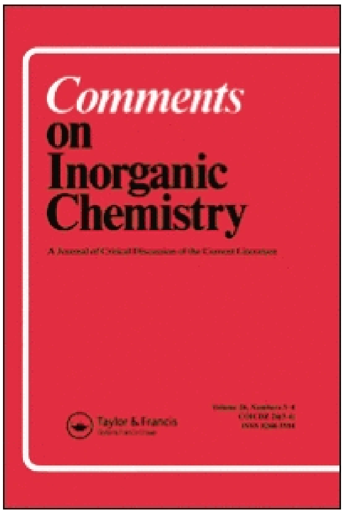

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Coordination Numbers Larger Than Six Among Electronegative Elements

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Coordination Numbers Larger Than Six Among Electronegative Elements

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A review of recent structure determination of non-metal anions containing simple ligands, mostly halogenes, is given, where the total number of ligands exceeds 6. It will be shown that these anions exist in the form of regular polyhedra, the pentagonal bipyramid and the square antiprism. A non-bonding electron pair (or two) will influence such geometries in a complex way: the general principle that such pairs are stereochemically active needs to be carefully revised in compounds of large coordination numbers.

Key Words: *fluoro anions, halogen fluorides, xenon fluorides, tellurium halides*

1. INTRODUCTION

Among main group compounds the Valence Shell Electron Pair Repulsion Model, as first described by Gillespie and Nyholm,[1] serves as a reliable model for predicting molecular geometries. Nowadays one can say that the structure of any main group compound is qualitatively correctly predicted, if the coordination number 6 is not exceeded. The model also is useful in the solid state,

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when longer contacts and their directions need to be discussed. Very often also qualitative predictions about bond lengths and angles can be made. The reason for this success is, of course, the underlying principle of the universal law of electrostatic attraction and repulsion.

A peculiarity of this model is that non-bonding electron pairs are regarded as additional ligands. Very recent theoretical works have shown that one can define an "electron localisation function" that is large in areas of the nuclei, the bonding electron pairs and also the non-bonding electron pairs.[2,3]

In the following discussion it will be discussed how these principles hold if coordination numbers larger than 6, including nonbinding electron pairs, are considered.

2. MOLECULAR FLUORIDES AND FLUOROANIONS WITH COORDINATION NUMBERS LARGER THAN 6 WITHOUT NONBINDING ELECTRON PAIRS

It is the nature of the chemical bond that coordination numbers larger than 6 among binary main group compounds can only be reached with the fluoride ligand. In fact IF_7 remains the only molecular species of this kind. Since the formal oxidation state cannot be increased numerically beyond the numbering of the old periodic system, one has to look for fluoroanions of earlier elements, such as TeF_7^-, IOF_6^-, TeF_8^{2-} and IF_8^-.

For a homoleptic, seven coordinated species four different geometries are conceivable: The pentagonal bipyramid, (1:5:1 model) the capped octahedron (1:3:3 model), the 1:4:2 and the 1:2:2:2 model (see Fig. 1). Without much bending energy all these models

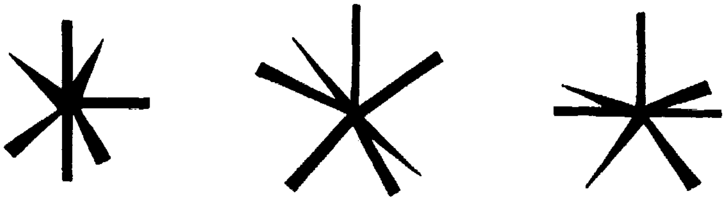

FIGURE 1 Possible geometries for the homoleptic seven coordination.

can be interconverted, so complicated problems of nonrigidity can be expected, much more complicated than in the well established case of five coordinated species.[4]

IF_7 as the only molecular main group species of this type has clearly a pentagonal bipyramidal structure, as was found out long ago.[5] The apical bonds are *shorter* than the equatorial ones, as is predicted by the previously mentioned model. However, the electron diffraction measurement indicated deviations from the idealized geometry. The five equatorial fluorine atoms are probably puckered (comparable to the ring puckering of cyclopentane) and the apical fluorine atoms may follow this movement. ^{19}F n.m.r. experiments reveal only one very broad resonance, at least partially due to collapse of coupling to the $J = 5/2$ of ^{127}I by the large quadrupole momentum.

