A Thiocyanate Complex of Rhenium(V), and the Identity of the Reduction Products of Perrhenate in Thiocyanate Solutions[1]

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

The new compound $Cs[Re(SCN)_6]$ was prepared from the reaction of $ReCl_5$ with molten KSCN. Infrared evidence for the mode of bonding of the thiocyanate groups in $[Re(SCN)_6]^-$ and $[Re(SCN)_6]^{2-}$ ions strongly favors attachment through the sulfur end. Studies of the reduction products of hydrochloric acid solutions of ReO_4^- with Sn(II) in the presence of excess KSCN, or reduction by KSCN itself, show that the hexathiocyanatorhenate(IV) and/or -(V) compounds are the major products, depending on the amount of reducing agent. No oxythiocyanate complexes were found.

Introduction

It has been well known for many years[2] that the reduction of a hydrochloric acid solution of potassium perrhenate in the presence of potassium thiocyanate (notably with $SnCl_2$) produces an intensely red coloration. Although it is this coloration that is the basis for the colorimetric determination of amounts to 1 μg of rhenium,[2] the precise nature of the species formed has not yet been elucidated. In fact, speculation on the composition and oxidation state of these species has led to many ambiguous interpretations. All of the compounds suggested have contained oxygen. Druce[3] postulated the complex to be $ReO(SCN)_4$, containing hexavalent rhenium. Holeman[4] concluded the oxidation state to be about 5. More recent potentiometric and coulometric investigations[5] have shown that the average oxidation state in the complex is about 4.5 leading to the suspicion that more than one species is present. Ryabchikov and others[6-10] have studied this system extensively in solution and have isolated salts of the complex anion claimed to be $[ReO_2(SCN)_4]^{3-}$, analogous to the rhenium(V) oxycyanide characterized by Klemm.[11] Some thiocyanate complexes of rhenium with phosphine[12] or carboxylate ligands,[13] or of Re(III) cluster compounds,[14] have been reported, but the only other adequately characterized rhenium thiocyanate complex ion is $[Re(SCN)_6]^{2-}$ described by Bailey and Kozak[15] and by Cotton, *et al.*[16]

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(15) R. A. Bailey and S. L. Kozak, *Inorg. Chem.*, **6**, 419 (1967).

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Experimental Section

$Cs[Re(SCN)_6]$ was prepared by allowing $ReCl_5$ to react with molten KSCN at 230° for 1 hr and isolated by the method described earlier[15] for $Cs_2[Re(SCN)_6]$. The specimen was carefully freed of any traces of $[Re(SCN)_6]^{2-}$, a by-product of the preparative reaction, and any unreacted $ReCl_5$ by washing with ethanol and ether, in which these impurities have a much greater solubility. The washings are readily monitored spectroscopically. All chemicals used were reagent grade. The product was obtained as a medium brown powder.

Anal. Calcd for $Cs[Re(SCN)_6]$: Re, 27.9; S, 28.8; N, 12.5. Found: Re, 28.0; S, 29.0; N, 12.4.

Solubilities: insoluble in water, slightly soluble in ethanol and ether, very soluble in acetone, and soluble in dilute acids and alkalies. Yield, about 50%.

Rhenium thiocyanate complexes were prepared in solution by adding perrhenic acid, potassium thiocyanate, and stannous chloride to 2 N hydrochloric acid according to the schedule in Table III. The reactions were allowed to proceed with stirring at 25° for periods up to 20 hr. No change in the peak positions in the observed spectra with time took place over reaction periods of 10 min to 20 hr.

Spectral Measurements.—Ultraviolet–visible spectra were taken on a Unicam SP 700 spectrophotometer, and extinction coefficients were obtained with a Beckman DU spectrophotometer. Spectra were taken on the reaction solution itself and on an ether extract of this. Both gave essentially the same results, but spectra in ether were more distinct and are the ones reported. In some instances, the ether extract was slowly evaporated to dryness and the residue was redissolved in absolute ethanol in order to extend the range of study beyond the cutoff due to the ether (30,000 cm^{-1}). In all cases, the spectra remained unchanged by such treatment.

