PENTACO-ORDINATION

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THE subject of pentaco-ordinate structures has received scant attention in textbooks and reviews, and with some justification since few of these structures were recognised until recent years. Examples of pentaco-ordination were once limited to Group V elements and to iron pentacarbonyl but it is now apparent that pentaco-ordination pervades the Periodic Table. There are pentaco-ordinate structures based on such diverse elements as magnesium, boron, carbon, tin, aluminium, nickel, and rhodium. Although the rare label no longer applies to pentaco-ordinate compounds, it still holds for definitive information on stereochemistry in this structural class. Trigonal bipyramidal geometry will probably prove to be the most common ground-state structure. However, the difference in energy between the trigonal bipyramid and the tetragonal pyramid for most electronic configurations should be small, and there may be specific ligand stabilisation of the tetragonal pyramidal state. Additionally there is the possibility of a low-energy process that can interconvert the two idealised geometries. Thus, pentaco-ordinate structures are potentially non-rigid in a stereochemical sense, and the time scale must be specified in any discussion of stereochemistry. It is also especially critical in discussing structures of pentaco-ordinate species to identify the physical state; there is no assurance that a given configuration will be maintained through the various physical states.

Since the stereochemical problem is yet to be resolved, it is premature to enter upon any discourse on bonding in pentaco-ordinate structures. Pauling's hybrid bond approach, electrostatics or Gillespie-Nyholm non-bonding repulsion considerations, and simple molecular orbital treatments yield similar conclusions about geometry, *i.e.*, they favour trigonal bipyramidal geometry at least for d^0, d^8, or d^{10} configurations but, as might be expected, these relatively simple analyses present different characterisations of the bonding. There have been attempts to analyse spectroscopic information, *e.g.*, nuclear magnetic resonance data, in an approximate fashion for characterisation of the bonding framework but these very crude and essentially mechanistic approaches are rather far removed from reality. The subject of bonding will not be pursued in this Review.

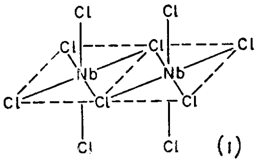
There are four major sections to this Review. In the first, pentaco-ordination is defined and discussed in the contexts of aggregation, geometry, structural rigidity, and reaction mechanism. Next, established structures are discussed in terms of idealised geometries and stereochemical correlations. Details of structural data are critically presented in the third section. In the fourth, a reference section, there is a tabulation of established and of potential pentaco-ordinate structures. For organisation, pentaco-ordinate compounds are divided into groups: the various classes of pentaco-ordinate structures with unidentate ligands, those with multidentate ligands, and cage or cluster aggregates in which pentaco-ordination is only a part of the overall structural problem.

I. General Principles

A. Definition of Pentaco-ordination.—Pentaco-ordination comprises those structures in which an atom is within reasonable bonding distance of five ligands. Ligand definition includes non-bonding electron pairs that reside in directed valence orbitals. Thus, our definition excludes such compounds or ions as BrF_5, SF_5^-, and SbF_5^{2-} and embraces SF_4, ClF_3, and SbF_4^-. The qualification is not completely arbitrary in that non-bonding electron pairs confer a structural rigidity to ML_5 species that is not an intrinsic property of a pentaco-ordinate structure. This reasoning is not extended to transition elements because the impact of *d* electron configuration on stereochemistry or structural rigidity is an experimental unknown.

B. Determination of Pentaco-ordinacy.—Composition is far from sufficient to establish pentaco-ordination. Although the most elementary formulation prevails for most four- and six-co-ordinate systems, this is not true for ML_5 compositions because of the tendencies toward (1) association to give octahedral dimers or polymers,* (2) solvation to octahedral structures in the solution state, and (3) rearrangement to ionic aggregates in the solid state. For such reasons, many of the compounds or ions listed in the Tables of Part III cannot be described as pentaco-ordinate structures at least for the condensed physical states.

In ML_5 compounds where the ligand is strongly electro-negative, a positive charge is generated about the central atom, and the compounds exhibit significant electron-acceptor properties. The acceptor activity may be sufficiently large that the molecules will be associated in the liquid or solid states through bridging ligand atoms (1). Such behaviour is typical of heavy-metal halides, *e.g.*, TaF_5,[1] and $MoCl_5$,[2] and the chlorides are usually dimers and the fluorides tetramers in the solid state. Antimony(V) halides



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* Penta co-ordination may be found in condensed states for nominally tetracoordinate species.

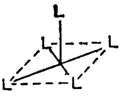
[1] A. J. Edwards, *J. Chem. Soc.*, 1964, 3714.

[2] D. E. Sands and A. Zalkin, *Acta Cryst.*, 1959, **12**, 723.

such as SbF_5[3] and SbF_3Cl_2[4] are associated in the liquid state, and liquid-state association is suspected in the other heavy-metal pentahalides.[5] Species present in the vapour state of the heavy-metal penta- and tetrahalides have not been established and it is critical that these vapour states be assessed with gas density and mass spectral studies. Association in ML_4 species does in some cases yield pentaco-ordinate arrays. For example, the trialkyltin halides,[6] hydroxides,[7] and carboxylates[8] have pentaco-ordinate tin atoms through tin–ligand–tin bonds.

Some potential pentaco-ordinate transition-metal compounds or ions associate through metal–metal bonding. For example, $Co(CN)_5{}^{3-}$ appears to be pentaco-ordinate in dilute solution; however, attempts to isolate crystalline salts have been unsuccessful. The solid phases[9] obtained from solution contain only dimeric octahedral anions $(NC)_5CoCo(CN)_5{}^{6-}$. Similarly, $Co(CNCH_3)_5{}^{2+}$ is paramagnetic and presumably monomeric in solution and in the blue perchlorate salt,[10] but it is dimeric and octahedral in the red form of the perchlorate salt.[11] This proclivity of d^7 ML_5 species to exist as octahedral dimers is evident in other systems such as $Mn_2(CO)_{10}$.

A problem arises for ML_5 structures in solution because of the difficulty in characterising solvation phenomena. For example, one cannot often rigorously distinguish between a tetragonal pyramidal (2) and a weak solvate–octahedral structure (3) in solution. However, comparison of



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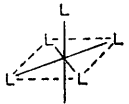

(3)

liquid and solution state spectral data may in some cases afford a reasonably clear distinction. A case in point: the ^{19}F n.m.r. data for liquid PF_5 and for ethereal solutions of PF_5 clearly establish a labile octahedral solvate as the primary species in solution.[12] The co-ordination number in ML_4 species in solution can be elusive. For example, there is a symmetry identity for the *cis*-octahedral disolvate with an equatorially solvated trigonal bipyramid. Stoicheiometry is again insufficient to define co-ordination number since a 1:1 complex may actually be hexaco-ordinate

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[3] C. A. Hoffmann, B. E. Holder, and W. L. Jolly, *J. Phys. Chem.*, 1958, **62**, 364.

[4] E. L. Muetterties, W. Mahler, K. J. Packer, and R. Schmutzler, *Inorg. Chem.*, 1964, **3**, 1298.

[5] F. Fairbrother, K. H. Grundy, and A. Thompson, *J. Chem. Soc.*, 1965, 761.

[6] H. C. Clark, R. J. O'Brien, and J. Trotter, *J. Chem. Soc.*, 1964, 2332.

[7] N. Kasai, K. Yasuda, and R. Okawara, *J. Organometallic Chem.*, 1965, **3**, 172.

[8] R. Okawara and M. O'Hara, *J. Organometallic Chem.*, 1964, **1**, 360.

[9] A. Adamson, *J. Amer. Chem. Soc.*, 1951, **73**, 5710.

[10] A. Sacco and M. Freni, *Gazzetta*, 1959, **89**, 1800.

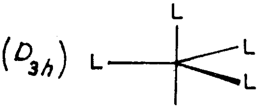
[11] F. A. Cotton, T. G. Dunne, and J. S. Wood, *Inorg. Chem.*, 1964, **3**, 1495.

[12] E. L. Muetterties, T. A. Bither, M. Farlow, and D. D. Coffman, *J. Inorg. Nuclear Chem.*, 1960, **16**, 52.

through M–L–M bonding as in the amine complexes of tin and titanium tetrafluorides.

Compounds which are pentaco-ordinate in the gaseous state may rearrange into ion aggregates upon condensation to the solid state. The classic example is phosphorus pentachloride[13] which is unimolecular in the gas state but forms a crystalline lattice comprised of PCl_4^+ and PCl_6^- ions. It is not at all evident what factors tend to promote such rearrangements. Solid-state structures of ML_5 compositions cannot be anticipated and structural analyses provide the only test of pentaco-ordination for this physical state.