The only method that may give exact answers is crystallography. However, IF_7 undergoes a solid–solid phase transition at $-120°C$, the normal melting point is 6°C, so that growing of single crystals of the low temperature phase is very difficult (the high temperature phase is of plastic nature, which means it is highly disordered). The reported data do not give clear insight into the structure.[6,7]

The search for analogues to IF_7 in order to find the structure principle of seven coordination reveals TeF_7^-. It has long been known as a Cs^+ sale.[8,9] However, in such ionic compounds the structure may be strongly influenced by cationic–anionic interactions. It is therefore advisable to have as large a cation as possible. Very recently the first *pure* $(CH_3)_4N^+F^-$ has been described, which turned out to have a remarkable stability against oxidative attack: The positive charge is delocalized over all 16 protons, so the "surface" of this cation is protected.[10] We are convinced that this remarkable material will in the future replace much of the often used CsF as a catalyst.

Indeed $(CH_3)_4N^+TeF_7^-$ can be grown in large crystals.[11,12] The vibrational analysis indicate clearly a pentagonal bipyramidal structure of the anion. Unfortunately, the almost spherical shapes of both cation and anion bring up a strongly disordered crystal structure which so far has withstood any solution. But lattice constants seem to be very close to $(CH_3)_4N^+IOF_6^-$ (see below). The ^{19}F- and ^{125}Te-.n.m.r. show all fluorine atoms being equivalent, so we have here a *nonrigid* species.

Indeed, IOF_5 is also complexed with $(CH_3)_4N^+F^-$ giving the novel anion IOF_6^-.[11,12] This, however, is a rigid species, as indicated by the doublett/sextett ^{19}F-n.m.r. spectra, giving a pentagonal bipyramidal structure with apical positioned oxygen: Any intramolecular exchange would place the oxygen into an equatorial position which seems to be energetically unfavourable. The crystal structure of this anion is shown in Fig. 2. The axial fluorine bond and the oxygen bond distances are shorter than the equatorial bonds, as was expected.

So while it seems that the pentagonal bipyramidal structure is the building principle for seven coordination, it remains to be seen what the situation is for the eight coordination: Models predict the cube, the square antiprism and the trigonal dodecahedrane (see Fig. 3). The cube is known to have larger repulsions between ligands than the others. From theory it cannot surely be predicted which of the remaining two has more stable geometry. Among homoleptic main group compounds there are two examples, IF_8^- and TeF_8^{2-}. The related XeF_8^{2-} will be discussed later since it has

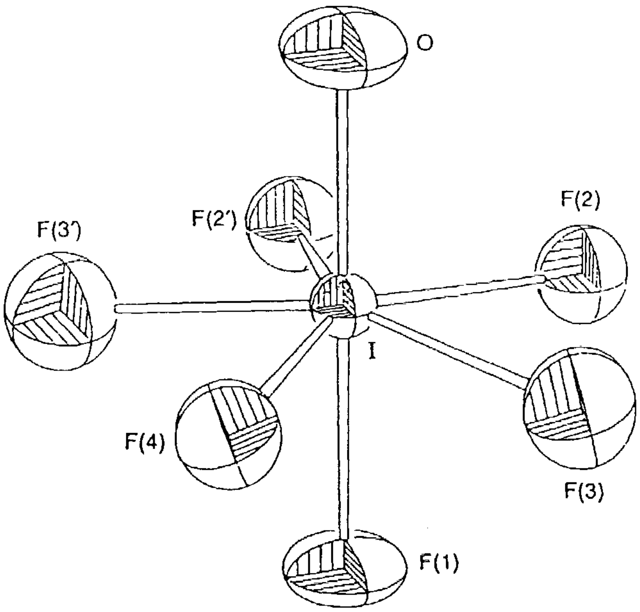

FIGURE 2 Structure of the IOF_6^- anion, from the $(CH_3)_4N^+IOF_6^-$ crystal structure. Reprinted with permission of the Chemical Society, London.

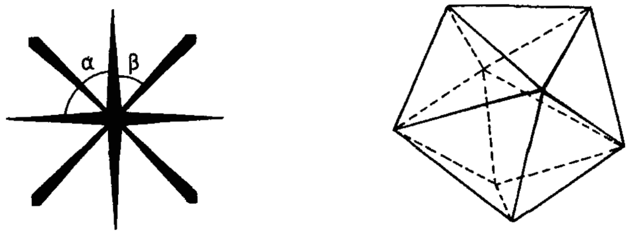

FIGURE 3 Possible geometries for the homoleptic eight coordination.

