azole ring acts as a bridging ligand. It is quite possible that our complexes have a similar structure.

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Electronic Spectra and Magnetism of Some Vanadium(III) Halogeno Complexes

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The electronic spectra of a number of octahedral and tetrahedral complexes of vanadium(III) have been recorded over the range 5500–45,000 cm^{-1}, and the relevant ligand field parameters were derived. Of special interest are the values found for $10Dq$ for the tetrahedral VCl_4^- and VBr_4^- ions; these are 5530 and 5200 cm^{-1}, respectively. The magnetic susceptibilities of the complexes have also been determined in the range 300–90°K. The magnetic moments of the tetrahedral species VCl_4^- and VBr_4^- are essentially independent of temperature, after allowance is made for temperature-independent paramagnetism, as expected for species possessing $^3A_2$ ground terms. The magnetically dilute octahedral complexes of vanadium(III) (ground term $^3T_{1g}$) have magnetic moments which fall slightly with decreasing temperature (from ~2.7 to ~2.5 BM in the range stated). The splitting of the ground term due to the asymmetry of the ligand field is estimated to be ~800 cm^{-1} in the ions $VX_4 \cdot 2CH_3CN^-$ (X = Cl or Br). The magnetism of the complex $[(C_2H_5)_4N]_3V_2Cl_9$ has been interpreted in terms of the binuclear spin system with $S_1 = S_2 = 1$. The exchange integral J is estimated to be ~ -40 cm^{-1}.

Introduction

The electronic spectra and magnetism of vanadium(III) complexes have been less extensively studied than those of the later, first-row transition elements.[1] As part of a continuing program of research in this area, it was thought desirable to obtain the spectra of the unusual tetrahedral species[2] VCl_4^- and VBr_4^- under good resolution (the counterions are $(C_6H_5)_4As^+$ for the VCl_4^- ion and $(C_6H_5)_4As^+$ and $(C_2H_5)_4N^+$ for the VBr_4^- ion). Moreover, the magnetic moments of these ions over a temperature range should be of interest in comparison with those of octahedral vanadium(III) complexes. The spectral and magnetic properties of two magnetically dilute octahedral complexes have also been investigated, and these are compared with previous results on related complexes.[3]

The binuclear species $[(C_2H_5)_4N]_3V_2Cl_9$ has also been studied, and it is found that both its spectral and magnetic properties imply appreciable vanadium–vanadium interaction. Surprisingly, the salt $[(C_2H_5)_4N]VCl_4$ has similar magnetic behavior, and, from this and other data, it is concluded that the anion is octahedral polymeric in this salt, whereas it is tetrahedral monomeric in the tetraphenylarsonium salt.

Experimental Section

Compounds.—The compounds were prepared under oxygen-free nitrogen in a vacuum system by methods outlined previously.[2,4] The compounds gave satisfactory analysis for C, H, N, Cl or Br, and V in each case.

One compound is characterized here for the first time, although its existence was implied previously.[2] It is $(C_6H_5)_4As[VCl_4 \cdot 2CH_3CN]$, prepared by addition of $(C_6H_5)_4AsCl$ to a solution of VCl_3 in acetonitrile. It is yellow, like other salts of the $VCl_4 \cdot 2CH_3CN^-$ ion. *Anal.* Calcd for $C_{28}H_{26}AsCl_4N_2V$: C, 50.3; H, 3.55; Cl, 21.9; N, 3.0; V, 8.25. Found: C, 51.1; H, 4.0; Cl, 21.5; N, 4.25; V, 7.75.

Spectra.—The electronic spectra of the compounds were recorded on a Cary 14 spectrophotometer both by diffuse reflectance and also, where possible, in solution. All of the complexes are very unstable to air and to moisture, and therefore their diffuse reflectance spectra were recorded on samples held between silica plates, the edges of which had been greased.

Magnetism.—The magnetic susceptibilities of the compounds were recorded by use of an electromagnet with a field strength of 8150 ± 50 Oe; the field strength was checked every six runs. The thermocouple was calibrated by reference to the susceptibility of $HgCo(NCS)_4$. The temperatures are believed to be correct to ±0.5° at 300°K and to ±0.8° at 90°K.

