the following equation, to which the actual mmole quantities of reactants and products are appended.

$$\underset{0.447}{Sb_2(CH_3)_4} + \underset{0.885}{2HCl} \longrightarrow \underset{0.892}{2(CH_3)_2SbCl} + \underset{0.414}{H_2}$$

The only assumption here was the identity of the colorless liquid $(CH_3)_2SbCl$; its mercury-reactivity made a mol. wt. determination difficult.

Two samples of the bistibine were fully analyzed by carrying on the HCl reaction for 15 hr. at 250°. The HCl requirement was determined by measuring the initial amount and the remainder. The methane–hydrogen mixture was analyzed by CuO-combustion. The $SbCl_3$ was determined by oxidimetric titration, using standard $KBrO_3$ solution. The results are summarized in Table V, listing all products in mmoles.

TABLE V

ANALYSIS OF $Sb_2(CH_3)_4$

Sample (mg.)	HCl used Found	HCl used Calcd.	H_2 Found	H_2 Calcd.	CH_4 Found	CH_4 Calcd.	$SbCl_3$ Found	$SbCl_3$ Calcd.
182.0	3.598	3.600	0.598	0.600	2.390	2.400	1.201	1.200
242.2	4.786	4.788	0.795	0.798	3.174	3.192	1.595	1.596

This very clean demonstration of the reaction $Sb_2(CH_3)_4 + 6HCl \rightarrow H_2 + 6CH_4 + 2SbCl_3$ dispels any possible doubt of the identity of the bistibine, the formation of which was the most direct evidence of the identity of dimethylstibine.

No such cleavage of $Sb_2(CH_3)_4$ occurred when H_2S was used instead of HCl: there was no reaction during 18 hr. at 100°.

Cleavage by Boron Trichloride.—The fairly clean low-temperature cleavage of $Sb_2(CH_3)_4$ by HCl encouraged the hope of making $(CH_3)_2SbBCl_2$ by the action of BCl_3. However, two experiments at room temperature gave only an adduct empirically formulated as $Sb_2(CH_3)_4 \cdot 0.83BCl_3$. One sample was heated *in vacuo* to 100°, giving a 10% yield of $(CH_3)_2BCl$ (proved by hydrolytic analysis), a black solid, a pale yellow oil and a white sublimate. After destruction of the oil by shaking with mercury, the white sublimate was analyzed, showing two B per Cl. The other sample of the adduct was heated only to 60°, giving a little $(CH_3)_2BCl$, the black solid, and the slightly yellow oil without the sublimate. A chloride analysis on the oil gave 18.61%; calcd. for $(CH_3)_2SbCl$, 18.95%. Thus it seemed that the desired cleavage occurred, but the desired $(CH_3)_2SbBCl_2$ appeared only in the form of its decomposition products, some of which were not intelligible.

In a third experiment on this cleavage the boron trichloride was employed in excess and the mixture was heated for 42 hr. at 60°. In this case the main effect was a methylation of the boron trichloride: 4.696 mmoles of BCl_3, reacting with 3.810 mmoles of $Sb_2(CH_3)_4$, gave 4.318 mmoles of $(CH_3)_2BCl$, representing 95% of the unrecovered BCl_3 (4.541 mmole) and 57% of the methyl groups. Neither the oil nor the sublimate appeared; hence the black solid could contain 0.31 mmole of $SbCl_3$ and a material empirically formulated as $Sb(CH_3)_{1.46}$.

Thermal Decomposition.—A 0.433 mmole sample of $Sb_2(CH_3)_4$ was made by the nearly quantitative conversion of 0.883 mmole of $(CH_3)_2SbH$, and withstood one week of heating in a sealed tube at 100°. Incipient decomposition was observed after 17 hr. at 160°: a trace of metallic mirror had appeared. After 20 hr. at 200°, the mirror had increased and the yellow liquid had become colorless. The yield of $(CH_3)_3Sb$ (mol. wt. 166.8; v.t. 31 mm. at 0°) was 0.571 mmole. The metal weighed 32 mg. (0.263 mg. atom Sb). These results cleanly indicate the equation $3Sb_2(CH_3)_4 \rightarrow 2Sb + 4(CH_3)_3Sb$, which requires 0.289 mg. atom of Sb and 0.578 mmole of $(CH_3)_3Sb$.

Grease-catalyzed Decomposition.—The bistibine proved to be unstable when stored at room temperature with the vapor in contact with a stopcock lubricated with Apiezon T grease. The yellow liquid slowly formed a white solid while the remaining liquid turned bright red. After two days the liquid had turned colorless and the solid was black. The yield of $(CH_3)_3Sb$ now was 0.513 mmole per mole of the original bistibine. Hence the non-volatile black solid had the empirical composition $Sb(CH_3)_{1.65}$.

