Cl_4), the σ and π contributions to the Re–Cl bonds are not rigorously separable by molecular symmetry. Thus, the values of σ and π Re–Cl bonds in Table IV are accurate only insofar as they represent an upper limit of π bonding and lower limit of σ bonding within the framework of rigorous σ–π separability. The total Re–Cl bond order, 0.40, is, of course, not subject to the separability of σ and π orbitals.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASSACHUSETTS 02139

Some Reactions of the Octahalodirhenate(III) Ions. IV. Reactions with Sodium Thiocyanate and the Preparation of Isothiocyanate Complexes of Rhenium(III) and Rhenium(IV)[1]

BY F. A. COTTON, W. R. ROBINSON, R. A. WALTON, AND R. WHYMAN

Received December 27, 1966

The reaction of sodium thiocyanate with the $Re_2Cl_8^{2-}$ ion gives the complex anions $Re_2(NCS)_8^{2-}$ or $Re(NCS)_6^{2-}$, depending upon the reaction conditions. The use of acidified media favors the dinuclear rhenium(III) species, while the use of acetone as solvent resulted in oxidation to rhenium(IV) and the isolation of $Re(NCS)_6^{2-}$. Magnetic susceptibilities, spectral data, and electrolytic conductances for these two anions are reported and shown to be consistent with structures proposed for them. Infrared spectral measurements indicate that the thiocyanate groups are nitrogen bonded in each case. A complex of empirical formula $[(C_4H_9)_4N]_3[Re_2(NCS)_{10}(CO)_2]$ was isolated as a by-product during the preparation of $[(C_4H_9)_4N]_2Re(NCS)_6$. The carbonyl groups which appear to be present are presumably derived from the solvent (acetone). Solutions containing $Re_2(NCS)_8^{2-}$ react with triphenylphosphine to give a green complex which apparently has the formula $[(C_4H_9)_4N]_2[Re_2(NCS)_8(P(C_6H_5)_3)_2]$. Available evidence suggests that a direct Re–Re bond is not present in this compound. The magnetic moment of this complex (~4.1 BM per rhenium) is unusual and difficult to interpret.

Introduction

We have recently[2-4] investigated the reactivity of the $Re_2X_8^{2-}$ ions, where X = Cl or Br, toward a variety of donor molecules. One of the most interesting results of these studies is that in a wide variety of ligand substitution reactions (with carboxylic acids, phosphines, and sulfur ligands) the Re–Re bond is normally preserved even though it may not remain a quadruple bond, as is present in the dinuclear $Re_2Cl_8^{2-}$ ions.[5,6] Thus a crystallographic investigation[7] has revealed that a Re–Re triple bond, not a quadruple bond, is present in the dinuclear 2,5-dithiahexane ($CH_3SCH_2CH_2SCH_3$) complex, $Re_2Cl_5(DTH)_2$.

Changing X from Cl to Br usually has little effect upon the reactivity of the $Re_2X_8^{2-}$ species and the formation and stability of the resulting complexes. This is of course not unexpected. Consequently, we have investigated the reaction of $[(C_4H_9)_4N]_2Re_2Cl_8$ with sodium thiocyanate in an attempt to isolate salts of octathiocyanatodirhenate(III) ions and thereby obtain more information about the effect that the nature of X has upon the stability and reactivity of the $Re_2X_8^{2-}$ species. The results of these investigations are now reported and several new complexes of rhenium described.

Experimental Section

$[(n\text{-}C_4H_9)_4N]_2Re_2Cl_8$ was prepared as previously described.[2] All other reagents and solvents were commercially available. Analyses were performed by the Galbraith Microanalytical Laboratories, Knoxville, Tenn.

Preparation of Compounds. **$[(n\text{-}C_4H_9)_4N]_2Re_2(NCS)_8$.**—This complex was prepared by two procedures, both of which are described below. The second is by far the more convenient method.

(a).—To 150 ml of tetrahydrofuran under nitrogen was added 5.0 g of $[(C_4H_9)_4N]_2[Re_2Cl_8]$ and 4.0 g of NaSCN. The brown solution was stirred for 1 hr, then refluxed for 30 min. The solvent was removed on a rotary evaporator, and the resulting thick oil was filtered to recover a brown precipitate. After this precipitate had been washed with 20 ml each of water, ethanol, and ether, it was dissolved in a minimum amount of acetonitrile, passed through an alumina column to remove some small amounts of by-products, and recovered by evaporation of the solvent. The compound was dried under vacuum at 80°; yield 77%.

Anal. Calcd for $C_{40}H_{72}N_{10}S_8Re_2$: C, 36.34; H, 5.48; N, 10.60; S, 19.41. Found: C, 36.0; H, 5.32; N, 10.7; S, 19.3.

(b).—$[(C_4H_9)_4N]_2Re_2Cl_8$ (0.15 g) and NaSCN (0.10 g) were dissolved in 15 ml of methanol. Acetic acid (1 ml) and acetic anhydride (2 ml) were added, and the reaction mixture was stirred under nitrogen for 6 hr. The dark red solution was filtered and reduced to a small volume at room temperature. The resulting red crystalline material was filtered off, washed freely with ethanol, water, and ether, and dried *in vacuo;* yield 0.17 g.

Anal. Calcd for $C_{40}H_{72}N_{10}S_8Re_2$: C, 36.34; H, 5.48; N, 10.60; S, 19.41. Found (for separate preparations): C, 36.0, 36.6; H, 5.37, 5.57; N, 10.7, 10.5; S, 19.1.

An identical product was isolated when tetrahydrofuran, acidified with a few drops of acetic acid, was used as the solvent.

---

[1] Research supported in part by the United States Atomic Energy Commission.

[2] F. A. Cotton, N. F. Curtis, and W. R. Robinson, *Inorg. Chem.*, **4**, 1696 (1965).

[3] F. A. Cotton, C. Oldham, and W. R. Robinson, *ibid.*, **5**, 1798 (1966).

[4] F. A. Cotton, C. Oldham, and R. A. Walton, *ibid.*, **6**, 214 (1967).

[5] F. A. Cotton and C. B. Harris, *ibid.*, **4**, 330 (1965).

[6] F. A. Cotton, *ibid.*, **4**, 334 (1965).

[7] M. J. Bennett, F. A. Cotton, and R. A. Walton, *J. Am. Chem. Soc.*, **88**, 3866 (1966).

Anal. Found: C, 36.5; H, 5.63; N, 10.5; S, 19.2.