The magnetic parameters for the $VCl_4 \cdot 2CH_3CN^-$ and $VBr_4 \cdot 2CH_3CN^-$ ions were initially derived by graphical procedures and then refined by Dr. D. J. Machin by use of the University of Manchester Atlas computer.

Results

Spectra.—The band maxima found for the tetrahedral complexes are given in Table I, while those for the octahedral complexes are given in Table II.

Magnetism.—The magnetic susceptibilities and moments of the tetrahedral complexes at the various measured temperatures are given in Table III, together with the suceptibilities and moments corrected for a temperature-independent contribution to the susceptibility (TIP) of 300 cgsu. The magnetic data for the octahedral species are given in Table IV. The appropriate diamagnetic corrections are indicated in each case and are subtracted from the observed sus-

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[1] R. J. H. Clark, "The Chemistry of Titanium and Vanadium," Elsevier Publishing Co., Amsterdam, 1968.

[2] R. J. H. Clark, R. S. Nyholm, and D. E. Scaife, *J. Chem. Soc.*, *A*, 1296 (1966).

[3] D. J. Machin and K. S. Murray, *ibid.*, 1498 (1967).

[4] G. J. Wessel and D. J. W. Ijdo, *Acta Cryst.*, **10**, 466 (1957).

TABLE I

BAND MAXIMA IN THE DIFFUSE REFLECTANCE SPECTRA OF $(C_6H_5)_4AsVCl_4$ AND $(C_2H_5)_4NVBr_4$ (CM^{-1})

	VCl_4^-		VBr_4^-		$Cs(Al,V)Cl_4$[a]
ν_2	8,230	s	7,560	s	8,250
	9,120	s	8,330	s	9,400
	~10,000	sh, br	9,220	ms, sh	10,250
ν_3	14,670	s	13,740	s	15,000
	16,230	sh	...		
	20,360	m	~19,000	sh	
	25,750	sh			
	29,250	m, br	~22,000	vs, sh	
	37,200	s	29,200	vs	
	42,450	s	35,900	vs	
			41,700	vs	

[a] Single crystal; see D. M. Gruen and R. Gut, *Nature*, **190,** 713 (1961).

TABLE II

BAND MAXIMA IN THE DIFFUSE REFLECTANCE SPECTRA OF OCTAHEDRAL VANADIUM(III) COMPLEXES (CM^{-1})

$(C_6H_5)_4As^+$ $VCl_4\cdot 2CH_3CN^-$	$(C_2H_5)_4N^+$ $VBr_4\cdot 2CH_3CN^-$	$[(C_2H_5)_4N^+]_3$ $V_2Cl_9^{3-}$	$(C_2H_5)_4N^+$ VCl_4^-
13,710 m	12,920 m	15,280 m	10,810 m, br
20,320 sh	19,350 ms	18,820 vs	16,560 ms
26,060 s	22,490 s	22,350 s, sh	20,000 m
28,570 sh	24,490 s	27,600 m	29,610 vs
30,620 vs		32,060 m	~43,500 vs
37,160 s		41,930 s	

TABLE III

MAGNETIC DATA ON THE TETRAHEDRAL COMPLEXES

$(C_6H_5)_4AsVCl_4$ (χ_{dia} = 321 cgsu)

	Temp, °K						
	290.5	270	250.5	238	225	205	187.5
$10^6\chi_M'$, cgsu	3101	3277	3504	3650	3821	4130	4461
μ, BM	2.68	2.66	2.65	2.64	2.62	2.60	2.59
μ', BM[a]	2.55	2.54	2.53	2.53	2.52	2.51	2.50

	Temp, °K						
	175	166.5	150.5	140	126	114	92.5
$10^6\chi_M'$, cgsu	4854	4834	5398	5830	6494	7048	8449
μ, BM	2.61	2.54	2.55	2.55	2.56	2.53	2.50
μ', BM[a]	2.52	2.46	2.48	2.49	2.50	2.48	2.46

