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Chemistry of Polynuclear Metal Halides. VI. Magnetic Susceptibility Studies of Some Niobium and Tantalum Halide Cluster Derivatives[1a]

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Magnetic susceptibilities have been measured for a series of niobium and tantalum halide compounds containing the $M_6X_{12}{}^{n+}$ (n = 2–4) cluster ions. Derivatives of the cluster anions $(M_6X_{12})Y_6{}^{3-}$ exhibited simple Curie behavior with magnetic moments somewhat less than the spin-only value of 1.73 BM for one unpaired electron. Some derivatives where the $M_6X_{12}{}^{3+}$ cluster units were interlinked through bridging halogen atoms exhibited Curie–Weiss behavior. This was interpreted as evidence for electron delocalization and exchange coupling between cluster units *via* the bridging atoms. However the compound $(Ta_6Cl_{12})Cl_3 \cdot 6H_2O$ also provided evidence for strong exchange coupling, even though the structure was not thought to involve such bridging atoms. Large temperature-independent paramagnetic susceptibilities (χ_{TIP}) were found for all compounds after special corrections for the diamagnetic atomic core and delocalized metal–metal bonding electron contributions were subtracted from the molar susceptibilities. For the $Nb_6X_{12}{}^{n+}$ and $Ta_6X_{12}{}^{n+}$ clusters, respectively, $10^6\chi_{TIP}$ values of *ca.* 600 and 500 cgsu were derived.

Introduction

Recent work[2-8] has shown that the niobium and tantalum halide cluster units $M_6X_{12}{}^{n+}$ can adopt the three oxidation states with n = 2–4. In the characterization of compounds or solutions containing these cluster units most of the reported studies have centered on the vibrational[9-11] or electronic spectra[12-16] and interpretations of the electronic structure.[12-14,17,18] On the other hand relatively little work has been published on the magnetic properties of these interesting species.

In one of the earliest reports on magnetic properties Krylov[19] reported the susceptibilities for $M_6Cl_{14} \cdot 7H_2O$ (M = Nb, Ta). Both compounds were reported to be paramagnetic with temperature-dependent moments. These data were interpreted as implying the existence of two paramagnetic and four diamagnetic metal atoms in the cluster unit. Likewise Robin and Kuebler[13] found $Nb_6Cl_{14} \cdot 7H_2O$ to be paramagnetic but reported that the molar susceptibility was independent of temperature. After making the diamagnetic electron core corrections they obtained an unusually large temperature-independent paramagnetic susceptibility (χ_{TIP}) of 850×10^{-6} cgsu for this compound.

Subsequent work by Spreckelmeyer[7] has shown that the previous results were in error and that the hydrated compounds $M_6X_{14} \cdot nH_2O$ (n = 8, 9) are diamagnetic, with negligible temperature dependence of the susceptibility when the compounds are carefully protected from oxidation during their preparation. Thus compounds containing the $M_6X_{12}{}^{2+}$ cluster units have been established as having a singlet ground state. Similarly compounds containing the 4+ cluster units have been found to be diamagnetic,[4,5] hence also having singlet ground states.

Compounds of the $M_6X_{12}{}^{3+}$ units, as might be expected, are paramagnetic and exhibit magnetic moments close to that expected for the spin-only value of one unpaired electron.[4-7] Corroborative results from a study of the epr spectra[5] demonstrated that the unpaired electron resides in an orbital singlet level which, because of the observed strong hyperfine interaction equally with all six metal atoms, is a molecular orbital centered primarily on the octahedron of metal atoms.

The purpose of the present work was to examine more closely the behavior of the magnetic properties as systematic changes of M, X, and the terminal ligands bound to the cluster units were affected. Also it was hoped that a clearer understanding of the large χ_{TIP} term in the molar susceptibility could be obtained.

Experimental Section

Preparation of Compounds.—Most of the compounds used in this investigation were samples specifically set aside for this study. The methods by which they were prepared and the analytical data for them are the same as those given in the reference for each compound. The exceptions are noted below.

$[(Nb_6Cl_{12})Cl_2(H_2O)_4] \cdot 4H_2O$.—This compound was prepared from $K_4Nb_6Cl_{18}$ as previously described.[20] *Anal.* Calcd: Nb,

(1) (a) Work performed in the Ames Laboratory of the U. S. Atomic Energy Commission. (b) A portion of the Ph.D. thesis of J. G. Converse, Department of Chemistry, Iowa State University, 1968.

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46.53; Cl, 41.44. Found: Nb, 46.53; Cl, 41.53; Cl:Nb, 2.34.