C. Geometry.—For a structure in which five like ligands are bonded to a central atom, there are only two idealised geometries worthy of serious consideration, the trigonal bipyramid (D_{3h}) (4) and the tetragonal pyramid (C_{4v}) (5). On substitution of one ligand by a unique atom or group, the possible structures are increased to four. All four idealised structures (6)—(9) possess different symmetries but each of the two trigonal bipyramidal models have a closely related tetragonal pyramidal counterpart. For an ML_3X_2 pentaco-ordinate structure, there are three possible isomers in trigonal bipyramidal geometry, and for each of these there is a closely related isomer in tetragonal pyramidal geometry (10)—(15). Only one geometry (10; D_{3h} model) within this group can be established by spectroscopic analyses that rely wholly upon symmetry argu-



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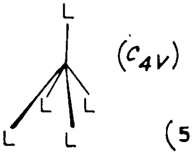

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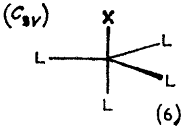

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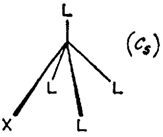

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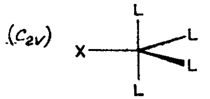

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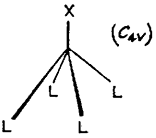

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[13] D. Clark, H. M. Powell, and A. F. Wells, *J. Chem. Soc.*, 1942, 642.

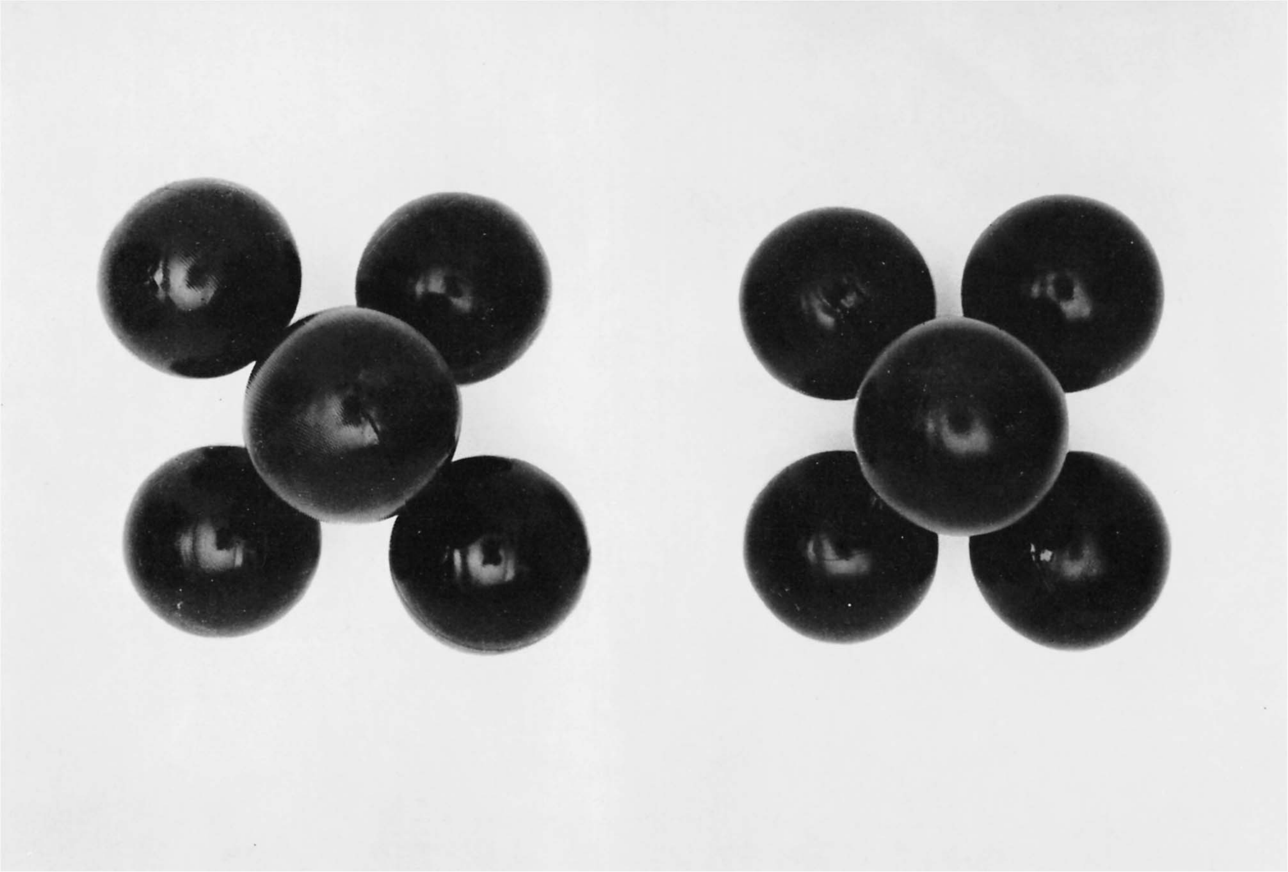


FIG. 1. *Alternative perspective of the trigonal bipyramid (left) and the tetragonal pyramid looking down* C_2 *and the* C_4 *axes, respectively.*

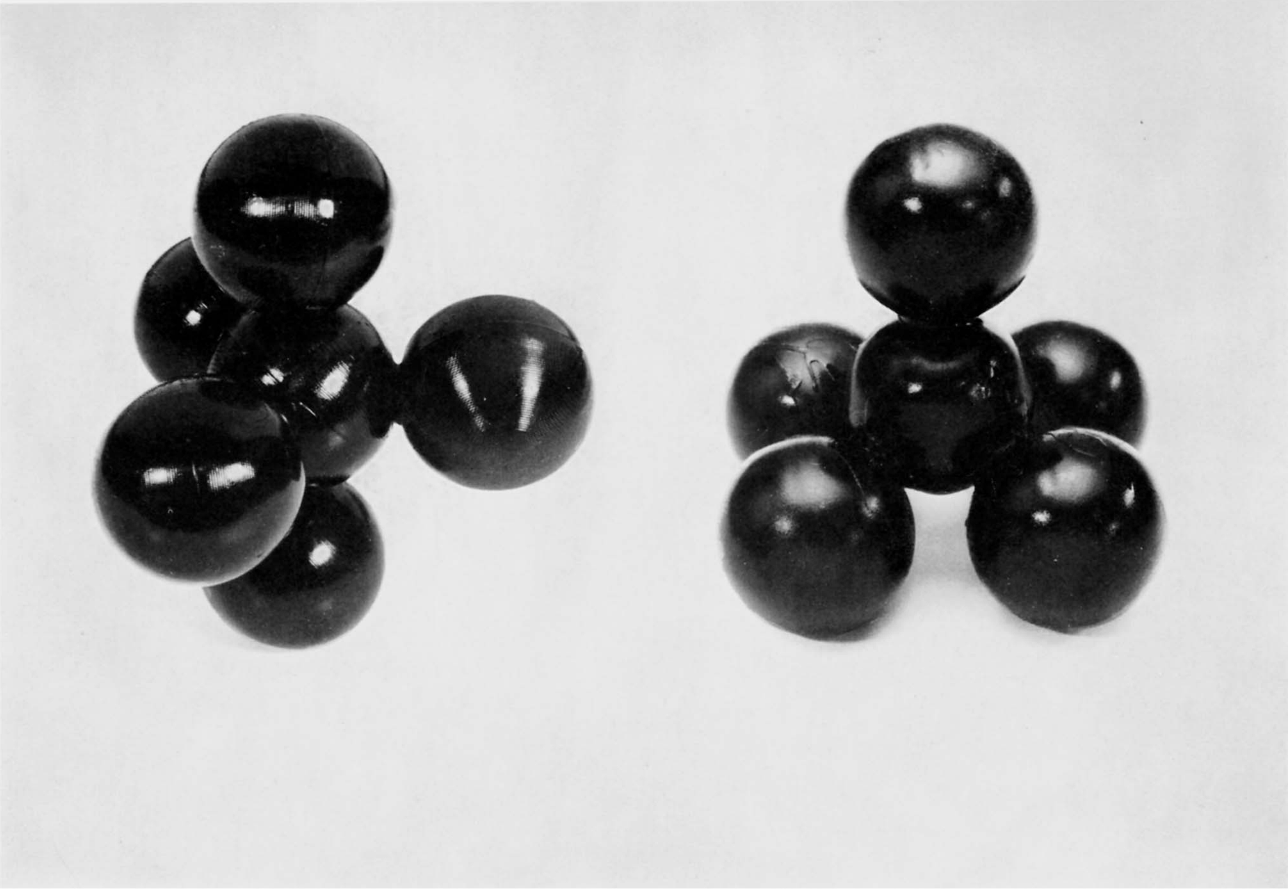
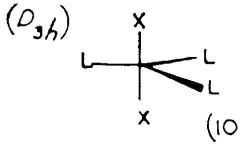


FIG. 2. *Perspectives usually employed for the trigonal bipyramid and the tetragonal pyramid.*



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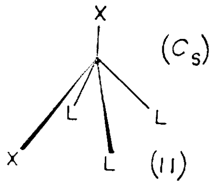

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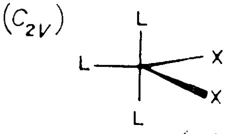

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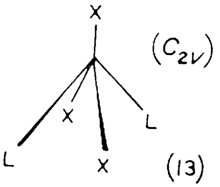

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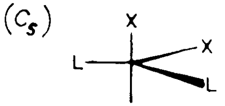

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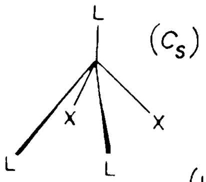
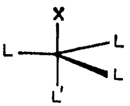


(15)

ments. The symmetry identities within this group greatly complicate establishment of ground-state geometries for the liquid and solution states. Microwave studies of the gas state are virtually the only reliable recourse here, and extensive preparation of isotopically labelled compounds will be required for a precise and accurate assay of molecular parameters. Even then the distinction between trigonal bipyramidal and tetragonal pyramidal geometry will be veiled.