Solubility.—This complex was soluble in tetrahydrofuran, acetonitrile, acetone, and nitromethane, slightly soluble in ethanol, but insoluble in water, ether, chloroform, and benzene. It could be recovered unchanged from acetonitrile.

$[(C_6H_5)_4As]_2Re_2(NCS)_8$.—$[(C_4H_9)_4N]_2Re_2Cl_8$ (0.15 g) and NaSCN (0.10 g) were dissolved in 15 ml of methanol. Four drops of glacial acetic acid were added and the reaction mixture stirred under nitrogen for 1 hr. The dark red solution was filtered into a methanol solution (10 ml) containing 0.20 g of tetraphenylarsonium chloride. Glistening orange plates immediately separated and were filtered off, washed with methanol and ether, and dried *in vacuo;* yield 0.20 g.

Anal. Calcd for $C_{56}H_{40}N_8S_8As_2Re_2$: C, 41.95; H, 2.52; N, 6.99; S, 15.99. Found: C, 41.9; H, 2.70; N, 6.79; S, 15.8.

When tetrahydrofuran was used as solvent the crystalline product was apparently contaminated with rhenium(IV) impurities.

Anal. Found: C, 46.3; H, 3.28; N, 6.30.

Solubility.—The complex was soluble in acetonitrile, acetone, and nitromethane, slightly soluble in tetrahydrofuran, and insoluble in water, ethanol, ether, chloroform, and benzene.

$[(C_6H_5)_3CH_3As]_2Re_2(NCS)_8$.—This complex was prepared as above for the tetraphenylarsonium salt; the solution containing $Re_2(NCS)_8^{2-}$ was filtered into 10 ml of methanol containing 0.20 g of triphenylmethylarsonium iodide; yield 0.153 g of dark red crystals.

Anal. Calcd for $C_{46}H_{36}As_2N_8S_8Re_2$: C, 37.34; H, 2.45; N, 7.58; S, 17.33. Found: C, 37.3; H, 2.65; N, 7.69; S, 17.1.

Solubility.—The solubility was very similar to that of its $[(C_6H_5)_4As]^+$ analog.

$[(n\text{-}C_4H_9)_4N]_2Re(NCS)_6$ and $[(n\text{-}C_4H_9)_4N]_3[Re_2(NCS)_{10}(CO)_2]$.—$[(C_4H_9)_4N]_2Re_2Cl_8$ (0.20 g) and NaSCN (0.15 g) were dissolved in 15 ml of acetone, and the reaction mixture was stirred under nitrogen for 2 hr. The dark brown solution was filtered from the precipitated sodium chloride and allowed to evaporate to dryness at room temperature. The dark brown residue that remained was extracted several times with absolute ethanol and then washed freely with water. These washings were discarded and the solid that remained on the filter pad was washed several times with tetrahydrofuran to give a deep red-brown filtrate and an insoluble dark green microcrystalline product (A). After the filtrate had been allowed to stand at room temperature for 1 hr it was again filtered to remove a further small yield of crystalline A and then allowed to evaporate very slowly to about half volume. After about 2 days large red-brown crystals of B separated, and these were filtered off, washed sparingly with tetrahydrofuran and then with ether, and finally dried *in vacuo.*

The yields of A depended upon the reaction time; shorter times favoring a higher yield of A. *E.g.*, 0.087 g of A and 0.045 g of B from 3 hr reaction; 0.028 g of A and 0.050 g of B from 6.5 hr reaction.

(i) *Anal* for A. Calcd for $C_{60}H_{108}N_{13}O_2S_{10}Re_2$ ($[(C_4H_9)_4N]_3[Re_2(NCS)_{10}(CO)_2]$): C, 41.50; H, 6.27; N, 10.48; S, 18.46. Found (for three separate preparations): C, 41.3, 41.5, 41.9; H, 6.46, 6.49, 6.60; N, 10.7, 10.0, 11.2; S, 17.7, 17.8, 18.5.

This material could be recrystallized as glistening dark green needles by adding an excess of ether to an acetonitrile solution of the crude product and cooling to 0°.

Anal. Found: C, 41.9; H, 6.77; N, 10.6; S, 18.6. The addition of tetraphenylarsonium chloride to an acetonitrile solution of this compound followed by an excess of ether gave crystalline dark green $[(C_6H_5)_4As]_3[Re_2(NCS)_{10}(CO)_2]$.

Anal. Calcd for $C_{84}H_{60}N_{10}O_2S_{12}As_3Re_2$: C, 46.74; H, 2.80; N, 6.49; S, 14.85. Found: C, 47.5; H, 3.05; N, 6.69; S, 14.2.

(ii) *Anal* for B. Calcd for $C_{38}H_{72}N_8S_6Re$ ($[(C_4H_9)_4N]_2Re(NCS)_6$): C, 44.75; H, 7.12; N, 10.99; S, 18.87. Found (for separate preparations): C, 44.6, 44.7; H, 7.04, 7.07; N, 10.9, 11.0; S, 18.2.

Solubility.—The complex A is soluble in acetonitrile, acetone, and tetrahydrofuran but insoluble in water, ether, chloroform, benzene, and ethanol.

$[(C_6H_5)_4As]_2Re(NCS)_6$.—A methanol solution (10 ml) of tetraphenylarsonium chloride (excess) was added to the tetrahydrofuran filtrate obtained above after the separation of A. An immediate red-brown precipitate (0.082 g) formed and this was filtered off and washed with methanol and ether.

Anal. Calcd for $C_{54}H_{40}N_6S_6As_2Re$: C, 49.84; H, 3.10; N, 6.46; S, 14.79. Found: C, 49.2; H, 3.23; N, 6.24; S, 14.3.

$[(C_4H_9)_4N]_2[Re_2(NCS)_8(P(C_6H_5)_3)_2]$.—$[(C_4H_9)_4N]_2Re_2Cl_8$ (0.20 g) and NaSCN (0.15 g) were dissolved in 25 ml of methanol containing four drops of 6 *N* hydrochloric acid and the reaction mixture stirred under nitrogen for 30 min. Triphenylphosphine (0.20 g) was then added and the stirring continued for a further 2 hr. The reaction flask was stoppered and allowed to stand overnight, and the bright green insoluble product was filtered off, washed freely with water, ethanol, and ether, and dried *in vacuo;* yield 0.12 g.

Anal. Calcd for $C_{76}H_{102}N_{10}S_8P_2Re_2$: C, 49.44; H, 5.57; N, 7.59; S, 13.89. Found (for separate preparations): C, 48.8, 48.3; H, 5.24, 5.11; N, 7.73; S, 13.9.

