Holloway[16] to rationalize the greater stability of *cis*-dialkoxybis(acetylacetonato)titanium(IV) complexes relative to the *trans* isomers.

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Magnetic and Spectroscopic Studies of Salts of $M_2X_9^{3-}$

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Preparative procedures for certain enneahalodimetalates ($M_2X_9^{3-}$), containing first-row transition metal ions, are reported. Many of these had been previously mentioned in the literature, but details in their preparation were lacking. The new compounds $Cs_3Cr_2X_9$ (X = Br or I) are described. All alkali metal salts appear to be isomorphous. The temperature dependence of their paramagnetic suscepibility has been measured between 80 and 300°K. It is shown that magnetic dilution with salts of $Cr_2Cl_9^{3-}$ is attained only with alkylammonium cations. The small, positive susceptibility of $Cs_3W_2Cl_9$ has been attributed to temperature-independent paramagnetism. Single-crystal spectra of $Cs_3M_2Cl_9$ (M = Ti, Cr, and V) are reported and interpreted in terms of transitions which are essentially localized on adjacent metal atoms, in contrast to the transitions in $W_2Cl_9^{3-}$ which are believed to be due to delocalized electrons. A further sharp contrast is provided in the reactions of $Cr_2Cl_9^{3-}$ and $W_2Cl_9^{3-}$ with pyridine.

The enneahalodimetalates are an interesting but small class of compounds which can simultaneously embody a general structural similarity and a significant structural difference. The structures of $Cs_3Cr_2Cl_9$ and $K_3W_2Cl_9$ have been fully characterized by X-ray analyses.[1,2] In both, the anion can be described as two octahedra sharing a common trigonal face. However, considerable differences in detail are present in the two structures. The chromium atoms in $Cr_2Cl_9^{3-}$ do not lie exactly at the centers of their respective octahedra but are displaced away from each other along the trigonal axis, so that their interatomic distance is 3.1 Å. On the other hand, this phenomenon is exactly reversed in $K_3W_2Cl_9$. The metal atoms are displaced toward each other causing the shared face to be somewhat larger than those on the periphery. The interatomic separation of the metal atoms is only 2.4 Å. Cotton[3] has presented a clear and convincing criterion for metal–metal bonding in general and in particular for its presence in $W_2Cl_9^{3-}$ and its absence in $Cr_2Cl_9^{3-}$. Since there appears to be a force operating between the tungsten atoms such that the metal atoms approach one another more closely than the bridging geometry would appear to require, metal–metal bonds are likely to exist in $W_2Cl_9^{3-}$. Conversely in $Cr_2Cl_9^{3-}$, the structure indicated a net repulsion and the lack of any major metal–metal interaction. Magnetic data obtained at room temperature are believed to reflect these properties. It is often claimed that $K_3W_2Cl_9$ is diamagnetic; however, Klemm and Steinberg[4] actually found a small, positive susceptibility corresponding to a magnetic moment of 0.47 BM. On the other hand, the magnetic moment[1] of $Cs_3Cr_2Cl_9$ has been reported as 3.82 BM per chromium atom. The magnitude of the spin interaction, if any, was not determined. However, a study of the temperature dependence of the magnetic susceptibility[5] of $[(CH_3CH_2)_4N]_3Cr_2Cl_9$ has indicated that the exchange constant is only −5°K or 0.01 kcal/mol, an insignificant quantity in terms of chemical bonding. It should be noted that the magnetic moment of 3.96 BM at room temperature reflects a considerable difference in the paramagnetic susceptibility when compared to that obtained for $Cs_3Cr_2Cl_9$.

While $Cs_3Tl_2Cl_9$ is well known,[6] other examples of compounds of similar stoichiometry, but containing paramagnetic metal atoms, are not plentiful. The existence of $K_3M_2Cl_9$ (M = Nd or Pr) has been indicated in a phase study,[7] but only $Cs_3M_2Cl_9$ (M = Ti or V) and $Cs_3Ti_2Br_9$ have been isolated.[1,8] Each of these are isomorphous with $Cs_3Cr_2Cl_9$, but no detailed structural or magnetic information was presented. However, the similarity of the lattice constants suggests that the interatomic separation of the metal atoms is also about 3.1–3.2 Å in each case, so that metal–metal bonding would not exist according to Cotton.

