Stereochemistry of Complex Halides of the Transition Metals[*]

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The aim of this lecture is to provide a survey of the stereochemistry of the tetrahalogeno complexes of the metal ions of the first transition series. In particular we wish to consider which non-bonding electron configurations favour the formation of regular tetrahedral complexes but we pass from this to examine the shape of four-coordinate complexes with other non-bonding electron arrangements. Recent experimental studies dealing with the preparation of various metal complexes having d^2, d^5, d^6 and d^8 non-bonding configurations will be summarised and the results of the investigations of the structures of these complexes are discussed.

Three common approaches to the study of the stereochemistry of molecules and complex ions are: (i) the valence bond theory which uses directed atomic orbitals; (ii) the electron pair repulsion model originally enunciated by Sidgwick and Powell[1] and (iii) the crystal field theory which provides an understanding of transition metal complexes. The latter is now more generally expresed as the ligand field theory in which allowance is made for covalent character in the metal ligand bond. We shall find it most convenient to start with an essentially electrostatic (electron pair repulsion) model and then pass to a consideration of the crystal field picture. A valence bond approach will be shown to be valuable as the metal-ligand bonds become more covalent. At the outset, we wish to stress our view that these approaches are complementary rather than contradictory.

For complex halides of the non transition elements, *e. g.* B^{III}, Al^{III}, Si^{IV} *etc.* the stereochemistry can be simply assigned in terms of an electron pair repulsion model. Taking metal atoms in which there are no non-bonding electron pairs (lone pairs) in the valency shell the shape is that expected on the grounds of symmetry, as shown in Figure 1.[2,3] Where there are lone pairs these can be allowed for by regarding them as "de facto" σ bonds; they have, however, greater repelling power than σ bonds and hence some distortion occurs from perfect symmetry. When we pass to consider transition metal complexes, allowance must be made for the fact that the non bonding d electrons in the metal atom do not necessarily give rise to a spherically symmetrical shell around which the halogen ligands are arranged. These d orbitals are of two types, the so called d_γ orbitals pointing t o w a r d s the ligands in an octahedral complex and the d_ε orbitals pointing between

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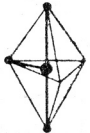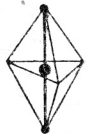
No. of electron pairs and corresponding hybrid orbitals	Number of lone pairs			
	0	1	2	3
2 sp	Linear e.g. HgCl$_2$			
3 sp^2	Triangular plane e.g. BCl$_3$	V-shape e.g. SnCl$_2$ gas		
4 sp^3	Tetrahedron e.g. CH$_4$	Trigonal pyramid e.g. NH$_3$	V-shape e.g. H$_2$O	
5 $sp^3d_{z^2}$	Trigonal bipyramid e.g. PCl$_5$	Irregular tetrahedron* e.g. TeCl$_4$	T-shape* e.g. ClF$_3$	Linear* e.g. [ICl$_2$]$^-$
6 $sp^3d_{z^2}d_{x^2-y^2}$	Octahedron e.g. SF$_6$	Square pyramid e.g. IF$_5$	Square plane* e.g. [ICl$_4$]$^-$	
7 $sp^3d_{z^2}d_{x^2-y^2}d_{xy}$	Pentagonal bipyramid e.g. IF$_7$	Irregular octahedron e.g. [SbBr$_6$]$^{3-}$		

Fig. 1. Shapes of molecules (non-transitional elements).

the ligands (see Figure 2).[4] In such an octahedral complex the originally dege-
nerate five d orbitals are split as shown in Figure 3. In this diagram we
show also the corresponding splitting for a tetrahedral arrangement. It is
important to observe that (a) the $d_\varepsilon - d_\gamma$ splitting is inverted in passing from
an octahedron to a tetrahedron and (b) the separation Δ is much less in the