Occasionally the product that separated from the reaction mixture was a darker green in color and analysis indicated that it was impure. Recrystallization and purification were carried out by dissolving the product in tetrahydrofuran or acetonitrile, adding an excess of ether to the filtered solution, and then maintaining the solution at ~0° for 30 min. The golden yellow crystals that separated were filtered off, washed with ether, and dried *in vacuo.*

Anal. Found: C, 48.34; H, 5.34; N, 7.26.

Solubility.—It was soluble in tetrahydrofuran, acetonitrile, and acetone, slightly soluble in chloroform, but insoluble in water, ether, benzene, and ethanol.

Other Reactions. (a).—The reaction of triphenylarsine and 2,5-dithiahexane with the solutions obtained from the reaction of NaSCN with $[(C_4H_9)_4N]_2Re_2Cl_8$ in methanol–acetic acid did not give products in which the ligand molecules were coordinated. In both instances only $[(C_4H_9)_4N]_2Re_2(NCS)_8$ was isolated.

Anal. Found: C, 36.2; H, 5.49; N, 10.7; S, 19.3.

(b).—Hydrogen peroxide (0.8 ml of a 30% solution) was added to a methanol solution (20 ml) containing 0.10 g of $[(C_4H_9)_4N]_2Re_2Cl_8$ and 0.10 g of NaSCN. After stirring under nitrogen for 1 hr the reaction mixture was filtered into a methanol solution of tetraphenylarsonium chloride (0.15 g). The red filtrate was allowed to evaporate slowly during which time it faded in color and an insoluble white product separated. This was filtered off, washed with methanol and acetone, and dried *in vacuo.*

Anal. Calcd for $C_{24}H_{20}O_4AsRe$ ($[(C_6H_5)_4As]ReO_4$): C, 46.26; H, 3.56. Found: C, 46.1; H, 3.45. The infrared spectrum of this complex showed a strong band at 910 cm^{-1}, assigned to ν(Re–O), characteristic of the ReO_4^- group.[8]

Physical Measurements.—Infrared spectra were recorded in the range 4000–400 cm^{-1} using Perkin-Elmer 237B and 337 grating spectrophotometers. Visible and ultraviolet spectra were obtained with Beckman DU and Cary Model 14 spectrophotometers.

Conductivities were measured on a Serfass bridge using a cell calibrated with a 1 *M* aqueous potassium chloride solution. Solutions were prepared in Spectrograde acetonitrile in the concentration range 10^{-2} to 10^{-4} *M*.

Magnetic susceptibility measurements were carried out at the University of North Carolina by the Faraday method, using the balance described previously.[9] Diamagnetic corrections were estimated from Pascal's constants,[10] and the magnetic moments were calculated using the expression

$$\mu_{\text{eff}} = 2.84(\chi_{\text{m}}^{\text{cor}}T)^{1/2}$$

---

[8] F. A. Cotton and S. L. Lippard, *Inorg. Chem.*, **5**, 9 (1966).

[9] W. E. Hatfield, C. S. Fountain, and R. Whyman, *ibid.*, **5**, 1855 (1966).

[10] B. N. Figgis and J. Lewis, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience, Publishers Inc., New York, N. Y., 1960, Chapter 6.

Results and Discussion

Preparative Procedures.—Initial attempts to prepare the octaisothiocyanatodirhenate(III) ions using reagent grade acetone or tetrahydrofuran as solvents yielded products in which appreciable oxidation to rhenium(IV) species had occurred. However, $[(n\text{-}C_4H_9)_4N]_2Re_2(NCS)_8$ could be isolated from the reaction mixture by a suitable chromatographic separation of the products. On the other hand, in acidified methanol the conversion of $[Re_2Cl_8]^{2-}$ to $[Re_2(NCS)_8]^{2-}$ occurred smoothly and in high yield. Thus the use of an acidified solvent (12 *M* hydrochloric acid or glacial acetic acid) retards or represses the oxidation Re(III) → Re(IV) and enables the thiocyanate complexes to be prepared conveniently and rapidly.

The reaction of triphenylphosphine with the deep brown solution formed from the reaction of $Re_2Cl_8^{2-}$ with sodium thiocyanate in methanol–hydrochloric acid afforded a small yield of a bright green compound. Analytical data are consistent with the formula $[(n\text{-}C_4H_9)_4N]_2[Re_2(NCS)_8(P(C_6H_5)_3)_2]$, although with a formula so complex there is a finite possibility that it may not be entirely correct even though it fits the analytical data.

TABLE I

CONDUCTANCE DATA FOR RHENIUM THIOCYANATE COMPLEXES

Complex	Λ_e[a]	C_e[b]	Λ_0	A_{exptl}	A_{theor} (1:1)	A_{theor} (1:2)
$[(C_4H_9)_4N]_2Re(NCS)_6$	163	6.52×10^{-4}	...	...	...	...
$[(C_6H_5)_4As]_2Re(NCS)_6$	146	8.92×10^{-4}	...	...	...	...
$[(C_4H_9)_4N]_2Re_2Cl_8$	137	4.85×10^{-3}	189	711	369	763
$[(C_4H_9)_4N]_2Re_2(NCS)_8$	141	9.64×10^{-4}	170	970	355	722
$[(C_6H_5)_4As]_2Re_2(NCS)_8$	134	6.14×10^{-4}	...	...	...	...
$[(C_6H_5)_3AsCH_3]_2Re_2(NCS)_8$	136	9.02×10^{-4}	...	...	...	...
$[(C_4H_9)_4N]_2[Re_2(NCS)_8(P(C_6H_5)_3)_2]$	113	2.20×10^{-3}	140	577	333	659
$[(C_4H_9)_4N]_3[Re_2(NCS)_{10}(CO)_2]$	234	6.80×10^{-3}	210	1320	384	1502[c]

[a] In $ohm^{-1}\ cm^2$. [b] Equivalent concentration. [c] Theory for 3:1 electrolyte.

A very interesting and novel reaction occurred when the $Re_2Cl_8^{2-}$ ion was treated with sodium thiocyanate in acetone. As mentioned before, the use of this solvent results in some oxidation to Re(IV). Dark red and green crystals were isolated from the reaction mixture and while the former product was shown to be $[(C_4H_9)_4N]_2Re(NCS)_6$, the analysis of the latter corresponded closely to the formula $[(C_4H_9)_4N]_3[Re_2(NCS)_{10}(CO)_2]$. This green substance could be recrystallized in the form of glistening green needles by adding diethyl ether to an acetonitrile solution of the complex.

