896. *The Stereochemistry of Five-co-ordination. Part II.*[1] *Transition Elements.*

By R. J. GILLESPIE.

The stereochemistry of five-co-ordination in molecules of the transition elements is discussed in terms of the theory of valency-shell electron-pair repulsions. For transition elements with d^0 and d^{10} configurations, as for non-transition elements, the trigonal-bipyramidal shape, determined by the interactions between the five electron pairs in the valency shell, is preferred. For other, less symmetrical *d*-shell configurations it is necessary to consider the interaction of the valency-shell electron pairs with the *d*-shell as well as with each other. It is shown that generally this additional interaction results in the square-pyramid's becoming more stable than the trigonal bipyramid. Examples of both trigonal-bipyramidal and square-pyramidal molecules of the transition metals are described and discussed, and the few cases of five-co-ordinated molecules whose shapes do not conform to the general rules are accounted for.

IN order to apply the ideas developed in Part I[1] to molecules of the transition elements it is necessary to take into account the interaction of the valency-shell electron pairs with the non-bonding *d*-shell in addition to their interactions with each other. A spherically symmetric *d*-shell such as that of the d^0, d^{10}, and d^5 (spin-free) configurations will have no effect on the arrangement of the valency-shell electron-pairs and thus, as for non-transition elements, five pairs will have a trigonal-bipyramidal arrangement and six pairs an octahedral arrangement. However, in other cases there will generally be some distortion of the preferred arrangement of the valency-shell electron-pairs, the magnitude of which will depend on the relative importance of their interaction with each other and with the non-bonding *d*-shell.

The d^0 *Configuration*.—The pentachlorides and pentabromides of niobium and tantalum have the expected trigonal-bipyramidal structures in the vapour state.[2] Although it is expected that the axial bonds would be longer than the equatorial bonds,[1] no differences have been reported in the lengths of the axial and equatorial bonds in these molecules. However, as the data was obtained in an electron-diffraction study carried out over twenty years ago, re-investigation of these structures would be of interest. A recent *X*-ray determination of the structure of solid niobium and tantalum pentachloride[3] has shown that they contain dimeric molecules with two bridging chlorine atoms (Fig. 1), whose stereochemistry is therefore based on an octahedral arrangement of six electron pairs rather than the trigonal-bipyramidal arrangement of five pairs. It is of interest that the deviations of the bond angles in this molecule from the ideal value of 90° can be satisfactorily accounted for in terms of electron-pair repulsions. The bridging chlorine atoms which are sharing two electron-pairs rather than one will have a higher effective electronegativity which will pull the electron pairs in the bridge bonds further away from the metal atom and also contract the orbitals that they occupy so that their interactions with each other and with the other electron-pairs will be less than the interactions between the electron-pairs of the non-bridging bonds. Evidently the angle between the bridge bonds will be less than 90°, allowing the other angles to increase to values slightly greater than 90° in exactly the observed manner.

In crystalline KVO_3,H_2O the vanadium is surrounded by five oxygen atoms with a distorted trigonal-bipyramidal arrangement.[4] Each trigonal bipyramid shares two edges

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[1] Part I, Gillespie, preceding paper.

[2] Skinner and Sutton, *Trans. Faraday Soc.*, 1940, **36**, 681.

[3] Zalkin and Sands, *Acta Cryst.*, 1958, **11**, 615.

[4] Christ, Clark, and Evans, *Acta Cryst.*, 1954, **7**, 801.

with neighbouring trigonal bipyramids to form an infinite chain as shown in Fig. 2. If we assume that the bonding is essentially covalent the atoms must carry the formal charges shown. The VO^1 bonds are only 1·63 Å long while there are two other VO bonds of length 1·93 Å and one of length 1·99 Å. The latter bonds are to oxygen atoms each of which is bonded to three vanadium atoms, and they must therefore be essentially single bonds; the other two bonds are to oxygen atoms that are not bonded to other vanadiums and it seems reasonable to suppose that they have at least 50% double-bond character, in agreement with their short length. The partial double-bond character of the VO^1 bonds will distort the trigonal bipyramid by pushing the other bond pairs together and decreasing the angle that they make with each other to less than 90°; the observed value is 74°. This effect is accentuated by the high electronegativity of the O^+ atoms to which the other bond-pairs are attached—the bond pairs are pulled strongly towards the O^+ atoms, which decreases their repulsions on each other and enables them more easily to move together under the influence of the VO^1 bonds.