It is remarkable that general preparative methods for the enneahalodimetalates which contain first-row transition metal atoms have not been reported in detail. Furthermore, with the exception of $[(CH_3CH_2)_4N]_3Cr_2Cl_9$, data pertaining to their temperature-dependent paramagnetism have not been available. Initially, we obtained these data for $Cs_3Cr_2Cl_9$, and the wide dis-

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parity between our results and those reported for the alkylammonium salt led us to investigate the dependence of the paramagnetic susceptibility on the nature of the cation. The synthesis of $Cs_3Cr_2X_9$ (X = Br or I) enabled us at least partially to evaluate the effect due to the nature of the halide ligand. The investigation was subsequently extended to $Cs_3M_2Cl_9$ (M = Ti or V) whose magnetic moments at room temperature were then unknown. Finally, we believed the magnetic susceptibility of salts of $W_2Cl_9^{3-}$ to be important in assessing Cotton's criterion for metal–metal bonding. Presuming the sample of Klemm and Steinberg to have been magnetically pure, the small paramagnetism which was observed[4] for $K_3W_2Cl_9$ could be due to temperature-independent paramagnetism or could indicate the thermal population of low-lying paramagnetic states. Thus, contrary to Cotton's opinion, metal–metal bonding may not be appreciable in $W_2Cl_9^{3-}$. Our investigation, while not providing complete confirmation for his view, does emphasize the sharp contrast that exists in the magnetic, spectroscopic, and chemical properties of the $W_2Cl_9^{3-}$ and $Cr_2Cl_9^{3-}$ ions.

Experimental Section

Materials.—Cesium chloride (99+%) as obtained from Matheson Coleman and Bell showed strong absorptions in its infrared spectrum at 3350, 2650, and 1100 cm^{-1}. These were removed by passing solutions of the salt through an anion-exchange resin in the chloride form, evaporating to dryness, and heating the salt to 200° for 1 hr. All other alkali metal halides were dried at 100° prior to their use. The anhydrous chlorides of Ti(III), V(III), and Cr(III) were obtained from Alfa Inorganics, Inc., and were used without further purification. Samples of $CrBr_3$ were kindly provided by G. Waasdorp, while CrI_3 was prepared according to the method of Gregory and Handy.[9] The preparation of $K_3W_2Cl_9$ was previously described.[10]

All compounds were prepared in sealed Vycor tubes which had been evacuated under high vacuum for 6–8 hr. In some instances, the tubes were preconditioned by sublimation of the anhydrous alkali metal halide. However, this procedure produced no noticeable effect on either the magnetic or spectroscopic properties of the compounds. Stoichiometric quantities were used in all cases.

Preparation of $M'_3Cr_2Cl_9$ (M' = K, Rb, and Cs).—Reaction conditions, color, and analytical results are given in Table I. In each case the violet crystals were composed of thick prisms and thin hexagonal plates which did not extinguish when rotated under crossed polarizers. Magnetic moments obtained from these samples agreed to within 1% of those taken on samples which were resublimed. Both $K_3Cr_2Cl_9$ and $Rb_3Cr_2Cl_9$ could be exposed for short periods to the dehumidified conditions of the laboratory without decomposition, but $Cs_3Cr_2Cl_9$ appeared to be indefinitely stable.

$Cs_3Cr_2X_9$ (X = Br and I).—Pertinent data for these compound are given in Table I. In the case of $Cs_3Cr_2Br_9$, the product was resublimed after mechanically separating some dark, inhomogeneous material from the fine, dark, blue-green crystals. The final product consisted of large single crystals which appeared to be completely uniform. Subsequent resublimation did not change the magnetic moment. With $Cs_3Cr_2I_9$, its sensitivity to atmospheric moisture required that all manipulations be performed under dry nitrogen. The reaction product consisted of I_2 and CrI_2 in addition to a quantity of large crystals, which were long and extremely dark. These were washed with CCl_4 and dried under vacuum. Resublimation was always accompanied by the formation of I_2 and salts of Cr(II). However, the magnetic moments of samples taken before and after resublimation agreed excellently. The crystals consisted of thick rods and flat black plates which appeared to possess a regular hexagonal shape.

$Cs_3Ti_2Cl_9$.—At the end of a reaction using the conditions given in Table I, the tube contained both the desired product and a noticeable quantity of $TiCl_4$. The latter was condensed in one end of the tube by bathing in liquid nitrogen before opening the other end. This procedure avoids inevitable fogging of the desired crystals with TiO_2. The product consists of both green prisms and plates, but some of the latter were not hexagonally shaped and extinguished under cross polarizers. In polarized light there was a green to amber dichroism, while the hexagonally shaped crystals were uniformly green. Thus, in the green polarization, the *c* axis of the hexagonal crystal lies perpendicular to the plane of polarized light.

This compound has been kept in a desiccator over $CaCl_2$ for 1 year without decomposition. The crystals are stable for short periods of time in dehumidified air, but they will decompose readily upon grinding in air. Powdered samples, showing apparently no decomposition, can be obtained by shock.