$(C_2H_5)_4NVBr_4$ (χ_{dia} = 261 cgsu)

	Temp, °K				
	295	281	263	238	218
$10^6\chi_M'$, cgsu	2759	2886	3047	3317	3548
μ, BM	2.55	2.55	2.53	2.51	2.49
μ', BM[a]	2.41	2.41	2.40	2.40	2.38

	Temp, °K				
	197	171	146	115	96
$10^6\chi_M'$, cgsu	3903	4479	5351	6667	7874
μ, BM	2.48	2.47	2.50	2.48	2.46
μ', BM[a]	2.38	2.39	2.43	2.42	2.41

[a] μ' is the magnetic moment calculated from the experimental susceptibility after an allowance of 300 cgsu has been made for temperature-independent paramagnetism.

TABLE IV

MAGNETIC DATA ON OCTAHEDRAL COMPLEXES

$(C_6H_5)_4As[VCl_4\cdot 2CH_3CN]$ (χ_{dia} = 374 cgsu)

	Temp, °K							
	292	271	253	240	228	208.5	200	191
$10^6\chi_M'$, cgsu	3244	3264	3551	3690	3964	4170	4367	4644
μ, BM	2.75	2.66	2.68	2.66	2.69	2.64	2.64	2.66

	Temp, °K							
	176	165	152.5	138.5	136	113.5	100	92.5
$10^6\chi_M'$, cgsu	4956	5263	5625	6310	6494	7302	8264	8752
μ, BM	2.64	2.64	2.62	2.64	2.60	2.57	2.57	2.55

$(C_2H_5)_4N[VBr_4\cdot 2CH_3CN]$ (χ_{dia} = 314 cgsu)

	Temp, °K						
	291	275	255	235.5	213	193	171
$10^6\chi_M'$, cgsu	3083	3208	3423	3663	4006	4400	4874
μ, BM	2.68	2.66	2.64	2.63	2.61	2.61	2.58

	Temp, °K					
	161	146	130	117	105	93.5
$10^6\chi_M'$, cgsu	5263	5726	6410	7107	7813	8318
μ, BM	2.60	2.59	2.58	2.58	2.56	2.45

$[(C_2H_5)_4N]_3V_2Cl_9$ (χ_{dia} = 567 cgsu)

	Temp, °K					
	291	280	259	244	221	203
$10^6\chi_M'$, cgsu	2455	2505	2561	2731	2831	2906
μ, BM	2.39	2.37	2.31	2.31	2.24	2.17

	Temp, °K				
	184	150	134.5	116	92
$10^6\chi_M'$, cgsu	3007	3414	3778	4217	5064
μ, BM	2.10	2.02	2.02	1.98	1.93

$(C_2H_5)_4NVCl_4$ (χ_{dia} = 216 cgsu)

	Temp, °K						
	293	258	242	231	210.5	195	178
$10^6\chi_M'$, cgsu	2259	2496	2593	2676	2827	2968	3105
μ, BM	2.30	2.27	2.24	2.22	2.18	2.15	2.10

	Temp, °K					
	165	152	134	115	100	92.5
$10^6\chi_M'$, cgsu	3306	3632	3826	4242	4587	4755
μ, BM	2.09	2.10	2.02	1.98	1.92	1.88

ceptibilities to give the quantity $10^6\chi_g'$; if the latter is multiplied by the molecular weight of the compound, the quantity $10^6\chi_M'$ is obtained.

Discussion

Tetrahedral Complexes. Spectra.—It was recently demonstrated for the first time,[2] on the basis of X-ray and other evidence, that tetrahedrally coordinated vanadium(III) is present in the salts $(C_6H_5)_4AsVCl_4$ and $(C_2H_5)_4NVBr_4$. We now report the diffuse reflectance spectrum of the VCl_4^- ion over a much wider range (5500–45,000 cm^{-1}) than was previously possible, and at higher resolution, and also for the first time we report the spectrum of the VBr_4^- ion. As neither of the salts could be obtained as suitable single crystals and, moreover, because complex equilibria are set up in solution, diffuse reflectance spectroscopy is the only practicable method for obtaining the spectra of these very interesting d^2 species.