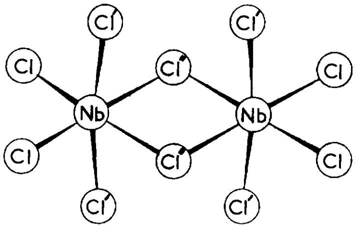

FIG. 1. The structure of $(NbCl_5)_2$, $(TaCl_5)$, and $(MoCl_5)_2$.

Bond angles: Cl'NbCl' 168·2°, ClNbCl 101·1° NbCl''Nb 101°, Cl'MoCl' 167°, ClMoCl 96°, MoCl''Mo 99°.

Bond lengths: NbCl'' 2·55, NbCl' 2·30, NbCl 2·25, MoCl'' 2·53, MoCl' 2·25, MoCl 2·24.

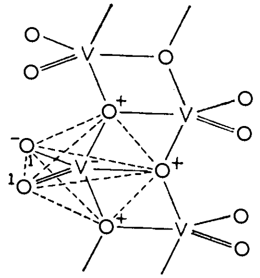

FIG. 2. The structure of the vanadate ion in KVO_3,H_2O.

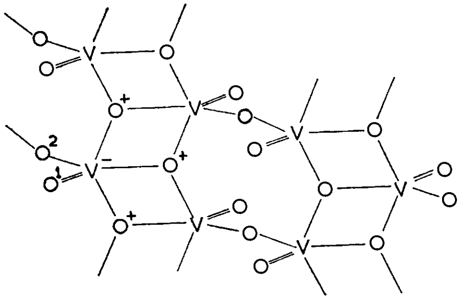

FIG. 3. The structure of V_2O_5.

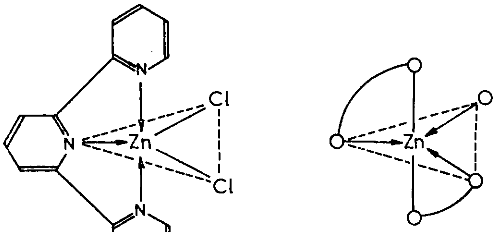

FIG. 4. The structures of Zn(terpyridyl)Cl_2 and Zn(acetylacetone)$_2$,H_2O.

The structure of V_2O_5 is clearly similar to that of the VO_3^- ion (Fig. 3).[5] It contains the same infinite chains of trigonal bipyramids sharing edges, but these chains are joined together by sharing of another oxygen at a corner to give a three-dimensional complex. Thus there are in this case three different types of oxygen atom surrounding the vanadium. O^1 is bonded to only one vanadium and the bond VO^1 which has a length of 1·54 Å is presumably a double bond. This length is close to the V–O distance in $VOCl_3$. The oxygen atom O^2 is linked to two vanadium atoms by bonds with some double-bond character; these bonds repel each other more strongly than single bonds and hence the

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[5] Bystrom, Wilhelmi, and Brotzen, *Acta Chem. Scand.*, 1950, **4**, 1119.

bond angle (125°) is appreciably greater than the tetrahedral angle.[6] The other three bonds are single bonds to very electronegative O^+ atoms and are correspondingly longer; two have a length of 1·85 Å and one a length of 2·02 Å. The arrangement of the oxygen atoms around the vanadium in V_2O_5 may be regarded as a somewhat distorted form of the arrangement expected for the five atoms around the sulphur in SOF_4.[1]

The d^{10} *Configuration.*—Two five-co-ordinated complexes of zinc, Zn(terpyridyl)Cl_2 and Zn(acetylacetone)$_2$,H_2O, both have the expected trigonal-bipyramidal structure [7,8] with axial bonds longer than the equatorial bonds, as shown in Fig. 4.