Infrared measurements were made with Perkin-Elmer 421 and 337 spectrophotometers by the KBr pressed-disk method and checked in hexachlorobutadiene and Nujol mulls. Peak intensity measurements in solution were made in 0.005-cm NaCl cells.

The magnetic susceptibility of $Cs[Re(SCN)_6]$ was found at 25° by the Gouy technique, using $Hg[Co(SCN)_4]$ as calibrant.

Results and Discussion

Characterization of $Cs[Re(SCN)_6]$.—Analytical data indicate that this complex is a compound of Re(V). It has been found to possess an effective magnetic moment, μ_{eff}, of 1.38 BM, which is independent of field strength and is in the range reported for several other Re(V) compounds,[17-19] *i.e.*, from 1.41 to 1.88 BM.

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The infrared spectra of the $Cs_2[Re(SCN)_6]$ and $Cs[Re(SCN)_6]$ complexes have been measured (Table I, Figure 1) over the range 4000–400 cm^{-1}. We have previously reported[15] the spectrum of $Cs_2[Re(SCN)_6]$ over the 4000–550-cm^{-1} range to be indicative of coordination through the sulfur atom of the ligand. This was based upon consideration of the shift of the C=S stretching mode from 749 cm^{-1} ("free" SCN$^-$) to 699 cm^{-1} which, according to the arguments of Tramer[20] and Lewis, *et al.*,[21] is consistent with sulfur bonding to the rhenium. Only very weak indications of bands appeared in the 800-cm^{-1} region; these could be attributed to overtones and in any event are much less distinct than the 699-cm^{-1} peak. Recently, Cotton, *et al.*,[16] prepared $[(C_6H_5)_4As]_2[Re(NCS)_6]$ and $[(C_4H_9)_4N]_2-[Re(NCS)_6]$ and pursued the infrared measurements to 400 cm^{-1}. These authors reported the N–C–S bending mode to be at 484 cm^{-1}, which Sabatini, *et al.*,[22] consider to be indicative of bonding to the metal through the thiocyanate nitrogen. The C=S stretching mode is reported for one compound at 865 cm^{-1}, although the 600–800-cm^{-1} region was obscured by cation bands. In view of this new evidence, we have extended our own

TABLE I[a]

Compound	C≡N str	C=S str	N—C—S bend
KSCN	2049 s	749 s	470 m
$Cs_2[Re(SCN)_6]$	2040 s 2022 s	699 w	476 w, br
$Cs[Re(SCN)_6]$	2052 s 1858 m	702 w, sp	...

[a] Values in cm^{-1}; s, strong; m, medium; w, weak; br, broad; sp, sharp.

investigations of the cesium compound to this region and have found a broad, weak band at 476 cm^{-1} which appears to be attributable to the bending mode. A comparison of this band with the previously reported band at 699 cm^{-1} is seen in Figure 1. The ambiguity of the situation is further exemplified by our studies of the low-energy region in the case of $Cs[Re(SCN)_6]$. Here, we observe no definite bands in the 400–500-cm^{-1} region but do observe a comparatively strong absorption at 702 cm^{-1} which we must attribute to the C=S stretching mode. The 702-cm^{-1} band is the predominant one in this region and its sharpness would seem to eliminate the possibility of its being an overtone of some lower frequency band (*e.g.*, Re–S). No definite absorptions were observed in the 800–1000-cm^{-1} region indicating, first, that there are no Re=O linkages present and, second, that there is no evidence from this region to support nitrogen bonding in this complex. The C≡N stretching mode occurs at 2052 cm^{-1}. While a value less than 2100 cm^{-1} has been considered characteristic of nitrogen bonding, this has been shown to be unreliable.[23] A second band at 1858 cm^{-1} remains unidentified, as it seems to be too low for any C≡N