For pentaco-ordinate structures with three kinds of ligand, there are too many possible isomers to illustrate here. In the case of XML$_2$L'$_2$ compounds, there are five possible geometrical isomers, one optically active, for a trigonal bipyramid and six for a tetragonal pyramid with two that have no plane of symmetry. For XML$_3$L' species, there are four possible isomers, one optically active, for a trigonal bipyramid and the same for a tetragonal pyramid. Of the nineteen geometrical isomers, only one, the C_{3v} trigonal bipyramid model (16) can be uniquely defined from



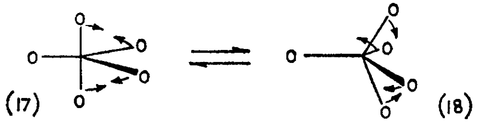
(16)

symmetry arguments. Generally, for these two classes of pentaco-ordinate species, structure can be accurately determined only for the solid state.

Because of the complexity of such highly substituted species, a distinction between tetragonal pyramidal or trigonal bipyramidal geometry (C_{3v} an exception) is not very meaningful. Geometry may be primarily determined by non-bonding repulsions between ligands particularly where the ligands are bulky as in triphenylphosphine.

D. Stereochemical Rigidity.—The two idealised geometries, trigonal bipyramid and tetragonal pyramid, appear unrelated in the traditional perspective as shown in Figure 1. However, even though they possess obviously different symmetry elements, they are strikingly similar when viewed down the C_2 axis of the trigonal bipyramid and the C_4 axis of the tetragonal pyramid as in Figure 2. The difference in energy levels for the two configurations may be small with respect to lattice-energy factors or packing forces in the solid state or to solvation energies in solution, and in some cases may be comparable to association energies in the liquid state. Only the gas state provides an unambiguous view of the electronically preferred configuration. Clearly, structural discussions of any pentaco-ordinate species must be referenced to a particular physical state.

As pointed by Berry,[14] interconversion of the two idealised geometries requires only a bending process as outlined in (17) and (18). This is a genuine vibration for an ML_5 species. Thus, there is a possibility that the lifetime of the ground-state geometry for a pentaco-ordinate compound or ion is short.[4,14,15,16] It is virtually impossible to predict the potential-energy surface of such complicated systems but three general situations may be recognised:


(17) (18)

(1) The amplitude of the bending vibration is so small that the probability of interconversion between (17) and (18) is very low and the ground-state lifetime is very long. This situation may occur for ML_5 structures which contain very heavy atoms. Thus $Pt(SnCl_3)_5^{3-}$, in the absence of intermolecular ligand exchange, may have a relatively long-lived ground-state geometry.

(2) The amplitude of the bending vibration is so large that interconversion occurs with each vibration. This is an improbable situation.

(3) Interconversion occurs through higher vibrationally excited states. Traversing of the energy barrier may be classical with molecular or wall collisions providing the final push or there may be a tunnelling of the barrier. Ground-state lifetimes here may vary from something longer

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[14] S. Berry, *J. Chem. Phys.*, 1960, **32**, 933

[15] E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, 1963, **2**, 613.

[16] E. L. Muetterties, *Inorg. Chem.*, 1965, **4**, 769.

than the 10^{-12} to 10^{-13} sec. for case (2) to something shorter than years for case (1). Berry[14] has estimated for PF_5 and PCl_5 rates of interconversion of about 10^5 sec.$^{-1}$ and 10^{-4} sec.$^{-1}$, respectively. Fast interconversion is the only plausible explanation for the n.m.r. spectroscopic equivalence of fluorine atoms in PF_5.

Stereochemical nonrigidity is clearly outlined in the temperature-dependence of the ^{19}F n.m.r. spectra of dialkylaminophosphorus tetrafluorides[4] and in CF_3NSF_4,*[4] and there are indications that lifetimes of ground-state geometries are very short for alkylphosphorus tetrafluorides,[15] $Fe(CO)_5$,[17,18] and AsF_5.[4,19] Classic examples of stereochemical non-rigid molecules are PF_3Cl_2 and PF_3Br_2.[4,15,20] These two fluorides have C_{2v} symmetry in the liquid, solution, and gas states.[4,15,20,21] Studies of the temperature-dependence of the ^{19}F n.m.r. spectra of PF_3Cl_2 and PF_3Br_2 have shown that there is a rapid intramolecular exchange of fluorine atoms in these molecules. The lifetimes of the ground-state geometry are about 10^{-1} and 10^{-2} sec., respectively, for PF_3Cl_2 and PF_3Br_2 at −50°, and the activation energy for the intramolecular rearrangement is 7·2 kcal./mole.[22] Hopefully, through techniques of this type, the energy surfaces of more pentaco-ordinate structures can be mapped.

The potentially easy rearrangement process in pentaco-ordinate structures lowers the probability of isolation of isomers in substituted ML_5 species. However, single crystals of isomeric species can be isolated. For example, if the energy levels of the C_{3v} and C_{2v} isomers (6 and 8) of some XML_4 species are comparable it is conceivable that either form may be stabilised in a particular crystalline lattice.

The question of structural rigidity must be kept clearly in mind whenever comparing structural information for a pentaco-ordinate structure, particularly when the data come from two physical techniques of significantly different time scales.[16] Structural rigidity is also a critical point if a pentaco-ordinate reaction intermediate is invoked because all stereospecificity may be lost in a long-lived intermediate.

E. Pentaco-ordination Postulated in Reaction Mechanism Schemes.—There appear to be pentaco-ordinate intermediates or transition states in many types of organic and inorganic reations. The most detailed informa-

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* Description is not straightforward because the rearrangement cannot be dissociated from the rotations about the P–N and S–N bonds.

[17] F. A. Cotton, A. Danti, J. S. Waugh, and R. W. Fessenden, *J. Chem. Phys.*, 1958, **29**, 1427.

[18] R. Bramley, B. N. Figgis, and R. S. Nyholm, *Trans. Faraday Soc.*, 1962, **58**, 1893.

[19] E. L. Muetterties and W. D. Phillips, *J. Amer. Chem. Soc.*, (*a*) 1957, **79**, 322; (*b*) 1959, **81**, 1084.

[20] R. R. Holmes, R. P. Carter, jun., and G. E. Peterson, *Inorg. Chem.*, 1964, **3**, 1748.

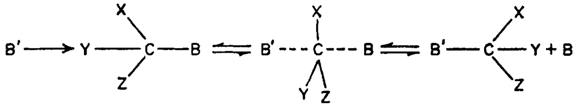
[20a] L. C. Hoskins, *J. Chem. Phys.*, 1965, **42**, 2631.

[20b] K. W. Hansen and L. S. Bartell, *Inorg. Chem.*, 1965, **4**, 1775.

[21] J. E. Griffeths, R. P. Carter, jun., and R. R. Holmes, *J. Chem. Phys.*, 1964, **41**, 863.

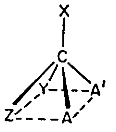
[22] W. Mahler and E. L. Muetterties, *Inorg. Chem.*, 1965, **4**, 1520.

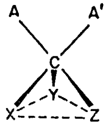
tion is found in substitution reactions at a tetrahedral carbon atom.[23] In bimolecular substitution involving nucleophilic attack of any asymmetric carbon atom, there is inversion of configuration. A model of the transition state consistent with these observations is a trigonal bipyramid:



On the other hand, electrophilic attack of an asymmetric carbon atom occurs with retention of configuration. In this pentaco-ordinate system derived from electrophilic attack, there are only eight electrons to describe five bonds, a situation formally analogous to that found in the boron hydrides. Thus, one might take either of the two geometries (19) or (20)

(19)





(20)

as models of the transition state since both of these have precedence in boron chemistry* and since either (19) or (20) meets the requirement for retention of configuration. A distinction between the two idealised geometries (19) and (20) is not too meaningful. Unless the X, Y, and Z groups are sterically and electronically very similar, actual bond angles may be primarily determined by non-bonding ligand repulsions. Only if X, Y, and Z are identical is there a symmetry distinction between (19) and (20).

Reactions of tetrahedral silicon have been examined[24–27] although not as extensively as in the case of carbon. Some nucleophilic substitutions at an asymmetric silicon atom occur with configurational inversion as found for all analogous carbon reactions. However, there are also examples of nucleophilic substitution on silicon with no configurational change. Inversion generally prevails in $R^1R^2R^3SiX$ species in which X is a good leaving group such as chloride ion whereas either retention or inversion is found for poor leaving groups like hydride or alkoxide ion. The experimental observations have, in general, been surveyed in terms of a pentaco-

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* For example, the apical boron atom in B_5H_9 and the 6 or 9 boron atom in $B_{10}H_{12}$-base have configurations (19) and (20) respectively; see section III, F.