The spectra of the two ions are shown in Figure 1. Near 6000 cm^{-1} lie the weak CH overtone and combination bands associated with the cations. Centered at ~9000 cm^{-1} in the spectrum of the VCl_4^- ion and at ~8370 cm^{-1} in that of the VBr_4^- ion is a strong band with three components; the band system is assigned in each case to the $^3T_1(F) \leftarrow {}^3A_2(\nu_2)$ transition. The structure of the band, and also its frequency, is closely similar to that found for the vanadium(III) ion when inserted in the $CsAlCl_4$ lattice.[5] This is to be expected, as the environment of the vanadium ion is similar in the lattice to that in the VCl_4^- ion. The bands at ~15,000 cm^{-1} (VCl_4^- ion) and at 13,740 cm^{-1} (VBr_4^- ion) are assigned to the $^3T_1(P) \leftarrow {}^3A_2(\nu_3)$ transitions in each case. The higher energy bands have not been assigned but are probably charge transfer in origin (bearing in mind that the technique of diffuse reflectance spectroscopy

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(5) D. M. Gruen and R. Gut, *Nature*, **190,** 713 (1961).

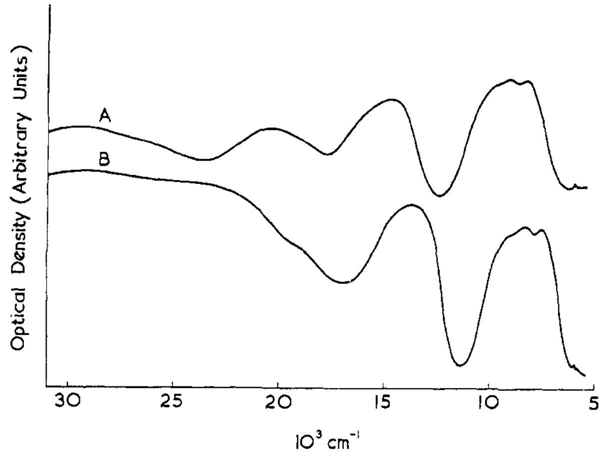

Figure 1.—Diffuse reflectance spectra of the complexes (A) $(C_6H_5)_4AsVCl_4$ and (B) $(C_2H_5)_4NVBr_4$.

discriminates against very strong bands, particularly in the ultraviolet region).

Using the above assignments, the ligand field splitting parameter ($10Dq$) and Racah parameter (B) are calculated by first-order perturbation theory,[6] which amounts to finding the solution to the simultaneous equations

$$15B = \nu_2 + \nu_3 - 30Dq \qquad (1)$$

$$340Dq^2 - 18(\nu_2 + \nu_3)Dq + \nu_2\nu_3 = 0 \qquad (2)$$

In this way we find for $10Dq$ and B the values 5530 and 494 cm^{-1}, respectively (VCl_4^- ion), as well as 5200 and 435 cm^{-1} (VBr_4^- ion). Thus bromide is lower than chloride in the spectrochemical series for tetrahedral ions, a fact which is well known for octahedral ions.[7] Moreover, the nephelauxetic ratios for the VCl_4^- and VBr_4^- ions (0.57 and 0.51, respectively) are also in the expected order.[7,8]

The symmetries of both the cation and the anion in the salt $(C_6H_5)_4AsFeCl_4$, with which the analogous vanadium complex is isomorphous,[2] are S_4 rather than T_d, and the site symmetries of both ions are likewise S_4 (the ClFeCl bond angles are 114.5 and 107.0°).[9] Thus the orbital triplet terms in the energy level diagram appropriate to the VCl_4^- ion are expected to split, $T_2 \rightarrow B + E$ and $T_1 \rightarrow A + E$. In practice, both $^3T_1$ terms show splittings, but the $^3T_1(F)$ term is actually split into three components; *cf.* the spectrum[5] of Cs(Al,V)Cl_4. Spin–orbit coupling, which should itself split the $^3T_1$ term by 3λ, probably causes this extra splitting, but a full interpretation of the additional structure would require studies at liquid-nitrogen or liquid-helium temperatures.

