

Figure 4. Photoelectron valence band spectra of W foil, $\text{WO}_2 + \text{WO}_3$, and WO_3 . The surface of the W foil was mechanically ground in vacuum.

When the $\text{W}_2\text{B} + \text{WB}$ or WC samples were made amorphous by Ar ion sputtering, their area ratios changed significantly. In these cases the area ratio becomes greater due to the increase in area of the broadened and diffuse valence bands. Perhaps the conflict for the $\text{W}_2\text{N} + \text{WN}$ sample lies within its amorphous nature or is due to the fact that it is a mixture. Unfortunately, a more reliable numerical result along this line has to be deferred until a later time.

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Registry No. W, 7440-33-7; $\text{W}_2\text{B} + \text{WB}$, 57016-62-3; WC, 12070-12-1; $\text{W}_2\text{N} + \text{WN}$, 57016-63-4; WO_2 , 12036-22-5; WO_3 , 1314-35-8; $\text{WO}_2 + \text{WO}_3$, 57016-64-5.

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Vibrational Spectra of Binuclear Molybdenum Sulfate Complexes of High Bond Order

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Numerous molybdenum(II) compounds discovered in the last decade have a Mo-to-Mo quadruple bond. The central group in all these compounds, Mo-Mo^{4+} , is coordinated to monodentate ligands, such as chloride¹ (in $\text{Mo}_2\text{Cl}_8^{4-}$), or bidentate bridging ligands, such as acetate² (in $\text{Mo}_2(\text{CH}_3\text{COO})_4$) or sulfate^{3,4} (in $\text{Mo}_2(\text{SO}_4)_4^{4-}$). Most of the relevant information on these binuclear molybdenum(II) compounds was derived from x-ray crystallography. The very short metal-metal bond length in Mo_2^{4+} (2.10 to 2.15 Å), in conjunction with other structural data and theoretical considerations,^{1,5} furnished the main evidence for the existence of a quadruple bond between the two metal atoms.

The use of vibrational spectroscopy, mainly Raman scattering, in the study of binuclear Mo(II) species was mainly oriented toward the characterization of the metal-metal stretching fundamental ν_1 . This frequency was found to be in most compounds between 406 cm^{-1} (in the tetraacetate) and 335 cm^{-1} (in the octabromide ion).^{4,6,7} The overtones $n\nu_1$ of this fundamental were observed in $\text{Mo}_2\text{Cl}_8^{4-}$ by resonance Raman spectroscopy.^{4,8,9} Observation of an overtone progression in ν_1 out to $5\nu_1$ enables the deduction of the harmonic frequency ω_1 and the anharmonicity constant X_{11} .

Cotton, Frenz, and Webb^{10,11} discovered the remarkable compound $\text{K}_3\text{Mo}_2(\text{SO}_4)_4 \cdot 3.5\text{H}_2\text{O}$ in which the Mo-to-Mo bond order is 3.5. They carried out an extensive x-ray crystallographic study of the pink $\text{K}_4\text{Mo}_2(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ and the blue $\text{K}_3\text{Mo}_2(\text{SO}_4)_4 \cdot 3.5\text{H}_2\text{O}$. The important structural unit in each compound is the $\text{Mo}_2(\text{SO}_4)_4^{4-}$ ion, in which four bidentate sulfate ions, related by a fourfold axis, serve as bridges across the strongly bonded pair of molybdenum atoms. Thus, in spite of the difference in color, and in oxidation state, caused by the removal of one electron from the quadruple bond, the two complex ions have qualitatively identical structures.

The vibrational spectra of $\text{K}_4\text{Mo}_2(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ and the newly reported spectra of $\text{K}_3\text{Mo}_2(\text{SO}_4)_4 \cdot 3.5\text{H}_2\text{O}$ have been recorded. A variation of the experimental procedures of their preparations¹² enabled us to obtain crystalline samples suitable for Raman spectroscopy. The ir spectrum of the Mo(II) compound is in general agreement with that reported by Bowen and Taube.³ In addition to assigning the Mo-Mo frequency in the Mo_2^{5+} complex, the spectra of both compounds are interpreted in terms of the various skeletal and ligand modes. Spectroscopic evidence is provided for the existence of two crystallographically¹¹ distinct species in the Mo_2^{5+} complex. The effects of stresses present in the ring structures of both these compounds are also discussed.