[23] C. K. Ingold, "Structure and Mechanism in Organic Chemistry", G. Bell and Sons, London, 1953.

[24] A. D. Allen and G. Modena, *J. Chem. Soc.*, 1957, 3671.

[25] L. H. Sommer, C. L. Frye, M. C. Musolf, G. A. Parker, P. G. Rhodewald, K. W. Michael, Y. Okaya, and R. Pepinsky, *J. Amer. Chem. Soc.*, 1961, **83**, 2210.

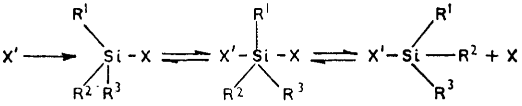
[26] L. H. Sommer, P. G. Rhodewald, and G. A. Parker, *Tetrahedron Letters*, 1962, 821.

[27] L. H. Sommer, C. L. Frye, and G. A. Parker, *J. Amer. Chem. Soc.*, 1964, **86**, 3276.

ordinate transition state although (solvated) hexaco-ordination is also conceivable.

On the basis of stereochemical data (see page 258) that exist for phosphorus compounds, we would expect any nucleophilic substitution at a silicon atom in a triorganosilane that proceeds through a pentaco-ordinate transition state to result in inversion of configuration, *i.e.*, the most probable transitional configuration comprises a trigonal bipyramid with near-planar alkyl or aryl groups. The substitutions that occur with retention of configuration appear anomalous within the framework of a pentaco-ordinate transition state; Sommers and his co-workers have postulated quasicyclic pentaco-ordinate transition states to account for these seemingly anomalous substitutions.

It has been suggested that racemisation of phosphine oxides under acidic conditions comprises an intramolecular rearrangement of a quinquecovalent intermediate $R^1R^2R^3POHCl$.[28] A similar process is one of two envisaged for acid-catalysed racemisation of sulphoxide; the suggested intermediate is $R^1R^2\ddot{S}Cl_2$ (the alternative state is $R^1R^2\ddot{S}Cl^+Cl^-$).[29]



In co-ordination chemistry, pentaco-ordinate intermediates and transition states have been postulated for many systems including octahedral, tetrahedral, and square-planar complexes. Square-planar complexes, particularly those of platinum(II), undergo a number of exchange reactions which seem to be best described by an associative mechanism with a transition state of essentially trigonal bipyramidal geometry. In such systems, the pentaco-ordinate state may be sufficiently stabilised for specific cases as to allow experimental identification. Fairly good evidence exists in support of a pentaco-ordinate transition state for some substitution reactions of cobalt(III). There is, at present, an intensive study of reactions of transition metals by a number of research groups. Space restrictions preclude a discussion of these elegant studies.[30,31,32,33]

[28] D. B. Denney, A. K. Tsolis, and K. Mislow, *J. Amer. Chem. Soc.*, 1964, **86**, 4486.

[29] K. Mislow, T. Simmons, J. T. Mefillo, and A. L. Ternay, *J. Amer. Chem. Soc.*, 1964, **86**, 1452.

[30] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", John Wiley and Sons, New York, 1958.

[31] J. O. Edwards, "Inorganic Reaction Mechanisms", W. A. Benjamin, Inc., New York, 1964.

[32] Inorganic Reaction Mechanism Conference, Univ. of Kansas, Inorg. Div., June, 1964, "Mechanisms of Inorganic Reactions", Advances in Chemistry series No. 49, Amer. Chem. Soc., 1965.

[33] R. S. Nyholm and M. L. Tobe, "Essays in Co-ordination Chemistry", Birkhäuser, Basel, 1964.

II. Discussion of Structural Results

A. Geometry.—Complete structural formulation, either from *X*-ray diffraction analyses of the crystalline state or from microwave or modern electron diffraction studies of the gaseous state has been found for forty-one pentaco-ordinate molecules or ions with unidentate ligands. To this may be added four molecules whose symmetry determination by vibrational analysis establishes geometry. Nine of this group have five identical ligands and eight of these have trigonal bipyramidal geometry. The exception is pentaphenylantimony,[34] a rather surprising result in that the analogous phosphorus and arsenic compounds as well as a number of organoantimony halides have trigonal bipyramidal geometry. Unfortunately, the complexity of $Sb(C_6H_5)_5$ precludes a unique structural interpretation for the gaseous or liquid states.

A total of thirty-five of the forty-five structurally established pentaco-ordinate species have trigonal bipyramidal geometry (Table 1). Electronic states encompassed for the central metal in these trigonal bipyramidal structures are d^0, d^8, d^9, and d^{10}. A large number of other pentaco-ordinate species have been structurally investigated but the results do not permit rigorous structural conclusions. Nevertheless, with but few exceptions, the results suggest trigonal bipyramidal geometry.

TABLE 1. *Established pentaco-ordinate structures with trigonal bipyramidal geometry.*

Compound or ion	d^x	State*	Ref.
$H_3Al[N(CH_3)_3]_2$	d^0	sln–c	35-38
ClF_3	d^0	c–g–l	19*a*, 39-41
$(CH_3)_2PF_3$	d^0	g	42
$FPCl_4$	d^0	g–l	20
CH_3PF_4	d^0	g	42
CF_3PCl_4	d^0	g–l	43
PF_5	d^0	g–l	20, 20*a*, 20*b*
$P(C_6H_5)_5$	d^0	c	44
SF_4	d^0	g–l	19*b*, 45-47
OSF_4	d^0	l–g	48, 49, 50
$Co(NCCH_3)_5^+$	d^8	c	51
$RhH(CO)[P(C_6H_5)_3]_3$	d^8	c	52, 52*a*
$Fe(CO)_5$	d^8	g–l–c	53, 54
$Pt(SnCl_3)_5^{3-}$	d^8	c	55
$Ir[(C_6H_5)_3P]_2Cl(CO)(O_2)$	d^8	c	56
$CuCl_5^{3-}$	d^9	c	57
AsF_5	d^{10}	g–l	58
$As(C_6H_5)_5$	d^{10}	c	44
$SbCl_5$	d^{10}	c	59
$(CH_3)_3SbCl_2$	d^{10}	c	60

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[34] P. J. Wheatley, *J. Chem. Soc.*, 1964, 3718.

For references 35 to 70, please see footnotes to Table 1.

TABLE 1.—*continued*

Compound or ion	d^x	State*	Ref.
$(CH_3)_3SbBr_2$	d^{10}	c	60
$(CH_3)_3SbI_2$	d^{10}	c	60
$(C_6H_5)_3SbCl_2$	d^{10}	c	62
$(C_6H_5)_2SbCl_3$	d^{10}	c	63
$(ClCH{=}CH)_3SbCl_2$	d^{10}	c	64
$[(CH_3)_3SnF]_n$	d^{10}	c	6
$[(CH_3)_3SnOH]_n$	d^{10}	c	7
$(CH_3)_3SnCl(C_5H_5N)$	d^{10}	c	65
$(C_6H_5)_2SeCl_2$	d^{10}	c	66
$(C_6H_5)_2SeBr_2$	d^{10}	c	67
$(p\text{-}CH_3C_6H_4)_2SeCl_2$	d^{10}	c	68
$(p\text{-}CH_3C_6H_4)_2SeBr_2$	d^{10}	c	68
$(CH_3)_2TeCl_2$	d^{10}	c	61
$(C_6H_5)_2TeBr_2$	d^{10}	c	69
BrF_3	d^{10}	g–l	40, 70

* sln, solution; c, crystal; l, liquid; g, gas.