An apparent exception to our prediction that five-co-ordinated zinc(II) complexes should have a trigonal-bipyramidal structure is provided by bis-salicylaldehyde-ethylenediiminezinc monohydrate which has the square-pyramidal structure shown in Fig. 5.[9] The zinc atom is above the basal plane of the square pyramid with the angle α between the basal bonds and the bond to the water molecule at the apex = 100°. By constructing a model of this complex it is easily seen that it is not possible to have all four co-ordinating groups of the tetradentate ligand at four of the corners of the trigonal bipyramid. Since, as we have shown in the preceding paper,[1] the square pyramid with $\alpha = 100°$ is only slightly less stable than the trigonal-bipyramid, and since for this configuration it is possible for the four co-ordinating groups of the tetradentate ligand to take up the four positions around the base of the square pyramid, it is not surprising that this is the observed structure. This may be regarded as one of the special situations referred to in the introduction to the preceding paper [1] in which steric requirements of the ligand force an unusual stereochemistry on the metal. It may be noted that in this complex the metal atom is above the basal plane of the square pyramid in contrast to the square-pyramidal molecules of the non-transition elements in which the central atom is in all cases below this plane. The former is the most probable form of a square-pyramidal arrangement of a total of five electron pairs all of which are bonding, while the latter is the shape derived from six electron pairs of which five are bonding and one non-bonding.[1]

The d^1—d^9 *Configurations.*—One method of treating the interactions between the ligand electron pairs and the non-bonding *d*-shell is by means of the ligand-field theory. This, in fact, considers the electrostatic interaction between the ligands, treated as point negative charges, and the *d*-electrons on the central metal, but the conclusions of this theory should, nevertheless, be qualitatively correct for the type of interaction that we are considering between bonding electron-pairs and the non-bonding *d*-shell in an essentially covalent complex.

The ligand-field stabilisation energies given in the Table show that in every case from d^1 to d^9 the energy of the *d*-electrons is less for the square-pyramidal arrangement of the ligands than for the trigonal-bipyramidal.[10] However, the interactions between the bonding electron-pairs themselves favour a trigonal-bipyramidal arrangement.[1] When the interaction between the ligand electron-pairs is relatively more important than their

Ligand-field stabilisation energies for trigonal-bipyramidal and square-pyramidal complexes.

	Trigonal bipyramid	Square pyramid		Trigonal bipyramid	Square pyramid
d^0	0 *Dq*	0 *Dq*	d^6	12·56	20·00
d^1	2·72	4·57	d^7	13·38	19·14
d^2	5·44	9·14	d^8	14·14	18·28
d^3	6·24	10·00	d^9	7·07	9·14
d^4	8·06	9·14	d^{10}	0	0
d^5	10·78	13·71			

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[6] Gillespie, *J. Amer. Chem. Soc.*, 1960, **82**, 5978.

[7] Corbridge and Cox, *J.*, 1956, 594.

[8] Lippert and Truter, *J.*, 1960, 4996.

[9] Hall and Moore, *Proc. Chem. Soc.*, 1960, 256.

[10] Basolo and Pearson, "Mechanisms of Inorganic Reactions," Wiley, New York, 1958.

interaction with the non-bonding *d*-electrons, which is probably the case in complexes with a large amount of " covalent " character, a trigonal-bipyramidal structure is to be expected, but when the interaction between the bonding electron-pairs and the *d*-shell predominates, as is probably the case in complexes with essentially " ionic " binding, then a square-pyramidal structure would be expected. When all the interactions are comparable an intermediate structure might be expected.

The structure of oxobisacetylacetonevanadium(IV) (d^1) has been shown to be a square pyramid, as shown in Fig. 6.[11] The bond to the apical-oxygen atom is much shorter than the bonds to the oxygen atoms of the acetylacetone molecules and is probably best represented as a double bond although it could have some triple-bond character. The extra repulsion produced by this double bond causes the angle α that it makes with the other VO bonds to have the rather large value of 106°. Evidently in this molecule the interaction of the bond electron-pairs with the single non-bonding *d* electron on the metal is sufficiently great to cause the square-pyramidal structure to be preferred to the trigonal-bipyramidal. It might be expected that in order to minimise its interactions with the bonding electron-pairs the non-bonding *d*-electron would occupy an orbital that is not symmetrical with respect to the vanadium atom but is to some extent directed away from the base of the square pyramid. The five bonds and the non-bonding *d*-electron may then be regarded as having an approximately octahedral arrangement. The extra repulsion due to the double bond and the weak repulsion associated with the single non-bonding *d* electron are responsible for the considerable deviation from a regular octahedral arrangement. The structure closely resembles that of the complex $2SeOCl_2,2C_5H_5N$,[1] except that the probably higher order of the VO compared with the SeO bond, and the presence of a single non-bonding electron in the vanadium complex compared with the non-bonding pair in the selenium complex, cause the angle α to be greater for the vanadium complex.