$Cs_3V_2Cl_9$.—Using the reaction conditions given in Table I, a heterogeneous product was obtained. The tube contained a white material, a zone composed of feathery crystals with a pink appearance, and a dark red zone. After mechanical separation, the latter proved to be the desired compound. After resublimation, the product consisted of dark red plates which did not extinguish when rotated under crossed polarizers. The pink crystals appeared to be Cs_3VCl_6. *Anal.* Calcd for Cs_3VCl_6: Cl, 32.11. Found: Cl, 32.40. With this assumption, the magnetic moment was found to be 2.78 BM. However, this compound was not the object of further investigation. Crystals of $Cs_3V_2Cl_9$ were stable to the dehumidified conditions of the laboratory for at least 48 hr. Grinding shortened the stability to about 1 hr.

$Cs_3W_2Cl_9$.—Olsson's method[11] was used to prepare this compound from freshly prepared and recrystallized $K_3W_2Cl_9$. The cesium salt was considerably more stable toward prolonged exposure to air than $K_3W_2Cl_9$.

Attempts to Prepare $[(C_2H_5)_4N]_3Cr_2Cl_9$.—This compound was prepared from $CrCl_3 \cdot 6H_2O$ and $(C_2H_5)_4NCl$ according to the procedure given by Earnshaw and Lewis.[5] Satisfactory analytical results were never obtained. Attempts to recrystallize this compound resulted in decomposition.

$[(n\text{-}C_4H_9)_4]_3Cr_2Cl_9$.—A modified version of the procedure described above was used to prepare this compound. To 50 ml of acetonitrile was added 1.0 g of $CrCl_3 \cdot 6H_2O$ and 1.6 g of $(n\text{-}C_4H_9)_4NCl$. The mixture was stirred until the crystals had dissolved and a deep blue solution remained. After evaporating to dryness, the glasslike material which remained was dissolved in a minimum quantity of CH_2Cl_2 (*ca.* 15 ml). The slow addition of ether produced a fine crystalline precipitate. The mixture was cooled to ice temperature and filtered under nitrogen. The crystals were washed with a CH_2Cl_2–ether mixture (4:1), and recrystallization was accomplished by the same procedure. The purple needles, which are extremely sensitive to moisture, were dried under vacuum at 80° for 2 hr. Magnetic data from separately prepared samples were in excellent agreement.

The Reaction of $K_3Cr_2Cl_9$ with Pyridine.—When small quantities of $K_3Cr_2Cl_9$ were refluxed in anhydrous pyridine, a green solution was obtained. After filtration, the slow addition of ether resulted in the characteristic green crystals of $CrCl_3(py)_3$. *Anal.* Calcd for $CrC_{15}H_{15}N_3Cl_3$: Cr, 13.20. Found: Cr, 13.25.

Crystallography.—All crystallographic data were obtained with nickel-filtered copper Kα radiation. The powder patterns of $M'_3M_2Cl_9$ (M' = K, Rb, or Cs; M = Ti, V, or Cr) are shown in Table II. The lattice constants given by Wessel and Ijdo[1]

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[9] N. W. Gregory and L. L. Handy, *Inorg. Syn.*, **5**, 128 (1957).

[10] R. Saillant, J. L. Hayden, and R. A. D. Wentworth, *Inorg. Chem.*, **6**, 1497 (1967).

[11] O. Olsson, *Ber.*, **46**, 566 (1913).

Table I

Reaction Conditions and Analytical Results for $M'_3M_2X_9$

Compound	Reaction conditions Temp, °C	Reaction conditions Time, days	% X Calcd	% X Found	% M Calcd	% M Found
K_3CrCl_9	850	6	59.04	59.08	...	...
$Rb_3Cr_2Cl_9$	710	4	46.95	46.85	...	...
$Cs_3Cr_2Cl_9$	650	2	38.83	38.86	...	...
$Cs_3Cr_2Br_9$	800	3	58.85	58.79	8.51	8.48
$Cs_3Cr_2I_9$	725	3	69.43	69.42	6.32	6.15
$Cs_3Ti_2Cl_9$	695	5	39.22	39.17	...	...
$Cs_3V_2Cl_9$	650	5	38.92	38.82	...	...
$Cs_3W_2Cl_9$	*a*	*a*	29.39	29.53	...	...
$[(C_4H_9)_4N]_3Cr_2Cl_9$	*a*	*a*	27.73	27.87	9.05	9.10

[a] Prepared in solution.

Table II

X-Ray Diffraction Data for $M'_3M_2Cl_9$

hkl	$Cs_3Ti_2Cl_9$[a]	$Cs_3V_2Cl_9$[a]	$Cs_3Cr_2Cl_9$[a]	$Rb_3Cr_2Cl_9$[a]	$K_3Cr_2Cl_9$[a]
010	...	...	6.12 w	5.88 w	5.51 s
011	...	...	5.74 w	5.62 m	
012	5.14 m	5.00 m	5.03 m	4.90 w	4.80 w
013	4.31 w	4.26 m	4.26 m	4.19 w	...
014	3.63 s	3.57 s	3.56 s	3.44 s	3.38 s
005					
110					
015	3.01 m	3.07 m	3.08 m	3.01 m	2.99 w
200					
201				2.90 m	2.88 w
202	2.97 s	2.95 s	2.96 m	2.83 s	2.79 s
006			2.92 s		2.75 s
114	2.78 m	2.75 m	2.79 vw	2.66 s	2.63 s
203			2.75 s		
016	2.74 m	...	2.70 m	...	...
007	2.57 m	2.54 m	2.54 s	2.47 s	2.44 s
a, Å	7.32[c]	7.24[c]	7.22[c]	6.86	6.84
c, Å	17.97[c]	17.94[c]	17.93[c]	17.15	16.53
ρ[b]					
Calcd	3.24	3.33	3.37	3.24	2.66
Found	3.29	3.33	3.36[c]	3.13	2.52