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[CONTRIBUTION FROM VENABLE HALL OF CHEMISTRY, UNIVERSITY OF NORTH CAROLINA]

Chemistry of Rhenium and Technetium. II. Magnetic Susceptibilities of $ReCl_5$, $ReCl_3$, $TcCl_4$ and $MoCl_5$

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The magnetic susceptibilities of $ReCl_5$, $ReCl_3$, $TcCl_4$ and $MoCl_5$ have been measured by the Gouy technique from liquid nitrogen at room temperature. The pentachlorides follow the Curie–Weiss relationship with these constants: $ReCl_5$, $\mu_{eff} = 2.21$, $\Delta = 164°$; $MoCl_5$, $\mu_{eff} = 1.52$, $\Delta = -23°$. The $1/\chi$ *vs.* T plots for $ReCl_3$ and $TcCl_4$ are not straight lines. Exchange interaction between the magnetic moments probably is significant for all of these compounds.

Introduction

Magnetic susceptibilities have proven to be useful in inorganic chemistry for interpretations of the electronic structures of compounds, especially those of the first transition series. Not so much is known about the theoretical magnetic behavior of compounds of the heavier transition elements, partly because of a lack of data on a sufficiently wide variety of compounds. We have measured the susceptibilities of several chlorides in order to investigate the magnetic behavior of compounds in this region of the periodic table.

Experimental

The methods described previously[2] were used to prepare $ReCl_5$, $TcCl_4$ and $MoCl_5$. Rhenium trichloride was prepared by (1) the thermal decomposition of $ReCl_5$ at 250° and (2) the reaction between $ReCl_5$ and Re at 450° in a sealed tube. Based on the conversion of $ReCl_5$, (1) gave yields around 50% whereas (2) yields around 85%. After purification by vacuum sublimation at 450°, the products of both reactions were the same. Analysis of several different preparations by essentially the same procedure used previously for $ReCl_5$[2] gave these average results with their standard deviations

% Re (theory 63.66)	% Cl (theory 36.34)	Cl/Re
63.66 ± 0.59	36.25 ± 0.28	3.00 ± 0.04

The compounds were loaded into calibrated Pyrex tubes in the dry box and weighed. The stoppered tubes were sealed off immediately after removal from the dry box.

The magnetic susceptibility measurements were made by the Gouy method in fields of up to 5000 oersted in an apparatus previously described.[3] None of the compounds had a field dependent susceptibility within experimental error. The reproducibility of the results on a single sample

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[1] Bell Telephone Laboratories, Inc., Murray Hill, New Jersey.

[2] K. Knox, S. Y. Tyree, Jr., *et al.*, THIS JOURNAL, **79**, 3358 (1957).

[3] C. E. Coffey, Ph.D. Thesis, University of North Carolina, Chapel Hill, North Carolina, 1956.

was 1% or better. The main source of error, however, lies in the purity of the compounds. An idea of the accuracy of the measurements may be derived from the results on three different preparations of $MoCl_5$, which had a spread of about 4%. Thus, the accuracy in χ is probably a few per cent.

Results and Discussion

The corrected molar magnetic susceptibilities of $ReCl_5$, $ReCl_3$, $TcCl_4$ and $MoCl_5$ are given in Table I. The diamagnetic corrections used are those of Klemm, recommended by Selwood.[3a] In addition, these various values were interpolated from those given in ref. 4: Tc(IV), 18×10^{-6}; Re(V), 21×10^{-6}. Along with each value of χ is given the standard deviation of many measurements on the same sample. For $MoCl_5$, the susceptibilities of three different samples, I, II and III, are given separately.