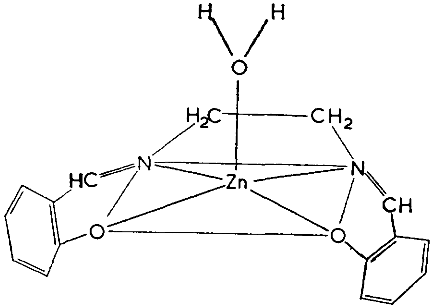

FIG. 5. The structure of bis-salicylaldehyde-ethylenedi-iminezinc monohydrate.

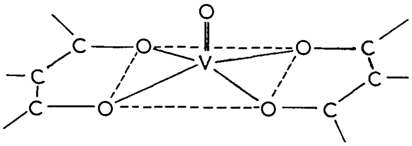

FIG. 6. The structure of oxobisacetylacetonevanadium(IV).

Molybdenum pentachloride (d^1) has been reported to have a trigonal-bipyramidal shape with equal equatorial and axial bond lengths.[12] A re-investigation of the structure of the molecule would obviously be of interest. In the crystal, the molecule is dimeric and has the same structure as $(NbCl_5)_2$ [13] in which each molybdenum atom has an approximately octahedral configuration and the single non-bonding *d*-electron does not appreciably affect the stereochemistry (Fig. 1).

The only other five-co-ordinated structures of transition metals that have been studied are some complexes of iron, cobalt, nickel, platinum, and copper with d^7, d^8, and d^9 configurations. For the d^7 (low-spin), d^8, and d^9 configurations it is possible to regard the *d* shell as having an ellipsoidal rather than a spherical shape, as for a d^{10} configuration. It is

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[11] Dodge, Templeton, and Zalkin, *J. Chem. Phys.*, 1961, **35**, 55.
[12] Ewens and Lister, *Trans. Faraday Soc.*, 1938, **34**, 1358.
[13] Sands and Zalkin, *Acta Cryst.*, 1959, **12**, 723.

not possible to say *a priori* if this ellipsoid would be oblate corresponding to the $d_{x^2-y^2}^{\,1}, d_{x^2-y^2}^{\,2}$ or $d_{x^2-y^2}^{\,2}, d_{z^2}^{\,1}$ configurations or prolate corresponding to the $d_{z^2}^{\,1}, d_{z^2}^{\,2}$ or $d_{z^2}^{\,2}, d_{x^2-y^2}^{\,1}$ configurations. The well-known tetragonal distortions of octahedral complexes of transition-metal ions with d^7, d^8, and d^9 configurations can most often be associated with a prolate rather than an oblate ellipsoidal *d*-shell, *i.e.*, the bonds along the tetragonal axis are generally longer than the four planar equatorial bonds, rather than shorter.

It was pointed out in Part I that a square-pyramidal arrangement of five electron pairs with $\alpha = 100°$ is not much less stable than the trigonal bipyramid.[1] It is clear that the interaction between the valency-shell electron-pairs and a prolate ellipsoidal *d*-shell will cause the valency-shell electron pairs to tend to avoid the ends of the ellipsoid since in these positions they will be subject to the greatest repulsion. This interaction with the *d*-shell will have a greater destabilising effect on the trigonal-bipyramid, which places two electron pairs opposite the ends of the *d*-shell ellipsoid, than on the square pyramid, which places only one electron pair in such a position (Fig. 7). Thus it is reasonable to suppose that when there is strong interaction between the valency-shell electron-pairs and a d^7, d^8, or d^9 shell the square-pyramidal configuration for five electron pairs may become more stable than the trigonal-bipyramidal. The extra repulsion exerted on the axial electron-pair by the *d*-shell would be expected to cause the axial bond to be longer than the basal bonds. If the trigonal-bipyramidal arrangement is retained, the ratio of the axial to the equatorial bond lengths would be expected to be even greater than it is for trigonal-bipyramidal molecules of the non-transition elements. The interaction between the bonding electron-pairs and an oblate ellipsoidal *d*-shell would, however, further stabilise the trigonal bipyramid with respect to the square pyramid and would be expected to cause the equatorial bonds to have approximately the same length as, or perhaps a slightly greater length than, the axial bonds. Thus, if the trigonal-bipyramidal configuration is found for a d^7, d^8, or d^9 transition element ion the difference between the axial and the equatorial bond lengths is likely to be small and perhaps in the opposite direction to that observed in the case of trigonal-bipyramidal molecules of the non-transition elements (Fig. 7).