Magnetism.—The magnetic moment (μ) of a tetrahedral d^2 complex is given by the formula[10]

$$\mu = \mu_{so}\left(1 - \frac{4k^2\lambda_0}{10Dq}\right)$$

where μ_{so} is the spin-only moment (2.83 BM), k is the orbital reduction factor, and λ_0 is the free ion value of the spin–orbit coupling constant (105 cm^{-1}).[11] The assumption is made that, in the complex, λ_0 is reduced to the value $k\lambda_0$. If $k = 1$ and $\lambda = \lambda_0$, the expected magnetic moment for the VCl_4^- ion would be 2.615 BM and for the VBr_4^- ion it would be 2.60 BM (this calculation employs the appropriate values for $10Dq$ for the ions as derived from their spectra). However, previous magnetic studies have invariably shown that k must be reduced below unity in order to describe the magnetic properties of complexes.[10] We have arbitrarily taken $k = 0.892$ for the VCl_4^- ion and 0.864 for the VBr_4^- ion (this being the usual relative order of k values for chlorides and bromides), and, in this way, μ is then calculated to be 2.655 for both ions. The values of k assumed for each ion have no special significance except that they are likely maximum values in each case,[10] and the ratio k/Dq for chloride is thereby equal to that for bromide.

The magnetic susceptibilities of the ions at the various measured temperatures are given in Table III. The magnetic moments calculated directly therefrom are temperature dependent, but this is principally because temperature-independent magnetism (TIP) has not yet been allowed for. For these species TIP is given by the expression[10] $8k^2N\beta^2/10Dq$. If $k = 1$, this leads to the TIP values 377 cgsu for the VCl_4^- ion and 401 cgsu for the VBr_4^- ion. By use of the previously mentioned values of k for each ion, the TIP is then reduced to 300 cgsu in both cases. The recalculated magnetic moments for both ions are then essentially independent of temperature, as expected for the ground $^3A_2$ term; the values are $\sim$2.50 and $\sim$2.40 BM for the VCl_4^- and VBr_4^- ions, respectively.

The discrepancy between the calculated moment (2.655 BM) and the experimentally found ones is possibly due to a small amount of oxidation of these highly air-sensitive salts during the loading of the Gouy tubes. However, this is not indicated by oxidation state determinations.

Octahedral Species (Magnetically Dilute). Spectra.—Only two magnetically dilute octahedral complexes were studied; these were the species $(C_6H_5)_4As[VCl_4\cdot 2CH_3CN]$ and $(C_2H_5)_4N[VBr_4\cdot 2CH_3CN]$. The band maxima are listed in Table II.

The visible spectrum of the $VCl_4\cdot 2CH_3CN^-$ ion has been recorded previously,[2] but the present measurements cover a wider frequency range. That of the $VBr_4\cdot 2CH_3CN^-$ ion is reported for the first time. The two lowest frequency bands in the spectrum of each complex are assigned[1] to the $^3T_{2g} \leftarrow {}^3T_{1g}(F)$ and the $^3T_{1g}(P) \leftarrow {}^3T_{1g}(F)$ transitions, the latter being at higher energies. An analysis of the spectra, similar to that employed in the tetrahedral cases, leads to the following values for $10Dq$ and B for each ion

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(6) C. J. Ballhausen, *Z. Physik. Chem.* (Frankfurt), **11**, 205 (1957).

(7) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding," Pergamon Press Ltd., London, 1962.

(8) F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *J. Am. Chem. Soc.*, **83**, 4690 (1961).

(9) B. Zaslow and R. E. Rundle, *J. Phys. Chem.*, **61**, 490 (1957).

(10) B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p 427; B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, **6**, 37 (1964).

(11) T. M. Dunn, *Trans. Faraday Soc.*, **57**, 1441 (1961).