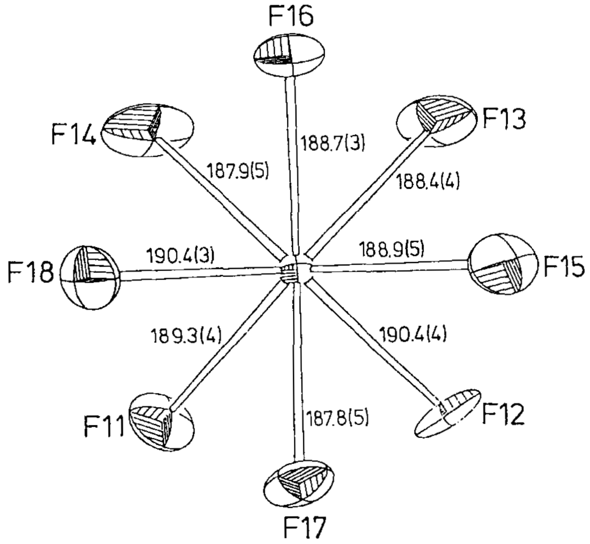

FIGURE 4 Structure of IF$_8^-$ anion, from the NO$^+$(NOF)$_2$IF$_8^-$ crystal structure. Reprinted with permission of VCH Verlag, Weinheim, New York.

one non-bonding electron pair. Both anions were described some time ago,[8,9,13] but the structures, again, were not clearly established. This we succeeded doing for the IF$_8^-$ anion.[14] It exists as Cs$^+$, NO$^+$(NOF)$_2$, and (CH$_3$)$_4$N$^+$ salt. The precicest structure is that of the nitrosyl compound, whereas the (CH$_3$)$_4$N$^+$IF$_8^-$ exhibits another case of severe disorder and twinning, which could be solved, however.[14] In all cases IF$_8^-$ has a regular square antiprism (see Fig. 4), and the TeF$_8^{2-}$ anion seems to have a similar structure, if one looks at its vibrational spectra.[9]

A regular square antiprism is a peculiar configuration since it has 8 equal bond lengths, but one remaining free parameter that defines its elongation or its flatness. We defined the angle α between adjacent fluorine atoms within one hemisphere as such a parameter. It turned out that the dependent angle β between adjacent fluorine atoms of different hemispheres is almost the same $\approx 75°$. This tells us that the IF_8^- anion is neither elongated nor flattened but has the closest packing required by the electron pair repulsion model. (*The structure of* $NO^+(NOF)_2IF_8^-$ *exhibits another peculiarity: a square pyramidal nitrogen coordination in the cation.*)

So there is an indication, but no proof yet, that the square antiprism is the structural principle for the homoleptic main group eight coordination.

For non-homoleptic compounds with coordination eight we cannot say anything so far. Also we can say nothing about the coordination number nine.

3. MOLECULAR HALIDES AND ANIONS WITH COORDINATION NUMBERS LARGER THAN 6 WITH NONBONDING ELECTRON PAIRS

If the pentagonal bipyramid and the square antiprism are the principle geometries for coordination numbers 7 and 8, then it ought to be simple to predict geometries for molecules and ions with non-bonding electron pairs, if the electron pair repulsion model still holds. As will be shown, this is not the case any longer. Obviously a large number of ligands with the subsequent sterical crowding results in a compression of the volume available for the non-bonding electron pair. This can already be seen with the old and famous case of gaseous XeF_6: The simple prediction would be pentagonal pyramidal structure with the non-bonding pair in an apical position opposite the apical fluorine atom. However, the molecule is known to have C_{3v} symmetry, close to an octahedron, with the non-bonding electron pair on the center of one plane, opening the angles between adjacent fluorine atoms and closing the angles between opposite fluorine atoms (adjacent and opposite with respect to the assumed location of the free electron pair).