$(Nb_6F_{12})F_{6/2}$.—This was prepared by equilibration of resublimed NbF_5 with niobium metal at 800° in a sealed niobium tube. *Anal.* Calcd for Nb_6F_{15}: Nb, 33.83. Found: Nb, 33.79. An X-ray diffraction powder pattern of this material agreed with the structure published by Schäfer, *et al.*[21]

$(Ta_6Cl_{12})Cl_{6/2}$.—This compound, previously described by Schäfer,[22] was prepared by disproportionation of $TaCl_4$ in a sealed Vycor tube under a temperature gradient of 425–290° for 10 days, followed by heating under a gradient of 550–25° for 3 days. The product then was washed with methanol and dried *in vacuo*. *Anal.* Calcd for Ta_6Cl_{15}: Ta, 67.12. Found: Ta, 67.09.

$(Ta_6Br_{12})Br_{6/2}$.—An initial material prepared by the method of Schäfer, *et al.*,[23] was found to be contaminated with a small amount of $TaBr_{2.83}$.[24] Consequently the latter impurity was removed by heating the mixture *in vacuo* at 500° for a few hours. *Anal.* Calcd for Ta_6Br_{15}: Ta, 47.53; Br, 52.47. Found: Ta, 47.06; Br, 52.07.

$(Ta_6Cl_{12})Cl_2(OH)_2$.—This compound was obtained from $[(Ta_6Cl_{12})Cl_4(H_2O)_2]\cdot 7H_2O$[8] by maintaining the latter on the high-vacuum line for several days at room temperature. *Anal.* Calcd for $Ta_6Cl_{14}(OH)_2$: Ta, 67.18; Cl, 30.71. Found: Ta, 66.71; Cl, 30.60; Cl:Ta, 2.34. The spectrum of this compound in ethanol–HCl confirmed that the cluster remained in the 4+ oxidation state.[15,16]

$((C_2H_5)_4N)_2[(Nb_6Cl_{12})Cl_5(DMSO)]\cdot DMSO$.—A product of this composition was obtained from the reaction of $((C_2H_5)_4N)_3[(Nb_6Cl_{12})Cl_6]$ in dimethyl sulfoxide (DMSO) with 1 equiv of $AgClO_4$.[25] *Anal.* Calcd for $[(C_2H_5)_4N]_2[(Nb_6Cl_{12})Cl_5(C_2H_6SO)]\cdot C_2H_6SO$: Nb, 35.3; Cl, 38.2; C, 15.2; H, 3.32. Found: Nb, 35.3; Cl, 38.4; C, 15.4; H, 3.49. The spectrum in DMSO confirmed that the cluster remained in the 3+ oxidation state.

Diammoniumhexaaquonickel(II) Sulfate.—The compound $(NH_4)_2[Ni(H_2O)_6](SO_4)_2$ was prepared by mixing equimolar solutions of $NiSO_4$ and $(NH_4)_2SO_4$ in water. The solution was allowed to evaporate slowly at room temperature until large crystals were obtained. The crystals were washed with water, dried at room temperature, and ground to a fine powder. *Anal.* Calcd for $(NH_4)_2[Ni(H_2O)_6](SO_4)_2$: Ni, 14.86. Found: Ni, 14.94.

Magnetic Susceptibilities.—Susceptibility measurements were made using a Faraday balance constructed and calibrated in this laboratory. The method of Honda and Owen[26] for determination of field dependence was applied. In this case force measurements were made at five field settings between 6 and 12 kOe at each temperature. A procedure described by Donoghue[27] was used to establish the internal consistency of the instrument, and field measurements were performed to determine the profile and reproducibility of the magnetic field. The salt $(NH_4)_2[Ni(H_2O)_6](SO_4)_2$ was used for calibration of the magnetic field as recommended by Simmons,[28] who made an investigation of susceptibility standards. The sample container was machined from Teflon rod to form a thin-walled, cylindrical bucket with a threaded cap. One container was used for all samples and periodic measurements of its susceptibility were made to ensure that the container corrections were accurate.

Susceptibility values for the paramagnetic 3+ cluster compounds usually exhibited an uncertainty of less than 1% as determined from a least-squares fit of χ_g(apparent) *vs.* reciprocal field strength. The very weak forces encountered in measurements of the diamagnetic 2+ and 4+ cluster compounds yielded uncertainties of 1–10% in the susceptibilities. For the diamagnetic derivatives susceptibility measurements were made at liquid nitrogen and room temperatures and in some cases at several other temperatures. The reported values of χ_M were obtained as the intercept of χ_M *vs.* T^{-1} plots, where small, but significant slopes were found only in the cases of $((C_2H_5)_4N)_2[(Nb_6Cl_{12})Cl_6]$ and $Nb_6X_{14}\cdot 8H_2O$ (X = Cl, Br).