[35] C. W. Heitsch, C. E. Nordman, and R. W. Parry, *Inorg. Chem.*, 1963, **2**, 508. [36] C. W. Heitsch and R. N. Kniseley, *Spectrochim. Acta.*, 1963, **19**, 1385. [37] G. W. Fraser, H. N. Greenwood, and B. P. Straughan, *J. Chem. Soc.*, 1963, 3742. [38] I. R. Beattie and T. Gilson, *J. Chem. Soc.*, 1964, 3528. [39] D. F. Smith, *J. Chem. Phys.*, 1953, **21**, 609. [40] H. H. Claasen, B. Weinstock, and J. G. Malm, *J. Chem. Phys.*, 1958, **28**, 285. [41] R. D. Burbank and F. N. Bensey, *J. Chem. Phys.*, 1953, **21**, 602. [42] L. S. Bartell and K. W. Hansen, *Inorg. Chem.*, 1965, **4**, 1777. [43] J. E. Griffiths, *J. Chem. Phy.*, 1964, **41**, 3510. [44] P. J. Wheatley, *J. Chem. Soc.*, 1964, 2206. [45] W. M. Tolles and W. D. Gwinn, *J. Chem. Phys.*, 1962, **36**, 1119. [46] R. E. Dodd, L. A. Woodward, and H. L. Roberts, *Trans. Faraday Soc.*, 1955, **52**, 1052. [47] F. A. Cotton, J. W. George, and J. S. Waugh, *J. Chem. Phys.*, 1958, **28**, 994. [48] P. L. Goggins, H. L. Roberts, and L. A. Woodward, *Trans Faraday Soc.*, 1961, **57**, 1877. [49] M. Radhakrishnan, *J. Mol. Spect.*, 1963, **10**, 111. [50] K. Kimura and S. H. Bauer, *J. Chem. Phys.*, 1963, **39**, 3172. [51] F. A. Cotton, T. G. Dunne, and J. S. Wood, *Inorg. Chem.*, 1956, **4**, 318. [52] S. J. LaPlaca and J. A. Ibers, *J. Amer. Chem. Soc.*, 1963, **85**, 3501. [52a] S. J. LaPlaca and J. A. Ibers, *Acta Cryst.*, 1965, **18**,511. [53] J. Donohue and A. Caron, *Acta Cryst.*, 1964, **17**, 663. [54] H. Stammreich, O. Sala, and Y. Tavares, *J. Chem. Phys.*, 1959, **30**, 856. [55] R. D. Cramer, R. V. Lindsey, jun., C. T. Prewitt, and U. G. Stolberg, *J. Amer. Chem. Soc.*, 1965, **87**, 658. [56] S. J. LaPlaca and J. A. Ibers, *J. Amer. Chem. Soc.*, 1965, **87**, 2581. [57] M. Mori, Y. Saito, and T. Watanabe, *Bull. Chem. Soc., Japan*, 1961, **34**, 295. [58] R. C. Lord and L. C. Hoskins, to be published. [59] S. M. Ohlberg, *J. Amer. Chem. Soc.*, 1959, **81**, 811. [60] A. F. Wells, *Z. Krist.*, 1938, **99**, 367. [61] G. D. Christofferson, R. A. Sparks, and J. D. McCullough, *Acta Cryst.*, 1958, **11**, 782. [62] T. N. Polynova and M. A. Porai-Koshits, *J. Struct. Chem.*, 1960, **1**, 146. [63] T. N. Polynova and M. A. Porai-Koshits, *J. Struct. Chem.*, 1961, **2**, 445. [64] Yu. T. Struchov and T. L. Khotsyanova, *Doklady Akad. Nauk S.S.S.R.*, 1963, **91**, 565. [65] R. Hulme, *J. Chem. Soc.*, 1963, 1524. [66] J. D. McCullough and G. Hamburger, *J. Amer. Chem. Soc.*, 1942, **64**, 508. [67] J. D. McCullough and G. Hamburger, *J. Amer. Chem. Soc.*, 1941, **63**, 803. [68] R. E. Marsh and J. D. McCullough, *Acta Cryst.*, 1950, **3**, 41. [69] G. D. Christofferson and J. D. McCullough, *Acta Cryst.*, 1958, **11**, 249. [70] D. W. Magnuson, *J. Chem. Phys.*, 1957, **27**, 223.

The tetragonal pyramidal molecules are transition metal complexes with the exception of $Sb(C_6H_5)_5$ which was cited above. The most notable feature of this group is the presence of large bulky ligands such as triphenylphosphine or diphenylmethylarsine oxide.† A trisphosphine com-

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† Some of these may be considered as hexaco-ordinate structures with an axial interaction between the central metal and an *ortho*-hydrogen atom of one of the phenyl rings.

plex of palladium dibromide[71] has one apical bromine atom and a second slightly below the plane described by the three phosphorus atoms. An analogous d^6 ruthenium complex has a different stereochemistry in that one of the phosphorus atoms is at the apical position.[72] The rather unusual iridium–sulphur dioxide complex $Ir(CO)Cl(SO_2)[P(C_6H_5)_3]_2$ has an S-bonded SO_2 group at the apical positions.[56] Curiously, a closely related complex in which O_2 is substituted for SO_2 has trigonal bipyramidal geometry with axial phosphine ligands.[56] There is an isostructural series of six metal complexes, ranging from manganese(II) to zinc(II) which have four diphenyl(methyl)arsine oxide ligands at basal positions and a perchlorate oxygen atom at the apical position.[73]

These structural data though somewhat sparse and not too representative for the Periodic Table clearly indicate that trigonal bipyramidal geometry will be the more common ground-state geometry at least for d^0, d^8, and d^{10} configurations.†

In one sense, the predominance of trigonal bipyramidal geometry is somewhat surprising. Consider the following argument. Fast intramolecular exchange of fluorine atoms in PF_5 requires a tetragonal pyramidal transition state. The barrier to exchange cannot be significantly larger than 6 kcal./mole. Therefore, the difference in energy levels between the trigonal bipyramidal and the tetragonal pyramidal states cannot be greater than this figure for PF_5. Although this fortuitously may be a most favourable case for small energy differentiation between the two states,* the point is that this particular value is small or at least comparable with values that might be expected for specific ligand stabilisation of tetragonal pyramidal geometry or to perturbation forces generated by the ordering process in the solid or liquid state. Clearly, any attempt to rationalise geometry for a particular pentaco-ordinate species on the basis of crude qualitative considerations such as π bonding and the like is quite unrealistic in view of the subtle energy differentiation between the two idealised geometries.

Critical to a more definitive picture of ground-state geometry is a more rigorous characterisation of the solution or gas state for pentaco-ordinate molecules with small, simple ligands. Exemplary molecules are SbF_3Cl_2 (g), $MoCl_5$ or MoF_5 (g), $HCo(CO)_4$ or $CH_3Co(CO)_4$ and $TiCl_3[N(CH_3)_3]_2$ or $VCl_3[N(CH_3)_3]_2$. Particularly worthy of structural analyses are the gaseous molybdenum pentahalides and $TiCl_3[N(CH_3)_3]_2$; all these have a d^1 configuration and would be amenable to fairly detailed theoretical studies. The gaseous pentahalides of d^0, d^1 through d^5, and d^{10} configuration should be systematically investigated for effect of electronic configuration on geometry.

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† Pentaco-ordination is more commonly found in these three electronic configurations.

* Certainly it is a favourable case for low barrier to intramolecular fluorine exchange.

[71] J. W. Collier, F. G. Mann, D. G. Watson, and H. R. Watson, *J. Chem. Soc.*, 1964, 1803.

[72] S. J. LaPlaca and J. A. Ibers, *Inorg. Chem.*, 1965, **4**, 778.

[73] P. Pauling, G. B. Robertson, and G. A. Rodley, *Nature*, 1965, **207**, 73.

In trigonal bipyramidal geometry, the axial bond distance, in general, is greater than the equatorial bond distance. For pentaco-ordinate species in which all five ligands are identical, the differentiation in bond length is small or non-detectible within experimental error. However, on substitution, particularly with electropositive groups, the bond-distance differential increases significantly. For example, the difference is 0·043 Å in PF_5, 0·069 Å in CH_3PF_4, and 0·101 Å in $(CH_3)_2PF_3$. This differentiation, first suggested in n.m.r. studies,[15] is probably at a maximum in $(CH_3)_3PF_2$ as evidenced by the ^{19}F n.m.r. coupling constant data. For tetragonal pyramidal geometry, it appears that apical bond distance is the larger. This is particularly evident in chelate structures as noted below.

Accurate solid-state structural data are available for twenty-six pentaco-ordinate structures containing polyfunctional ligands. The majority of these present a basic geometry of fairly close correspondence to one of the two idealised geometries. Eleven of these chelates have near trigonal bipyramidal geometry. The complexes include an alkoxyphosphorane (d^0),[74] iodobisbipyridylcopper(II) cation (d^9),[75] a quadridentate arsinoplatinum complex (d^8),[76] terpyridyl complexes of the dichlorides of copper (d^9), cadmium (d^{10}) and zinc (d^{10}),[77] and *N*-methylsalicylaldimine complexes[78] of manganese(II) (d^5), cobalt(II) (d^7), and zinc(II) (d^{10}). The remaining two trigonal bipyramids are peroxide complexes of chromium[79] containing ethylenediamine (d^0) or *o*-phenanthroline (d^2) in which the O_2^{2-} group may be considered as occupying only one bonding position.

Fifteen of the twenty-six pentaco-ordinate chelates have square-pyramidal geometry. This fraction seems disproportionately large with respect to the cumulative structural information for pentaco-ordinate species based solely on unidentate chelates. Six of these square-pyramidal structures have copper(II) as the central atom. Peculiar to the copper complexes is a relatively long bond between copper and the apical atom. The apical bond length varies from 2·41 Å in the dimeric *NN'*-disalicylidene-ethylenediaminecopper(II)[80] to 2·76 Å in diaquoacetylacetonatocopper(II) picrate[81] while the basal bond lengths vary from 2·01 to 1·88 Å, respectively. It is tempting to consider these d^9 complexes as quasi-octahedral structures with the weakly bonded ligand atom and the unpaired *d* electron on the d_z axis. Preference for a square-pyramidal configuration may also reflect the strong covalent ligand–metal bonding possible in a more nearly coplanar arrangement of metal and ligand atoms in chelate complexes.

[74] W. C. Hamilton, S. J. LaPlaca, and F. Ramirez, *J. Amer. Chem. Soc.*, 1965, **87** 127.
[75] G. A. Barclay and C. H. L. Kennard, *Nature*, 1961, **192**, 425.
[76] G. A. Mair, H. M. Powell, and L. M. Venanzi, *Proc. Chem. Soc.*, 1961, 170.
[77] D. E. C. Corbridge and E. G. Cox, *J. Chem. Soc.*, 1956, 594.
[78] P. L. Orioli, M. DiVaira, and L. Sacconi, *Chem. Comm.*, 1965, 103.
[79] R. Stomberg, *Nature*, 1965, **207**, 76.
[80] D. Hall and T. N. Waters, *J. Chem. Soc.*, 1960, 2644.
[81] R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 1963, 5399.