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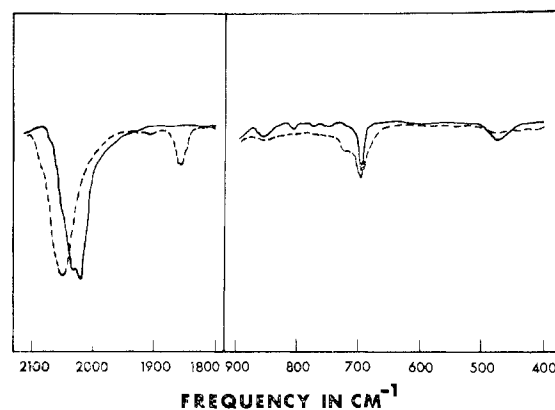
Figure 1.—Infrared spectra of $Cs_2[Re(SCN)_6]$ (solid line) and $Cs[Re(SCN)_6]$ (dashed line).

band. A combination band is a possibility, although the sharpness and intensity do not indicate this.

Pecile[24] has shown that the product $A = \epsilon_{max}\Delta\nu_{1/2}$ (extinction coefficient × width at half-maximum, an approximation of the integrated intensity) for the C≡N stretching mode is indicative of the coordination. Bonding through sulfur gives values of A near 2×10^4 M^{-1} cm^{-2} or less, while N-bonded values are in the neighborhood of 9×10^4 M^{-1} cm^{-2}. The results of Table II clearly imply S bonding. X-Ray analysis of these compounds would be valuable to establish the structures unambiguously.

TABLE II

FREQUENCY, APPARENT HALF-BAND WIDTH ($\Delta\nu_{1/2}$), AND INTEGRATED INTENSITY (A) OF THE INFRARED ABSORPTION AT 2048–2078 CM^{-1} FOR COMPLEXES

Compound	Medium	$\nu_{C≡N}$, cm^{-1}	$\Delta\nu_{1/2}$, cm^{-1}	ϵ_{max},[a] M^{-1}cm^{-1}	$10^{-4}A$,[a] M^{-1} cm^{-2}
$Cs_2[Re(SCN)_6]$	C_2H_5OH	2057	41	5.61×10^2	2.30
	CH_3COCH_3	2048	21	1.39×10^3	2.90
$Cs[Re(SCN)_6]$	C_2H_5OH[b]	2078	56	1.58×10^2	0.89
	CH_3COCH_3	2067	40	5.88×10^2	2.35

[a] Calculated per mole of coordinated SCN group. [b] Accuracy limited by low solubility.

The ultraviolet–visible region shows only one peak (Figure 2) at 27,600 cm^{-1}. The extinction coefficient for this band was determined in H_2O (acidified with HCl) to be 6.12×10^3 M^{-1} cm^{-1}. This band is most likely attributed to charge transfer. No ligand field bands were observed in aqueous or in ether solutions, these probably being hidden under the charge-transfer band. The spectrum of the Re(IV) compound shows two bands, at 38,300 and 23,800 cm^{-1}, both about 10 times as intense.[15] It also exhibits a number of weaker bands below 12,000 cm^{-1}, so that a distinction between the two compounds is made easily. The composition of the Re(V) compound indicates a simple, probably octahedral complex, although this is of course not proven by the above data. Attempts to study the conductance of this species in acetonitrile were unsuccessful. Apparently solvolysis reactions take place, giving anomalously high conductivity values and changing the spectrum.