The above complexes were also isolated as their tetraphenylarsonium salts by cation exchange in suitable solvents.

Only a few thiocyanate complexes of rhenium have previously been reported in the literature. These include the rhenium(V) complexes $ReO(SCN)_3L_2$, where L = $(C_2H_5)_2(C_6H_5)P$ or $(C_6H_5)_3P$,[11] the alleged rhenium(IV) complex $ReO(SCN)_2(py)_3$,[12] the compound $K_3[ReO_2(SCN)_4]$,[13] the rhenium(III) carboxylates $Re_2(O_2CR)_4(SCN)_2$,[3,14] and the trinuclear $[Re_3Cl_3(CNS)_{6+n}]^{n-}$ ions.[15] The new complexes described here suggest that the possible range of thiocyanate complexes of rhenium may be almost as large and varied as that of their chloride and bromide analogs, particularly in their structural variations.

Several properties of these new complexes are listed in Tables I–IV and these will now be discussed in detail.

Conductance Studies.—Equivalent conductances of acetonitrile solutions of the complexes are shown in Table I. Feltham and Hayter[16] have recently emphasized the need to carry out such measurements over a concentration range, since molar conductances measured at one concentration do not distinguish between [R][ML], a 1:1 electrolyte, and $[R]_2[M_2L_2]$, a 2:1 electrolyte. According to the Onsager limiting law

$$\Lambda_0 - \Lambda_e = (a\Lambda_0 + b)\sqrt{c} = A\sqrt{c}$$

Thus, Λ_0 can be determined by plotting Λ_e as a function of $\sqrt{c}$, where c is the equivalent concentration. Such plots were made for several of the compounds listed in Table I and the experimentally determined values of Λ_0 are listed. The slopes, A, were also determined and compared with the theoretical values calculated for different types of electrolytes.[17] With the exception of $[(C_4H_9)_4N]_3[Re_2(NCS)_{10}(CO)_2]$, the complexes behave as 2:1 electrolytes in acetonitrile. This is, of course, in keeping with the known structure of the octachlorodirhenate(III) anion.[5]

Davison, *et al.*,[17] have recently measured the conductances of several 1:1 and 1:2 electrolytes in acetonitrile. In Figure 1 their results are compared with those in the present work where plots of $\Lambda_0 - \Lambda_e$ against $\sqrt{c}$ clearly distinguish between 1:1, 1:2, and 1:3 electrolytes.

Below concentrations of $\sim 4 \times 10^{-4}$ g-equiv/l., both $Re_2Cl_8^{2-}$ and $Re_2(NCS)_8^{2-}$ give nonlinear $(\Lambda_0 - \Lambda_e)$ *vs.* $\sqrt{c}$ plots. We attribute this to solvolysis reactions of the type

$$Re_2X_8^{2-} + nCH_3CN \rightleftharpoons [Re_2X_{8-n}(CH_3CN)_n]^{(2-n)-} + nX^-$$

---

[11] J. Chatt and G. A. Rowe, *J. Chem. Soc.*, 4010 (1962).

[12] L. I. Evteev, *Zh. Neorgan. Khim.*, **10**, 2573 (1965).

[13] D. I. Ryabchikov, V. A. Zarinskii, and I. I. Nazarenko, *ibid.*, **6**, 641 (1961).

[14] F. Taha and G. Wilkinson, *J. Chem. Soc.*, 5406 (1963).

[15] B. H. Robinson and J. E. Fergusson, *ibid.*, 5683 (1964).

[16] R. D. Feltham and R. G. Hayter, *ibid.*, 4587 (1964).

[17] A. Davison, D. V. Howe, and E. T. Shawl, *Inorg. Chem.*, **6**, 458 (1967). This paper outlines the method used for such calculations.

TABLE II

INFRARED SPECTRA (4000–400 CM^{-1})[a]

Complex	Medium[b]	ν(C–N)	ν(C–S)	2 × δ (N–C–S)	δ(N–C–S)
$[(C_4H_9)_4N]_2Re(NCS)_6$	A	~2050 sh	*c*	*c*	485 m
$[(C_4H_9)_4N]_2Re_2(NCS)_8$	A	2050 vs, br	*c*	*c*	475 m
	B	2050 vs	. . .	. . .	. . .
$[(C_6H_5)_4As]_2Re(NCS)_6$	A	2030 vs, 2048 sh, 2060 sh	865 w	~950 w, br?	484 m
$[(C_6H_5)_4As]_2Re_2(NCS)_8$	A	2025 vs, br	~875 vw?	*c*	*c*
$[(C_6H_5)_3AsCH_3]_2Re_2(NCS)_8$	A	2025 vs, br	*c*	*c*	*c*
$[(C_4H_9)_4N]_2Re_2(NCS)_8(P(C_6H_5)_3)_2]$	A	2120 m, 2070 vs, 2045 vs, 2025 vs	842 mw?	*c*	*c*
	B, C	2065 vs, 2040 vs	. . .	. . .	. . .
$[(C_4H_9)_4N]_3[Re_2(NCS)_{10}(CO)_2]$	A	2075 vs, 2055 vs, 2038 vs	1920 vs,[d] 1889 s[d]	*c*	~480 mw, ~465 w
	C	2078 vs, 2050 vs	1920 vs,[d] 1880 m[d]	. . .	. . .
$[(C_6H_5)_4As]_3[Re_2(NCS)_{10}(CO)_2]$	A	2060 vs, 2040 vs	1910 s,[d] 1870 s[d]	*c*	*c*

[a] These assignments are based upon the results of K. N. Raymond and F. Basolo [*Inorg. Chem.*, **5**, 1632 (1966)] and W. R. McWhinnie [private communication to R. A. Walton (Oct 1966)]. [b] A = Nujol mull; B = acetonitrile; C = acetone. [c] Obscured by cation or ligand absorptions. [d] ν(C–O).