The structure, abbreviated as 1:3:3 type, is close to an octahedron, so that intramolecular rearrangement is predominant, resulting in a time averaged non-polar molecule.[15,16,17]

The only known covalent xenon(VI)derivative, $Xe(OTeF_5)_6$, probably has the same structure.[18]

The structures of the isoelectronic ions IF_6^- and BrF_6^- have only very recently been solved. IF_6^- is the closest relative to XeF_6. After overcoming the problems of a systematic twinning of $(CH_3)_4^+IF_6^-$ at low temperatures, the structure turned out to be a strongly C_{3v} distorted octahedron (see Fig. 5) very much like the gas structure of XeF_6.[19] The peculiarity is the loose dimer formation which indicates intermolecular fluorine exchange in the crystal at room temperature: the bridging fluorine atoms switch back and forth, and the other fluorine atoms follow this movement.

If, however, a small cation, NO^+, is chosen, then IF_6^- prefers a tetramer,[19] very much like crystalline $(XeF_6)_4$.[20] The differences between these two tetramers are marginal.

While XeF_6 and IF_6^- are very much alike, BrF_6^- is different: it is octahedral,[21,22] (see Fig. 6): The explanation can be that the MO scheme for octahedral complexes holds for BrF_6^-, since the A_{1g}^+ orbital is low enough in energy (see Fig. 7). This would be a consequence of the imperfect shielding of the nucleus by the first filled d-shell. The only result of the presence of a non-bonding electron pair is the 10% bond length increase in BrF_6^- as compared to BrF_6^+. The latter is, of course, also strictly octahedral.

The picture of a centrosymmetric (not necessarily spherical symmetric) non-bonding electron pair is certainly reasonable for BrF_6^-; but it seems that the unstable CCF_6^- has the same structure.[23] That would indicate that also sterical reasons have to be considered. The crowding of 6 fluorine atoms around Cl simply does not leave space for a non-bonding electron pair as seventh ligand.

The whole discussion reminds us of the problem of the geometry of the long known ions $SeCl_6^{2-}$, $TeCl_6^{2-}$, and alike. With simple cations these ions are octahedral. In the last few years this problem has been brought to a conclusion also: The series of ions has been extended to $SbCl_6^{3-}$ and $BiCl_6^{3-}$, and also bromides and iodides have been investigated.[24-27] In a series of papers W. Abriel has shown that the structures of these anions depend strongly on the

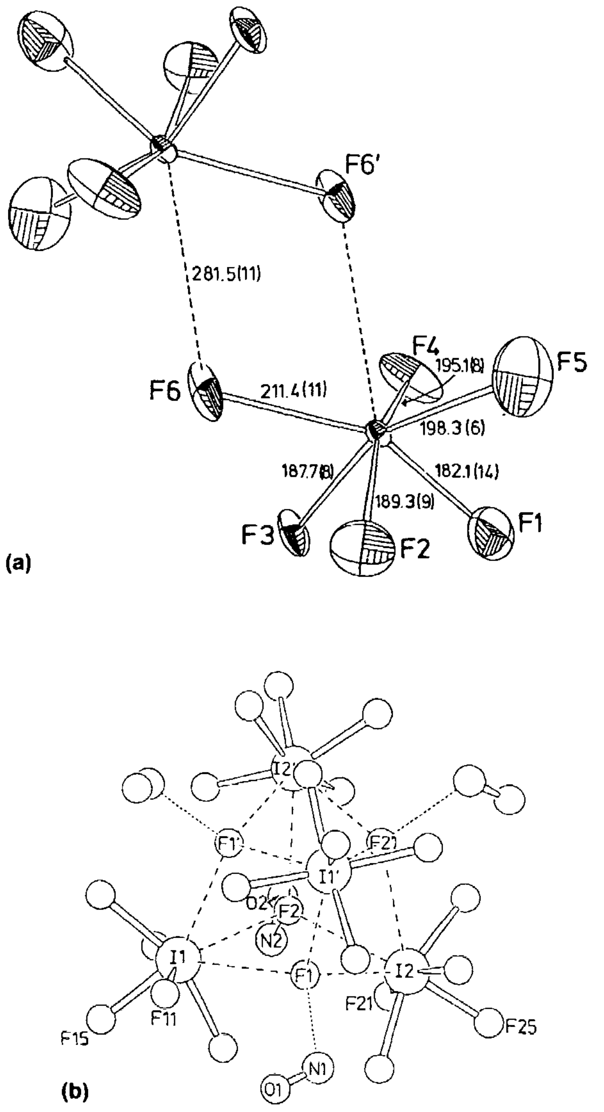

FIGURE 5 Structure of the IF_6^- dimer and tetramer anion, from the $(CH_3)_4N^+IF_6^-$ and $(NO^+IF_6^-)_4$ crystal structures. Reprinted with permission of VCH Verlag, Weinheim, New York.