second case. Indeed, it is reduced to about 1/3rd (theoretically 4/9ths) of the octahedral value. As a result the crystal field stabilisation energy is less for tetrahedral than for octahedral complexes and therefore, tetrahedral complexes would, in general be less likely to occur than octahedral ones *if* the crystal field stabilisation energy were the sole factor deciding this. In fact,
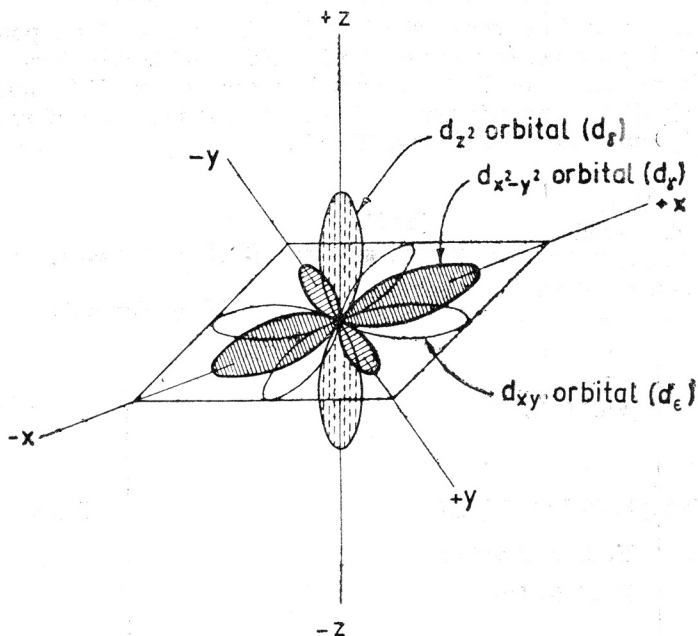
Fig. 2. Arrangement of d_ε and d_γ orbitals in octahedron. Both. d_γ but only one d_ε orbital (the d_{xy}) are shown.

since covalent bonding, amongst other factors, is quite important this simple model has to be modified when we consider complexes of the more electronegative ions such as bivalent nickel and copper.[5]

The formation of a regular octahedral or tetrahedral complex is favoured when the d_ε and d_γ shells are empty, half filled or filled with electrons. Thus, for spin free complexes regular octahedra are expected for spin free d^0, d^3, d^5, d^8 and d^{10} configurations. Regular tetrahedra are expected for the following d^0, $d_\gamma{}^2$, $d_\gamma{}^2 d_\varepsilon{}^3$, $d_\gamma{}^4 d_\varepsilon{}^3$ and d^{10}. Now a deviation from the above perfect electronic symmetry is expected to cause a slight distortion of the tetrahedron if the asymmetry is in the d_γ shell (because these d_γ orbitals point between the tetrahedrally disposed ligands). However, asymetry in the $d\varepsilon$ orbitals is expected to have a more serious effect upon shape and to cause considerable distortion. The shapes for various electron arrangements are summarised in Table I and II.

No reference is made in the above to the effects of "mixing in" excited states by spin-orbit coupling but this can be of some importance for ions with a large value of λ (the spin-orbit coupling constant). It is less important with ions at the beginning of the first transition series such as V^{III}. Also, no

allowance is made for possible distortions arising from other ions in the lattice, e.g. $[Et_4N]_2CoCl_4$ as compared with $[Ph_4As]_2CoCl_4$.

Tetrahedral d² Complexes

In collaboration with Dr. D. E. Scaife[6], work has been proceeding on the isolation of tetrahedral complexes having a $d_\gamma{}^2$ configuration.