	10*Dq*	15*B*
$VCl_4 \cdot 2CH_3CN^-$	14,750	7650
$VBr_4 \cdot 2CH_3CN^-$	13,950	7450
VCl_6^{3-}	12,650	7700 (data for the pyridinium salt at 160°[12])

These results clearly confirm the relative order of the ligands in the spectrochemical series, *i.e.*, $CH_3CN > Cl > Br$.

Magnetism.—The magnetic moments of the $VCl_4 \cdot 2CH_3CN^-$ and $VBr_4 \cdot 2CH_3CN^-$ ions fall with decrease in temperature; the variation is 2.75–2.55 BM, in the case of the former, and 2.68–2.45 BM, in the case of the latter, the temperature range studied being ∽292 to ∽93°K. This behavior is in agreement with that expected for $^3T_{1g}$ ground terms in the presence of a cubic or axially distorted cubic ligand field.[13]

The parameters of interest which can be determined from the magnetic data are:[13] $\nu = \Delta/\lambda$ (where Δ is the splitting, in cm^{-1}, of the ground $^3T_{1g}$ term by the axial ligand field), k, λ, and $A = (1.5 - c^2)/(1 + c^2)$, where c is the mixing coefficient in the ground-term $^3T_{1g}$ wave functions. The results are as follows

	A	*k*	λ	ν	Δ
$VCl_4 \cdot 2CH_3CN^-$	1.27	0.85	105	7.8	890
$VBr_4 \cdot 2CH_3CN^-$	1.27	∼0.7	110	7.0	∽770

(Δ and λ are given in cm^{-1}). The values for these parameters are similar to those found[3] for other octahedral complexes of vanadium(III) and, in particular, imply an appreciable (∼800 cm^{-1}) splitting of the ground $^3T_{1g}$ term by the axial ligand field, with the orbital singlet lying lowest. The quality of the fit is demonstrated in Figure 2. The value of *A* calculated from the spectral data by the method outlined in ref 13 is 1.27 for both ions, in agreement with the values derived from the magnetic data.

Octahedral Complexes (Magnetically Concentrated). Spectra.—Two complexes behave as though they are magnetically concentrated; they are $[(C_2H_5)_4N]_3V_2Cl_9$ and $[(C_2H_5)_4N]VCl_4$. The former is known to be isostructural with the corresponding chromium compound, for which a full X-ray analysis is available.[4] The binuclear anions consist of two MCl_6 octahedra with a common face.

The band maxima for $[(C_2H_5)_4N]_3V_2Cl_9$ are given in Table II, and the spectrum is shown in Figure 3. The spectrum is very different from that of the VCl_6^{3-} ion, as present[12] in the salt $(pyH)_3VCl_6$ at 160°, but shows some resemblance to that of vanadium trichloride, especially in the 18,000-cm^{-1} region.[14] The spectrum of the $V_2Cl_9^{3-}$ ion is not typical of those of magnetically dilute vanadium(III) complexes.[1] The unusual features are almost certainly indicative of cooperative phenomena in the anion, similar to those discussed by Morin in the case of metal oxides.[15]

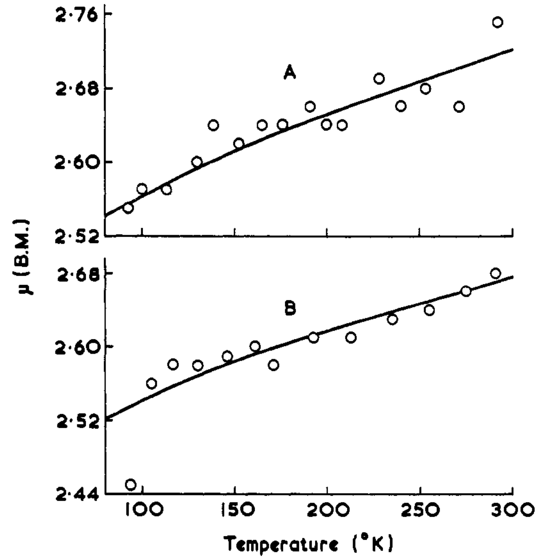

Figure 2.—Plots of μ_{eff} *vs.* temperature for the complexes (A) $(C_6H_5)_4As[VCl_4 \cdot 2CH_3CN]$ and (B) $(C_2H_5)_4N[VBr_4 \cdot 2CH_3CN]$. The curves are theoretical and correspond to the parameters of best fit as given in the Discussion. The circles are experimental points.

