5.8° (extrapolated), mol wt 180 (calcd 182.5), $\Delta H_{vap} = 5.86$ kcal/mole, and Trouton's constant = 21.0 cal/deg mole. Its infrared spectrum showed absorptions at 1227 (s, b), 1163 (m), 1064 (m), 1014 (m), 943 (w), 800 (m), and 702 (m) cm^{-1}. The ultraviolet spectrum exhibited a maximum at 372 mμ, indicating the presence of an azo linkage. The F^{19} nmr spectrum showed two absorptions at −21.2 ppm ($CClF_2$) and −1.0 ppm (CF_3), referred to CF_3COOH, with relative areas in the ratio of 2.0:3.2.

The Indirect Fluorination of ClCN by AgF_2 in the Presence of Chlorine.—Approximately 30 g (0.4 mole) of ClCN and 6 g (0.08 mole) of chlorine were condensed onto 180 g (1.2 mole) of AgF_2 in the 300-cc steel cylinder at −196°. After evacuation, the bomb was closed, wrapped in glass wool, placed in an open brass cylinder, and rocked while warming gradually to room temperature. After 20 hr the contents of the cylinder was passed under reduced pressure through a series of glass traps maintained at −80, −126, and −196°, respectively. The coldest trap contained 6 ml of material which was shown by chromatography and infrared analysis to consist of CF_4, $CClF_3$, and $CF_3N=NCF_3$. The trap at −126° had collected 13 ml of crude product, which was passed through 10% aqueous NaOH to remove free chlorine, after which 5 ml of dried product was recovered. A completely vaporized sample of this was then analyzed by chromatography and infrared spectrum and shown to contain $CF_3N=NCF_3$ (40%), CCl_2F_2 (15%), and CCl_3F (15%), together with CF_3NCl_2 (15%) and $CClF_2N=NCF_3$ (13%) (see above). Percentages were calculated on the basis of chromatographic peak areas, assuming, as usual, equal thermal conductivities for all components. The trap at −80° (3 ml) contained three components which were separated in the manner just described. They were $CClF_2N=NCF_3$ (25%), CF_3NCl_2 (50%), and CCl_3F (25%). The over-all yield of CF_3NCl_2 was approximately 10%.

A second experiment designed to favor the formation of the dichloramine by increasing the Cl_2 concentration was conducted in a 75-cc stainless steel bomb. This was first charged with 7.3 g (0.05 mole) of AgF_2 and after evacuation 3.1 g (0.05 mole) of ClCN and 7.8 g (0.11 mole) of Cl_2 were condensed in successively. The vessel was then allowed to warm slowly to room temperature while being rocked and finally left to stand at room temperature for 2 days. Analysis of the crude product by the method outlined above showed that the major constituent boiling above −30° was CF_3NCl_2, which was obtained in an estimated yield of 30 ± 5%. The corresponding amounts of the two azo compounds $CF_3N=NCF_3$ and $CClF_2N=NCF_3$ had been markedly reduced, as expected.

Pure CF_3NCl_2 (2 ml) was isolated by repetitive chromatography on the Kel-F column. It was a faintly yellow liquid, bp 14.9° (extrapolated), mol wt 157 by gas density (calcd 154), $\Delta H_{vap} = 6.1$ kcal/mole, and Trouton's constant = 21.3 cal/deg mole. Its infrared spectrum showed major absorptions at 1399 (w), 1250 and 1229 (s), 1188 (s), 895 (w), 806 (m), and 704 (m) cm^{-1}. The vapor-phase ultraviolet spectrum exhibited a single maximum centered at 287 mμ (NCl_2). The mass spectrum exhibited the following principal *m/e* values in order of decreasing relative intensity (Cl^{37} ions omitted): 69 (CF_3^+), 99 ($CClF_2N^+$), 70 (Cl_2^+), 80 ($CClFN^+$), 49 (NCl^+), 31 (CF^+), 35 (Cl^+), 64 (CF_2N^+), 153 ($CCl_2F_3N^+$) (parent ion), 45 (CFN^+), 118 ($CClF_3N^+$), and 50 (CF_2^+). The F^{19} nmr spectrum showed only one peak at −19.4 ppm (CF_3), relative to CF_3COOH. This compound readily oxidized neutral KI solution, was fairly stable toward dilute alkali, and has been stored in glass for 6 months at ambient temperature with only slight decomposition.