In the first transition series the ions Ti^{2+}, V^{3+} and Cr^{4+} are potentially of interest for this purpose. In view of the instability of tetrahalides of Cr^{4+} and of the high reactivity of Ti^{2+}, interest has centred on V^{3+}. Starting with vanadium trichloride and tribromide, the following sequence of reactions has yielded the complex ions $[VCl_4]^-$ and $[VBr_4]^-$.
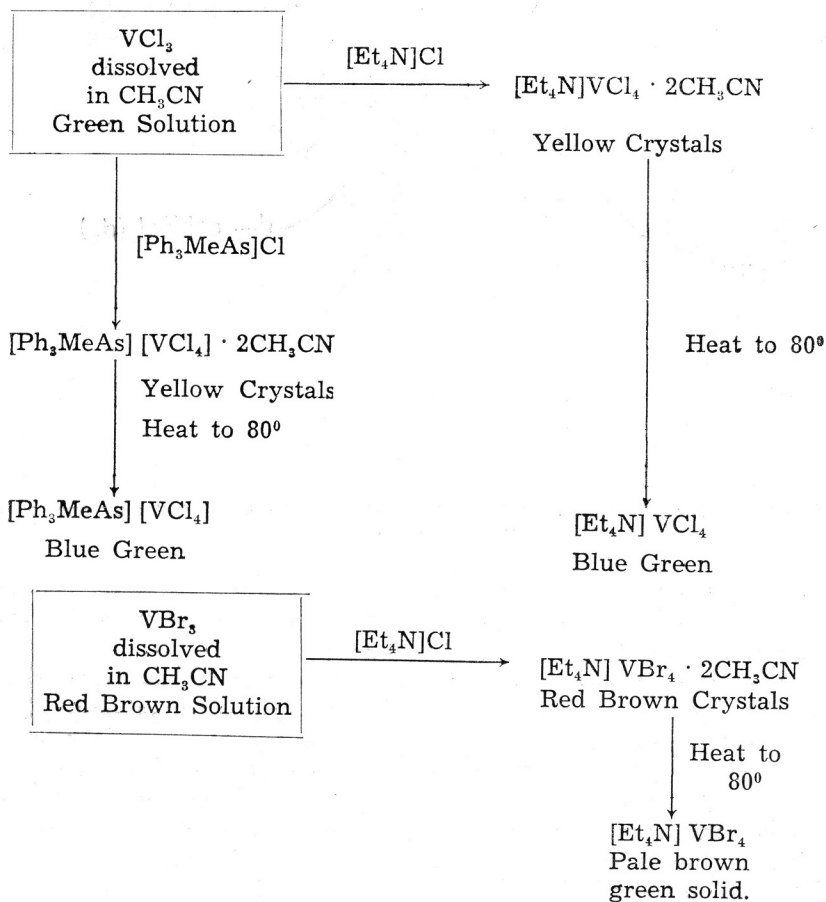
Attempts to prepare the corresponding $[Et_4N]VI_4$ were not successful. Although the adduct $[Et_4N]VI_4 \cdot 2CH_3CN$ could be prepared, heating of this caused decomposition rather than simple dissociation into the expected $[Et_4N]VI_4$.

One must avoid water or alcohol as the solvent because solvolysis occurs; methylcyanide has proved convenient for this investigation. Whilst it dissolves

ORBITAL   SPLITTINGS
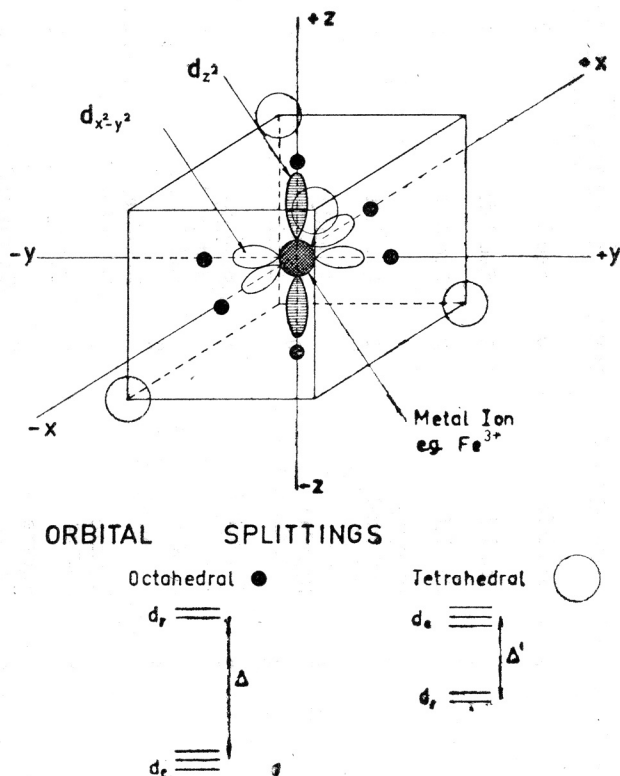
Fig. 3. Orbital splittings for a metal ion.

the vanadium trihalides it coordinates fairly weakly with V^{III} and can be removed by heating.