For the paramagnetic 3+ derivatives which exhibited Curie behavior the magnetic moments calculated at individual temperatures from the relation $\mu = 2.828[(\chi_M - \chi_{TIP} - \chi_D)T]^{1/2}$ were in agreement within 1–3% with the average moment calculated from the slope of χ_M *vs.* T^{-1} over the range 77–300°K. All data processing for the Honda–Owen and χ_M *vs.* T^{-1} least-squares calculations were performed with the IBM 360 computer. The uncertainties given for the values of μ and χ_{TIP} are standard deviations derived from these least-squares treatments.

Results and Discussion

Paramagnetic $M_6X_{12}^{3+}$ Derivatives.—Usually the diamagnetic component (χ_D) of the susceptibility for paramagnetic materials is small compared to the sum of the paramagnetic components, *viz.*, χ_T, the temperature-dependent term, and χ_{TIP}, the temperature-independent term. Thus diamagnetic corrections using additive constants introduce only small errors into the paramagnetic susceptibilities from which the magnetic moments are calculated. However, the diamagnetic term in the compounds discussed here may be unusually large because of the evident delocalization of electrons over the large, highly symmetrical cluster units. Furthermore the χ_T term is relatively small because only one unpaired electron resides in the paramagnetic 3+ cluster units. Hence it becomes important to obtain a more accurate estimate of the diamagnetic correction to be employed.

The atomic constants are based on the assumption that bonding is ionic (localized electrons) rather than covalent in most inorganic compounds. Hameka[29] has concluded that it is generally not possible to express molecular diamagnetism accurately as a sum of atomic contributions since interatomic terms are of major importance. As an example, Kaczmarczyk and Kolski[30] have shown that the diamagnetism in boron cluster compounds was significantly larger than the value calculated from atomic constants. Their conclusion was that the delocalized electrons in molecular orbitals of a cluster generate an enhanced diamagnetism in the same manner as the π electrons of organic aromatic compounds.

The $M_6X_{12}^{2+}$ ions according to the molecular orbital scheme of Cotton and Haas[18] would have 16 atomic electrons delocalized over the metal octahedron in eight molecular orbitals. Assuming the effective radius of each electron to be that of a sphere passing through the six metal atoms, one can calculate the excess diamagnetism due to delocalization. While this is not an exact method because of uncertainties in the theoretical model and electron orbits, it should be a better empirical approach than using atomic constants for a molecular

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problem. The value of 2.05×10^{-8} cm was taken as the mean radius $\bar{r}$ of the M_6 octahedra; it was computed from the M–M distances of 2.92 Å found in $K_4[(Nb_6Cl_{12})Cl_6]$[31] and 2.93 Å in $(Ta_6Cl_{12})Cl_{6/2}$.[32] Although these distances do vary slightly with change of oxidation state and halogen in the $M_6X_{12}^{n+}$ units, no attempt was made to include these variations in the value of $\bar{r}$.

The molecular diamagnetism χ_D^m of the octahedron of six metal atoms then was determined from eq 1,[33] where χ_D^{core} is the core diamagnetism of Nb(V) and Ta(V) given by Selwood.[34] In this equation the sum

$$\chi_D^m = (-2.83 \times 10^{10}\sum \bar{r}_i^2) + 6\chi_D^{core} \qquad (1)$$

extends over the number of bonding electrons i in the metal–metal molecular orbitals, *viz.*, 16, 15, and 14 for the 2+, 3+, and 4+ cluster ions, respectively. The values of χ_D^m obtained in this way were greater by *ca.* 100×10^{-6} cgsu than the values estimated from atomic core constants for the six metal atoms in the appropriate oxidation state. These values of χ_D^m and the other atom core corrections used in this work are listed in Table I. Note that no correction has been introduced for the delocalized electrons of the bridging halides which certainly must contribute more to the diamagnetism of the cluster ion than they would in a localized atomic orbital.

The $M_6X_{12}^{2+}$ and $M_6X_{12}^{4+}$ ions exhibited negative susceptibilities while the $M_6X_{12}^{3+}$ ions showed positive values. The least-squares intercept of a χ_M *vs.* T^{-1} plot was used to obtain the total temperature-independent susceptibility composed of the two components, χ_D and χ_{TIP}. A value of χ_D was determined from the data of Table I, and the difference between the intercept and

TABLE I

DIAMAGNETIC CORRECTIONS

Cluster	$10^6(-\chi_D^m)$, cgsu	Ion	$10^6(-\chi_D)$, cgsu	Group	$10^6(-\chi_D)$, cgsu
Nb_6 (2+)	244	Nb(V)	9	$(C_2H_5)_4N^+$	108
Nb_6 (3+)	232	Ta(V)	14	$(C_6H_5)_4As^+$	225
Nb_6 (4+)	220	F^-	11	$(CH_3)_2SO$	43
Ta_6 (2+)	274	Cl^-	26	H_2O	13
Ta_6 (3+)	262	Br^-	36	OH^-	12
Ta_6 (4+)	250				

χ_D yielded χ_{TIP}. This method reliably established the value of χ_{TIP} only in those cases where Curie law behavior was found. Compounds which did not exhibit this simple behavior were Ta_6Cl_{15}, Ta_6Br_{15}, $[(Ta_6Cl_{12})Cl_3(H_2O)_3]\cdot 3H_2O$, and Nb_6F_{15}. However, because Nb_6F_{15} exhibited very weak Curie–Weiss behavior with a value for $\Theta = -1°$, χ_{TIP} was estimated by the intercept method for this compound.