TABLE III

ELECTRONIC ABSORPTION SPECTRA

Complex	Medium[a]	Absorption maxima, cm^{-1} [b]
$[(C_4H_9)_4N]_2Re_2(NCS)_8$	A	9,200; ~18,200 sh; 20,400 br
	B	10,000 (1960); 15,200 (1280); ~19,200 (3800); 21,700 (15,900); 27,900 (23,500); 29,400 (21,600); 38,500 sh; 41,670 (51,610)
$[(C_6H_6)_4As]_2Re_2(NCS)_3$	A	9,500; 18,900; 21,300; 25,000
$[(C_6H_5)_3AsCH_3]_2Re_2(NCS)_8$	A	9,400; 19,100 sh; 21,700; 26,300
$[(C_4H_9)_4N]_2[Re_2(NCS)_8(P(C_6H_5)_3)_2]$	A	~11,000 sh?; 12,990; ~15,400 sh; 21,280 sh; 23,800
	B	13,510 (813); 15,870 (488); 23,800 (21,500); 39,220 (43,900); 43,480 (50,800)
$[(C_4H_9)_4N]_3[Re_2(NCS)_{10}(CO)_2]$	A	~10,810 sh; ~13,700; 17,090; ~20,400; 23,800
	B	7,600 (558); 14,930 (4250); ~21,050 sh; 23,810 (39,590); ~26,700 sh; ~37,000 sh; 43,370 (95,800)
$[(C_4H_9)_4N]_2Re(NCS)_6$	A	9,750; 10,870; 20,830; 24,390
	B	9,900 (4.0); 11,360 (5.3); 23,640 (56,200); 38,170 (62,000)
$[(C_6H_5)_4As]_2Re(NCS)_6$	A	9,524 sh; 10,810 sh; 20,000; 23,800

[a] A = diffuse reflectance; B = acetonitrile. [b] Molar extinction coefficients in parentheses.

TABLE IV

MAGNETIC PROPERTIES OF RHENIUM THIOCYANATE COMPLEXES OVER THE TEMPERATURE RANGE 300–77°K

$[(C_4H_9)_4N]_2Re(NCS)_6$														
T, °K	295	283	271	257	244	231	217	201	182	164	140	120	99	77
$\chi_g \times 10^6$	4.480	4.695	4.912	5.192	5.505	5.820	6.237	6.790	7.502	8.249	9.583	11.14	13.68	17.20
μ_{eff}	3.50	3.50	3.50	3.49	3.49	3.49	3.49	3.49	3.48	3.45	3.42	3.40	3.41	3.35
$[(C_6H_5)_4As]_2Re(NCS)_6$														
T, °K	299	289	272	258	245	231	218	201	182	165	145	123	98	77
$\chi_g \times 10^6$	3.150	3.270	3.485	3.695	3.895	4.175	4.385	4.760	5.350	5.815	6.595	7.775	9.540	11.89
μ_{eff}	3.38	3.37	3.37	3.36	3.36	3.36	3.34	3.33	3.34	3.30	3.28	3.26	3.21	3.16
$[(C_4H_9)_4N]_2[Re_2(NCS)_8(P(C_6H_5)_3)_2]$														
T, °K	299	287	272	255	245	234	212	198	182	166	152	127	104	83
$\chi_g \times 10^6$	6.836	6.836	6.898	6.940	6.987	7.001	7.081	7.147	7.207	7.264	7.307	7.401	7.491	7.603
μ_{eff}	5.73	5.62	5.49	5.33	5.24	5.13	4.91	4.76	4.58	4.39	4.17	3.88	3.53	3.17
$[(C_4H_9)_4N]_2[Re_2(NCS)_{10}(CO)_2]$														
T, °K	303	286	272	256	243	229	216	197	178	154	134	115	98	77
$\chi_g \times 10^6$	1.014	1.089	1.160	1.240	1.328	1.416	1.517	1.676	1.849	2.130	2.434	2.761	3.133	3.789
μ_{eff}	2.57	2.56	2.55	2.53	2.52	2.50	2.49	2.47	2.44	2.40	2.36	2.30	2.24	2.16

leading to an increase in conductance of the solutions at these low concentrations.

As previously discussed,[16] a solvent which is suitable for conductance measurements should be unreactive and have a high dielectric constant and a low viscosity. It may be noted that from the latter two criteria, acetonitrile is a more suitable solvent than either nitromethane or nitrobenzene.[18]

Infrared Spectra.—In the infrared spectra of the complex anions $Re(NCS)_6^{2-}$ and $Re_2(NCS)_8^{2-}$, the thiocyanate C–N stretching frequency was observed as a very strong band between 2070 and 2025 cm^{-1} (Table II). Its position and rather broad nature are

---

(18) Acetonitrile, nitromethane, and nitrobenzene have the following dielectric constants (ϵ) and viscosities (η at 15°).[19] CH_3CN: $\epsilon = 37.5$, $\eta = 0.375$; CH_3NO_2: $\epsilon = 35.87$, $\eta = 0.694$; $C_6H_5NO_2$: ϵ, 34.82, $\eta = 2.165$.

(19) See "Techniques of Organic Chemistry," Vol. VII, "Organic Solvents," A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., pp 219, 223, 224.

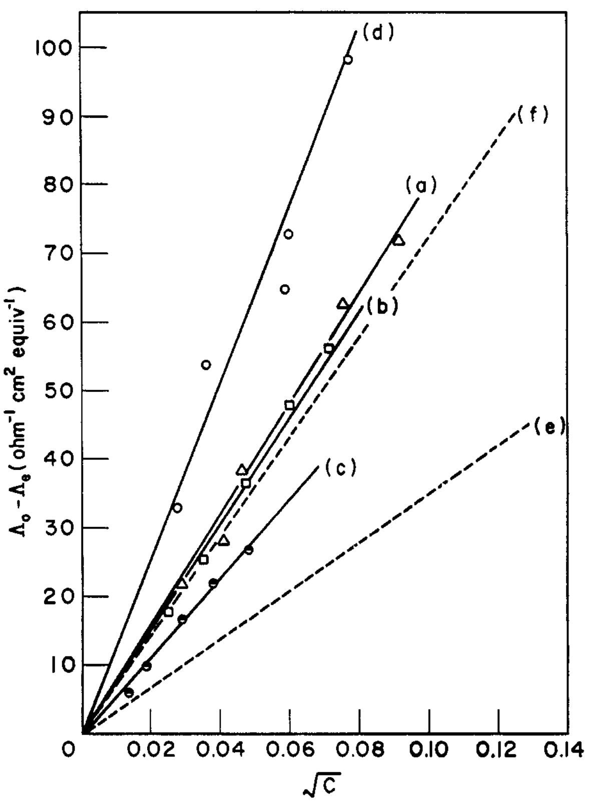


Figure 1.—The equivalent conductances of rhenium–thiocyanate complexes in acetonitrile: (a) $[(C_4H_9)_4]_2Re_2Cl_8$, (b) $[(C_4H_9)_4N]_2Re_2(NCS)_8$, (c) $[(C_4H_9)_4N]_2[Re_2(NCS)_8(P(C_6H_5)_3)_2]$, (d) $[(C_4H_9)_4N]_3[Re_2(NCS)_{10}(CO)_2]$, (e) typical 1:1 electrolyte (see ref 17), (f) typical 1:2 electrolyte (see ref 17).

characteristic[20,21] of N-bonded thiocyanate. In several instances the N–C–S bending mode was observed, and its position (490–460 cm^{-1}) afforded further confirmation that the thiocyanate groups were N-bonded.[20] In S-bonded complexes this vibration occurs between 440 and 410 cm^{-1} and is split into several components.[20] Unfortunately the C–S stretching vibration was not observed with certainty in any of the complexes listed in Table II because of the presence of cation absorptions in the appropriate region (900–700 cm^{-1}) of the spectrum.