The remaining nine chelates of near square-pyramidal geometry include metal complexes of d^1, d^5, d^7, d^8, and d^{10} electronic configuration. Vanadyl bisacetylacetone[82] complex has a very short (1·56 Å) axial bond. Maximum multiple VO bonding is possible in this particular geometry and this stabilisation alone may be sufficient to account for the overall configuration that is adopted for this complex. Two d^5 iron–porphyrin complexes have the iron atom located about 0·5 Å above the plane of the porphyrin skeleton with an apical methoxy-group[83] or chlorine atom.[84] The d^7 (or d^8) example is based on cobalt(II) with two dithiocarbamate ligands and a nitrosyl group;[85] the cobalt atom is substantially out of the plane described by the four chelate sulphur atoms. A triarsinonickel dibromide complex is basically square-pyramidal.[86] The arsenic atoms are bridged by $-(CH_2)_3-$ groups and the basal and axial nickel–bromine distances are quite different (2·37 as against 2·69 Å). This result for a d^8 metal ion is somewhat surprising. Because of the disparate Ni–Br distances, it is not easy to rationalise this geometry on the basis of distortion imposed by steric requirements of the terdentate ligand. This geometry may, in fact, be quite distinctive because it is found in a d^8 palladium bromide–trisphosphine complex in which all ligands are unidentate.[71] The Schiff base *N*-β-diethylaminoethyl-5-chlorosalicylaldimine forms 2:1 tetragonal pyramidal complexes with cobalt(II) and nickel(II)[87,87a] in which one of the potentially terdentate ligands is only bidentate. *NN'*-Disalicylidene-ethylenediaminezinc monohydrate has a tetragonal pyramidal configuration[88] with the water molecule at the apex. The remaining square-pyramidal structure is the monohydrate of zinc bisacetylacetone. In this structure all Zn–O bond lengths are the same within the precision and accuracy of the determination. There has been some debate[89a,b] whether this complex more closely approximates a trigonal bipyramid. Perhaps the departure from either model is severe enough to invalidate any discussion based on idealised geometries. In fact, the possibility of constraints introduced by steric requirements of polyfunctional ligands makes it rather difficult to analyse the significance of structural data for pentaco-ordinate chelates in general.

A variety of atoms attain a co-ordination number of five in molecular polyhedra or periodic lattices. Such structures include boron, carbon, magnesium, copper, mercury, iron, vanadium, germanium, or palladium

[82] R. P. Dodge, D. H. Templeton, and A. Zalkin, *J. Chem. Phys.*, 1961, **35**, 55.

[83] J. L. Hoard, M. J. Hamor, T. A. Hamor, and W. S. Caughey, *J. Amer. Chem. Soc.*, 1965, **87**, 2312.

[84] D. F. Koenig, Ph.D. Thesis, Johns Hopkins University, 1962; *Acta Cryst.*, 1965, **18**, 663.

[85] P. R. H. Alderman, P. G. Owston and J. M. Rowe, *J. Chem. Soc.*, 1962, 668.

[86] G. A. Mair, H. M. Powell, and D. E. Henn, *Proc. Chem. Soc.*, 1960, 415.

[87] L. Sacconi, P. L. Orioli, and M. DiVaira, *J. Amer. Chem. Soc.*, 1965, **87**, 2059.

[87a] L. Sacconi, P. Nannelli, N. Nardi, and U. Campigli, *Inorg. Chem.*, 1965, **4**, 943.

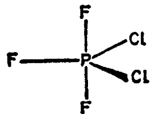
[88] D. Hall and F. H. Moore, *Proc. Chem. Soc.*, 1960, 256.

[89a] E. L. Lippert and M. R. Truter, *J. Chem. Soc.*, 1960, 4996.

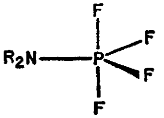
[89b] H. Montgomery and E. C. Lingafelter, *Acta Cryst.*, 1963, **16**, 748.

as the pentaco-ordinate atom. In molecular polyhedra, the preferred stereochemistry, with but one exception, is tetragonal pyramidal; the exception is the magnesium atom in $Mg_4Br_6O(Et_2O)_4$[90] which has a nearly regular trigonal bipyramidal configuration. In periodic lattices both configurations, usually distorted, have been observed.

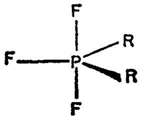
B. Stereochemistry.—The question arises as to whether there may be a set of empirical rules of some predictive value in pentaco-ordinate stereochemistry. The answer is yes at least for structures in which the central atom is a light element of d^0 configuration. The extensive studies of phosphorus fluorides by Muetterties, Mahler, and their co-workers[4,15] clearly indicate that the more electronegative ligands tend to assume the axial or apical positions in trigonal bipyramids, *e.g.* (21—25). It is tempting to draw the conclusion that maximum *s* character resides in the equatorial bonds particularly in view of supporting PF spin–spin coupling* data[4,15] but however meaningful such a conclusion might be it would not escape the qualitative label.



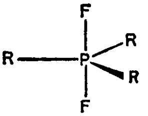
(21)



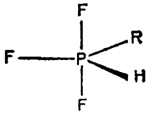
(22)



(23)



(24)



(25)

The consistency in stereochemistry found for phosphorus fluorides will probably prove applicable to other pentaco-ordinate light atoms of d^0 configuration and there appears to be no exception in the aluminium and sulphur compounds that have been studied. There is no basis to assume that this generality will survive extension to pentaco-ordinate heavy atoms of d^0 configuration or to any atoms of d^x or d^{10} configuration. In fact, there are bases to expect exceptions to preferential occupancy of axial position by the more electronegative ligands; one single reason of import is that the participation of *s*, *p*, and *d* metal orbitals in the sigma bonding framework must vary for these various electronic configurations. Nevertheless, there appears to be no pentaco-ordinate species, whose structure is known with reasonable certainty, in which the more electronegative ligands do not occupy the axial sites.

* Additionally, the trend towards equatorial bonds being shorter than axial bonds is consistent with such an empiricism.

[90] G. Stucky and R. E. Rundle, *J. Amer. Chem. Soc.*, 1964, **86**, 4821.

A great number of structural analyses must be made before extensive generalisations can be presented for pentaco-ordinate stereochemistry. In many cases, critical structures must first be synthesised. This is particularly true for d^x configurations, exclusive of d^8 and d^{10}.

III. Structural Data

A. ML_5 Species (See Table 3).—1. *Solid-state geometry.* Precise solid-state structural data exist for only eight pentaco-ordinate ML_5 species, $P(C_6H_5)_5$, $As(C_6H_5)_5$, $Sb(C_6H_5)_5$, $SbCl_5$, $Fe(CO)_5$, $Pt(SnCl_3)_5^{3-}$, $Co(CNCH_3)_5^+$, and $CuCl_5^{3-}$. Pentaphenylphosphorus (d^0) has trigonal bipyramidal geometry in a crystalline lattice[44] although the molecule itself has no symmetry because of asymmetric orientation of the benzene rings. The axial and equatorial P–C bond lengths are 1·987 Å and 1·850 Å, respectively. Pentaphenylarsenic (d^{10}) is isomorphous with the phosphorus compound.[44] However, pentaphenylantimony (d^{10}) has near-tetragonal pyramidal geometry;[34] the pertinent parameters are Sb–C distances of 2·14 ± 0·07 Å, equatorial C–Sb–C angles of 88 ± 2°, and equatorial–axial C–Sb–C angles of 102 ± 6°. Antimony pentachloride, on the other hand, has regular trigonal bipyramidal geometry[69] at —30°c in the solid state with apical Sb–Cl distances of 2·34 Å and equatorial Sb–Cl distances of 2·29 Å'

In the solid state, iron pentacarbonyl is a trigonal bipyramid with no significant deviation from this idealised model.[53] The average Fe–C distance is 1·79 Å. There are no apparent differences in the axial and equatorial Fe–C distances. (See Note added in proof.) In the electronically related $Pt(SnCl_3)_5^{3-}$ anion (methyltriphenylphosphonium salt), there is a trigonal bipyramid of platinum and tin atoms with little or no difference in the axial and equatorial platinum–tin distances.[55] The pentakis(methylisonitrile)cobalt(I) cation is a nearly regular trigonal bipyramid[51] with an average Co–C distance of 1·87 Å. The axial and equatorial distances are equal within experimental error. The $CuCl_5^{3-}$ ion, d^9 configuration, also has trigonal bipyramidal geometry.[57] The axial Cu–Cl distance (2·32 Å) is reported to be 0·03 Å shorter than the equatorial CuCl distances. The $Ni(CN)_5^{3-}$ ion is reported to have 3 CN stretching fundamentals, and it was suggested that only a tetragonal pyramid is consistent with these data.[91] However, the analysis is not definitive and the conclusion is in conflict with the findings for all other d^8 nonchelate pentaco-ordinate structures.