Magnetic susceptibility data and μ_{eff} values for all of the 3+ cluster compounds are presented in Table II. For all of the compounds which exhibited Curie be-

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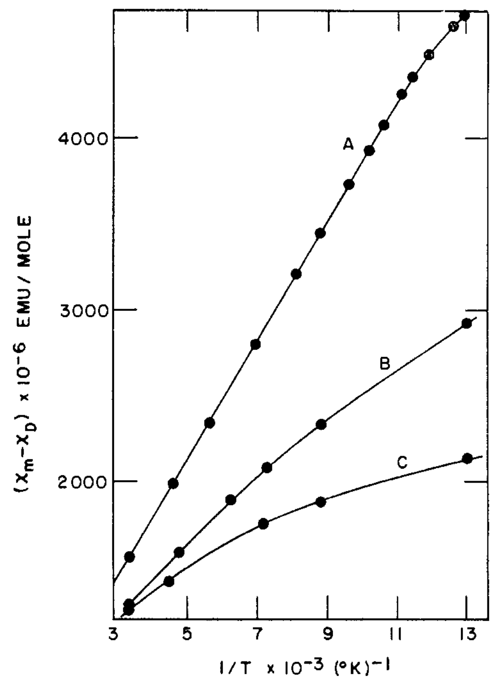

Figure 1.—Magnetic susceptibilities of (A) Nb_6F_{15}, (B) Ta_6Cl_{15}, and (C) Ta_6Br_{15}.

havior the μ_{eff} values at room temperature were significantly greater than the value 1.73 BM for one unpaired electron. This effect is caused by the rather large contribution of χ_{TIP} to μ_{eff}, as shown by the data in Table III. Note that the permanent magnetic moments obtained from the susceptibility data are in good agreement with moments calculated from the measured g factors for the compounds containing the $(M_6Cl_{12})Cl_6^{3-}$ ions. In these latter two cases the reduction of the magnetic moments below the free electron moment is small but real. Apparently there is a small residual orbital contribution to the moments resulting from second-order mixing of the d-orbital functions *via* spin–orbit coupling. The slightly lower g factors of the tantalum derivatives provide evidence for this, since the spin–orbit coupling constants are in the order $\lambda_{Ta} > \lambda_{Nb}$. The much lower moments of the two derivatives of $Nb_6Cl_{12}^{3+}$ which have terminally substituted ligands are most likely caused by contamination of these with a diamagnetic 2+ or 4+ cluster. Adequate methods for obtaining these substituted cluster anions in high purity have not been developed.

The deviations from Curie law behavior which were observed for the remaining compounds given in Table III have suggested another possible application of the susceptibility data, *viz.*, as a test for the presence of ligands bridging between the cluster units. Single-crystal structure analyses have shown that Nb_6F_{15},[21] Ta_6Cl_{15},[32] and Ta_6Br_{15}[32] have halogen bridging between cluster units (as indicated by the formulas $(M_6X_{12})X_{6/2}$) which could cause Curie–Weiss behavior *via* superexchange interactions. Their molar susceptibilities corrected for diamagnetism are shown in Figure 1 as a function of reciprocal temperature. The observed trend toward increased exchange coupling going from