Experimental Section

$\text{K}_4\text{Mo}_2(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ was prepared from a solution of $\text{K}_4\text{Mo}_2\text{Cl}_8 \cdot 2\text{H}_2\text{O}$ in 2 M H_2SO_4 by precipitation with saturated K_2SO_4 .³ $\text{K}_3\text{Mo}_2(\text{SO}_4)_4 \cdot 3.5\text{H}_2\text{O}$ was prepared as described previously.¹² Both substances are obtained by these procedures as a finely powdered

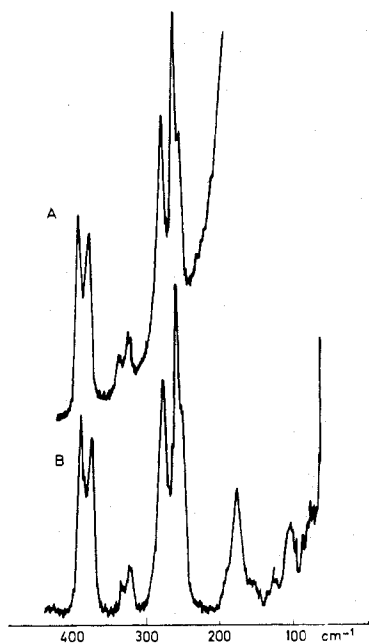


Figure 1. Demonstration of effectiveness of third monochromator. Spectrum of $K_3Mo_2(SO_4)_4 \cdot 3.5H_2O$: (A) without TTM, and (B) with TTM.

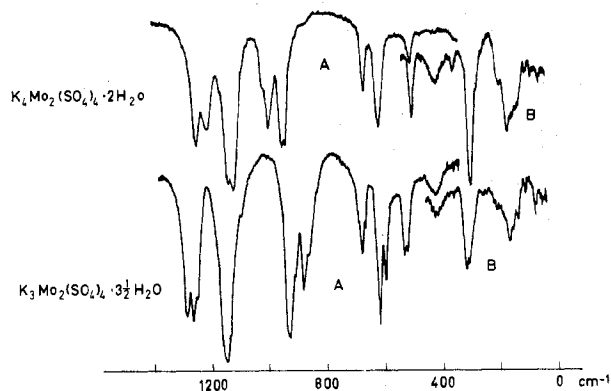


Figure 2. Infrared spectrum of $K_2Mo_2(SO_4)_4 \cdot 2H_2O$ and $K_3Mo_2(SO_4)_4 \cdot 3.5H_2O$: (A) KBr disk and (B) Nujoll mull on polyethylene window.

precipitate. It was found that Raman spectra of acceptable quality could not be obtained with these powdered samples. Therefore, both salts were recrystallized by slow cooling of their respective saturated hot solutions in 2 M H_2SO_4 . Each substance precipitated as small but well-formed crystals which were subsequently filtered, washed with cold water and absolute ethanol, and dried in vacuo over KOH.

Raman spectra were recorded of the complexes in these crystalline forms. As these substances are colored, we used the rotating sample technique of Kiefer and Bernstein.¹³ A ring-shaped crystal powder pellet was formed in a stainless steel mold that was then rotated at an angle toward the incident laser beam. Rather low pressures were used in forming the ring pellet in order not to crush the crystalline structure. The best spectra were obtained with the 4880-Å exciting line of a Spectra Physics 164 Ar⁺ laser. The spectrometer used was a Spex 1401 double monochromator with a third monochromator (TTM, Spex 1442) in tandem. The latter reduced scattered light considerably, generally improving the spectra and enabling us to record bands to well below 100 cm^{-1} . The effectiveness of the TTM is demonstrated in Figure 1. The signal was detected by a thermoelectrically cooled RCA C13034 Class II photomultiplier and monitored by photon counting.

Infrared spectra were recorded from KBr pellets of the complexes in the mid-infrared region. Nujol mulls spread on a polyethylene window were used as samples for far-infrared spectra. The spectrophotometers used were a Perkin-Elmer 457 and a Perkin-Elmer 180 equipped with the far-infrared option.