We attribute any splitting of the C–N stretching frequency in complexes containing the $Re(NCS)_6^{2-}$ and $Re_2(NCS)_8^{2-}$ ions to solid-state effects.

The salts $[(C_4H_9)_4N]_2[Re_2(NCS)_8(P(C_6H_5)_3)_2]$ and $[(C_4H_9)_4N]_3[Re_2(NCS)_{10}(CO)_2]$ have more complex spectra in the C–N stretching region than the other complexes discussed above (see Table II and Figure 2). Although this complexity was reduced when measurements were carried out in solution (acetonitrile or acetone), a splitting of bands in the latter media points to the nonequivalence of the thiocyanate groups even in solution. It should be noted that although the C–N stretching vibration of a sulfur-bonded thiocyanate group usually occurs at a higher frequency than in its nitrogen bonded analog,[20] the presence of nonbridging nitrogen- *and* sulfur-bonded species in the same molecule cannot be ruled out.[22]

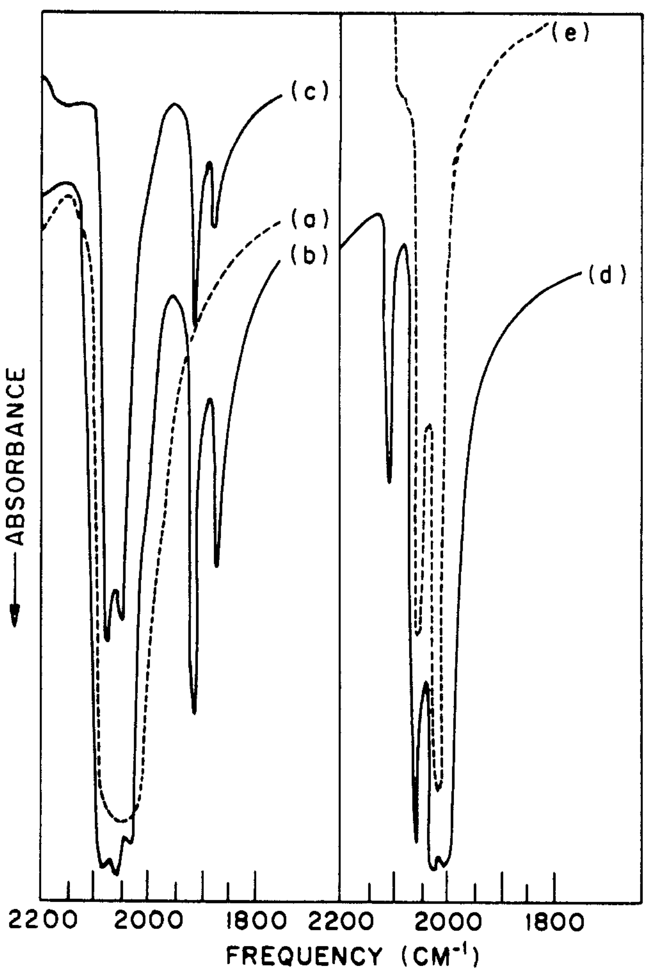
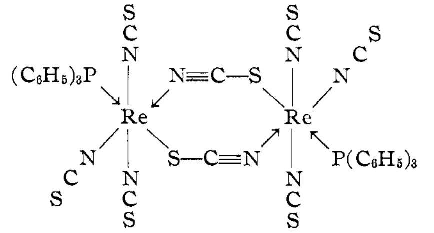


Figure 2.—Infrared spectra (2200–1800 cm^{-1}) of $[(C_4H_9)_4N]_2Re_2(NCS)_8$ ((a) Nujol mull); $[(C_4H_9)_4N]_3[Re_2(NCS)_{10}(CO)_2]$ ((b) Nujol mull, (c) acetonitrile); $[(C_4H_9)_4N]_2[Re_2(NCS)_8(P(C_6H_5)_3)_2]$ ((d) Nujol mull, (e) acetonitrile).

Although the electronic absorption spectrum of $[(C_4H_9)_4N]_2[Re_2(NCS)_8(P(C_6H_5)_3)_2]$ is consistent with a structure based upon the $Re_2X_8^{2-}$ dimer, with the vacant terminal positions (along the line of the Re–Re bond) occupied by triphenylphosphine molecules, the magnetic properties of this molecule (see later) rule out such a structure. The complexity of the infrared spectrum in the C–N stretching vibration region would seem to confirm this, and we are tempted to suggest that this molecule may contain a dimeric anion (see conductivity data) with a structure similar to I, in



I

---

[20] A. Sabatini and I. Bertini, *Inorg. Chem.*, **4**, 959 (1965), and earlier references therein.

[21] A. Sabatini and I. Bertini, *ibid.*, **4**, 1665 (1965).

[22] Several thiocyanate complexes of copper(II) have recently been considered to contain nitrogen- and sulfur-bonded thiocyanate groups.[23,24]

[23] K. N. Raymond and F. Basolo, *Inorg. Chem.*, **5**, 1632 (1966).

[24] W. R. McWhinnie, private communication to R. A. Walton (Oct., 1966).

which bridging and nitrogen-bonded thiocyanate groups are present.[25] The bridging C–N stretching frequency could then be assigned to the band at 2120 cm^{-1}. However, some sort of reaction or isomerization occurs in solution since the 2120 cm^{-1} band disappears while two bands of equal intensity are observed at 2065 and 2040 cm^{-1}. Further speculation about the structure of this compound does not appear justified at present.