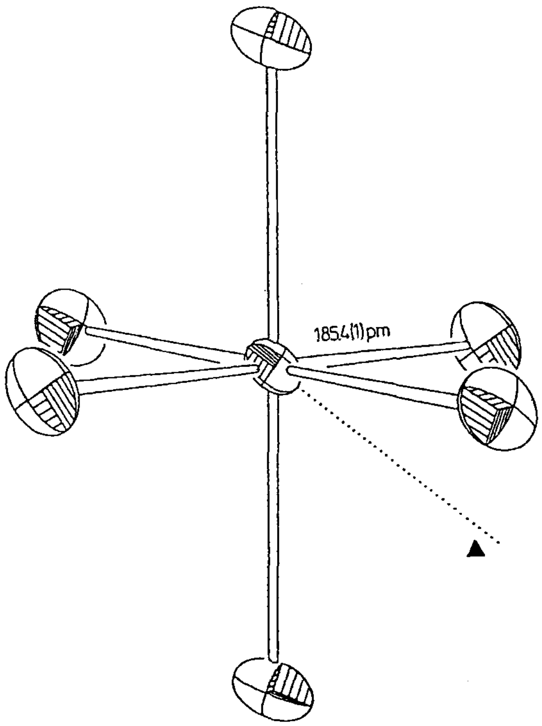

FIGURE 6 Structure of the BrF_6^- anion, from the $Cs^+BrF_6^-$ crystal structure. Reprinted with permission of VCH Verlag, Weinheim, New York.

counterion. Simple or highly symmetric cations enforce an octahedral structure. The same anions in combination with less symmetric cations are always, sometimes strongly, distorted from octahedral symmetry (see Table I). It is also shown that the vibrational ellipsoids of the crystallographic determinations of the octahedral cases may in fact be superimpositions of dynamically distorted (or at low temperature, statically distorted and then disordered) non-octahedral structures.[25] While this argument often goes to the limits of precision of the x-ray determination, a strong argument is obtained by comparison of i.r. spectra of $TeCl_6^{2-}$ and $SnCl_6^{2-}$. In $TeCl_6^{2-}$ the two i.r. active bands of a regular octahedron collapse to a very intense, broad absorption, indicating large amplitude motions that rapidly interconvert different slightly non-octahedral structures.[25]

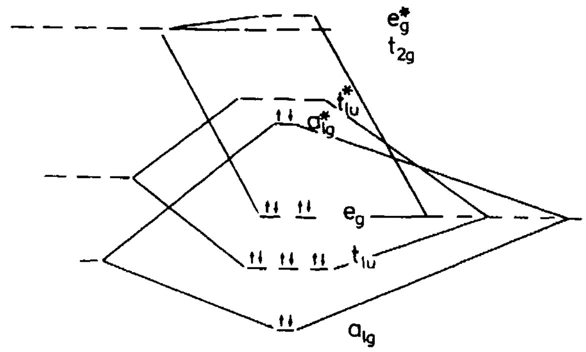

FIGURE 7 Schematic MO diagram for octahedral main group compounds and 14 electron.

TABLE I

Listing of maximal and minimal Te–Cl bond lengths in $TeCl_6^{2-}$ salts (excerpt from Ref. 24).

Compound	Space Group	R_{max}[Å]	R_{min}[Å]	$\Delta \times 10^5$
$[(CH_3)_4N^+]_2TeCl_6$	Fd3c	2.538	2.538	0
$[(C_6H_5)_4As]_2TeCl_6$	$P\bar{1}$	2.548	2.518	2.75
$N_2C_3H_{12}TeCl_2$	Pnma	2.672	2.426	68.4
$[(MeHN_2)_2CS]_2TeCl$	$Pna2_1$	2.740	2.420	186.53

O. Knop *et al.* have discussed this problem in detail also.[28] They favour a C_{3v} symmetry (as in gaseous XeF_6 or crystalline IF_6^-) as the genuine geometry for these systems, which may degenerate to the octahedral geometry. The latter will increasingly be favoured in the sequence Te, I, Xe, as computational results indicate.[29] Also the larger halogenes will favour the higher symmetry. Both findings are in accord with simple considerations of size. The remaining uncertainty is due to crystal forces.