A number of physical measurements were carried out on these complexes and all lead to the conclusion that ions of the type $[VCl_4]^-$ and $[VBr_4]^-$ are present in the compounds and that these ions are regular tetrahedra. Conductivity data are shown in Figure 4. Whereas VCl_3 is virtually a non-electrolyte, VBr_3 shows some conductivity presumably owing to auto-complex formation, perhaps yielding some $[VBr_2(CH_3CN)_4][VBr_4]$ in solution in CH_3CN. However, the conductivities of the other complexes are such as to suggest that 1:1 electrolytes are formed. Molecular weight data in solution were not available owing to the low solubility and reducing power of the $[VX_4]^-$ ions towards most convenient solvents. Studies of the spectra of $[Ph_3Me\ As]\ VCl_4$ in PhCN and CH_3CN were carried out and bands in the visible region of considerable intensity were obtained. Thus ε at 17000 cm^{-1} varies from 70 to 105 in $PhNO_2$ depending upon the temperature. In general, whilst the ε values for octahedral complexes lie in the region 2 — 10, the corresponding values for tetrahalogeno complexes are of the order of 100 — 1000 depending upon the metal and halogen. (We exclude from this generalization the $[Mn(halogen)_4]^{2-}$ spectra which have much lower values of ε because transitions are both La Porte and Spin Forbidden, because Mn^{2+} has a d^5 configuration.)

TABLE I

Stereochemistry and Electron Configuration
(Based on crystal Field Theory)

Number of Non-Bonding d Electrons	SPIN FREE Expected Stereochemistry				SPIN PAIRED Expected Stereochemistry			
	Coord. No. 4	U.E.*	Coord. No. 6	U.E.*	Coord. No. 4	U.E.*	Coord. No. 6	U.E.*
0	**Regular** Tetrahedron	0	**Regular** Octahedron	0	See left	0	See left	0
1	Slightly distorted Tetrahedron	1	Slightly distorted Octahedron	1	See left	1	See left	1
2	**Regular** Tetrahedron	2	Slightly distorted Octahedron	2	See left	2	See left	2
3	Distorted Tetrahedron	3	**Regular** Octahedron	3	Slightly distorted Tetrahedron	1	See left	3
4	Square Planar	4	Tetragonal	4	**Regular** Tetrahedron	0	Slightly distorted Octahedron	2
5	**Regular** Tetrahedron	5	**Regular** Octahedron	5	Distorted Tetrahedron	1	Slightly distorted Octahedron	1
6	Slightly distorted Tetrahedron	4	Slightly distorted Octahedron	4	Distorted Tetrahedron	2	**Regular** Octahedron	0
7	**Regular** Tetrahedron	3	Slightly distorted Octahedron	3	Square Planar	1	Tetragonal	1
8	Distorted Tetrahedron	2	**Regular** Octahedron	2	Square Planar	0	Tetragonal	0
9	Square Planar	1	Tetragonal	1	See left	1	See left	1
10	**Regular** Tetrahedron	0	**Regular** Octahedron	0	See left	0	See left	0

* Unpaired Electrons.

TABLE II

Stereochemistry and Electron Configuration

(Expected from Crystal Field Theory — assuming no mixing
of excited states.)

Shape	Spin Free	Spin Paired
Perfect Octahedron	d^0, d_ε^3, $d_\varepsilon^3 d_\gamma^2$, $d_\varepsilon^6 d_\gamma^2$, d^{10}	d_ε^6
Slightly Distorted Octahedron (Unsymm. d_ε)	d_ε^1, d_ε^2, $d_\varepsilon^4 d_\gamma^2$ $d_\varepsilon^5 d_\gamma^2$	d_ε^4, d_ε^5
Square or Tetragonal (Unsymm. d_ε)	$d_\varepsilon^3 d_\gamma^1$, d_ε^6, d_γ^3	$d_\varepsilon^6 d_\gamma^1$ $d_\varepsilon^6 d_\gamma^2$
Perfect Tetrahedron	d^0, d_γ^2, $d_\gamma^2 d_\varepsilon^3$ $d_\gamma^4 d_\varepsilon^3$, d^{10}	d_γ^4
Slightly Distorted Tetrahedron (Unsymm. d_γ)	d_γ^1, $d_\gamma^3 d_\varepsilon^3$	d_γ^3
Distorted Tetrahedron (Unsymm. d_ε)	$d_\gamma^2 d_\varepsilon^1$, $d_\gamma^2 d_\varepsilon^2$ d_ε^4, d_γ^4	$d_\gamma^4 d_\varepsilon^1$, $d_\gamma^4 d_\varepsilon^2$

These figures are summed up in the Table III. The magnetic moment of these $[VX_4]^-$ complexes (~ 2.7 B.M.) is not diagnostic of stereochemistry at 20°C, as may be seen from Fig. 5.