[a] d_{hkl} values are given. [b] Density in g/cm.^{3} [c] See ref 1.

for $Cs_3M_2Cl_9$ (M = Ti, V, or Cr) allowed the powder photographs of these compounds to be indexed without difficulty. Furthermore, the similarity of these patterns to those of $M'_3Cr_2Cl_9$ (M′ = K or Rb) suggests that the latter are isomorphous. When the lattice constants are compared, they exhibit the expected decrease: Cs > Rb > K. The striking similarity of the strongest lines in the powder photographs of $Cs_3Cr_2X_9$ (X = Br or I) to those of $Cs_3Cr_2Cl_9$ suggested that all were isomorphous. This was confirmed by precession photographs of shellac-encased single crystals. For each, the point symmetry is 6/mmm and systematic extinctions occur only when $l \neq 2n$ for $hh\bar{2h}l$ reflections. The last observation restricts the space group to that of $Cs_3Cr_2Cl_9$, *viz.*, D_{6h}^4-P6$_3$/mmc. The lattice dimensions are: for $Cs_3Cr_2Br_9$, $a = 7.51$ and $c = 18.68$ Å; for $Cs_3Cr_2I_9$, $a = 7.90$ and $c = 19.60$ Å. The observed density for each is greater than that of CH_2I_2 (3.33 g/cm^3). For two formula units per unit cell, as are found in $Cs_3Cr_2Cl_9$, the calculated densities are 4.20 g/cm^3 for the bromide and 5.18 g/cm^3 for the iodide.

In addition, our results for $Cs_3W_2Cl_9$ (not shown) could be indexed using the hexagonal lattice constants given by Brosset.[12] The *d* spacings exhibit a strong resemblance to those published recently for $K_3W_2Cl_9$[13] and suggest that these compounds are isomorphous.

Instrumentation.—The magnetic susceptibility equipment,[10] as well as the experimental apparatus[14] for measuring the electronic spectra of single crystals, have been described elsewhere. The hygroscopic nature of some of the compounds required that they be handled in an inert atmosphere when making the physical measurements.

Discussion of Results

With the exception of $Cs_3W_2Cl_9$, all alkali metal salts of the $M_2X_9^{3-}$ anion were prepared in sealed tubes at high temperatures from the anhydrous metal halide and the appropriate alkali metal halide. It is especially noteworthy that the commercially available CsCl contains several contaminants which must be removed in order to obtain pure products. The infrared spectrum of the impure CsCl indicates that the major contaminants were probably H_2O and NO_3^-. The latter must be removed if successful reactions with $TiCl_3$ and VCl_3, which are both easily oxidized, are to be obtained. The presence of trace quantities of water in this salt, or in the other alkali metal salts, does not noticeably affect the analytical results for the final products; however, their infrared spectra contained bands which must be attributed to the hydroxide ligand. Presumably, small quantities which result from the hydrolysis of the transition metal halide are then able to replace the halide ligand in the salts of the $M_2X_9^{3-}$ anion. With CsCl, traces of water are tenaciously held even at 100° but are removed by prolonged heating at 200°. With the other alkali metal halides, less stringent conditions are required. The order of stability of the salts of $Cr_2Cl_9^{3-}$ toward atmospheric moisture was qualitatively observed as Cs > Rb > K >> $(C_4H_9)_4N$. Under similar reaction conditions, it was possible to prepare the new compounds $Cs_3Cr_2Br_9$ and $Cs_3Cr_2I_9$, which are isomorphous with $Cs_3Cr_2Cl_9$. Both of these compounds are sensitive to atmospheric moisture and the following qualitative order of stability has been observed: Cl > Br > I.