TABLE II

MOLAR MAGNETIC SUSCEPTIBILITIES OF SOME $M_6X_{12}^{3+}$ DERIVATIVES

$((C_2H_5)_4N)_3[(Nb_6Cl_{12})Cl_6]$	T^a	77	113	133	175	222	243	270	299
($10^3\chi_D = -1.024$)	$10^3\chi_M{}^b$	4.03	2.71	2.13	1.60	1.17	1.01	0.906	0.758
(Ref 8)[d]	$\mu_{eff}{}^c$	1.74	1.80	1.78	1.86	1.90	1.91	1.96	1.97
$((C_6H_5)_4As)_2[(Nb_6Cl_{16}(OH)(H_2O)]$	T	77	113	140	183	299			
($10^3\chi_D = -1.123$)	$10^3\chi_M$	2.94	1.84	1.39	0.916	0.366			
(Ref 4)[d]	μ_{eff}	1.55	1.59	1.62	1.66	1.78			
$((C_2H_5)_4N)_2[(Nb_6Cl_{12})Cl_5(DMSO)]\cdot DMSO$	T	77	110	113	126	152	182	298	
($10^3\chi_D = -0.976$)	$10^3\chi_M$	3.33	2.22	2.15	1.87	1.50	1.21	0.627	
	μ_{eff}	1.62	1.67	1.67	1.69	1.73	1.77	1.94	
$((C_2H_5)_4N)_3[(Ta_6Cl_{12})Cl_6]$	T	77	113	131	149	299			
($10^3\chi_D = -1.054$)	$10^3\chi_M$	3.65	2.37	1.96	1.61	0.515			
(Ref 8)	μ_{eff}	1.68	1.73	1.74	1.75	1.87			
$[(Ta_6Cl_{12})Cl_3(H_2O)_3]\cdot 3H_2O$	T	77	113	155	157	186	215	267	302
($10^3\chi_D = -0.630$)	$10^3\chi_M$	1.89	1.52	1.20	1.18	1.02	0.886	0.694	0.601
(Ref 8)[d]	μ_{eff}	1.25	1.40	1.50	1.51	1.57	1.62	1.68	1.71
Nb_6F_{15}	T	77	79	83	87	89	93	97	103
($10^3\chi_D = -0.385$)	$10^3\chi_M$	4.41	4.34	4.20	4.06	3.96	3.78	3.64	3.44
	μ_{eff}	1.72	1.73	1.74	1.76	1.76	1.76	1.77	1.78
Nb_6F_{15}	T	113	122	142	176	217	294	298	
	$10^3\chi_M$	3.16	2.91	2.50	2.04	1.68	1.27	1.26	
	μ_{eff}	1.79	1.80	1.81	1.85	1.90	1.93	1.93	
Ta_6Cl_{15}	T	77	137	160	210	298			
($10^3\chi_D = -0.552$)	$10^3\chi_M$	2.36	1.77	1.25	1.03	0.709			
	μ_{eff}	1.34	1.45	1.56	1.63	1.73			
Ta_6Br_{15}	T	77	113	139	219	298			
($10^3\chi_D = -0.782$)	$10^3\chi_M$	1.34	1.09	0.972	0.650	0.470			
	μ_{eff}	1.15	1.30	1.40	1.59	1.73			

[a] Temperature in degrees Kelvin. [b] Calculated from $\chi_M = \chi_g M$, where M is the molecular weight and χ_g is the gram-susceptibility (cgsu/g). [c] Calculated from $\mu_{eff} = 2.828[(\chi_M - \chi_D)T]^{1/2}$. [d] The preparative method and analytical data for these compounds are given in the reference.

TABLE III

MAGNETIC CONSTANTS FOR $M_6X_{12}^{3+}$ DERIVATIVES

Compound	Θ, °K[a]	$10^6\chi_{TIP}$, cgsu	μ(obsd)[b]	μ(calcd)[c]	g[d]
$((C_2H_5)_4N)_3[(Nb_6Cl_{12})Cl_6]$	0	652	1.65	1.69	1.949
$((C_6H_5)_4As)_2[(Nb_6Cl_{12})Cl_4(OH)(H_2O)]$	0	594	1.46	...	...
$((C_2H_5)_4N)_2[(Nb_6Cl_{12})Cl_5(DMSO)]\cdot DMSO$	0	646	1.50	...	...
$((C_2H_5)_4N)_3[(Ta_6Cl_{12})Cl_6]$	0	497	1.67	1.66	1.922
$[(Ta_6Cl_{12})Cl_3(H_2O)_3]\cdot 3H_2O$	−110	...	...	1.64	1.897
Nb_6F_{15}	−1	482	1.67	...	...
Ta_6Cl_{15}	−50	...	...	...	...
Ta_6Br_{15}	−125	...	...	...	...

[a] Weiss constant determined from the χ^{-1} *vs.* T plot. [b] Calculated from the slope of the χ_M *vs.* T^{-1} plot; permanent magnetic moment in Bohr magneton units. [c] Calculated from $\mu = g[S(S+1)]^{1/2}$. [d] Experimental g factor from epr measurement.

the fluoride compound to the bromide compound perhaps is rationalized by increasing covalency in the metal–terminal halogen bonds and consequent greater cluster electron delocalization in the same order.