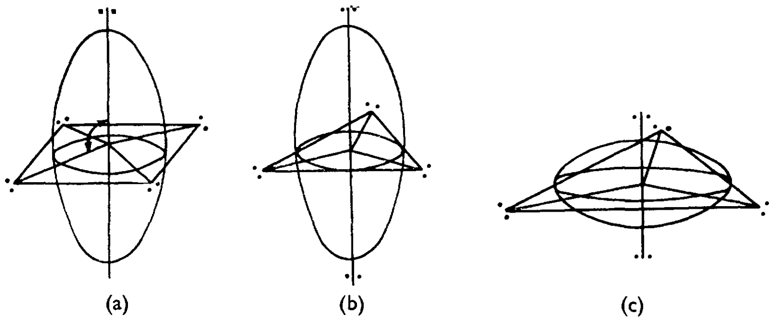

FIG. 7. (a) Prolate *d*-shell and square-pyramidal arrangement of valence-shell electron pairs. (b) Prolate *d*-shell and trigonal-bipyramidal arrangement of valence-shell electron pairs. (c) Oblate *d*-shell and trigonal-bipyramidal arrangement of valence-shell electron pairs.

The factors that determine whether or not the *d*-shell is to be regarded as having a prolate or an oblate ellipsoidal shape are not clear. However, one can predict that for the apparently more common prolate ellipsoid the square pyramid is favoured and if the trigonal bipyramid does occur the axial bonds will be considerably longer than the equatorial bonds, whereas for the oblate ellipsoidal *d*-shell the trigonal bipyramid is favoured and it will have approximately equal axial and equatorial bond lengths or even slightly shorter axial than equatorial bonds (Fig. 7).

Most five-co-ordinated complexes of transition metals with d^7, d^8, and d^9 configurations have a square-pyramidal structure corresponding to the prolate ellipsoidal *d*-shell. (Dimethyl dithiocarbonato)nitrosocobalt(II) has been shown to have the structure in Fig. 8 in which the cobalt is 0·54 Å above the plane of the sulphur atoms.[14] Copper dimethylglyoxime has been shown to be dimeric in the crystal, each copper atom being surrounded by a square-pyramidal arrangement of four nitrogen atoms from two dimethylglyoxime molecules and an oxygen atom from a dimethylglyoxime of a copper–dimethylglyoxime complex.[15] The square pyramid is distorted in the way described above, so that the copper is above the plane of the four nitrogen atoms and, as expected, the bond between the copper and the oxygen atom of the second dimethylglyoxime molecule is found to be 2·41 Å, which is longer than the " normal " Cu–O single bond distance of 2·0 Å. Similar structures have been observed for bis-salicylaldehydeisopropylidenedi-iminecopper monohydrate and bis-salicylaldehyde-ethylenedi-iminecopper.[16] The latter is a dimeric compound with Cu–O = 2·41 Å and the former has Cu–OH_2 = 2·53 Å. Again these long bonds along the axis of the square pyramid can be attributed to the greater repulsion exerted by the *d*-shell in this direction. A similar structure (Fig. 9) is also found for $NiBr_2$ (triarsine), except that in this case the four atoms at the base of the pyramid are not all equivalent so that there is no reason to expect a symmetrical structure; indeed it is found that the basal bromine atom is distorted out of the plane by 11° whereas the arsenic atoms are depressed below the plane by an average of only 3°.[17] Again the axial Ni–Br bond is much longer than the basal Ni–Br bond. It seems probable that the interaction between the apical electron-pair and the non-bonding *d*-shell will cause a distortion of the eliptical *d*-shell so that it bulges out more below the base of the square pyramid. This could be approximately described by placing five bond-pairs and one lone-pair in octahedral orbitals (d^2sp^3 hybrids in valence-bond theory), leaving six *d*-shell electrons in the d_{xy}, d_{yz}, and d_{xz} orbitals which are symmetrically disposed towards the six octahedral orbitals and therefore have no influence on their arrangement. The shape and electron

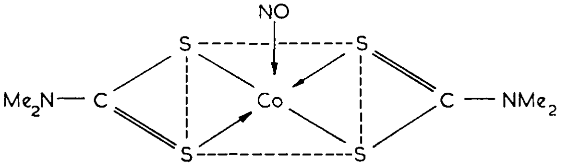

FIG. 8. The structure of (dimethyl dithiocarbonato)nitrosocobalt(II).