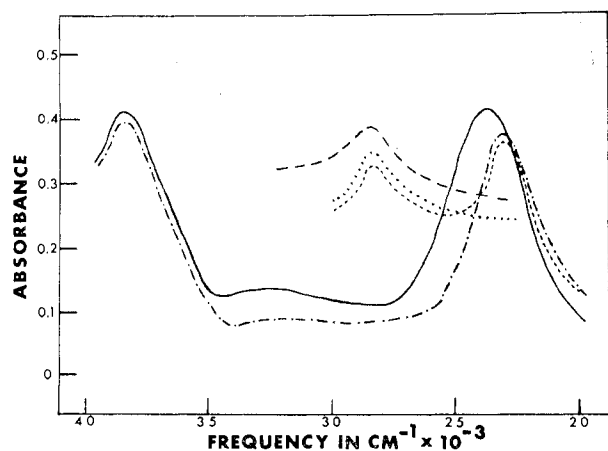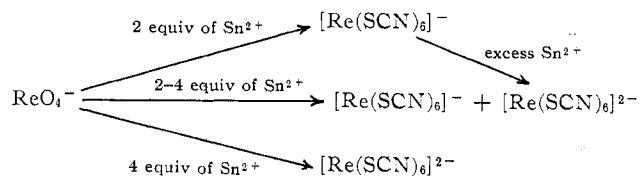(24) C. Pecile, *Inorg. Chem.*, **5**, 210 (1966).

Figure 2.—Ultraviolet–visible spectra of rhenium–thiocyanate systems: ———, Cs$_2$[Re(SCN)$_6$]; — —, Cs[Re(SCN)$_6$]; · · · ·, reaction 1; – – – –, reaction 3; – · – ·, reaction 4.

Identification of Rhenium Thiocyanate Species Formed in HCl Solutions.

—It has repeatedly been reported that solutions of KReO$_4$ in dilute HCl form upon addition of KSCN and SnCl$_2$ red to red-orange solutions, the colored species being easily and completely extracted by ether. The reported visible absorption spectra for these ether solutions have contained one or both of two bands,[10] one at 350 mμ (28,600 cm^{-1}) and the other at 420 mμ (23,800 cm^{-1}). Ryabchikov and Nazarenko have claimed[7] for some time that this coloration is due at least in part to the [ReO$_2$(SCN)$_4$]$^{3-}$ ion, which in fact they claim to have isolated as [Pt(NH$_3$)$_4$]$_3$[ReO$_2$(SCN)$_4$]$_2$, for example. The evidence for this, however, is not convincing. Since infrared techniques should be able to detect Re=O groups and the rhenium(IV) and -(V) hexathiocyanate complexes have now been characterized, we have undertaken the present study. We have shown that the red coloration is due to the presence of the [Re(SCN)$_6$]$^{2-}$ and/or the [Re(SCN)$_6$]$^-$ ion.

Repetition of the studies of the spectra of the ether extracts of the reaction mixtures studied by Yordanov and Pavlova[10] yielded similar results to those which they reported. The peak positions agree to within a few hundred wavenumbers. With 100-fold excess of KSCN and an Re concentration of 2 × 10^{-3} M, 2 equiv of Sn(II) gives a solution with only a single peak at 27,600 cm^{-1}. With higher Sn(II) concentrations, a second peak at 23,100 cm^{-1} appears. With 4.5 equiv of Sn(II), the 27,600-cm^{-1} peak disappears, leaving only the 23,100-cm^{-1} absorption. These bands are assigned to the rhenium(V) and -(IV) thiocyanate complexes. Reactions under identical conditions, but with different concentrations of rhenium, showed somewhat different results in that the Re(V) band was frequently missing or obscure. It appears that the relative amounts of Re(IV) and Re(V) formed are dependent on concentration and that at high concentrations the Re(V) band is obscured by the comparatively high background. Owing to the lower extinction coefficient of the latter, small amounts may not be detected in the presence of large amounts of Re(IV). Little

colored rhenium material was left in the aqueous phase after ether extraction.

KReO$_4$ reacts slowly with KSCN in 2 N HCl in the absence of any additional reducing agent (reaction 5, Table III). Two bands are observed in the visible spectrum of the product formed. These are at 27,600 and 23,100 cm^{-1}, respectively. The two bands do not change in relative intensity with time, but do increase gradually in over-all intensity as the reaction proceeds. These are obviously the same products as when SnCl$_2$ is used as reducing agent. Reduction by SCN$^-$ is not important when Sn^{2+} is present, owing to its slowness. When the Cs[Re(SCN)$_6$] prepared as described earlier was treated with excess Sn^{2+}, the peak at 27,600 cm^{-1} vanished and there appeared the band at 23,100 cm^{-1}. These observations led us to believe that the reactions involved in these systems could be represented by the equations