Table I. Infrared and Raman Frequencies of Mo_2^{4+} and Mo_2^{5+} Sulfato Complexes^a

$K_2Mo_2(SO_4)_4 \cdot 2H_2O$		$K_3Mo_2(SO_4)_4 \cdot 3.5H_2O$		Suggested assignments (see text)
Raman	Ir	Raman	Ir	
85 (37)	60 vw	76 (9)	80 m	Out-of-plane MoO_4 deformations
95 (28)	85 vw			
107 (46)	105 vw	106 (15)	105 m	
	140 sh	122 (2)	130 m	In-plane O-Mo-O bends
	165 s		160 m	
	193 sh	175 (37)	200 m	
225 (5)				Mo-O stretches
246 (27)		251 sh		
		256 (100)		
		274 (73)		Mo-O stretches
		292 s	300 sh	
			310 s	
322 (3)		319 (13)		Mo-Mo stretch
		331 (10)		
		352 w	350 vw	
364 sh				Mo-O stretches
371 (100)		373 (55)	412 m	
		386 (59)	425 sh	
		415 m		ν_2 bend of free SO_4
		442 (9)		
464 (9)		464 sh		ν_2 bend of coordinated SO_4
500 (9)	498 m			
		513 (9)	515 sh	
		529 (23)	530 m	ν_4 bend of SO_4
		589 sh	589 m	
604 (5)	600 s	598 (10)		
	610 s		610 s	Overtone of ν_{Mo-Mo}
622 (5)		618 (19)		
635 (3)		638 (24)		
		662 m	665 m	Free S-O stretches
670 (3)			675 m	
721 sh				Coordinated S-O stretches
744 (9)				
806 (3)				
			855 sh	Free S-O stretches
			875 s	
			905 sh	
		914 (12)	920 vs	Coordinated S-O stretches
		923 (19)	932 sh	
		931 (24)		
	940 sh			Coordinated S-O stretches
	950 vs	956 (84)		
	995 s			
1119 (9)	1015 sh			Coordinated S-O stretches
	1116 vs	1130 (9)	1130 vs	
	1140 vs		1150 vs	
1158 (14)		1167 (62)		Coordinated S-O stretches
1202 (9)		1193 (41)		
	1215 sh			
1243 (7)	1247 s	1248 (2)	1245 sh	Coordinated S-O stretches
		1272 (10)	1262 s	
			1285 s	
		1301 (5)		

^a Numbers in parentheses designate relative intensities; vs = very strong; m = medium; w = weak; vw = very weak; sh = shoulder.

Results and Discussion

The recorded infrared and Raman spectra of the Mo_2^{4+} and Mo_2^{5+} sulfates are presented in Figures 2 and 3, respectively. The numerical frequency values are tabulated in Table I. In general, the Mo_2^{5+} Raman spectrum is of considerably higher quality than that of Mo_2^{4+} . The greater number of bands

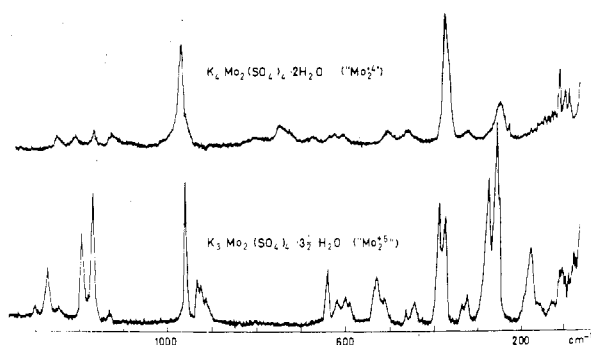


Figure 3. Raman spectrum of $K_4Mo_2(SO_4)_4 \cdot 2H_2O$ and $K_3Mo_2(SO_4)_4 \cdot 3.5H_2O$.

observed in both infrared and Raman spectra of the Mo_2^{5+} sulfate adds to their complexity. However, much of this complexity may be rationalized if most bands are considered to be split into two components. A straightforward interpretation of this splitting is possible by relating it to the existence of two crystallographically distinct species in the solid of this substance. One of these is packed as isolated units while the other forms an infinite chain.^{10,11} Nevertheless, the spectra are still quite complicated and simple symmetry considerations cannot be applied generally. Raman polarization measurements were not performed since the compounds are only sparingly soluble. As a result of these difficulties most bands cannot be completely characterized by assigning them to definite symmetry species. Nevertheless, we believe that they can still be attributed to the various motions within the functional groups and that a comparison between the spectra of the two related substances (Mo_2^{4+} and Mo_2^{5+}) helps in clarifying the structural effects on both.