TABLE III

Values of Extinction Coefficients for Octahedral Hexa-aquo and Tetrahalogeno Complexes (ε_{max} only given)

Metal	Hexaquo Complexes		Tetrachloro Complexes	
	λ_{max} in mμ	ε_{max}	λ_{max} in mμ	ε_{max}
Mn^{II}	532	0.017	445	0.71
Co^{II}	513	4.8	693	653
Ni^{II}	395	5.1	700 & 660	167
Cu^{II}	800	13	890 & 360	88 & 4,000

We may conclude that these at least support the existence of tetrahalogeno vanadium complexes in CH_3CN solution. Confirmation of the tetrahedral assignment comes from X — ray studies. It has been shown by Rundle[7] that in $[Ph_4As]FeCl_4$ the Fe^{III} atom is at the centre of an almost regular tetrahedron, the bond angles being 114.5° and 107.0° with Fe — Cl distances of 2.17 Å. We find that $[Ph_4As]VCl_4$, is strictly isomorphous with this Fe^{III} complex and conclude that it contains a regular $[VCl_4]^-$ anion. It has been shown also that $[Et_4N]VBr_4$ is isomorphous with $[Et_4N]FeBr_4$ and although the latter

has not been shown by X-rays to contain a tetrahedral $[FeBr_4]^-$ there is little doubt that this is true.

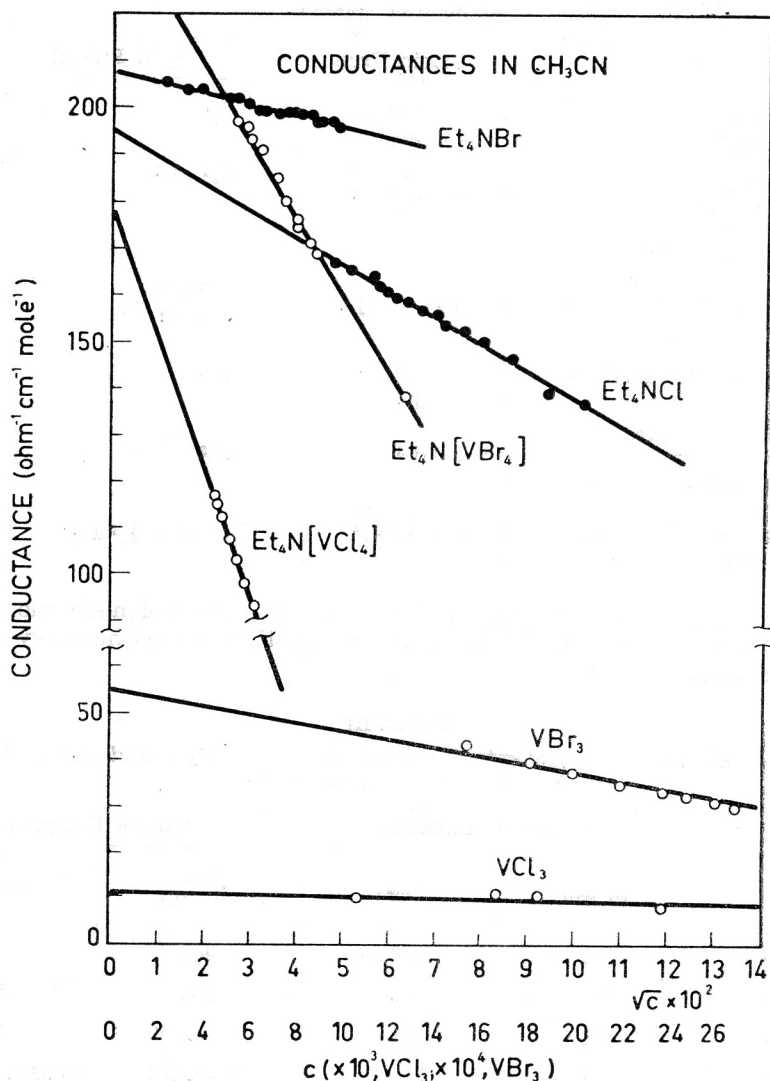Fig. 4. Conductances in CH_3CN.