Magnetic Properties.—The results of the measurement of the magnetic susceptibilities of the various compounds are given in Figures 1 and 2. In Table III we also record this data in terms of the constants from the Curie–Weiss equation. The susceptibilities of the chromium compounds, with two exceptions, obeyed this expression throughout the entire range of temperatures. In both figures, it can be seen that slight deviations from the Curie–Weiss behavior occurred with $Rb_3Cr_2Cl_9$ and $Cs_3Cr_2Br_9$ at temperatures less than 100°K. These results were verified on separately prepared samples. With the general class $M'_3Cr_2Cl_9$, however, the constants from the Curie–Weiss expression depended markedly on the nature of the cation. Evidently spin ordering can occur throughout the entire crystal and is not localized to each $Cr_2Cl_9^{3-}$ unit. The effect is lessened progressively as the size of the alkali metal ion is increased. Samples which were apparently magnetically dilute were obtained by substituting a larger alkylammonium cation for the alkali metal. In Figure 1, our results for $[(n\text{-}C_4H_9)_4N]_3Cr_2Cl_9$ are compared to those obtained by Earnshaw and Lewis for $[(C_2H_5)_4N]_3Cr_2Cl_9$. In each case, $\theta = 12°$. It should be noted that with the latter the experimental values of the reciprocal susceptibility exhibit a small curva-

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[12] C. Brosset, *Arkiv Kemi, Mineral. Geol.*, **12A** (4), 1 (1935).
[13] E. König, *Inorg. Chem.*, **2**, 1238 (1963).
[14] R. A. D. Wentworth, *ibid.*, **5**, 496 (1966).

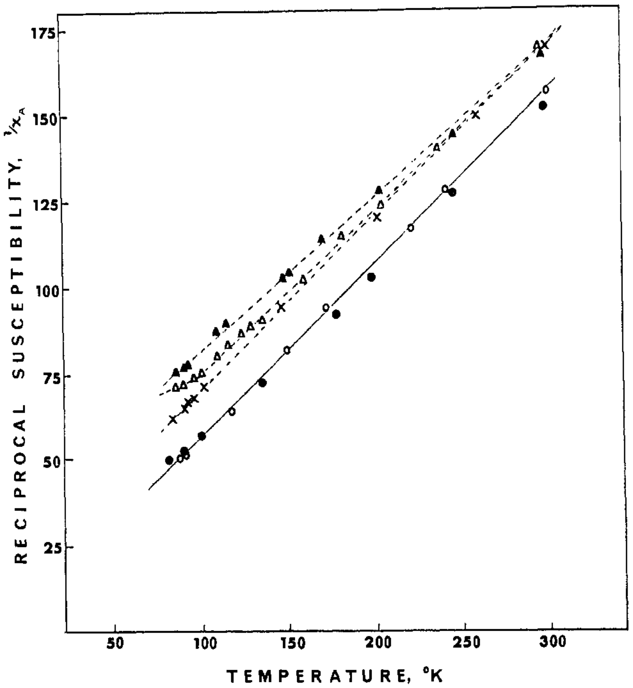

Figure 1.—Temperature dependence of the reciprocal susceptibility of various salts of $Cr_2Cl_9^{3-}$: ▲, $K_3Cr_2Cl_9$; △, $Rb_3Cr_2Cl_9$; ×, $Cs_3Cr_2Cl_9$; ○, $[(n\text{-}C_4H_9)_4N]_3Cr_2Cl_9$; ●, $[(C_2H_5)_4N]_3Cr_2Cl_9$.[5] The solid line is the theoretical variation with $-J/k = 4°$ and $g = 2.05$.

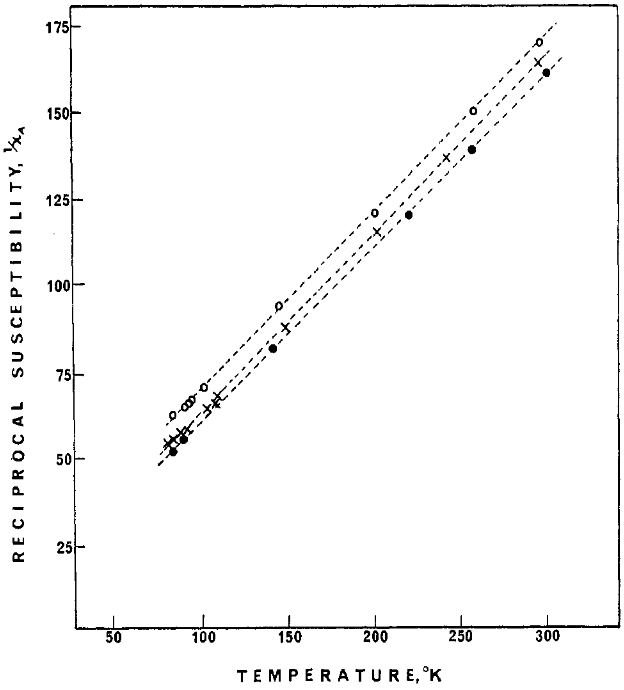

Figure 2.—Temperature dependence of the reciprocal susceptibility of: ○, $Cs_3Cr_2Cl_9$; ×, $Cs_3Cr_2I_9$; ●, $Cs_3Cr_2Br_9$.

ture at temperatures less than 120°K. We have attempted to prepare pure samples of this compound, but its instability to recrystallization has discouraged further attempts. It may be that trace quantities of antiferromagnetic contaminants were present in the compound examined by Earnshaw and Lewis.