Mo-Mo Vibrations. These vibrations are observed in the sulfate complex ions as a single Raman band at 371 cm^{-1} in Mo_2^{4+} and as a doublet at 373 and 386 cm^{-1} in the Raman spectrum of Mo_2^{5+} . The Mo-Mo vibration is observed as a very strong Raman band but is absent from the infrared spectra, in agreement with the existence of a center of symmetry inherent in the idealized symmetry of these substances.

The frequency for Mo_2^{4+} is in very good agreement with the previously reported value.⁴ The Mo-Mo vibration in complexes with monodentate ligands such as $K_4Mo_2Cl_8 \cdot 2H_2O$ occurs at frequencies lower than 350 cm^{-1} . When these ligands are replaced by bidentate bridging ligands such as sulfate, fluoroacetate, and acetate a substantial increase of this frequency to 371 , 397 , and 406 cm^{-1} , respectively, is observed.^{8,14} This increase is not necessarily evidence for a strengthening of the Mo-Mo bond. It is more reasonable to assume that it reflects the stresses introduced into the structure by the closed rings which the bridging ligands form with the two molybdenum atoms. In the bridging ligands the angles between the bridging bonds are distorted and narrower than in the free ligand. The Mo-Mo vibration frequency is even higher in Mo_2^{5+} sulfate than in Mo_2^{4+} sulfate. The higher oxidation state involves a decrease of the bond order and an accompanying increase in bond length,¹¹ implying a lowering of the Mo-Mo frequency. However, the greater distortion in the ring structure, as evidenced by the lowering of the coordinated OSO angle from 109.47° in the free ligand to 106.8° in Mo_2^{4+} and to 105.8° and 106.0° in Mo_2^{5+} ,¹¹ probably outweighs the former effect. The $\nu(Mo-Mo)$ band in the Mo_2^{5+} sulfate is distinctly split into a doublet separated by 13 cm^{-1} . This spectroscopic observation is in accord with the x-ray evidence of two distinct species as discussed above.

The 744-cm^{-1} band in the Raman spectrum of Mo_2^{4+} is assigned to the $2\nu_1(Mo-Mo)$ overtone. The corresponding

overtone in Mo_2^{5+} was not observed. This difference stems from the resonance Raman effect occurring in Mo_2^{4+} which has a strong absorption³ in the region of the exciting line.

SO_4 Vibrations. In the assignment of the sulfate group vibrations we generally follow Nakamoto.¹⁵ The symmetry of each coordinated SO_4 group cannot be higher than C_{2v} as compared with the T_d symmetry of the free ion. However, the spectra may be complicated as a result of interactions between the different SO_4 groups in the same molecule, by mode mixing, and by the existence of more than one structural species in the solid. The vibrations in the region between 900 and 1250 cm^{-1} probably originate in the SO stretching vibrations. The strongest Raman peaks in the $920\text{--}960\text{-cm}^{-1}$ region may be assigned to the symmetric stretching of the free SO bonds. The strongest ir bands in this frequency region are assigned to the asymmetric stretching of the same bonds. The bands in the higher portion of the spectra (around 1200 cm^{-1}) are assigned to vibrations of the coordinated SO bonds.

The bending vibrations are active in the $440\text{--}530\text{-cm}^{-1}$ and the $590\text{--}670\text{-cm}^{-1}$ regions, corresponding to the ν_2 and ν_4 bending modes of the free SO_4 ion, respectively. In the ν_2 region the bands of lower frequency, 464 (R) Mo_2^{4+} and 442 (R) and 464 (R) Mo_2^{5+} are assigned to the SO_2 in-plane, bending mode of the angle between free bonds, whereas the higher frequency bands, 500 (R) and 498 (ir) Mo_2^{4+} and 513 (R), 529 (R); 515 (ir), and 530 (ir) Mo_2^{5+} , are assigned to the corresponding bending angle between the coordinated bonds. It is impossible to make such distinction in the out-of-plane deformation originating from ν_4 as both coordinated and free bonds participate in these modes.