$$\text{ReO}_4^- \xrightarrow[\text{2 equiv of Sn}^{2+}]{} [\text{Re(SCN)}_6]^- \xrightarrow[\text{excess Sn}^{2+}]{}$$
$$\text{ReO}_4^- \xrightarrow{\text{2-4 equiv of Sn}^{2+}} [\text{Re(SCN)}_6]^- + [\text{Re(SCN)}_6]^{2-}$$
$$\text{ReO}_4^- \xrightarrow{\text{4 equiv of Sn}^{2+}} [\text{Re(SCN)}_6]^{2-}$$

To substantiate these identifications, the ether extract of reaction 4 (Table III) was allowed to evaporate to dryness and the ethanolic solution of the residue was scanned on the spectrophotometer. One clearly observes (*cf.* Table III) peaks nearly identical with those we reported for the Cs$_2$[Re(SCN)$_6$] which was isolated and definitely identified. The extract of reaction I was treated similarly, and, once again, the band at 27,600 cm^{-1} is the same as we obtained from the isolated and identified Cs[Re(SCN)$_6$] in this solvent.

Table III summarizes these results.

TABLE III

Reaction	10^3[Re], M	10[SCN$^-$], M	Equiv of Sn/equiv of Re	Absorption maxima, cm^{-1}
1	2.0	2	2.0	27,600^a
2	2.0	2	2.5	27,600
3	2.0	2	3.0	27,600, 23,100
4	2.0	2	4.5	38,300, 23,100^b
5	2.0	2	0	27,600, 23,100^c
6	Cs[Re(SCN)$_6$]	0	Excess	23,100

^{a} In ether or in alcohol. ^{b} In ether or in alcohol; low-intensity ligand field peaks below 12,000 cm^{-1} were also detected. ^{c} After 1 or 4 days.

Infrared spectra were taken of both residues and absolutely no trace of any Re=O linkages were observed. This would appear as a strong band between 900 and 1000 cm^{-1} [25] or in the 815–830-cm^{-1} region if a *trans*-O=Re=O group were present.[26] We next duplicated the preparation of the alleged [Pt(NH$_3$)$_4$]$_3$-[ReO$_2$(SCN)$_4$]$_2$ reported by Ryabchikov,[7] and its infra-

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red spectrum showed no Re=O to be present. In fact, if one considers the precipitate to be $[Pt(NH_3)_4]_2[Re(SCN)_6]$, one finds that the rhenium content determined by the Russian workers (23.30% Re) is indeed in much better agreement with that calculated for the hexathiocyanate(IV) salt (23.31%).

These results show that the colored rhenium thiocyanate compounds produced by reduction of perrhenate are made up of rhenium(IV) and/or rhenium-(V) hexathiocyanate species, depending on the amount of reducing agent used. An excess is clearly required for reproducible analytical use. No oxo species are formed unless in trace amounts in the acidity range considered here. In view of the fact that none of the previous workers in this field has given any direct evidence for the presence of oxygen in their compounds, it must be concluded that rhenium oxothiocyanates have not been observed as yet.

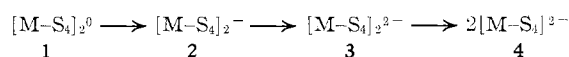# Cleavage Reactions of Cobalt and Iron Dithiolate Compounds. Five-Coordinate Complexes

