketone, methyl isopropyl ketone, salicylaldehyde, and ethyl acetoacetate. LiSCN was insoluble in N,N-dimethylaniline, N-methyldiphenylamine, 2,5-dimethylfuran, phenetole, *o*-xylene, *o*-nitrotoluene, benzene, and petroleum ether.

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α-Furildioxime Complexes of Rhenium

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Compounds formed by rhenium with α-furildioxime are poorly characterized.[1-4] A purple-red compound described by Martin, Meloche, and Webb[1] and subsequently isolated in an impure state[2] has been formulated by them as $\mathrm{Re^{II}}$(α-furildioxime)$_2$. On the other hand, the red compound of α-furildioxime observed in solution by Peshkova[4] is described as a complex of Re(III). Complexes of benzildioxime[5] and dimethylglyoxime,[6] however, are said to contain Re(IV).

Both of the oxidation states described for the α-furildioxime complexes are unusually low, considering the conditions of preparation; namely, the reduction of a perrhenate solution by stannous chloride in the presence of the ligand, which usually gives Re(IV)[7] except when the ligand itself is a reducing agent.[8,9]

Evidence is presented in this paper for a compound which can best be formulated as $\mathrm{Re^{IV}}$(dioxime)$_3$X, where X is a univalent ligand the nature of which is unknown. The low magnetic moment of this compound suggests considerable spin coupling[10] and its low conductivity indicates a nonelectrolyte.

The compound decomposes rapidly in acetone, alcohol, and aqueous hydrochloric acid solution, giving a shift in the visible absorption band from 493 to 511 mμ. In hydrochloric acid solutions more concentrated than 3 *N*, a coordinated α-furildioxime is liberated and hydrolyzed. The absorption spectrum of the resulting product is identical with that described by Martin, Meloche, and Webb.[1] Since no reduction is detectable in the acid solution, it is concluded that the compound of Martin, *et al.*, still contains Re(IV) rather than the Re(II) suggested earlier.[2]

Experimental

Preparation of the Rhenium–α-Furildioxime Complex.—Ammonia (2–3 drops, 14.3 *N*) was added with vigorous stirring to 30 ml. of a 0.035 *M* aqueous solution of potassium hexachlororhenium(IV) and 4 ml. of a 0.8 *M* acetone solution of α-furildioxime. The precipitate which appeared in the deep red solution was quickly filtered and dried over potassium hydroxide under vacuum for 2 hr. The dark red solid was extracted with chloroform twice to remove rhenium dioxide and excess α-furildioxime. Then it was dried in the air and finally over calcium chloride under vacuum; yield 0.17 g., 19%.

Anal. Calcd. for $\mathrm{ReC_{30}H_{21}N_6O_{12}}$: C, 42.7; H, 2.49; N, 9.95; Re, 22.1. Found: C, 43.15; H, 3.16; N, 9.52; Re, 22.1; Cl, 0.00. Rhenium was determined spectrophotometrically by the formation of the rhenium–α-furildioxime complex.[1] Interference from nitrate ions, which may be formed from the nitrogen in the ligand during fusion, was shown to be negligible. Analyses for carbon, nitrogen, and hydrogen were carried out by Dr. A. D. Campbell at the microanalytical laboratory, University of Otago.

A modification of Job's continuous variation method confirmed that there were three dioximes coordinated to each rhenium. The compound is readily soluble in most of the usual organic solvents, but with progressive decomposition.

At 25°, the specific conductivity is 0.19×10^{-5} ohm^{-1} in nitromethane ($c = 0.83 \times 10^{-3}$ g.-atom of Re/ml.). The compound has a gram susceptibility $\chi_g = 0.28 \times 10^{-6}$ c.g.s. at 22° (assuming Curie's law).

The infrared spectrum was very similar to that of the free ligand and bis(α-furildioximato)nickel(II). The ultraviolet and visible absorption spectra showed charge-transfer bands at 268 (due to the ligand) and 493 mμ.

Oxidation State of Rhenium–α-Furildioxime Complexes.—The tetravalent oxidation state of the rhenium was indirectly confirmed in both the tridioxime compound and the species absorbing at 532 mμ, by the isolation from them on treatment with *o*-phenylenebisdimethylarsine of the rhenium(III) chlorodiarsine complex.[9] The addition of hypophosphorous acid accelerated the formation of the arsine compound, indicating that reduction of rhenium is involved, presumably from Re(IV). Furthermore, neither Re(III) nor Re(V)[2] react with α-furildioxime.

Reaction of the Tridioxime Complex with Hydrochloric Acid.—Hydrogen chloride was passed through a solution of the tridioxime compound in chloroform and ether (2:1), and the resulting solution was evaporated to dryness. X-Ray powder photographs of the residue from different preparations showed that there were at least two species present, one of which was identified by its characteristic lines as furil; *d* values: 6.71 (w), 5.33 (m), 3.45 (m), 2.98 (w).

The formation of furil was also shown by the appearance of its ultraviolet absorption band (305 mμ), the intensity of which increased with increasing acid concentration. A calculation showed there to be at least 8% furil formed.

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(1) V. W. Meloche, R. L. Martin, and W. H. Webb, *Anal. Chem.*, **29**, 527 (1957).

(2) R. L. Martin and V. W. Meloche, *J. Inorg. Nucl. Chem.*, **6**, 210 (1958).

(3) V. M. Peshkova and M. I. Gromova, *Vestnik Moskov. Univ.*, **7**, No. 10, *Ser. Fiz.-Mat. i Estestven Nauk*, No. 7, 85 (1952).

(4) V. M. Peshkova, *Inst. Geokhim. i Anal. Khim.*, **8**, 75 (1958).

(5) S. Tribalat, *Ann. Chim.* (Paris), **4**, 289 (1949).

(6) M. B. Tougarinoff, *Bull. Soc. Chim. Belges*, **43**, 111 (1934).

(7) E. K. Mann and N. Davidson, *J. Am. Chem. Soc.*, **72**, 2254 (1950).

(8) M. Freni and V. Valenti, *J. Inorg. Nucl. Chem.*, **16**, 240 (1961).

(9) N. F. Curtis, J. E. Fergusson, and R. S. Nyholm, *Chem. Ind.* (London), 625 (1958).

(10) B. Jezowska-Trzebiatowska, Fifth International Conference on Coordination Chemistry, Special Publication No. 13, The Chemical Society, London, 1959, p. 156.