The previously discussed splittings into two components in the Mo_2^{5+} spectra were also observed in most bands of the SO_4 vibrations, whether bending or stretching modes.

The fact that the SO_4 bands associated with vibrations of the coordinated bonds are shifted to higher frequencies in Mo_2^{5+} than the corresponding bands in Mo_2^{4+} may be taken as additional evidence for the higher stresses in the ring structure of the former. On the other hand, the frequencies of the free bonds are shifted to lower frequencies.

Mo-O Vibrations. An idealized symmetry of D_{4h} may be assumed for the two MoO_4 groups with the center of the Mo-Mo bond as center of inversion. In this case three Raman and two ir active, mutually exclusive, stretching vibrations are expected. It would be reasonable to assign the 322 , 246 , and the 225 cm^{-1} Raman bands, and the 415 and 292 cm^{-1} ir bands of Mo_2^{4+} to these vibrations. The corresponding bands in Mo_2^{5+} are 331 , 319 ; 274 , 256 , and 251 cm^{-1} (Raman) and 425 , 412 ; 310 , and 300 cm^{-1} (ir). The splitting typical to the Mo_2^{5+} bands is again observed in this region.

Finally, the bending modes of the MoO_4 groups are observed in the region below 200 cm^{-1} . Of these 200 , 160 , and 130 cm^{-1} (ir) and 175 and 122 cm^{-1} (Raman) in Mo_2^{5+} and 193 , 165 , and 140 cm^{-1} (ir) in Mo_2^{4+} are probably due to the in-plane O-Mo-O bending. The corresponding Raman bands in Mo_2^{4+} have not been observed, possibly due to the poorer quality of the spectrum. The bands in the region below 100 cm^{-1} can be assigned to the out-of-plane deformation motion.

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Registry No. [$K_4Mo_2(SO_4)_4 \cdot 2H_2O$], 53293-19-9; [$K_3Mo_2(SO_4)_4 \cdot 3.5H_2O$], 53260-21-2.

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Group 3 Tetrahalide Salts, Lattice Energies and Thermodynamic Parameters. The AlCl_4^- and GaCl_4^- Ions

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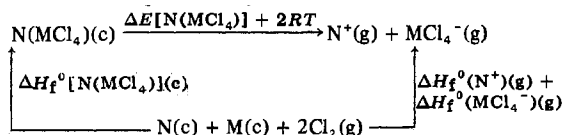
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Gearhart, Beck, and Wood,¹ in this journal, have evaluated the enthalpies of formation of the gaseous tetrachloroaluminate ion, $\Delta H_f^\circ(\text{AlCl}_4^-)(g)$, and the tetrachlorogallate ion, $\Delta H_f^\circ(\text{GaCl}_4^-)(g)$. Assuming a value of q_{Cl} , the charge on the chlorine atoms of the ions AlCl_4^- and GaCl_4^- , of -0.39 (equal to the average of the range of values selected for their calculations) the above workers obtain values $\Delta H_f^\circ(\text{AlCl}_4^-)(g) = -1188 \pm 28 \text{ kJ mol}^{-1}$ ($-284 \pm 7 \text{ kcal mol}^{-1}$) and $\Delta H_f^\circ(\text{GaCl}_4^-)(g) = -1029 \pm 28 \text{ kJ mol}^{-1}$ ($-246 \pm 7 \text{ kcal mol}^{-1}$) from a consideration of the lattice energies of representative salts. The contention of the present note is that the assumption regarding the constancy of q_{Cl} in the two ions, AlCl_4^- and GaCl_4^- , which seems at variance with published electronegativity values (Ga 1.82, Al 1.47),² (Ga 1.81, Al 1.61),³ and (Ga 1.95, Al 1.81),⁴ is unnecessary. Moreover, if q_{Cl} is retained as a variable parameter throughout the treatment it can be determined for each of the ions individually and coincident with the determination of the enthalpies of formation of the ions. The assigned thermodynamic parameters are then determined with more certainty.

The equivalence of the equation of Gearhart⁵ for the evaluation of the repulsion component of the lattice energy of a crystal lattice and the equation of Jenkins and Waddington⁶ is demonstrated.