Thus it has been possible to prepare the first d_{γ}^2 tetrahalogeno complexes of tervalent vanadium and as expected from crystal field theory these are tetrahedral.

Tetrahedral d[8] Complexes

As part of a related investigation, Dr. Naida A. Gill[8,9,10] has been studying tetrahedral complexes of the bivalent metals Mn^{II}, Co^{II} and Zn^{II} each of

which is expected to give regular tetrahedral complexes of the type $M^I_2 M^{II} X_4$. It has been found convenient to use for M^I a large organic cation such as the $[Et_4N]^+$ or $[Ph_3Me As]^+$ ions. Alcohol is a convenient solvent in which to mix the pseudo-alkali halide and the metal dihalide because water causes solvolysis — particularly in the case of Mn^{II}; indeed, it is very difficult to
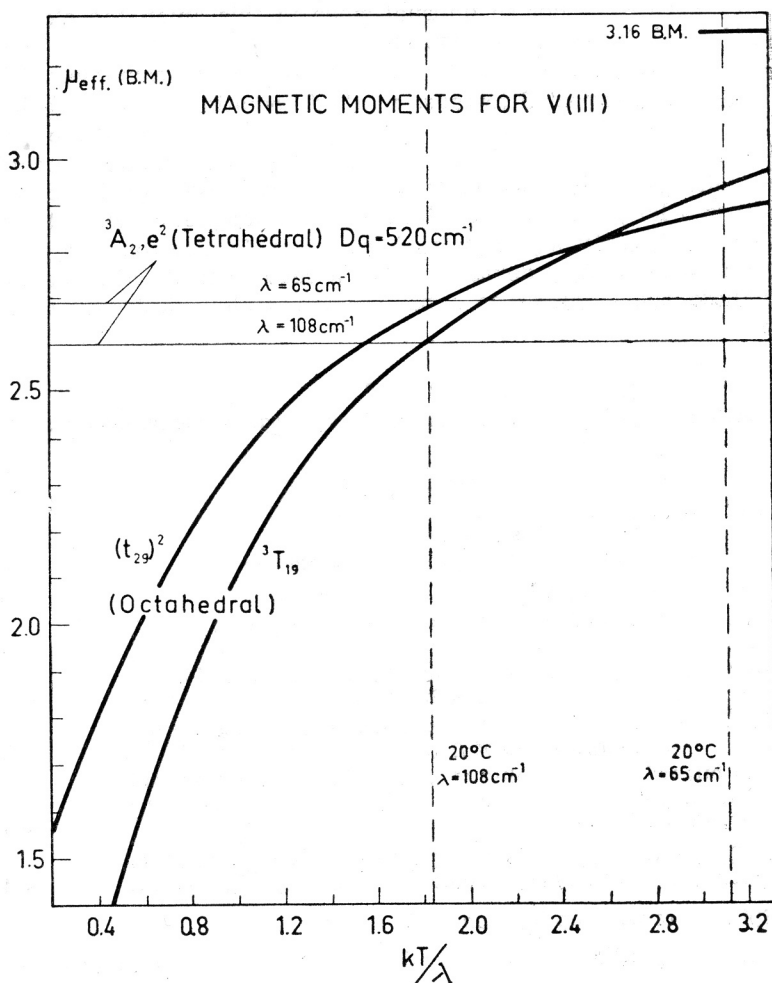
Fig. 5. Magnetic moments for V^{III}.