One fluorination of ClCN by AgF_2 in the absence of chlorine has been run. The reaction appeared to be much more vigorous than when chlorine was present and yielded a highly complex mixture of products which has not as yet been resolved, but no CF_3NCl_2 was formed.

Ultraviolet Irradiations.—These reactions were conducted in a Monel infrared gas cell, 10 cm in length and equipped with NaCl windows. The source employed was a 550-w high-pressure Hg lamp.

When the cell had been pressurized with 50 mm of CF_3NCl_2 and irradiated for 15 min, most of the reactant was consumed. The major products were $CF_3N=NCF_3$, identified by its infrared spectrum and chromatographic retention time, and Cl_2, identified by its chromatographic retention time, lack of any infrared absorptions, and its reaction with water followed by precipitation with $AgNO_3$. Traces of N_2O and COF_2 were also detected by infrared analysis.

When CF_3NCl_2 (at 50 mm) was mixed with an excess of CO (at 700 mm) and the mixture photolyzed for 10 min, the products were $CF_3N=NCF_3$ and $COCl_2$ together with traces of COF_2, the latter two compounds being identified by infrared, but no CF_3NCO was detected. In an analogous experiment in which O_2 (at 700 mm) was substituted for the CO, the products were $CF_3N=NCF_3$ and traces of COF_2, but no CF_3NO was produced.

The irradiation of CF_3NClF under analogous conditions proceeded somewhat more slowly than that of the dichloramine and after 0.5 hr produced $CF_3N=NCF_3$, together with COF_2, N_2O, and CO_2. The NaCl windows were badly attacked during this reaction, indicating the presence of a reactive intermediate such as ClF.

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Preparation of Hexathiocyanatorhenium(IV) Ion by a Fused-Salt Reaction[1]

BY R. A. BAILEY AND S. L. KOZAK

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A number of reports of rhenium thiocyanate complexes may be found in the literature. Most of these are prepared by the reduction of a perrhenate and apparently contain coordinated oxygens. They are generally not well characterized. Nelson and Boyd[2] have described the magnetic properties of a series of Re(IV) hexathiocyanates but have given no method for their preparation or analytical results. In fact, no other reference to these compounds can be found in the literature.[3] In view of this, we have taken advantage of the reactivity of molten salts to prepare compounds of $[Re(SCN)_6]^{2-}$ from K_2ReCl_6.

Experimental Section

K_2ReCl_6 was prepared by the method of Rulfs and Meyer.[4] All other chemicals were reagent grade.

The preparation was carried out in a large stoppered test tube which was surrounded by a cylindrical furnace. An electronic

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[1] Based on part of a thesis to be submitted by S. L. Kozak to the Graduate School of Rensselaer Polytechnic Institute in partial fulfillment of the requirements for the degree of Doctor of Philosophy. This work was partially supported by National Science Foundation Grant NSF-GP-5615.

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[3] R. Colton, "The Chemistry of Rhenium and Technetium," John Wiley and Sons, Inc., New York, N. Y., 1965, pp 148, 149.