The structure of crystalline $[(C_4H_9)_4N]_3[Re_2(NCS)_{10}(CO)_2]$ is unknown although nonequivalent SCN groups are present in this molecule. The two strong bands at 1920 and 1880 cm^{-1} (Figure 2 (a)) are assigned to C–O stretching vibrations. The presence of carbonyl groups in this molecule is based upon analytical data and infrared spectral evidence. This is not unreasonable since we can see no plausible alternative explanation for two strong bands in the 2000–1800 cm^{-1} region save for the possibility that some of the thiocyanate groups in the molecule are bonded through the π-electron system of the C≡N group. Such bonding seems unlikely although there are two recent reports[26,27] of complexes believed, but not proved, to contain π-bonded C≡N groups.

Electronic Absorption Spectra.—From the electronic absorption spectra of the $Re_2X_8^{2-}$ ions (see Figure 3 and ref 4) it can be seen that the energy of the first electronic transition increases in the order Cl > Br >> NCS. The solution and diffuse reflectance spectra of the $Re_2(NCS)_8^{2-}$ ion are similar (Table III) and may be assigned using the energy level diagram previously described.[6] The ground-state configuration is taken as $\sigma^2\pi^4\delta^2$ and the 9500 cm^{-1} band is assigned to the $\delta \rightarrow \sigma_n$ transition. This band has an oscillator strength of ~0.02, which is consistent with the above assignment.[6] Since the allowed $\delta \rightarrow \delta^*$ transition should probably correspond to the next absorption band, the absorption at ~21,000 cm^{-1} may be assigned to this transition. Its oscillator strength (~0.44) and energy (*i.e.*, $\delta \rightarrow \delta^* \sim 2(\delta \rightarrow \sigma_n)$)[6] are consistent with such an assignment.

The energy of the two-electron δ bond is then estimated to be ~20,000 cm^{-1}, or about 2.5 ev. Although this is less than the bond energy (3.7 ev) in the analogous chloride complex,[6] it would still be quite sufficient to stabilize the eclipsed rotational configuration. This is further confirmed by the diamagnetism of these complexes (see later).

The solution spectrum of $[(C_4H_9)_4N]_2Re_2(NCS)_8$ in acetonitrile did show one band not observed in its diffuse reflectance spectrum. This occurs at 15,200 cm^{-1} and its low oscillator strength (~0.02) suggests that it may be due to the $\delta \rightarrow \sigma_n$ transition of a species such as $[Re_2(NCS)_8(CH_3CN)_2]^{2-}$, with axially bonded solvent molecules. The effect of axial coordination upon the electronic spectra of the $Re_2X_8^{2-}$ ions has been dealt with elsewhere.[3,4]

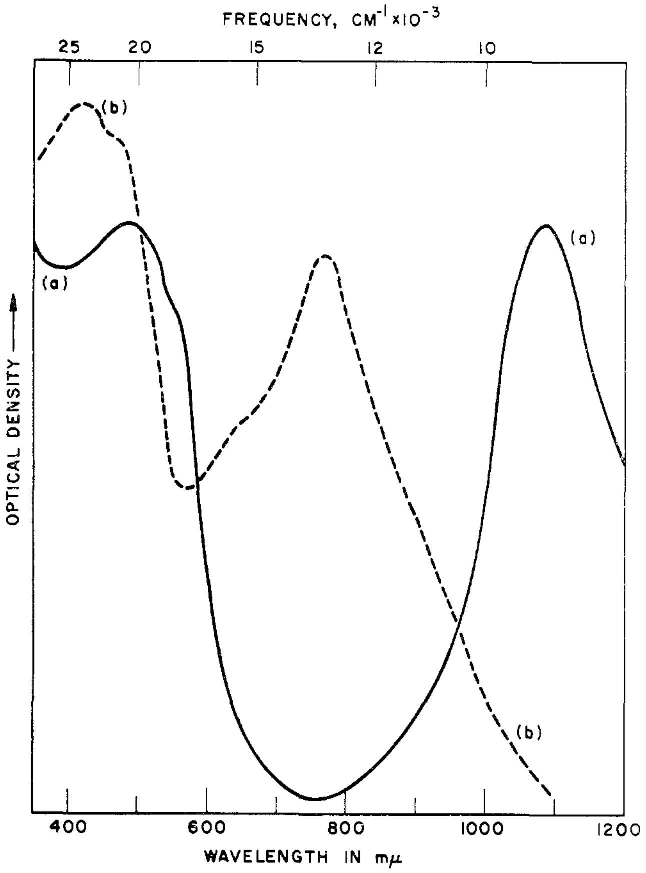


Figure 3.—Diffuse reflectance spectra (1200–350 mμ) of (a) $[(C_4H_9)_4N]_2Re_2(NCS)_8$; (b) $[(C_4H_9)_4N]_2[Re_2(NCS)_8(P(C_6H_5)_3)_2]$.

The spectrum of the $Re(NCS)_6^{2-}$ ion may readily be compared with that of the hexachlororhenate(IV) anion.[28] The two low-energy bands (Table III) are likely to be spin-forbidden quartet–doublet transitions, $^4A_2 \rightarrow {}^2T_1$, ^2E, typical of octahedral rhenium(IV). Five spin-forbidden transitions are predicted[29] for this species and while one is probably outside the range of our measurements, the remaining two are presumably obscured by the intense electron-transfer band at 20–23,000 cm^{-1}.

As shown in Figure 4, several bands of $[(C_4H_9)_4N]_3[Re_2(NCS)_{10}(CO)_2]$ are also typical of $Re(NCS)_6^{2-}$, so that the former could be formulated as $\{[(C_4H_9)_4N]_2Re(NCS)_6 \cdot [(C_4H_9)_4N][Re(NCS)_4(CO)_2]\}$. The previous isolation of salts with the general formula $M_2Re_4Br_{15}$, which were shown[30] to be the equimolar crystalline mixtures $[Re_3Br_9 \cdot M_2ReBr_6]$, does set a precedent for such a formulation. However, the magnetic properties of this complex cannot readily be interpreted in terms of this structure.

Unfortunately the spectrum of $[(C_4H_9)_4N]_2[Re_2(NCS)_8(P(C_6H_5)_3)_2]$ (Figure 3) does not permit us to assign a structure unambiguously to this molecule.

Magnetic Properties.—The diamagnetism of the octaisothiocyanatodirhenate(III) anions[31] is convincing

---

(25) J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1416 (1961); see this paper for a discussion of bridging SCN groups.

(26) M. F. Farona and N. J. Brener, *J. Am. Chem. Soc.*, **88**, 3735 (1966).

(27) R. B. King and M. B. Bisnette, *Inorg. Chem.*, **5**, 306 (1966).

(28) R. A. Bailey and J. A. McIntyre, *ibid.*, **5**, 964 (1966), and references therein.