For the summary of this discussion, see Fig. 8. It contains qualitatively the bending potential of the distortion from octahedral symmetry of different molecules and ions: TeF_6 and BrF_6^- are octahedral. $TeCl_6^{2-}$ adjusts itself to the environment, and XeF_6 and IF_6^- are non-octahedral under all circumstances.

Normally sterical effects bring the non-bonding electron into the

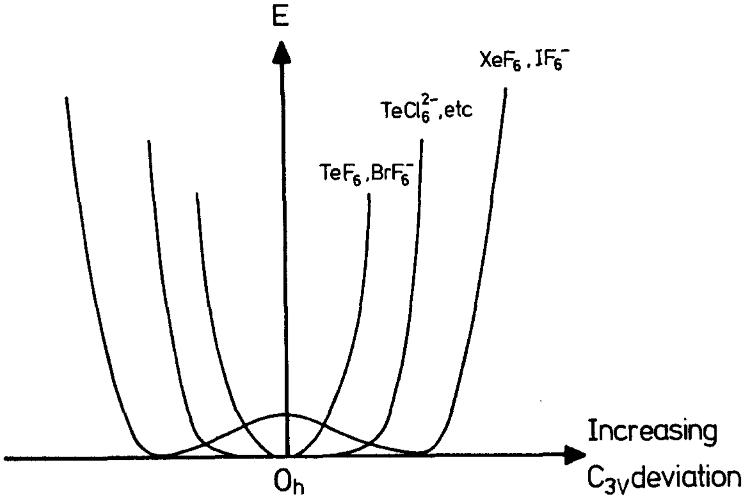

FIGURE 8 Potential curves for the C_{3v} distortion of octahedral main group halides.

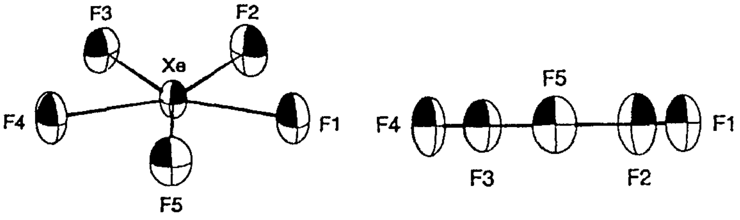

FIGURE 9 Structure of the XeF_5^- anion from the $(CH_3)_4N^+XeF_5^-$ crystal structure. Reprinted with permission of the American Chemical Society.

sterically most unhindered position. A perfect example is the newly detected anion XeF_5^-.[30] This anion may be considered as a derivative of a pentagonal bipyramid containing two non-bonding electron pairs in axial positions (see Fig. 9). Besides the beauty of the fully planar anion, it shows that the number of five real ligands around xenon is not large enough to block the sterical activity of the non-bonding pairs.

Xenon chemistry serves as another example for the contrary also. The known structure of XeF_8^{2-} [31] (one non-bonding electron pair) can be compared with IF_8^- (see previous section). Both are regular square antiprisms. Small deviations in the case of XeF_8^{2-}

are most likely caused by interactions with the small NO^+ cations. The average bond length in XeF_8^{2-} is larger than in IF_8^- although xenon is considered to be smaller than iodine: another case of a sterically inactive electron pair that only blows up the size of the anion.

4. SUMMARY

The valence shell electron pair repulsion model finds its limits with coordination numbers larger than 6. In certain cases the sterical activity of the non-bonding electron pairs disappears completely. If many more structures become known with different ligands, e.g., IOF_6^-, a very complicated stereochemistry will arise. Unfortunately chemical stability will not allow too many of such cases, since we are restricted to the large, electronegative non-metal elements and to a small number of different ligands. There is, however, a similar field of chemistry with coordination numbers larger than 6 among transition metal coordination compounds. This is also an unfinished story, but nevertheless beyond the scope of this survey.