[4] C. L. Rulfs and R. J. Meyer, *J. Am. Chem. Soc.*, **77**, 4505 (1955).

controller was used to maintain the desired temperature. Oxygen and moisture were eliminated from the system by means of a stream of nitrogen gas; the inlet for this reached to the bottom of the reaction tube so that the gas stream also served to stir the melt. About 8 g of KSCN was placed in the reaction tube and slowly fused at 225°. One gram of K_2ReCl_6 was added to the melt and the temperature maintained at 225° for 45 min. Under the stirring action of the N_2 stream, the K_2ReCl_6 quickly dissolved in the molten KSCN and reacted at once to yield a dark brown (almost black) mixture. After cooling, the solid was extracted with absolute ethanol and filtered to remove the KCl. The ethanol was evaporated under vacuum on a rotatory evaporator and the residue dissolved in a minimum of water. A solution of CsCl was immediately added, and the $Cs_2[Re(SCN)_6]$ was filtered off, washed twice with water, ethanol, and ether, and vacuum dried; yield, 69%. *Anal.* Calcd for $Cs_2[Re(SCN)_6]$: Cs, 33.2; Re, 23.3; S, 24.0. Found: Cs, 32.9; Re, 23.3; S, 23.9.

The product is dark brown, soluble in ethanol, water, ether, dilute acids, and alkalis but insoluble in chloroform and petroleum ether (bp 60–90°).

By dissolving the cesium salt in water and adding thallous acetate, $Tl_2[Re(SCN)_6]$ is precipitated. *Anal.* Calcd for $Tl_2[Re(SCN)_6]$: Re, 19.8; S, 20.4; Tl, 43.3. Found: Re, 20.0; S, 19.6; Tl, 43.2. This is slightly soluble in water and ethanol.

$AgNO_3$ produced the silver salt in a similar manner, but the infrared spectrum and the analysis indicated some AgSCN impurity. *Anal.* Calcd for $Ag_2[Re(SCN)_6]$: Re, 24.8; S, 25.6. Found: Re, 23.6; S, 24.1. This is almost insoluble in water and ethanol, but slightly soluble in acetone.

The filtrate remaining from the cesium precipitation was still dark brown. Almost all of the rhenium-containing material could be precipitated by the addition of tetraethylammonium chloride, but the brown product obtained was evidently a mixture of the $[Re(SCN)_6]^{2-}$ salt and another diamagnetic product. While the reaction is primarily one of ligand exchange, a secondary process is occurring.

Infrared spectra were taken by the KBr pellet technique on a Perkin-Elmer 421 infrared spectrophotometer and checked in Nujol mulls. Visible–ultraviolet spectra were obtained in ethanol on a Unicam SP 700 spectrophotometer, and the extinction coefficients were checked with a Beckman DU spectrophotometer.

Magnetic susceptibilities were found by the Gouy technique, using $Hg[Co(SCN)_4]$ as calibrant. These measurements were made at only one temperature, 25°.

Colton[3] has suggested that this complex might be prepared by treating K_2ReI_6 with SCN^- in an organic solvent. This was attempted in methanol and in acetone, but the products formed, while not yet identified, were not salts of $[Re(SCN)_6]^{2-}$. In any event, the method described above has proven to be quite convenient. It requires about 3 hr, gives a respectable yield, and can be scaled up readily.

TABLE I

MAGNETIC DATA FOR $[Re(SCN)_6]^{2-}$ COMPOUNDS

Compound	Gram susceptibility, $10^6\chi$	Gram-atomic susceptibility, $10^6\chi_m'$	μ_{eff}, BM
$Cs_2[Re(SCN)_6]$	6.76	5660	3.66
$Tl_2[Re(SCN)_6]$	4.74	4730	3.36

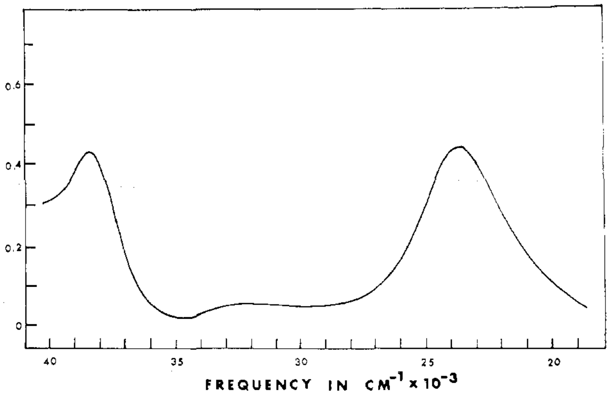

Figure 1.—Visible–ultraviolet spectrum of $Cs_2[Re(SCN)_6]$.