TABLE I

CORRECTED MOLAR MAGNETIC SUSCEPTIBILITIES OF $ReCl_5$, ReCl, $TcCl_4$ AND $MoCl_5$

Compound	T, °K.		$\chi_M \times 10^6$	$\chi_M \times 10^6$ (lit.)
$ReCl_5$	301		1315 ± 4	1225(293°K.)[4]
	253		1455 ± 3	
	196		1697 ± 4	1485(195°K.)[4]
	150		1944 ± 23	
	79		2664 ± 8	1925(90°K.)[4]
$ReCl_3$	305		404 ± 1	75(293°K.)[4]
	256		420 ± 1	
	195		449 ± 1	
	145		482 ± 1	
	78		552 ± 2	
$TcCl_4$	306		4939 ± 32	
	253		6275 ± 77	
	195		8538 ± 15	
	151		11,175 ± 82	
	78		17,348 ± 435	
$MoCl_5$	305	I	1019 ± 6	
	305	II	1077 ± 4	860(281°K.),[5] 965(293°K.),[6] 1090(289°K.)[7]
	305	III	982 ± 4	
	196	I	1640 ± 5	
	196	II	1739 ± 6	1260(198°K.),[5] 1690 195°K.)[6]
	196	III	1590 ± 3	
	78	I	5558 ± 14	
	78	II	5663 ± 26	3600(90°K.),[5] 4460 (90°K.)[6]
	78	III	4755 ± 9	

The reciprocals of the susceptibilities given in Table I are plotted *vs.* absolute temperature in Fig. 1. It is seen that $ReCl_5$ obeys the Curie–Weiss law down to a temperature slightly below 150°K. and then $1/\chi_M$ begins to drop below the Curie–Weiss value, χ_M becoming larger than expected. The deviation here is small and just outside the experimental error. Using only the first 4 points, with $\mu_{\text{eff}} = 2.83\sqrt{\chi(T + \Delta)}$, an effective magnetic moment of 2.21 ± 0.002 Bohr magnetons is calculated for $ReCl_5$ with a Weiss constant of 164 ± 5° (the standard deviations here represent the σ's of the constants of the least-square straight line, given the σ's of the 4 points). These values are in fair agreement with those of Schüth and Klemm,[4] who reported $\mu_{\text{eff}} = 2.3$ with $\Delta = 265°$. The differences are probably due to different amounts of impurities introduced in handling the compound, which is very reactive. The moments agree quite well since they depend only on the slope, while the Δ's and actual values of the susceptibilities, compared in Table I, are not in such good agreement.

Each sample of $MoCl_5$ came very close to a straight line over the whole temperature range. The average values of μ_{eff} and Δ are 1.52 ± 0.03 and −23 ± 5° (the standard deviations here represent the σ's of the average μ and Δ of the 3 different samples). Again the values are in fair agreement with the previous results,[5–7] of which Klemm and Steinberg's are probably the best. Their data, treated by the Curie–Weiss relationship, give $\mu_{\text{eff}} = 1.5$ with $\Delta = -30°$. Molybdenum pentachloride would be an interesting substance to take down to lower temperatures because there it must become ferromagnetic or abruptly anti-ferromagnetic.

For $ReCl_3$, our values are not in agreement with previous work although the main features of the behavior are the same. The present measurements show a low paramagnetic susceptibility only slightly dependent on temperature. Schüth and Klemm[4] found a net diamagnetism, probably temperature independent, which becomes slightly paramagnetic when corrected for the diamagnetism of the atoms. Perakis[8] found a temperature-dependent paramagnetism for $ReBr_3$ and questioned Schüth and Klemm's values, but he does not give quantitative results. The $1/\chi_M$ *vs.* T plot is more markedly concave toward the temperature axis than for $ReCl_5$. The two high temperature points in a crude Curie–Weiss calculation give $\mu_{\text{eff}} = 2.04$, $\Delta = 985°$.

Technetium tetrachloride has a high molar susceptibility which is strongly temperature dependent. The $1/\chi$ *vs.* T plot is again curved but for this compound in the direction of the $1/\chi$ axis. The two high temperature points give $\mu_{\text{eff}} = 3.14$ with $\Delta = -57°$.

A comparison of these results with various calculations for the free metal ions is given in Table II. The fourth and fifth columns give the ground state and moment calculated on the assumption of (j.j) coupling between the electrons, which is the rule for heavier elements, and multiplet spacing wide with respect to kT. The g values are those of the free metal ion.[9] The last four columns assume (L,S) coupling and give the ground state and the moments for wide multiplets, narrow multiplets and narrow multiplets with the orbital contribution quenched, *i.e.*, spin only, in that order. As can be seen, none of these simple theories is wholly satisfactory. It is interesting that (j.j) coupling with wide-multiplet spacing is a close approximation for $ReCl_5$. Of course, there is no question of coupling for Mo(V) with only one electron, but the wide multiplet spacing value is much better than

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[3a] P. W. Selwood, "Magnetochemistry," 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1956, p. 78.

[4] W. Schüth and W. Klemm, *Z. anorg. allgem. Chem.*, **220**, 193 (1934).

[5] W. Sucksmith, *Phil. Mag.*, **14**, 1115 (1932).