2. *Liquid and solution-state geometry.* Raman (and infrared) studies point strongly to D_{3h} symmetry for phosphorus[20,20a] and arsenic[58] pentafluorides and for iron pentacarbonyl.[54]

3. *Gaseous state.* Only one rigorous structural study has been made of a gaseous ML_5 compound. A recent electron diffraction study of PF_5 has established trigonal bipyramidal geometry[20b] with an equatorial P–F

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[91] J. S. Coleman, H. Peterson, jun., and R. A. Penneman, *Inorg. Chem.*, 1965, **4**, 135.

bond distance of 1·534 Å and an apical P–F distance of 1·577 Å. All of the other electron diffraction results listed in Table 3 are of a vintage that precludes acceptance. Infrared results for gaseous PF_5,[20,20a] AsF_5,[58] and $Fe(CO)_5$[54] point to D_{3h} symmetry.

B. XML_4 Species (See Table 4).—1. *Solid state.* In the potassium salt of $Sb_2F_7^-$, the two antimony atoms are joined by a single fluorine bridge bond.[92] The molecular parameters could be employed to argue for a distorted tetrahedron, a distorted trigonal bipyramid with a non-bonding electron pair at an axial site, or a distorted square pyramid with a non-bonding electron pair at a basal site. The distortion from these idealised geometries is sufficiently large as to preclude a distinction among the three possibilities.

The metal(II) perchlorates of manganese, iron, cobalt, nickel, copper, and zinc form a series[93] of isostructural complexes with diphenylmethylarsine oxide of the formula $[(C_6H_5)_2CH_3AsO]_4M(ClO_4)_2$. A preliminary account of a single-crystal structure analysis[73] of the cobalt complex shows it to contain both co-ordinated and unco-ordinated ClO_4^- groups and the cobalt atom to be in a distorted tetragonal pyramidal configuration. The four coplanar arsine oxide–oxygen atoms form the base of the pyramid each at a distance of 2·02 Å. The cobalt atom is located 0·32 Å above the centre of this plane. An oxygen atom of the co-ordinated ClO_4^- ion is displaced 0·72 Å to one side of the four-fold axis at a distance of 2·10 Å above the cobalt atom.

Crystal-structure analysis[94] of the salts $[(C_2H_5)_4N][ReBr_4O(H_2O)]$ and $[(C_6H_5)_4As][ReBr_4O(CH_3CN)]$ has shown them to have virtual C_{4v} symmetry with an apical (oxo) oxygen to rhenium distance of 1·80 Å. The rhenium atom is located slightly above the plane described by the four bromine atoms; the rhenium–bromine distance is 2·48 Å. The solvent molecule (H_2O or CH_3CN), located at the sixth, octahedral position at a distance of 2·3 Å, is described as being relatively weakly bonded to the rhenium. The solvent-free salts are presumed to have a similar tetragonal pyramidal geometry. Magnetic susceptibility measurements[94] of the anhydrous salts are consistent with the pentaco-ordinate tetragonal pyramidal model but these results are by no means definitive.

2. *Liquid or solution-state geometry.* SF_4,[19b,47] SeF_4,[19b] $(CH_3)_2NPF_4$,[95] $(C_2H_5)_2NPF_4$,[4] and $CF_3N{=}SF_4$[4] display low-temperature ^{19}F n.m.r. spectra which are consistent with but do not uniquely establish trigonal bipyramidal structures (26)—(29) in which two of the three equatorial sites are occupied by fluorine atoms. The same symmetry was first suggested for SF_4 from a vibrational analysis.[46]

Analysis[48,49] of the vibrational spectrum of OSF_4 indicates a C_{2v}

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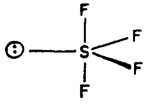
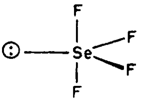
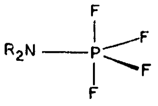
[92] A. Byström and K. Wilhemi, *Arkiv Kemi*, 1951, **3**, 373.
[93] J. Lewis, R. S. Nyholm, and G. A. Rodley, *Nature*, 1965, **207**, 72.
[94] F. A. Cotton and S. J. Lippard, *Chem. Comm.*, 1965, 245.
[95] D. H. Brown, G. W. Fraser, and D. W. A. Sharp, *Chem. and Ind.*, 1964, 367.



(26)



(27)



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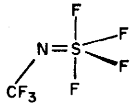
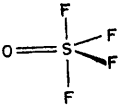
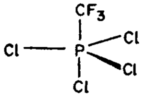


(29)

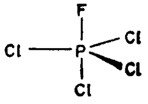
trigonal bipyramidal model (30). Similar studies of CF_3PCl_4[43] and $FPCl_4$[20] point to C_{3v} trigonal bipyramidal geometries with the unique substituent at an axial position (31, 32) Analogous models for $HCo(CO)_4$[96] and



(30)

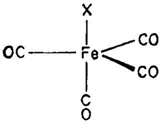


(31)



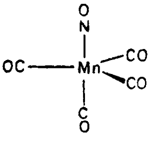
(32)

$HFe(CO)_4^-$ [97] have been suggested from symmetry arguments based on infrared and on Raman spectra, respectively. Solution infrared studies (analysis of the CO stretching region) of derivatives of iron pentacarbonyl,[98,99] nitrosylmanganese tetracarbonyl,[100] and substituted manganese carbonyl anions[101] suggest C_{3v} symmetry consistent with (33)—(35).

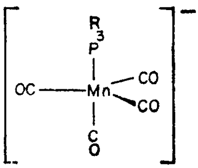


$X=PR_3, AsR_3, SbR_3$, RNC

(33)



(34)



(35)

None of these studies based solely on Raman data or solely on infrared data is definitive. There is a most curious paramagnetic d^7 manganese carbonyl $R_3PMn(CO)_4$ which also has 3 fundamental CO stretching frequencies, consistent with C_{3v} symmetry.[101,102]

The Raman spectra[103] of a number of 1:1 complexes of tin tetrachloride with organic donor molecules such as ethers, alcohols, and nitriles are

[96] W. F. Edgell, C. Magee, and G. Gallup, *J. Amer. Chem. Soc.*, 1956, **78**, 4185.

[97] H. Stammreich, K. Kawai, Y. Tavares, K. Krumholz, J. Behmoiras, and S. Bril, *J. Chem. Phys.*, 1960, **32**, 1482.

[98] F. A. Cotton and R. V. Parrish, *J. Chem. Soc.*, 1960, 1440.

[99] A. F. Clifford and A. K. Mukherjee, *Inorg. Chem.*, 1963, **2**, 151.

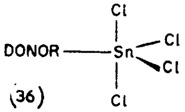
[100] P. M. Treichel, E. Pitcher, R. B. King, and F. G. A. Stone, *J. Amer. Chem. Soc.*, 1961, **83**, 2593.

[101] W. Hieber, G. Faulhaber, and T. Theubert, *Z. anorg. Chem.*, 1962, **314**, 125.

[102] W. Hieber and W. Freyer, *Chem. Ber.*, 1959, **92**, 1765.

[103] H. A. Brune and W. Zeil, *Z. phys. Chem.*, 1962, **32**, 384.

consistent with C_{2v} symmetry; presumably, the idealised geometry is trigonal bipyramidal (36). The titanium tetrachloride–trimethylamine

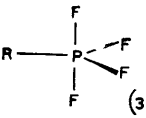


(36)

complex is volatile and presumably pentaco-ordinate, but no stereochemical data are available.[104] Silicon tetrachloride forms 1:1 complexes with tertiary amines that may be analogous to the tin complexes,[105,106] but the silicon adducts are apparently too highly dissociated in solution for spectroscopic studies.[107] The tetrafluorides of silicon, germanium, and tin also form 1:1 complexes with trialkylamines.[108,109] These complexes are relatively intractable, a point that appears inconsistent with a discrete pentaco-ordinate structure. Other, indirect data suggest that these fluoride complexes are polymeric octahedral complexes through fluorine atom bridges.[109]

Selenium and tellurium tetrachlorides have been characterised as salt-like structures $MCl_3^+Cl^-$ on the basis of Raman results;[110] however, there are no definitive structural results. It has been pointed out that the solubility of $TeCl_4$ in non-polar solvents is not particularly consistent with an ionic formulation.[111]

Chemical-shift and coupling-constant results[15] have been employed to argue for a C_{2v} trigonal bipyramidal model for mono-alkyl and -aryl derivatives of phosphorus pentafluoride (37) and this has been confirmed by electron diffraction for the specific case of CH_3PF_4.[42]



(37)

Salts of the ReX_4O^- anion (X = Cl, Br, I) are 1:1 electrolytes in nitromethane and acetonitrile[94] and are therefore presumably pentaco-ordinate. However, the crystal-structure analysis of $[(C_6H_5)_4As][ReBr_4O(CH_3CN)]$ shows the acetonitrile ligand to be weakly co-ordinated; the anion may exist as an octahedral solvate in solution.

[104] M. Antler and A. W. Laubengayer, *J. Amer. Chem. Soc.*, 1955, **77**, 5250.

[105] A. Burg, *J. Amer. Chem. Soc.*, 1954, **76**, 2674.

[106] J. E. Fergusson, D. K. Grant, R. H. Hickford, and C. J. Wilkins, *J. Chem. Soc.*, 1959, 99.