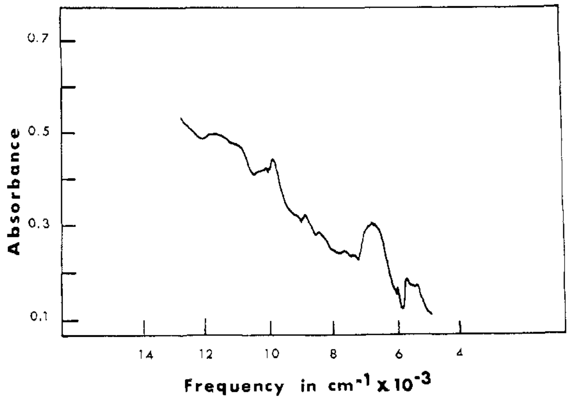

Figure 2.—Ligand field bands of $Cs_2[Re(SCN)_6]$.

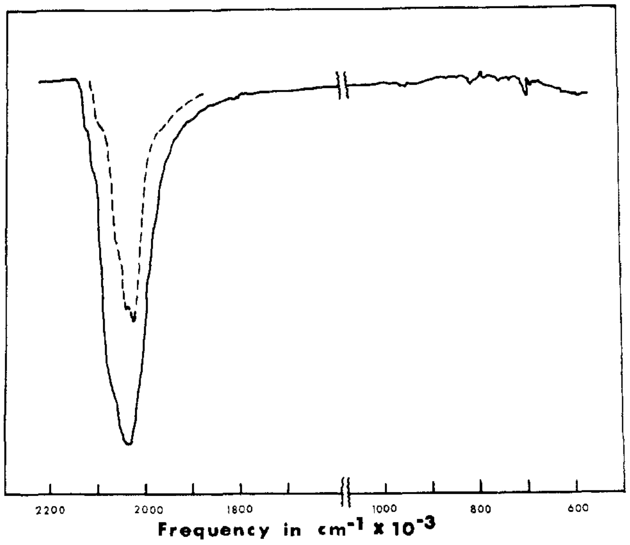

Figure 3.—Infrared spectrum of $[Re(SCN)_6]^{2-}$ compounds: solid line, Tl salt; dashed line, Cs salt.

TABLE II

ULTRAVIOLET AND VISIBLE SPECTRA OF $[Re(SCN)_6]^{2-}$ COMPOUNDS

Complex	Peak position, cm^{-1} (ϵ, M^{-1} cm^{-1})							
$Cs_2[Re(SCN)_6]$	38,300 (5.1×10^4)	23,800 (4.3×10^4)	11,600 (2.7)	11,050 (3.9)	10,070 (4.5)	9900 (6.9)		
	8880 (2.1)	8400 (1.2)	7700 (1.2)	7380 (2.4)	6800 (10.3)	6050 (2.1)	5750 (5.7)	5400 (5.7)
$Tl_2[Re(SCN)_6]$	38,100 (3.2×10^4)	23,700 (3.0×10^4)						
$Ag_2[Re(SCN)_6]$[a]		23,700						

[a] Measured in acetone.

Results and Discussion

The magnetic susceptibility or $Tl_2[Re(SCN)_6]$, Table I, is essentially the same as that reported by Nelson and Boyd.[2] That for $Cs_2[Re(SCN)_6]$ is also in the expected range, almost the same as reported for the potassium salt. It thus appears that these authors did, in fact, have authentic material.