Acknowledgments

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References

1. R. J. Gillespie and R. S. Nyholm, Q. Rev. **11**, 339 (1957).
2. A. D. Becke and K. E. Edgecombe, J. Chem. Phys. **92**, 5397 (1990).
3. A. Savin, A. D. Becke, J. Flad, R. Nesper, H. Preuss and H. G. v. Schnering, Angew. Chem. **103**, 421 (1991); Angew. Chem. Int. Ed. Engl. **30** (1991).
4. R. S. Berry, J. Chem. Phys. **32**, 933 (1960).
5. W. J. Adams, H. B. Thompson and L. S. Bartell, J. Chem. Phys. **53**, 4040 (1970).
6. R. D. Burbank and F. N. Bersey Jr., J. Chem. Phys. **56**, 5081 (1957).
7. J. Donohue, J. Chem. Phys. **58**, 1618 (1959), R. Burbank, *ibid.* **58**, 1619 (1959).

8. E. C. Muetterties, J. Amer. Chem. Soc. **79**, 1004 (1957).
9. H. Selig, S. Sarig and S. Abramovitz, Inorg. Chem. **13**, 1508 (1974).
10. K. O. Christe, W. W. Wilson, R. D. Wilson, R. Ban and J. Feng, J. Amer. Chem. Soc. **112** (1990).
11. A. R. Mahjoub and K. Seppelt, Chem. Comm., in press.
12. K. O. Christe, J. C. Sanders, J. J. Schrobilgen and W. W. Wilson, Chem. Comm., in press.
13. C. J. Adams, Inorg. Nucl. Chem. Lett. **10**, 831 (1974).
14. A. R. Mahjoub and K. Seppelt, Angew. Chem. **103** (1991); Angew. Chem. Int. Ed. Engl. **30** (1991).
15. L. S. Bartell, R. M. Gavin Jr., H. B. Thompson and C. L. Gerwich, J. Chem. Phys. **43**, 2547 (1965).
16. W. E. Falconer, M. J. Vasile and F. A. Stevie, J. Chem. Phys. **66**, 5335 (1978).
17. For a brief summary of the structure of XeF_6 see K. Seppelt and D. Lentz, *Progress Inorg. Chem.*, ed. S. Lippard. (J. Wiley & Sons, 1982), Vol. 29, p. 167.
18. E. Jacob, D. Lentz, K. Seppelt and A. Simon, Z. Anorg. Allg. Chem. **472**, 7 (1981).
19. A. R. Mahjoub and K. Seppelt, Angew. Chem. **103**, 309 (1991); Angew. Chem. Int. Ed. Engl. **30**, 323 (1991).
20. R. D. Burbank and J. R. Jones, J. Amer. Chem. Soc. **96**, 43 (1974).
21. A. R. Mahjoub, A. Hoser, J. Fuchs and K. Seppelt, Angew. Chem. **101**, 1528 (1989); Angew. Chem. Int. Ed. Engl. **28**, 1526 (1989).
22. K. O. Christe and W. W. Wilson, Inorg. Chem. **28**, 3275 (1989), W. W. Wilson and K. O. Christe, *ibid.* **28**, 4172 (1989).
23. K. O. Christe, R. V. Chirakal, J. C. P. Sanders, G. J. Schrobilgen and W. W. Wilson, Inorg. Chem. **29**, 3506 (1990).
24. W. Abriel, Z. Naturforsch. **40b**, 1691 (1987); **42b**, 415 (1988).
25. W. Abriel and E. J. Zehnder, Z. Naturforsch. **42b**, 1273 (1988).
26. W. Abriel, Acta Cryst. B **42**, 449 (1986).
27. W. Abriel and H. Ehrhardt, Angew. Chem. **96**, 965 (1984); Angew. Chem. Int. Ed. Engl. **23**, 963 (1984).
28. O. Knop, A. Linden, B. R. Vincent, S. C. Choi, T. S. Cameron and R. J. Boyd, Can. J. Chem. **67**, 1984 (1989).
29. M. Klobukowski, S. Husinga, L. Seijo and Z. Barondiaran, Theor. Chim. Acta **71**, 375 (1987).
30. K. O. Christe, E. C. Curtis, D. A. Dixon, H. P. Mercier, J. C. P. Sanders and G. J. Schrobilgen, J. Amer. Chem. Soc. **113**, 3351 (1991).
31. S. W. Peterson, J. H. Holloway, B. A. Coyle and J. M. Williams, Science **173**, 1238 (1971).