A question then arises about the origin of the strong Weiss behavior of the hydrate formulated as $[(Ta_6Cl_{12})Cl_3(H_2O)_3]\cdot 3H_2O$. This behavior is compared with that of related tantalum derivatives in Figure 2. In view of the behavior of the M_6X_{15} compounds one possibility is that a route for strong exchange coupling is provided by the presence of terminal chlorine atoms in bridging positions between the cluster units. However, the infrared spectrum of this compound showed a strong band at 404 cm^{-1} which is in the region expected for the M–O stretching vibration of oxygen donor ligands on the cluster[10,11] and here is indicative of coordinated water. At the same time the presence of a band indicative of coordinated Cl could not be identified positively. Thus it was concluded that at least one or more of the water molecules was coordinated, but coordination by chlorine, though expected, could not be confirmed. In the related $Ta_6Cl_{14}\cdot 7H_2O$, Burbank[35] has determined a structure which shows the two outer Cl atoms coordinated; thus formulation of the compound as $[(Ta_6Cl_{12})Cl_2(H_2O)_4]\cdot 3H_2O$ is indicated. If this structure is correct, then the coordination of the outer Cl atoms in the 3+ hydrate should be expected (as indicated by the formulation in this paper), but bridging of these Cl atoms between clusters should not be expected. Also, if the formulation given here is correct, then the compound should give evidence of being magnetically more dilute than the anhydrous M_6X_{15} compounds. Finally we note that the data presented here for Ta_6Cl_{15} and Ta_6Br_{15} are in reasonable agreement with those of Bauer and von Schnering,[32] and the strong Weiss dependence noted here for $[(Ta_6Cl_{12})Cl_3(H_2O)_3]\cdot 3H_2O$ is also evident in data presented by Spreckel-

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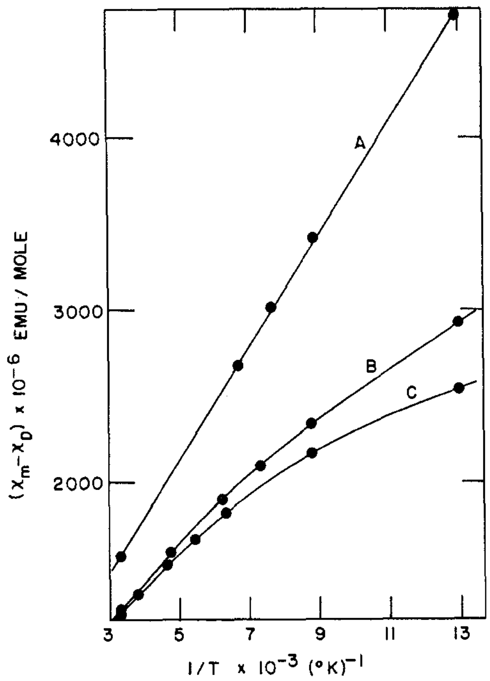

Figure 2.—Magnetic susceptibilities of (A) $((C_2H_5)_4N)_3[(Ta_6Cl_{12})Cl_6]$, (B) Ta_6Cl_{15}, and (C) $Ta_6Cl_{15} \cdot 6H_2O$.

meyer[6,7] for $Nb_6Cl_{15} \cdot 7H_2O$ and $Ta_6Cl_{15} \cdot 7H_2O$. It is obvious that further investigation will be required before the questions in regard to the structure and origin of the strong Weiss behavior in these hydrated derivatives can be answered.

Temperature-Independent Paramagnetism.—A large contribution to the total molar susceptibility of the $M_6X_{12}{}^{n+}$ cluster compounds was derived from the temperature-independent term χ_{TIP}, regardless of the oxidation state of the cluster. Van Vleck[36] referred to this term as the high-frequency term in the susceptibility expression, since as shown in eq 2 it arises from a mixing

$$\chi_{TIP} = 2N\sum_{n,m}(\Phi_{0,m}|\mu_i|\Phi_{n,m})^2/j_m(E_n - E_0) \qquad (2)$$

of excited-state functions with those of the ground state in the presence of the magnetic field, when $E_n - E_0 \gg kT$. In this equation n and m are quantum numbers, $\Phi_{0,m}$ is the ground-state wave function, $\Phi_{n,m}$ is an excited-state wave function, μ_i is the magnetic moment operator $\beta(\bar{L}_i + 2\bar{S}_i)$ with $i = x, y,$ or z, j_m is the multiplicity of the ground state, and $E_n - E_0$ is the energy separation between the indicated excited and ground states. The summation is over all states above the ground state. However, not all excited states will contribute since the matrix element $(\Phi_{0,m}|\mu_i|\Phi_{n,m})$ will be nonzero only when the product representation $\Gamma(\Phi_{0,m})\Gamma(\mu_i)\Gamma(\Phi_{n,m})$ contains the representation A_{1g}. Also when $E_n - E_0$ is very large, the upper state will contribute very little to χ_{TIP} even when the matrix element is nonzero. Thus investigation of χ_{TIP} for a series of cluster compounds should provide information which will be useful in understanding the electronic structure of the cluster ions.