The ultraviolet–visible spectra (Table II, Figures 1 and 2) show two intense charge-transfer bands and a series of low-intensity peaks which appear to be the ligand field transitions. These are superimposed on the tail of the 23,800-cm^{-1} band, and the extinction coefficients given in Table II were obtained by subtracting this background. There is a distinct similarity between the more intense bands of this region and those observed[5] for other octahedral Re(IV) complexes such as $[ReCl_6]^{2-}$. This latter spectra has been assigned.[6] However, a number of other peaks, all of low intensity, appear in the thiocyanate complex. The energies of this series of bands lie about 3000 cm^{-1} below those of the hexachloride.

TABLE III

INFRARED SPECTRA OF $[Re(SCN)_6]^{2-}$ COMPOUNDS (CM^{-1})

Compound	C≡N stretch	C—S stretch
KSCN	2049	749
$Cs_2[Re(SCN)_6]$	2040, 2022	699
$Tl_2[Re(SCN)_6]$	2038	694
$Ag_2[Re(SCN)_6]$	2038	695

The infrared spectra (Table III, Figure 3) show only the expected thiocyanate peaks. From the arguments of Tramer,[7] and Lewis *et al.*,[8] the decrease in the C–S stretching frequency to about 700 cm^{-1} in our products is indicative of sulfur bonding to the rhenium. The C–N frequency is unusually low, but no significance can be attributed to this at present. No trace of any Re=O can be seen in the spectra.

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Amides as Ligands. VII. Complexes of N-Methyl-γ-butyrolactam with Nontransition Metals

BY STANLEY K. MADAN

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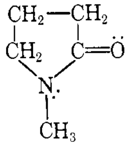
The first two papers of this series reported the formation and characterization of coordination compounds of several transition metals and a few nontransition metal ions with the ligands N,N-dimethylacetamide[1] and ε-caprolactam.[2,3] The present work is concerned with N-methyl-γ-butyrolactam (NMBuL) complexes of nontransition elements, especially alkali and alkaline earth elements. The structure of NMBuL is best represented by



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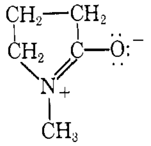

II

Few stable complexes of alkali metals have been reported. Complexes of the alkali metals with β-diketone derivatives, *o*-nitrophenol, and salicylaldehyde have been described in the literature.[4,5] The sodium compounds ranged from hydrated ionic salts such as $Na(acac)\cdot 2H_2O$ to adducts such as Na(Sal)HSal (HSal = salicylaldehyde). Pfeiffer[6] and others[7] have reported the isolation of a complex of sodium perchlorate with 1,10-phenanthroline. Brady and Badger[8] have presented evidence for chelation in sodium salts of *o*-hydroxybenzaldehydes. More recently, Popp and Joesten[9] have isolated and characterized a number of alkali metal and alkaline earth metal salts with the ligand octamethylpyrophosphoramide (OMPA). Gentile and co-workers[10] have also reported complexes of diacetamide with alkali and alkaline earth metal salts.

In line with our interest in substituted amides as ligands, we decided to extend our studies of NMBuL by studying reactions of NMBuL with nontransition metal ions. During the progress of this study a paper appeared in which a few NMBuL–transition metal complexes were described and characterized *via* their infrared spectra, magnetic moments, and electrical conductivity.[11]

Experimental Section

Reagents.—We are thankful to General Aniline and Film Corp. for furnishing us with a sample of NMBuL. This product was distilled under reduced pressure. The constant-boiling middle fraction, 80° (10 mm), $n^{25}D$ 1.4691, was collected. This refractive index is in agreement with the one reported in the literature.[12] Metal perchlorates were purchased from G. Frederick Smith Chemical Co.

Preparation of Complexes.—All of the NMBuL complexes with metal perchlorates with the exception of that of Mg(II) were prepared by the same procedure. The hydrated metal perchlorates were dehydrated with excess quantities of 2,2-dimethoxypropane by stirring (magnetic) for a minimum of 2 hr. Excess NMBuL was added and stirring continued for 40–50 min. Excess anhydrous ether was added, and crystalline product formed

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