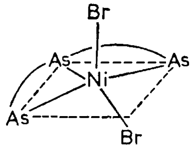

FIG. 9. The structure of $NiBr_2,Me_2As\cdot[CH_2]_3\cdot AsMe\cdot[CH_2]_3\cdot AsMe$.

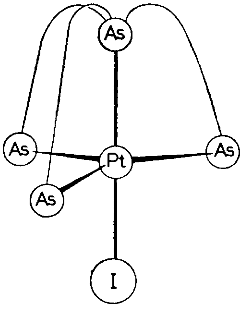

FIG. 10. The structure of PtI(QAS)$^+$.

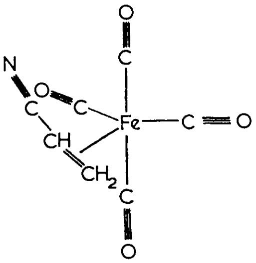

FIG. 11. The structure of tetracarbonylacrylonitrileiron.

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[14] Alderman, Owston, and Rowe, *J.*, 1962, 668.
[15] Frasson, Bardi, and Bezzi, *Acta Cryst.*, 1959, **12**, 201.
[16] Waters, Hall, and Llewellyn, *Chem. and Ind.*, 1958, 1203.
[17] Mair, Powell, and Henn, *Proc. Chem. Soc.* 1960, 415.

arrangement of these complexes is, therefore, related closely to that of the AX_5E molecules of the non-transition elements, except that, whereas for the non-transition elements the non-bonding pair exerts a greater repulsion than the bonding pairs, for the d^8 transition-metal complexes the equivalent non-bonding pair is at least partly " inside " the valency shell, or in other words retains considerable 3*d* character, and thus has a smaller repulsive effect on the ligand electron-pairs. Hence the four bonds in the base of the square pyramid are bent towards this lone-pair orbital, rather than away from it as in the case of non-transition elements.

The $CuCl_5^{3-}$ ion has been shown to have a trigonal-bipyramidal structure in which $d(Cu-Cl) = 2{\cdot}35$ Å for the equatorial bonds and 2·32 Å for the axial bonds.[18] This is consistent with our conclusion above, that an oblate ellipsoidal *d*-shell will stabilise the trigonal bipyramid and cause the axial to be shorter than the equatorial bonds. Mair, Powell, and Venanzi [19] have recently carried out the first structure determination of a five-co-ordinated platinum complex, namely, $[PtI(QAS)]BPh_4$, where QAS stands for the ligand tris-(*o*-diphenylarsinophenyl)arsine, $As(C_6H_4{\cdot}AsPh_2\text{-}o)_3$. Their preliminary results indicate that the cation has a trigonal-bipyramidal structure (Fig. 10). In this case the trigonal symmetry of the ligand may help to maintain the trigonal-bipyramidal structure. Bond lengths have not yet been reported.

Pentacarbonyliron [20-22] and tetracarbonylacrylonitrileiron [23] also have a trigonal-bipyramidal structure (Fig. 11). It is generally accepted that there is considerable double-bond character in the ligand–metal bonds in these molecules. Double-bond character increases the repulsions between the bonds, and by removing electrons from the non-bonding *d*-shell it reduces the interaction between the *d*-shell and the bonding electron pairs. Hence it is not unreasonable that in these molecules the interactions between the bonding-electron pairs predominates over their interaction with the *d*-shell so that the trigonal-bipyramidal structure is preferred. The axial bonds are longer than the equatorial bonds in tetracarbonylacrylonitrileiron, as in molecules of the non-transition elements. From an electron-diffraction study [20] the bonds in pentacarbonyliron have been reported to be all the same length, but this structure evidently needs accurate re-investigation.

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DEPARTMENT OF CHEMISTRY, MCMASTER UNIVERSITY,
HAMILTON, ONTARIO, CANADA.

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[18] Mori, Saito, and Watanabe, *Bull. Chem. Soc. Japan*, 1961, **34**, 295.
[19] Mair, Powell, and Venanzi, *Proc. Chem. Soc.*, 1961, 170.
[20] Ewens and Lister, *Trans. Faraday Soc.*, 1939, **35**, 681.
[21] Stammreich, Sala, and Tavares, *J. Chem. Phys.*, 1959, **30**, 856.
[22] Pistorius and Haarhoff, *J. Chem. Phys.*, 1959, **31**, 1439.
[23] Luxmore and Truter, *Proc. Chem. Soc.*, 1961, 466.