prepare the $[MnX_4]^=$ ion unless the solvent is a much poorer solvating one than water. Complexes of the type $[Ph_3MeAs]_2 M Cl_4$ where $M = Mn^{II}$, Co^{II} and Zn^{II} have been found to be strictly isomorphous as expected since these metals have respectively d^5, d^7 and d^{10} non-bonding electron configurations. Furthermore, there are many crystal structure studies which show that the $CoCl_4^{2-}$ ion is tetrahedral. The corresponding $[Ph_3MeAs]_2 CuCl_4$ complex was also prepared but this is not isomorphus; on crystal field theory this is to be

expected since a square planar arrangement in the anion is predicted. As we shall see later, however, the $[CuCl_4]^{2-}$ ion, whilst not a square planar ion, nevertheless deviates considerably from a regular tetrahedral arrangement. The corresponding $[FeCl_4]^{2-}$ and $[NiCl_4]^{2-}$ complexes were also prepared and surprisingly these were found to be isomorphous with the Mn^{II}, Co^{II} and Zn^{II} complexes. Hence, the $[FeCl_4]^{2-}$ and $[NiCl_4]^{2-}$ ions are also tetrahedral. Perhaps the case for $[FeCl_4]^{2-}$ is not so unusual since in this anion the electron configuration $(d_\gamma{}^3 d_\varepsilon{}^3)$ involves an asymmetry in the orbitals pointing in between the tetrahedral ligands. However, for $[NiCl_4]^{2-}$ we have an asymmetric d_ε shell $(d_\gamma{}^4 d_\varepsilon{}^4)$ and this is expected to cause marked deviation from a regular tetrahedral arrangement. The near perfect tetrahedron is supported also by magnetic data. As may be seen from Table IV the expected magnetic moment for a regular tetrahedral Ni^{II} complex is considerably larger (~ 4.0 B.M.). This arises because a large orbital contribution to the magnetic moment can occur only if the three d_ε orbitals (containing here f o u r $3d$ electrons) are degenerate or nearly degenerate. Any deviation from a regular tetrahedral arrangement will split these apart and cause a partial or complete destruction in orbital magnetism.

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TABLE IV

Predicted magnetic moments for spin-free bivalent nickel complexes.

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No.	Environment of Ni^{II} atom	μ_{eff}. (B.M.) (calc'd.)
1.	Free Ni^{2+} ion ($^3F_4$). No electrical field. $S = 1$, $L = 3$. Assume $\lambda = 0$.	4.47*
2.	As in (1) but assuming usual value of λ (~ -335 cm.$^{-1}$)	5.56
3.	As in (1) but assuming $\lambda = \infty$	5.59†
4.	Ni^{2+} ion in perfect octahedral field of negative charges; Assume $\lambda = 0$.	2.83
5.	Octahedral Ni^{II}, e.g., $[Ni(H_2O)_6]^{2+}$, using accepted value of λ (varies from ~ 200 to 324)	$\sim 3.1 - 3.2$
6.	Ni^{2+} in tetrahedral field of negative charges assuming $\lambda = 0$ and large value of Δ (assume $L = 1$)	3.16*
7.	As in (6) but using same value of λ as in octahedral case and assuming Δ is very large, i.e., only configuration to be considered is $d_\gamma{}^4 d_\varepsilon$	~ 3.6
8.	As in (7) but with Δ small enough to permit configuration interaction (i.e., weak filed). Moment can be as large as 4.1.	~ 4.1

$\lambda =$ Spin — orbit coupling constant

* Using $\mu = \sqrt{[4S(S + 1) + L(L + 1)]}$ † Using $\mu = g\sqrt{[J(J + 1)]}$.

Since Δ decreases in the sequence $[NiCl_4]^{2-} > [NiBr_4]^{2-} > [NiI_4]^{2-}$ the effect of mixing in of higher states becomes steadily more important as we pass from the chloro- to the bromo- to the iodo-complex. The effect of this is to cause a decrease in μ_{eff}. The experimental values are: $[NiCl_4]^{2-}$ 3.88 B.M.; $[NiBr_4]^{2-}$, 3.79 B.M.; $[NiI_4]^{2-}$ 3.49 B. M. These figures should be compared with $[CoCl_4]^{2-}$, 4.69 B. M.; $[CoBr_4]^{2-}$, 4.74 B.M.; $[CoI_4]^{2-}$, 4.85 B.M. Here the steadily decreasing value of Δ mixes in more of a triplet excited state as we pass from the chloro to the bromo to the iodo complex with a consequent i n c r e a s e in μ_{eff} along this sequence.