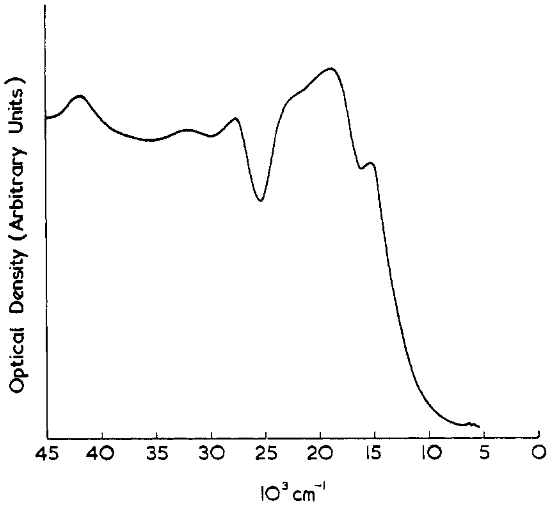

Figure 3.—Diffuse reflectance spectrum of the complex $[(C_2H_5)_4N]_3V_2Cl_9$.

The spectrum of the salt $(C_2H_5)_4NVCl_4$ is different from that of authentic salts of the tetrahedral VCl_4^- ion;[2] from the energies of the various bands, it would appear that the vanadium(III) ions are in a very distorted octahedral environment of chloride ions.

Magnetism.—The magnetic moments of the complexes $[(C_2H_5)_4N]_3V_2Cl_9$ and $[(C_2H_5)_4N]VCl_4$ are similar to one another over the range 300–90°K. In both cases, the magnetic moment at ∼292°K is about 0.5 BM below the spin-only value for two unpaired electrons (2.83 BM), and it falls to ∼1.9 BM at 92°K (Figure 4). It seems likely that these large reductions in the magnetic moments of the complexes are a consequence of metal–metal interaction.

The magnetic behavior of a number of polynuclear systems has now been investigated, and general expressions for the magnetic susceptibilities of the binuclear spin systems ($^1/_2$, $^1/_2$), ($^3/_2$, $^3/_2$), and ($^5/_2$, $^5/_2$), as well as of

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(12) D. M. Gruen and R. L. McBeth, *J. Phys. Chem.*, **66**, 57 (1962).

(13) B. N. Figgis, J. Lewis, F. E. Mabbs, and G. A. Webb, *J. Chem. Soc., A*, 1411 (1966).

(14) R. J. H. Clark, *ibid.*, 417 (1964).

(15) F. J. Morin in "Semiconductors," N. B. Hannay, Ed., Reinhold Publishing Corp., New York, N. Y., 1959.

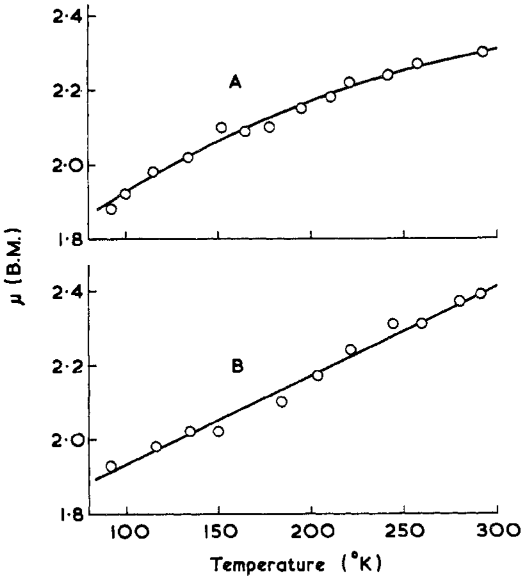

Figure 4.—Magnetic moments of (A) $[(C_2H_5)_4N]VCl_4$ and (B) $[(C_2H_5)_4N]_3V_2Cl_9$ as a function of temperature.