(29) J. C. Eisenstein, *J. Chem. Phys.*, **34**, 1628 (1961).

(30) F. A. Cotton and S. J. Lippard, *Inorg. Chem.*, **4**, 59 (1965).

(31) For $[(C_4H_9)_4N]_2Re_2(NCS)_8$, $\chi_g = -0.9330 \times 10^{-6}$ and $\chi'_m = -569 \times 10^{-6}$ cgsu; for $[(C_6H_5)_4As]_2Re_2(NCS)_8$, $\chi_g = -0.7892 \times 10^{-6}$ and $\chi'_m = -570 \times 10^{-6}$ cgsu.

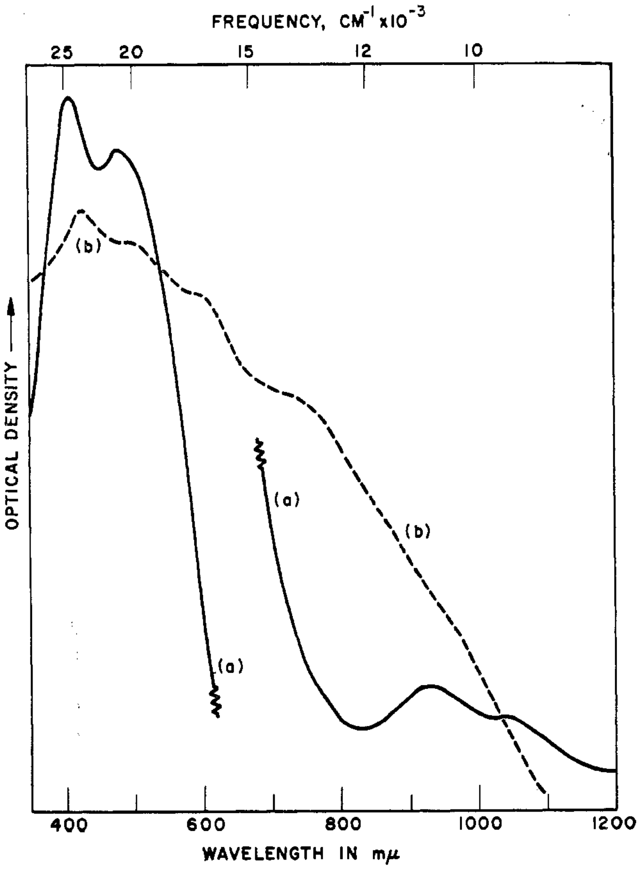


Figure 4.—Diffuse reflectance spectra (1200–350 mμ) of (a) $[(C_4H_9)_4N]_2Re(NCS)_6$; (b) $[(C_4H_9)_4N]_3[Re_2(NCS)_{10}(CO)_2]$.

confirmatory evidence for their dinuclear *eclipsed* configuration.

The magnetic properties of three complexes of the type $M^I_2[Re(NCS)_6]$, where M = K, Ag, or Tl, have previously[32] been investigated over the temperature range 400–77°K. Their magnetic moments vary more rapidly with temperature than do those of the corresponding hexahalorhenates(IV),[33] and the complexes have Curie–Weiss constants ranging from 212 to 41°; intermolecular magnetic exchange must be appreciable in these systems. These magnetic interactions vary with cation, and in the $[(C_4H_9)_4N]^+$ and $[(C_6H_5)_4As]^+$ salts is considerably reduced (θ = 10 and 16°, respectively). This is evidenced by an increase in μ_{eff} and its reduced variation with temperature.

The magnetic behavior of most magnetically dilute rhenium(III) complexes is not well understood,[34] and in many cases the expected behavior is difficult to predict. In the previous spectral section, we considered the possibility that $[(C_4H_9)_4]_3[Re_2(NCS)_{10}(CO)_2]$ could be formulated as $\{[(C_4H_9)_4N]_2Re(NCS)_6 \cdot [(C_4H_9)_4N][Re(NCS)_4(CO)_2]\}$, but the magnetic properties of this complex would appear to rule out such a formulation. It evidently does not behave as a simple mixture of these two components since the magnetic susceptibility of $[(C_4H_9)_4N]_2Re(NCS)_6$ (*i.e.*, one of the components) is much greater at all temperatures between 300 and 77°K than that of $[(C_4H_9)_4N]_3[Re_2(NCS)_{10}(CO)_2]$ (see Table IV). The Curie–Weiss law is obeyed, with θ = 50°, so that some magnetic exchange may be present in this system. Even allowing for the presumable diamagnetism of the salt $[(C_4H_9)_4N][Re(NCS)_4(CO)_2]$,[35] it would be difficult to explain the magnetic properties of the proposed rhenium(IV)–rhenium(III) mixture although the presence of rhenium species in still other oxidation states cannot be ruled out. The magnetic behavior of the triphenylphosphine compound, $[(C_4H_9)_4N]_2[Re_2(NCS)_8(P(C_6H_5)_3)_2]$, is remarkable. First, its paramagnetism rules out a structure based upon the $Re_2X_8^{2-}$ dimer (eclipsed or staggered). Second, the room-temperature magnetic moment (4.1 BM *per rhenium*) is unusually high in view of the general tendency of complexes of the heavy transition metals to have spin-paired configurations. One possible explanation might be the presence of *spin-free* rhenium(III).

Simple theory requires that for a spin-free d^4 configuration, the magnetic moment should lie below the spin-only value (4.90 BM) by the factor $(1 - 2\lambda/10Dq)$ and be independent of temperature. For rhenium(III) we might expect $\mu_{eff} \sim 4.6$ BM, but the operation of the intermediate coupling scheme makes this uncertain. From Table IV it is clear that μ_{eff} is not independent of temperature and that the Curie–Weiss law is not obeyed. This may be due to the presence of considerable magnetic interaction in this system. This complicated behavior is not necessarily inconsistent with the presence of spin-free rhenium(III).

Acknowledgments.—We thank Dr. F. E. Mabbs and Mr. E. T. Shawl for helpful discussions.

---

(32) G. E. Boyd, C. M. Nelson, and W. T. Smith, *J. Am. Chem. Soc.*, **76**, 348 (1954).

(33) B. N. Figgis, J. Lewis, and F. E. Mabbs, *J. Chem. Soc.*, 3138 (1961).

(34) B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, **6**, 151 (1964).

(35) Although several octahedral rhenium(III) species are paramagnetic, many other complexes are reported to be diamagnetic.[34] This has been attributed to the presence of a large asymmetric field in the latter compounds.