The spectra of the $[NiX_4]^{2-}$ complexes are again similar to those of other tetrahedral complexes in exhibiting large values of ε. Values of ε_{max} vary from 167 for $[NiCl_4]^{2-}$ to 173 for $[NiBr_4]^{2-}$ to 1096 for $[NiI_4]^{2-}$. Finally single crystal X-ray studies by Dr. Peter Pauling show that in the $[Ph_3MeAs]_2NiCl_4$ complex the Ni^{2+} atoms lie on a threefold axis of symmetry. Any deviation from a perfect tetrahedral arrangement is small and involves a lengthening of one bond by a maximum of 0.03 Å.

We now ask why simple crystal field theory has proven inadequate here. An answer is provided if we bear in mind that the Ni—Cl bonds involve a considerable degree of covalent character. The degree of covalency in $[MX_4]^{2-}$ complexes is in any case expected to increase as we pass from Ti^{2+} to Cu^{2+} along the first transition series because the effective electronegativity of the M^{2+} ion is increasing as we move from left to right. (The latter is measured by the rising sum of first and second ionisation potentials.) Experimental support for this covalent character is given also by studies of the change of λ, the spin-orbit coupling constant of a metal ion, when complex occurs. For an ion in an F state $\mu_{eff} = \mu$ spin only $(1 + 4\lambda/\Delta)$ where Δ is the splitting between d_ε and d_γ levels. If λ retained its free ion value, then one should be able to calculate μ_{eff} in metal complexes from a knowledge of Δ (obtained spectroscopically). However, it is found that when one attaches ligands to a metal ion λ decreases, moving in the direction such as to suggest that the bivalent metal ion is at least approaching electrical neutrality i. e. $M^{2+} \rightarrow M^0$. This is simply interpreted to imply charge transfer of electron pairs from the ligands to the metal ion, i. e. covalent binding. Now as these electron pairs get closer to the metal atom their mutual repulsion will become steadily more important. This repulsion favours a regular tetrahedral arrangement (Figure 1.) rather than the unsymmetrical tetrahedron suggested by the d^8 non-bonding configuration.

Alternatively, one could say that sp^3 bonding becomes steadily of greater importance. In $[NiCl_4]^{2-}$ it is clear that covalent binding is of greater importance in deciding shape than is the non-bonding configuration since the complex ion is shown experimentally to be an almost regular tetrahedron.

An extremely interesting test of these ideas is provided by the $[CuCl_4]^{2-}$ ion. For an essentially ionic structure crystal field theory suggests that a $[Cu(ligand)_4]^{2+}$ ion should be square. This is the case for $[Cu(H_2O)_4]^{2+}$. However, if easily polarisable ligands are used one might expect these to result in much more ligand — ligand repulsion owing to covalent binding and hence for the shape to more towards a tetrahedron. It is therefore of importance to notice that the $[CuCl_4]^{2-}$ in $Cs_2[CuCl_4]$ does indeed show this behaviour.* The structure of the anion is that of a slightly flattened tetrahedron with bond angles of 120^0 and 104^0.[11] Thus in this d^9 instance the expected shapes for a purely ionic crystal field model (square planar) and a perfect covalent model (regular tetrahedral) differ markedly and the resulting shape is intermediate between them. We return therefore to our opening remarks: in predicting stereochemistry it is not a question of which theory is correct. The valence bond and crystal field theories start at two different ends of a spectrum and which model is the more appropriate depends upon whether the bond is essentially ionic or essentially covalent in the complex being considered.

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* The $[CuBr_4]^{2-}$ is similarly distorted.

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IZVOD

Stereokemija kompleksnih halida prelaznih metala

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Iznesen je pregled stereokemije tetrahalogeno kompleksa metalnih iona prve prelazne serije. Razmatrane su elektronske konfiguracije nevezivnih elektrona, koje pogoduju stvaranju pravilnih tetraedrijskih kompleksa. Prikazani su oblici kompleksa s koordinacijom četiri, koji imaju drugačiji poređaj nevezivnih elektrona. Opisana su dobivanja i svojstva tetraedrijskih kompleksa trovalentnoga vanadija kao i tetraedrijskih kompleksa Mn^{II}, Co^{II}, Zn^{II}, Fe^{II} i Ni^{II}. U svijetlu teorije valentne veze i teorije kristalnoga polja razmatrana su magnetska svojstva i spektri ovih spojeva.

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