[6] W. Klemm and H. Steinberg, *Z. anorg. allgem. Chem.*, **227**, 193 (1936).

[7] B. Th. Tjabbes, *Proc. Acad. Sci. Amsterdam*, **35**, 693 (1932).

[8] N. Perakis, *J. Phys. Radium*, **15**, 191 (1954).

[9] See *e.g.*, H. E. White, "Introduction to Atomic Spectra," McGraw-Hill Book Co., New York, N. Y., 1934, pp. 287, 442.

TABLE II

MAGNETIC MOMENTS OF METAL CHLORIDES

			(j,j) Coupling		(L,S) Coupling			
Compound	μ_{eff} (obsd.)	Electron structure	Ground state	$g\sqrt{J(J+1)}$	Ground state	$g\sqrt{J(J+1)}$	$\sqrt{4S(S+1)+L(L+1)}$	$\sqrt{4S(S+1)}$
$ReCl_5$	2.21	$5d^2$	$(3/2,3/2)_2$	1.96	$^3F_2$	1.63	4.47	2.83
$ReCl_3$	2.04	$5d^4$	$(1/2,1/2,1/2,1/2)_0$	0.00	$^1D_0$	0.00	5.48	4.90
$TcCl_4$	3.14	$4d^3$	$(3/2,3/2,3/2)^3/_2$	1.55	$^4F^3/_2$	0.77	5 20	3.87
$MoCl_5$	1.52	4d	$(3/2)^3/_2$	1.55	$^2D^3/_2$	1.55	3.00	1.73

even the spin only. The d^4 configuration of Re(III) makes it the most likely to have multiplet spacing comparable to kT,[10] which could account for the wide discrepancies in Table II. For $TcCl_4$, the spin-only value seems the best, although the interaction of the moments is probably complicating the picture.

Deviations from the free-ion moments can be attributed to at least two factors: (1) crystal-field splitting of the ground state, and (2) exchange interaction between the magnetic moments. Since the structures in the solid state of the compounds under discussion are not known, it is impossible to attempt a complete theoretical treatment. The theory of Kotani[11] has been applied with some success to compounds of the heavier transition elements.[12] It does not fit the present compounds, however. The molybdenum and technetium chlorides do not follow the theoretical behavior while the rhenium chlorides have the qualitative behavior of the theory only. For $ReCl_3$ the spin-orbit coupling constant varies between 9000 and 15.000, improbably high values, while for $ReCl_5$ it varies between 1000 and 1800, improbably low values. It is probable that these compounds do not meet the requirements of Kotani's theory: (1) cubic symmetry for the crystal field and (2) negligible exchange coupling between magnetic ions.

The magnetic behavior of these compounds is in line with the general trend for compounds of the heavier transition elements, which exhibit low moments compared to the first transition series. These chlorides are not magnetically dilute enough, however, for exchange-interaction to be negligible.

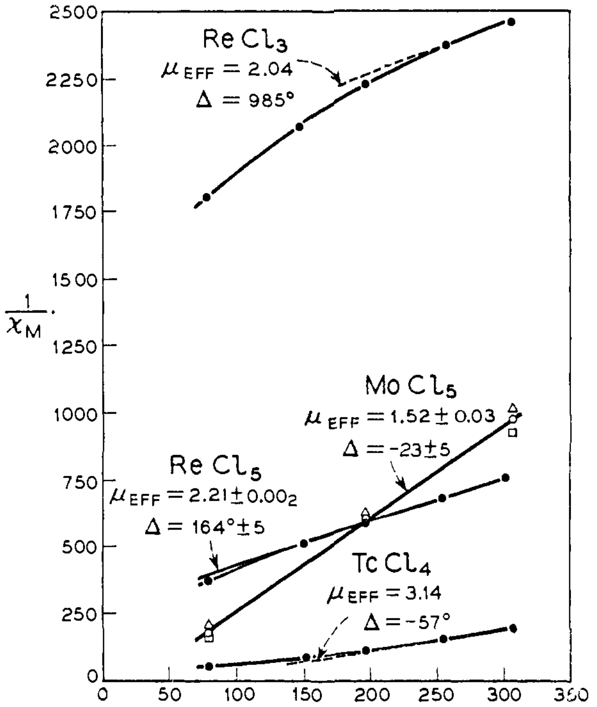

Fig. 1.—Reciprocal susceptibility *vs.* temperature.

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(10) J. H. Van Vleck. "The Theory of Electric and Magnetic Susceptibilities," Oxford, London, 1932, p. 312.

(11) M. Kotani, *J. Phys. Soc. Japan*, **4**, 293 (1949).

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