TABLE III

MAGNETIC DATA FOR $M'_3M_2X_9$

Compound	C^a	θ, °K^a	μ_{eff}(300°K), BM
$K_3Cr_2Cl_9$	2.30	90	3.77
$Rb_3Cr_2Cl_9$^{b}	2.13	61	3.77
$Cs_3Cr_2Cl_9$	1.96	38	3.76
$[(n\text{-}C_4H_9)_4N]_3Cr_2Cl_9$	1.98	12	3.91
$Cs_3Cr_2Br_9$	1.91	16	3.81
$Cs_3Cr_2I_9$	2.00	21	3.88
$Cs_3V_2Cl_9$^{c}	1.29	116	2.74
$Cs_3Ti_2Cl_9$^{d}	...	...	1.2-1.4
$Cs_3W_2Cl_9$^{e}	...	...	0.43

[a] Constants from the Curie–Weiss equation: $\chi = C(T + \theta)^{-1}$. [b] Curie–Weiss behavior above 100°K. At $T < 100°$, curvature is observed. $\chi(80°) = 14{,}370 \times 10^{-6}$ cgsu. [c] Curie–Weiss behavior above 90°K. At $T < 90°$, curvature is observed. $\chi(80°) = 7000 \times 10^{-6}$ cgsu. [d] Does not follow Curie–Weiss behavior. See text. [e] Only TIP observed. $\chi = (76 \pm 10) \times 10^{-6}$ cgsu.

The magnetic interaction in a weakly coupled spin system can be described by the Heisenberg exchange Hamiltonian

$$\mathcal{H}' = -2J\hat{S}_i \cdot \hat{S}_j$$

whose eigenvalues are

$$E(S') = -J[S'(S' + 1)]$$

where, for this case, $S' = 3, 2, 1$, or 0. The appropriate equation for the magnetic susceptibility has been given by Earnshaw and Lewis.[5] Fitting their equation to the experimental results obtained for $[(n\text{-}C_4H_9)_4N]_3Cr_2Cl_9$ requires that $-J/k = 4°$ and $g = 2.05$. The solid line in Figure 1 represents the calculated values of the reciprocal susceptibility using these parameters. These results agree reasonably well with those obtained by Earnshaw and Lewis for $[(C_2H_5)_4N]_3Cr_2Cl_9$. However, the best fit to the experimental data was obtained without employing a correction for temperature-independent paramagnetism. According to this model of weakly coupled spins, the state of maximum spin multiplicity ($S' = 3$) within the ground term is separated from the singlet state by $-12J/k$. Thus, the energy required to decouple the electrons is about 0.1 kcal/mol.

It is interesting to note that in the cases of $Cs_3Cr_2X_9$ (X = Br or I), as shown in Figure 2, the Weiss constants are considerably less than in $Cs_3Cr_2Cl_9$. This may simply indicate that magnetic dilution is more nearly approached in these compounds. However, it is strange that the Weiss constant decreases according to Cl > I > Br. Since alkylammonium salts of these anions have not yet been isolated, the extent of magnetic dilution remains undetermined and further discussion is not warranted. For similar reasons, a detailed discussion of the magnetic properties of $Cs_3M_2Cl_9$ (M = Ti or V) will not be attempted. However, several points should be noted. The reciprocal susceptibility of $Cs_3V_2Cl_9$ varied linearly with temperature above 90°K but exhibited a distinct curvature at lower temperatures. Since identical results were obtained on separately prepared samples, the phenomenon is not due to impurities and might be associated with a phase transition. On the other hand, we were unable to obtain reproducible results with samples of $Cs_3Ti_2Cl_9$. In 16 separate preparations, using hand-picked crystals, the magnetic moment at 300°K varied between 1.2 and 1.4 BM, while that at 80°K ranged from 0.5 to 0.8 BM. In each case a minimum in the susceptibility was observed at about 165°K. The nature of the contaminant is presently unknown, but it does not seem to result from oxidation of the sample since the susceptibility of samples kept for several hours in dry air remained unchanged.

Finally, the susceptibility of $Cs_3W_2Cl_9$ has been measured at temperatures between 80 and 300°K. Throughout this interval the susceptibility per tungsten atom remained constant at $76 \pm 10 \times 10^{-6}$ cgsu.[15] For example the results at 90, 149, and 298°K were 79, 72, and 75×10^{-6} cgsu, respectively. It is now certain that the observed paramagnetism is due to second-order Zeeman effects and not to the thermal population of low-lying paramagnetic states. Unfortunately, the nature of the observed paramagnetism would render fruitless any attempt to estimate the stability of the singlet state with respect to either the triplet state or the state of highest spin multiplicity.[16] Nevertheless, the fact that the observed paramagnetic susceptibility is independent of temperature removes the possible objection to Cotton's theory.