(36) J. H. Van Vleck, "The Theory of Electric and Magnetic Susceptibilities," Oxford University Press, Oxford, England, 1932, p 277.

Values of χ_{TIP} derived from this work for a number of niobium and tantalum cluster derivatives are listed in Table IV, along with the calculated values of χ_D (*vide supra*). For the diamagnetic compounds $\chi_{TIP} = \chi_M - \chi_D$, and for the paramagnetic ones $\chi_{TIP} = \chi_{T_\infty} - \chi_D$, where χ_{T_∞} is the value of the intercept of a χ_M *vs.* T^{-1} plot at $T^{-1} = 0$. Values of χ_{TIP} for the compounds which gave Curie–Weiss behavior are not presented because their estimation involved too many uncertainties. Additional values of χ_{TIP} can be derived from data given by other authors for related compounds. These values, as listed in Table V, were calculated from the published χ_M using an estimate of χ_D according to the method developed above for the metal cluster compounds and the corrections given in Table I.

TABLE IV

TEMPERATURE-INDEPENDENT PARAMAGNETISM OF SOME $M_6X_{12}{}^{n+}$ CLUSTER COMPOUNDS

Compound[a]	n[b]	$10^6(-\chi_D)$, cgsu	$10^6\chi_{TIP}$,[c] cgsu
$((C_2H_5)_4N)_2[(Nb_6Cl_{12})Cl_6]$[4]	4	904	618 (15)
$((C_2H_5)_4N)_3[(Nb_6Cl_{12})Cl_6]$[4]	3	1024	652 (21)
$((C_2H_5)_4N)_2[(Nb_6Cl_{12})Cl_5(DMSO)] \cdot DMSO$	3	976	646 (20)
$((C_6H_5)_4As)_2[(Nb_6Cl_{12})Cl_4(OH)(H_2O)]$[4]	3	1123	594 (45)
Nb_6F_{15}	3	397	482 (26)
$Nb_6Cl_{14} \cdot 8H_2O$	2	712	630 (13)
$Nb_6Br_{14} \cdot 8H_2O$[20]	2	852	662 (6)
$((C_6H_5)_4As)_2[(Ta_6Cl_{12})Cl_6]$[8]	4	1168	472 (44)
$((C_2H_5)_4N)_2[(Ta_6Cl_{12})Cl_6]$[8]	4	934	501 (23)
$((C_2H_5)_4N)_2[(Ta_6Cl_{12})Br_6]$[8]	4	994	526 (12)
$((C_2H_5)_4N)_2[(Ta_6Br_{12})Br_6]$[8]	4	1114	544 (26)
$(Ta_6Cl_{12})Cl_2(OH)_2$	4	638	440 (10)
$((C_2H_5)_4N)_3[(Ta_6Cl_{12})Cl_6]$[8]	3	1054	497 (29)
$((C_2H_5)_4N)_2[(W_6Cl_8)Cl_6]$[37]	4	876	331 (14)
$((C_2H_5)_4N)_2[(W_6Cl_8)Br_6]$[37]	4	916	295 (24)

[a] Reference numbers of papers where preparations and analytical data appear are given. [b] Oxidation state of the cluster. [c] Uncertainty in the value of χ_{TIP} is given in parentheses.

TABLE V

Compound	$10^6\chi_{TIP}$, cgsu	Compound	$10^6\chi_{TIP}$, cgsu
$((C_2H_5)_4N)_2[(Nb_6Cl_{12})Cl_6]$[5]	528	$Nb_6Cl_{14} \cdot 9H_2O$[7]	645
$((C_2H_5)_4N)_3[(Nb_6Cl_{12})Cl_6]$[5]	666	$Nb_6Br_{14} \cdot 8H_2O$[7]	702
Nb_6Cl_{14}[7]	678	$Ta_6Cl_{14} \cdot 8H_2O$[7]	522
$Nb_6Cl_{14} \cdot 8H_2O$[7]	652	$Ta_6Cl_{14} \cdot 9H_2O$[7]	495

These results can be compared to investigate the effect of the metal, the halogen, and the oxidation state upon the magnitude of χ_{TIP}. First, we note there is reasonable agreement among the values derived from this work and those from other published work for the same compounds, with the exception of the values for $((C_2H_5)_4N)_2[(Nb_6Cl_{12})Cl_6]$. Since the value derived for this compound in Table IV is more consistent with the other niobium compounds, it probably is more reliable. The value given for Nb_6F_{15} also is comparatively low, but in this case the unique features of the compound may account for this. Note that Nb_6F_{15} is the only such metal cluster compound containing inner fluorine atoms in the bridging positions of the cluster unit.