trinuclear systems, have been derived.[15–18] Recently[19] the explicit expression for the magnetic susceptibility of the metal–metal system relevant here has also been given, that is, the system in which two d^2 ions interact ($S_1 = S_2 = 1$). The expression for the susceptibility, per metal atom, is

$$\chi_A = \frac{N\beta^2}{3kT}\frac{1.5g^2}{T}\left[\frac{10 + 2\exp(-2J/kT)}{5 + 3\exp(-2J/kT) + \exp(-3J/kT)}\right]$$

where J is the exchange coupling constant, β is the Bohr magneton, k is the Boltzmann constant, g is the Landé splitting factor, and T is the temperature in degrees Kelvin. The energy level diagram of the appropriate system is given in Figure 5.

The best fit of the experimental data on the $V_2Cl_9^{3-}$ ion to the theoretical equation is obtained with $J = -40$ cm^{-1} and $g = 1.79$. With these values of the parameters, the general shape of the χ *vs.* T plot is correct, but the precise curvature cannot be reproduced. This is probably because the binuclear and polynuclear systems in question retain some orbital angular momentum. In the theoretical equation, the orbital angular momentum is equated to zero; this is a reasonable approximation for most low-symmetry vanadium(III) complexes, in which the splitting of the ground term by an asymmetric ligand field is found[3,20] to vary from 500 to 2000 cm^{-1}. By use of the above equation and $J = -40$ cm^{-1}, the Néel point is predicted to lie at 59°K. However this is unlikely to be an accurate estimate, owing to the limitations of the curve-fitting procedure. Studies to liquid-helium temperatures should provide more precise information.

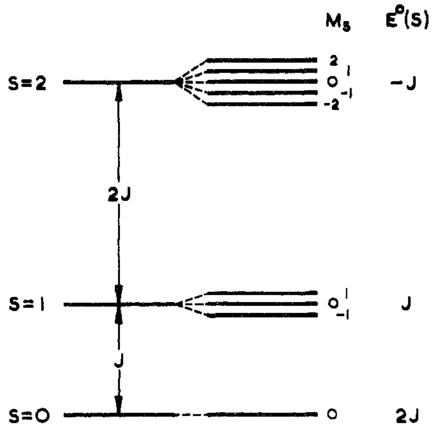

Figure 5.—Energy level diagram for two interacting $S_1 = S_2 = 1$ spin systems.

It is interesting that the J value found[18] for the chromium compound $[(C_2H_5)_4N]_3Cr_2Cl_9$ is only -3.5 cm^{-1} (−5°). The much larger J value for the isostructural vanadium compound is presumably a consequence of the larger wave functions of vanadium, leading to more extensive overlap and interaction between the two metal atoms. However exchange could also take place *via* a mechanism which involves the chlorine bridges. The magnetic behavior of the $V_2Cl_9^{3-}$ ion is thus intermediate between that of the $Cr_2Cl_9^{3-}$ ion and the $W_2Cl_9^{3-}$ ion. The latter is diamagnetic and presumed to have a direct W–W bond.

The close similarity between the magnetic behavior of the $V_2Cl_9^{3-}$ ion and the salt $(C_2H_5)_4NVCl_4$ implies that the latter is a polymeric molecule in agreement with the spectroscopic data; it possibly has the octahedral stereochemistry

This structure is found for NbI_4 in which the metal atoms move together in pairs,[21] and as a consequence the halide is diamagnetic.[22] It is concluded, therefore, that the structure of the VCl_4^- ion is determined by the cation, being tetrahedral with the large tetraphenylarsonium ion but polymeric octahedral with the smaller tetraethylammonium ion. On the other hand, the larger VBr_4^- anion remains tetrahedral with both these cations. Marked changes in the structure of anions with change in the cation have been found previously, for instance, for the salts $(NH_4)_2CuCl_4$ and Cs_2CuCl_4. The former[23] contains square-planar anions whereas the latter[24] contains distorted tetrahedral anions. The present results further emphasize the importance of lattice energy considerations in determining the structures of ionic compounds.

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