BY A. L. BALCH

Synthetic and polarographic studies indicate that triphenylphosphine, triphenylarsine, triphenylstibine, and triphenyl phosphite (L) cleave the dimeric complexes $[MS_4C_4R_4]_2^z$ (M = Co, Fe; R = CF_3, z = 0, −1, −2; R = CN, z = −2) to yield monomeric, five-coordinate $[LMS_4C_4R_4]^z$. Polarography of the $[LMS_4C_4R_4]^z$ species indicates the existence of three complexes (z = +1, 0, −1) for M = Co and R = CF_3 and at least two (z = 0, −1) for M = Co and R = CN and for M = Fe and R = CF_3 or CN. In solution $LCoS_4C_4(CF_3)_4$ exhibits magnetic and esr properties consistent with a doublet ground state. In the solid $(C_6H_5)_3PCoS_4C_4(CF_3)_4$ is diamagnetic and presumably dimerized. Magnetic studies show that $LFeS_4C_4(CF_3)_4$ and $[(C_6H_5)_3PCoS_4C_4R_4]^-$ are diamagnetic whereas $[(C_6H_5)_3PFeS_4C_4(CF_3)_4]^-$ has an S = $^3/_2$ ground state. No evidence of these five-coordinate species adding further ligands has been found.

Introduction

A recent investigation[1] of the complexes $[MS_4C_4R_4]_n^z$ with M = Co or Fe and R = CF_3 has revealed that in dichloromethane solution an electron-transfer series embracing the members 1–4 exists. When R = CN

$$[M-S_4]_2^0 \longrightarrow [M-S_4]_2^- \longrightarrow [M-S_4]_2^{2-} \longrightarrow 2[M-S_4]^{2-}$$
$$\quad 1 \qquad\qquad 2 \qquad\qquad 3 \qquad\qquad 4$$

only the three reduced species 2–4 have been detected. With $[CoS_4C_4(CF_3)_4]_2^2$ and $[FeS_4C_4(CN)_4]_2^{2-}$,[3] dimerization has been shown to occur through metal-to-sulfur bonds to give square-pyramidal coordination about each metal. This basic structure, depicted in Figure 1, is believed to persist throughout the electron-transfer series 1–3. However the most reduced member 4 with M = Co and R = CN has been shown to have monomeric, planar geometry.[4]

The present study is concerned with the interaction of several potential two-electron donors with dimers 1–3. Although addition—possibly stepwise—of donors to the intact dimers is feasible, previous studies indicate that cleavage of the dimers to give five- or six-coordinate complexes would be more likely. For example, it has been shown[5] that $[MS_4C_4(C_6H_5)_4]_n$ (M = Co, Fe) reacts with phosphines to yield monomeric [phosphine-$MS_4C_4(C_6H_5)_4$]. Reaction of $[CoS_4C_4(CN)_4]_2^{2-}$ with a variety of donors yields a variety of six- and apparently five-coordinate, monomeric species.[6] Five-coordination has also been observed in the novel gold dithiolato complex $[(C_6H_5)_3PAuS_4C_4(CF_3)_4]Cl$.[7]

Experimental Section

Preparation of Compounds.—Commercial samples of group V triaryls were recrystallized before use. Melting points are uncorrected.

$(C_6H_5)_3PCoS_4C_4(CF_3)_4$.—A solution of 0.263 g (1.00 mmole) of triphenylphosphine in 60 ml of dry pentane was added dropwise to a solution of 0.512 g (0.500 mmole) of $[CoS_4C_4(CF_3)_4]_2$[8] in 200 ml of dry pentane. The volume of the brown solution was reduced to 60 ml. The solution was filtered and cooled in a Dry Ice bath. The fine brown crystals which formed were collected by filtration and washed with pentane. Further purification was obtained by recrystallization from pentane followed by vacuum drying. The yield is 70–80%; mp 183–185°. *Anal.* Calcd: C, 40.37; H, 1.95; S, 16.58; P, 4.00; mol wt, 774. Found: C, 40.60; H, 2.00; S, 16.84; P, 4.08; mol wt, 757.

A similar procedure produced yields of 60–90% in the preparation of the following analogous compounds. For the iron compounds, $[FeS_4C_4(CF_3)_4]_2$[1] replaced its cobalt analog as starting material.

$(C_6H_5)_3AsCoS_4C_4(CF_3)_4$.—Brown crystals were obtained; mp 186.5–188°. *Anal.* Calcd: C, 38.29; H, 1.85; mol wt, 818. Found: C, 38.50; H, 2.05; mol wt, 785.

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