The niobium compounds clearly exhibit larger values of χ_{TIP} than the analogous tantalum compounds, by *ca.* 100×10^{-6} cgsu. Correlation of the absorption maxima in the electronic spectra[14–16] of niobium and tantalum cluster ions indicates that $E_n - E_0$ should be smaller for niobium. It can be seen from eq 2 that a decrease in the energy separation between the ground state and the excited states leads to an increase in χ_{TIP} as observed. Certain absorption maxima in the electronic spectra also exhibit a shift to lower energy upon successive unit oxidation of the cluster ions from 2+ to 4+. Accordingly, one might expect the 4+ ion to exhibit the largest value of χ_{TIP}. Comparison of values for analogous niobium and tantalum compounds containing the ions $(M_6Cl_{12})Cl_6^{n-}$ with $n = 2$ and 3, however, reveals no trend of this type within the uncertainty of the data. Such a trend may be obscured by compensating changes in χ_D which are not accounted for in the method used here for estimating this quantity. Alternately, the effect of oxidation upon the electronic levels contributing to χ_{TIP} is too small to give a discernible trend in these data.

It does appear that a small increase in χ_{TIP} results when Br is substituted for Cl in the cluster compounds. This can be seen by comparing the values for the compounds in the $(Ta_6X_{12})X_6^{2-}$ series and for $Nb_6X_{14}\cdot 8H_2O$ with X = Cl or Br. Again this effect correlates with observed changes in the electronic spectra, where a small shift of the "metal–metal" bands toward lower energy by *ca.* 1000 cm^{-1} results on replacement of Cl with Br in the cluster ions.[16] A further structural feature that might be expected to have some effect on the magnetic properties is the symmetry of the cluster species. No discernible effect on χ_{TIP} is evident, however, when values for the hydrated or terminally substituted derivatives are compared with the values for the corresponding clusters having O_h symmetry, *viz.*, the $R_n[(M_6X_{12})X_6]$ compounds. As demonstrated by the two tungsten cluster compounds[37] included in Table IV there is a large decrease in χ_{TIP} on switching from the $M_6X_{12}^{n+}$ series to the $M_6X_8^{4+}$ series. The bonding levels in the latter clusters for M = Mo or W are known to be more stable, and the excited states are at higher energies, as evidenced by the absence of bands in the visible region of their electronic spectra.

In conclusion it is noted that the values derived here for χ_D and χ_{TIP} may be useful in correcting the molar susceptibilities of new paramagnetic derivatives of the $M_6X_{12}^{n+}$ cluster ions prior to a calculation of the magnetic moment, especially in those cases where the temperature dependence of χ_M is not determined. In the case of diamagnetic derivatives measured values of χ_M may be compared with χ_M calculated from appropriately chosen values of χ_D and χ_{TIP} to test for the presence of paramagnetic impurities. Finally, when a more accurate knowledge of the molecular orbital structure of these interesting species becomes available it should be possible to calculate the magnetic susceptibility components for comparison with experiment.

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(37) R. D. Hogue and R. E. McCarley, *Inorg. Chem.*, **9**, 1354 (1970).

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Chemistry of Polynuclear Metal Halides. VII. Characterization of the Tantalum Chloride and Bromide Phases $TaX_{2.8}$ as Mixed-Valence Compounds[1]

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It has been shown that during equilibration of $TaCl_4$ or $TaBr_4$ at temperatures above their decomposition points TaX_3 phases are initially produced, but continued equilibration leads ultimately to phases of composition $TaX_{2.80}$. Data derived from reactions in aqueous solution, reflectance spectra (300–1000 nm), infrared spectra (50–400 cm^{-1}), epr, and magnetic susceptibilities indicate that the mixed-valence formulation $2Ta_6X_{15}\cdot 3TaX_4$ best describes the stoichiometry and structural features of the $TaX_{2.80}$ phases. Examination of the intermediate TaX_3 phases by similar methods revealed marked structural differences between $TaCl_3$ and $TaBr_3$. Apparently the $TaCl_3$ phase does not contain Ta_6Cl_{12} cluster units, in contrast to $TaBr_3$ which may be formulated as $(Ta_6Br_{12}^{2+})(TaBr_6^-)_2$.

Introduction

Compounds in the tantalum–tantalum chloride, bromide, and iodide systems have been investigated by Schäfer, *et al.*, and the lower phases $TaCl_4$, $TaCl_3$, Ta_6Cl_{15} in the chloride[2] system; $TaBr_4$, $TaBr_3$, and Ta_6Br_{15} in the bromide[3] system; and TaI_4 and Ta_6I_{14} in the iodide[4] system were reported. Each of these lower phases was obtained in crystalline form *via* deposition from vapor species formed in chemical transport reactions between the appropriate gaseous tantalum(V) halide and tantalum metal under the influence of a care-

(1) Work performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

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