Spectroscopic Properties.—In the cases of $Cs_3M_2Cl_9$ (M = Ti, V, or Cr) it was possible to grow crystals of excellent optical quality. The predominant type of crystal with each was a thin, hexagonal plate, in which the unique crystallographic axis is normal to the major face. Since the threefold axis of the $M_2X_9^{3-}$ anion is parallel to this crystallographic axis, the electric vector of the incident unpolarized radiation was always perpendicular to the threefold axis of the anion. With $Cs_3Ti_2Cl_9$, it was possible to obtain thin sections of the crystal which contained the unique axis. In this case, polarized incident radiation could be used to obtain the parallel and perpendicular spectra. The results are tabulated in Table IV. In addition, the spectrum of $[(n\text{-}C_4H_9)_4N]_3Cr_2Cl_9$ in CH_2Cl_2 solution is included for comparison.

TABLE IV

SPECTROSCOPIC DATA FOR $M'_3M_2X_9$

Compound	Polarization	Cm⁻¹ × 10⁻³
$Cs_3Cr_2Cl_9$	⊥	12.6, 14.0 sh, 17.9
$[(n\text{-}C_4H_9)_4N]_3Cr_2Cl_9$	a	12.75, 14.15 sh, 14.65 sh, 18.0
$Cs_3Cr_2Br_9$	b	11.9, 16.2, 24.4
$Cs_3V_2Cl_9$	⊥	11.0, 17.9
$Cs_3Ti_2Cl_9$	‖	13.3
	⊥	12.6

[a] Solution spectrum in CH_2Cl_2. [b] Reflectance spectrum.

Since the magnetic moments of $Cs_3M_2Cl_9$ (M = V or Cr) at 300°K are close to those expected for normal octahedral complexes, it follows that little metal–metal interaction occurs at this temperature. In each of these cases, the spectrum resembles that of MCl_6^{3-}. For example $CrCl_6^{3-}$ is reported[17] to have maxima at 13,200 and 18,700 cm⁻¹, while those of VCl_6^{3-} in a melt are found[18] at 11,000 and 18,000 cm⁻¹. Consequently, it is possible to assign the absorption in $Cs_3M_2Cl_9$ (M = V or Cr) as transitions predominantly within each isolated chromophore. It is interesting to note that the spin-forbidden $^4A_2 \rightarrow {}^2E$ transition in $Cs_3Cr_2Cl_9$ is particularly well resolved in the single-crystal spectrum, but not visible in the reflectance spectrum (not shown) and visible only in highly concentrated solutions of $[(n\text{-}C_4H_9)_4N]_3Cr_2Cl_9$. The magnetic moments of $Cs_3Cr_2X_9$ (X = Br or I) also point to little metal–metal interaction. Thus, their spectra should resemble those of the corresponding hexahalides. Since $CrBr_6^{3-}$ and CrI_6^{3-} are unknown, it is not possible to make a direct comparison of their spectra with those of $Cs_3Cr_2X_9$. However, at least with the bromide, an alternative method is available. By a comparison of the spectra of the *trans* isomers of $Cr(en)_2(H_2O)_2^{3+}$ and $Cr(en)_2(H_2O)Br^{2+}$, Krishnamurthy, Schaap, and Perumareddi[19] have estimated $10Dq$ for the bromide ligand to be 11,930 cm⁻¹. The first spin-allowed transition in $CrBr_6^{3-}$ should then occur at just these wave numbers, which is in remarkable agreement with the first transition in $Cs_3Cr_2Br_9$ which occurs at 11,900 cm⁻¹. Unfortunately, the extreme sensitivity of $Cs_3Cr_2I_9$ to atmospheric moisture precluded a reliable measurement of its spectrum.

The low magnetic moment of $Cs_3Ti_2Cl_9$ undoubtedly indicates considerably more spin coupling. Nevertheless, the observed absorptions are in good agreement with that recently reported[20] for $TiCl_6^{3-}$. The observed polarizations, however, should not be interpreted according to the local symmetry about each metal chromophore. It is probable that the mutual contamination, however small, of the orbitals of the neighboring metal atoms would render valueless such a crude approach. In other words, the interpretation of electric dipole phenomena is far more sensitive to the nature of wave functions than is the calculation of molecular energies.

It was not possible to observe the temperature dependence of the spectra since each crystal shattered at undetermined low temperatures. This phenomenon was not confined to the cesium salts but also occurred with $Rb_3Cr_2Cl_9$. While the magnetic data indicated the possibility of a phase transition in $Cs_3V_2Cl_9$ at about 90°K, no indication of a similar discontinuity

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[15] This result corresponds to a magnetic moment of 0.43 BM at 300°K in fair agreement with the result obtained for $K_3W_2Cl_9$. It should be noted, however, that for that salt a small diamagnetic contribution (-31×10^{-6} cgs) for the tungsten atom was included. We have not attempted to correct for the diamagnetism of any transition metal atom because its contribution would be uncertain. However, the inclusion of the diamagnetic correction would lead to a magnetic moment of 0.49 BM. Furthermore, any inaccuracies in Pascal's diamagnetic corrections cannot effect the conclusion that the residual paramagnetism must be independent of temperature.