Theoretical Section

For group 3 halides of general formula $\text{N}(\text{MCl}_4)$ the following thermochemical cycle can be employed:



where $\Delta E[\text{N}(\text{MCl}_4)]$ is the total internal energy change in the lattice energy step of the above cycle and is related to the total lattice potential energy, U_{pot} , defined as:

$$U_{\text{pot}}[\text{N}(\text{MCl}_4)] = U_{\text{elec}} + U_{\text{D}} - U_{\text{R}} \quad (1)$$

where U_{elec} , U_{D} , and U_{R} are the electrostatic, dispersion, and

repulsion energies of the crystalline lattice, respectively, by the equation:⁷

$$\Delta E[\text{N}(\text{MCl}_4)] = U_{\text{pot}}[\text{N}(\text{MCl}_4)] - 3RT \quad (2)$$

From the cycle therefore:

$$U_{\text{pot}}[\text{N}(\text{MCl}_4)] - RT = \Delta H_f^\circ(\text{N}^+)(g) + \Delta H_f^\circ(\text{MCl}_4^-)(g) - \Delta H_f^\circ[\text{N}(\text{MCl}_4)](c) \quad (3)$$

If, as described in detail elsewhere,⁸⁻¹⁰ we write the electrostatic lattice energy of the complex salt as a function of the distributed charge on the terminal chlorine atoms of the complex ion:

$$U_{\text{elec}} = \sum_{i=0}^2 A_i q_{\text{Cl}}^i \quad (4)$$

then we write the enthalpy of formation of the complex ion also as a function of q_{Cl} :

$$\Delta H_f^\circ(\text{MCl}_4^-)(g) = \sum_{i=0}^2 B_i q_{\text{Cl}}^i \quad (5)$$

A plot of $\Delta H_f^\circ(\text{MCl}_4^-)(g)$ vs. q_{Cl} for compounds where the gegenion N^+ varies, can be used to estimate not only the enthalpy of formation of the complex ion, which is independent of the nature of N^+ , but also of the charge distribution on the ion as defined by q_{Cl} .

Results

Gearhart, Beck, and Wood¹ have considered, inter alia, the salts $\text{Na}(\text{AlCl}_4)$, $\text{Cs}(\text{AlCl}_4)$, $\text{Cs}(\text{GaCl}_4)$, and $\text{Ga}(\text{GaCl}_4)$, for which they have calculated the electrostatic energy, U_{elec} , for the three specified charge distributions (corresponding to q_{Cl} values of 0.0, -0.2, and -1.0). U_{R} , the repulsion energy, was calculated from the equation⁵

$$U(\delta^{\text{OK}})_{\text{rep}} = -\left(\frac{\rho}{a_0}\right) \left[U_{\text{coul}} + 6U_{\text{vdw}} + e^2 \left(\frac{\partial M_\delta}{\partial \delta} \right) \right] \quad (6)$$

where, using the notation of eq 1:

$$U(\delta^{\text{OK}})_{\text{rep}} = U_{\text{R}} \quad (7)$$

$$U_{\text{coul}} = -U_{\text{elec}} \quad (8)$$

$$U_{\text{vdw}} = -U_{\text{D}} \quad (9)$$

and a_0 is the lattice constant, ρ is the repulsion constant (0.345 Å), and M_δ is the electrostatic Madelung constant referred to δ , the cube root of the molecular volume. From the above equation it can be inferred that if U_{elec} can be written in the form of eq 4 then U_{R} is also a quadratic function of q_{Cl} , within the applicability of eq 6

$$U_{\text{R}} = \sum_{i=0}^2 C_i q_{\text{Cl}}^i \quad (10)$$

and hence in eq 5;

$$B_0 = A_0 - C_0 + U_{\text{D}} - RT - \Delta H_f^\circ(\text{N}^+)(g) - \Delta H_f^\circ[\text{N}(\text{MCl}_4)](c) \quad (11)$$

$$B_1 = A_1 - C_1 \quad (12)$$

$$B_2 = A_2 - C_2 \quad (13)$$

The above workers have also calculated the dispersion energy of the lattices.

As described below we can carry the parameter q_{Cl} through the calculation and determine it along with the thermodynamic parameters of the problem.

From the U_{elec} and U_{R} values quoted by Wood et al. we can obtain the constants in eq 4 and 10. These two equations are then combined, via the relationships 11, 12, and 13, into equations of the form of (5) for each complex ion. Solution