[16] In the cases of true chemical bonding, the spin-dependent energy is no longer linear in $S'(S' + 1)$. Therefore, an estimate of the stability of the singlet state in $W_2Cl_9^{3-}$, using the Heisenberg formalism, would probably be of little value.

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occurred with the chromium compounds. It may be that the thermal instability in all cases is due to anisotropic contractions of the lattice.

The spectrum of $W_2Cl_9^{3-}$ has been previously discussed.[10] The first observed absorption, which appears at 13,200 cm^{-1} (ϵ 50), would not correspond to a reasonable estimate of the wave numbers of the same absorption in the unknown WCl_6^{3-}. For this reason, it was believed that the absorptions are the result of transitions between d orbitals which are delocalized between the two metal atoms.

Possible Chemical Significance.—A comparison of the properties of $Cr_2Cl_9^{3-}$ and $W_2Cl_9^{3-}$ reveals three distinct differences: structural, magnetic, and spectroscopic. It is not difficult to believe that these differences occur because of electron localization in the former and electron delocalization in the latter. The effect of these properties on the chemical reactivity of each ion is a subject which is currently receiving our attention. However, several points related to this subject can be discussed. In salts of $Cr_2Cl_9^{3-}$, the energy associated with the intraionic coupling of spins is not chemically significant, and it is not expected that the long-range spin coupling alone will prevent the degradation of the dinuclear ion into mononuclear units during the course of a chemical reaction. On the other hand, bonding between the adjacent metal atoms in $W_2Cl_9^{3-}$ could reasonably be expected to deter, if not prevent, the conversion to mononuclear complexes of trivalent tungsten. The products of the reactions of $Cr_2Cl_9^{3-}$ and $W_2Cl_9^{3-}$ with pyridine are in full accord with this reasoning. When $K_3Cr_2Cl_9$ is allowed to react with hot pyridine, mononuclear $CrCl_3(py)_3$ is obtained. However, in the corresponding reaction with $K_3W_2Cl_9$, it was shown[10] that at least one-third of the product was diamagnetic $W_2Cl_6(py)_4$, in which it was presumed that adjacent octahedra were joined by two chlorine bridges. The three-dimensional X-ray study of Jackson and Streib[21] confirmed this hypothesis and showed that the metal–metal internuclear distance had increased to only 2.6 Å. Thus, the product retains a considerable amount of interaction between the metal atoms in their adjacent octahedra. It may be that kinetic factors alone are responsible for the different products. However, the special nature of $W_2Cl_9^{3-}$ can be further exemplified. The remarkable stability of this ion toward degradation was recently demonstrated[22] in the mass spectrum of $K_3W_2Cl_9$, wherein $W_2Cl_6^+$ and $W_2Cl_5^+$ were observed. Although mass spectroscopic data for $Cr_2Cl_9^{3-}$ are not available, similar ions were not found in the mass spectrum of $MoCl_3$. Furthermore, it is noteworthy that the only reported reactions of $W_2Cl_9^{3-}$ which lead to mononuclear compounds are those involving oxidation or the loss of some of the electrons which are thought to be extensively involved in metal–metal bonding. Thus, the reaction of this ion with the cyanide ligand[23] leads to $W(CN)_8^{4-}$, while the pyrolysis of $(NH_4)_3W_2Cl_9$ with 8-hydroxyquinoline yields[24] the eight-coordinate tetrakis derivative of W(IV).

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Solubility of Silver Chloride and Bromide and the Formation of Silver Halide Complexes in Molten Ammonium Nitrate Dihydrate

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The solubilities of silver chloride and bromide as a function of the corresponding ammonium halide concentration were determined in molten $NH_4NO_3 \cdot 2H_2O$, at 55, 70, and 85°. Solubility measurements were made using a radioactive-tracer technique with ^{110}Ag. The solubility product K_{sp} and the consecutive stability constants of the complexes AgX, AgX_2^-, and AgX_3^- ($X^- = Cl^-, Br^-$) were computed. The results are discussed in terms of a quasi-lattice model of molten salts.

Introduction

The solubility of silver chloride[1–5] and bromide[2,4,6–8] in water at various halide ion concentrations has been extensively studied. From solubility data it was conconclued that soluble silver complexes of the type $AgX_n^{-(n-1)}$ were formed (X^- denotes the halide ion, $n = 1$–4) and in some cases the stability constants of the complexes were calculated. The association of silver(I) ions with halide ions was also studied at high

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