[107] I. R. Beattie and M. Webster, *J. Chem. Soc.*, 1963, 4285.

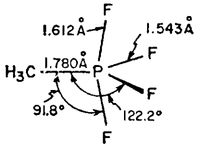
[108] C. J. Wilkins and D. K. Grant, *J. Chem. Soc.*, 1953, 927.

[109] E. L. Muetterties, *J. Amer. Chem. Soc.*, 1960, **82**, 1082.

[110] H. Gerding and H. Houtgraaf, *Rec. trav. Chim.*, 1954, **73**, 737, 759.

[111] A. W. Cordes, R. F. Kruh, E. K. Gordon, and M. K. Kemp, *Acta Cryst.*, 1964, **17**, 756.

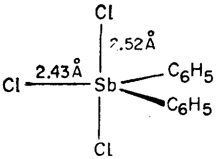
3. *Gaseous state.* A microwave study[45] has shown sulphur tetrafluoride to be a slightly distorted trigonal bipyramid with bond angles of 187° for $SF_{ax}F_{ax}$, and 101° for $SF_{eq}F_{eq}$. The axial SF bond distance is greater than the equatorial one, 1·646 Å *vs.* 1·545 Å. A similar conclusion about geometry was reached from an electron diffraction study.[112] Trigonal bipyramidal geometry has been confirmed[42] for CH_3PF_4 by electron diffraction; the methyl group is at an equatorial position as was initially suggested from n.m.r.[15] Molecular parameters are given in (38). Analogous geometry has been suggested for SeF_4[113] and $TeCl_4$[114] from electron diffraction analyses but the bond angles and bond distances are not precisely known and these studies are not definitive. Electron diffraction[50] of OSF_4 suggested a C_{2v} model as was suggested from vibrational spectra.

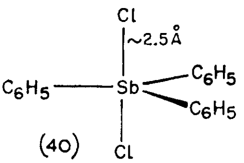


(38)

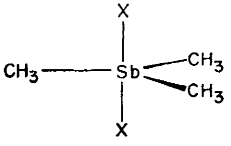
C. X_2ML_3 Species (See Table 5).—1. *Solid state.* Trigonal bipyramidal geometry has been established by *X*-ray analysis for twelve X_2ML_3 species. Six are organoantimony halides[60,62–64] and in each of these the alkyl or aryl groups occupy equatorial positions. Several are represented in (39), (40), and (41) with some of the molecular parameters.

(39)





(40)



(41)

X = Cl, Br, I

SbCl = 2.49 Å
SbBr = 2.63 Å
SbI = 2.88 Å
SbC = ~2.1 Å

Crystal structure analysis[64] of tris-(2-chlorovinyl)dichlorostibine, $(ClCH{=}CH)_3SbCl_2$, shows the axial chlorine atoms to be located at a distance of 2·45 Å from the antimony and the equatorial Sb–C distance to be 2·15 Å. Infrared spectra of the dihalides and dihydroxides of $(CH_3)_3Sb^{2+}$ and

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[112] K. Kimura and S. H. Bauer, *J. Chem. Phys.*, 1963, **39**, 3172.
[113] H. J. M. Bowen, *Nature*, 1953, **172**, 171.
[114] D. P. Stevenson and V. Shomaker, *J. Amer. Chem. Soc.*, 1940, **62**, 1267.

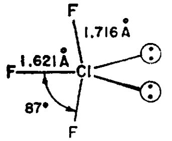
$(C_2H_5)_3Sb^{2+}$ have also suggested a D_{3h} trigonal bipyramidal structure for the solid state.[115]

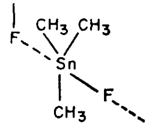
The bistrimethylamine adduct of alane, $H_3Al\cdot[N(CH_3)_3]_2$, has essentially D_{3h} symmetry with the hydrogen atoms at the equatorial sites.[35] The Al–N bond distance is 2·18 Å.

X-Ray diffraction of ClF_3[41] has shown a distorted trigonal bipyramidal configuration about chlorine with the two non-bonding electron pairs at equatorial sites. Molecular parameters are shown in (42).

In trimethyltin fluoride, the tin and carbon atoms are coplanar and the fluorine atoms are shared between tin atoms in such a fashion as to generate near-trigonal bipyramidal geometry about the tin atom (43). The Sn–F and Sn–C distances are 2·1—2·6 Å and 2·1 Å, respectively.[6] A similar structure has been found in crystalline trimethyltin hydroxide in which the oxygen atoms bridge the $(CH_3)_3Sn$ groups.[7] Detailed parameters have not been presented. Analogous structures have been suggested for a number of trialkyltin derivatives including formates,[8] acetates,[8] hydroxides,[116] triazoles,[117] and glyoxalines.[117] Support for these proposals comes from chemical properties and infrared data. Trimethyltin nitrate forms a stable diammoniate which is a salt, $(CH_3)_3Sn(NH_3)_2{}^+NO_3{}^-$. The infrared data for this salt are consistent with a trigonal bipyramidal cation in which the ammonia ligands are at axial sites.[118]

(42)





(43)

Dichlorotris(triphenylphosphine)ruthenium(II) is a slightly distorted square pyramid with the chlorine atoms at *trans* positions in the square base.[72] The base is not planar; the phosphorus atoms are slightly above and the chlorine atoms are slightly below their mean plane. Bond distances are Ru–Cl = 2·387 Å, $Ru\text{–}P_{ax}$ = 2·37 and 2·41 Å, and $Ru\text{–}P_{eq}$ = 2·23 Å. The authors[72] noted that the "unused" octahedral site is effectively blocked by a phenyl ring and may account for the stability of this d^6 pentaco-ordinate structure.

The tertiary phosphine 2-phenylisophosphindoline (44) forms a complicated series of complexes with platinum(II), palladium(II), and nickel(II) halides.[71] The trisphosphine palladium dibromide complex, for example, exists in two isomeric forms, an orange tetraco-ordinate ionic complex and a red pentaco-ordinate species. The crystal structure of the red isomer[71]

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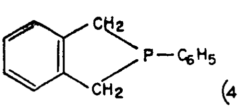
[115] G. G. Long, G. O. Doak, and L. D. Freeman, *J. Amer. Chem. Soc.*, 1964, **86**, 209.

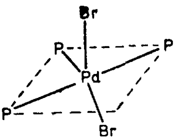
[116] R. Okawara and K. Yasuda, *J. Organometallic Chem.*, 1964, **1**, 356.

[117] M. J. Janssen, J. G. A. Luijten, and J. M. Van der Kerk, *J. Organometallic Chem.*, 1964, **1**, 286.

[118] H. C. Clark and R. J. O'Brien, *Inorg. Chem.*, 1963, **2**, 740.



(44)



(45)

shows the palladium atom to be in a distorted tetragonal pyramidal environment as in (45) where P represents the 2-phenylisophosphindoline ligand. The average Pd–P distance is 2·26 Å and the apical Pd–Br distance is 2·93 Å. The remaining Pd–Br distance is 2·52 Å and this bromine atom is displaced about 10° from the plane of the palladium and phosphorus atoms. The structure bears a marked similarity to that of (triars)$NiBr_2$ (see Section F).

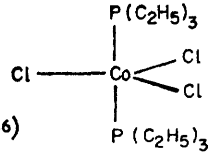
A series of derivatives of iron carbonyl, in which two of the carbonyl groups are replaced by ligands such as phosphines, arsines, and stibines, display an infrared CO stretching region consistent with a trigonal bipyramid with equatorial CO ligands.[98,99]

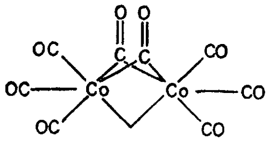
2. *Liquid and solution state.* A number of transition-metal trihalides form monomeric pentaco-ordinate complexes with organic donor molecules.[119,120] For example, nitrosyl halides convert the nickel and cobalt(II) halide–bisphosphine complexes into the tervalent complexes:

$$CoCl_2[P(C_2H_5)_3]_2 + NOCl \rightarrow NO + CoCl_3[P(C_2H_5)_3]_2$$

In pentane solution, the cobalt chloride adduct has essentially zero dipole moment.[120] This result was taken as evidence for the trigonal bipyramidal model (46).

(46)





(47)

However, calculations of dipole moments for inorganic compounds from their dielectric constants in solution are notoriously inexact because of the uncertainty in the correction for atomic polarisation. Analogous to the cobalt and nickel complexes are the bistrimethylamine complexes of $TiCl_3$[104] and VCl_3.[121,122] These two volatile species form isomorphous lattices in the solid state. The vanadium complex is monomeric in nitrobenzene solution but there could be an interaction between solute and solvent in this case.[121]

The carbonyl stretching absorption in the infrared spectra of $Fe(CO)_3L_2$ complexes in solution is consistent with trigonal bipyramidal geometry

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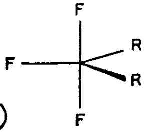
[119] K. A. Jensen and B. Nygaard, *Acta Chem. Scand.*, 1949, 3, 474.
[120] K. A. Jensen, B. Nygaard, and C. T. Pedersen, *Acta Chem. Scand.*, 1963, **17**, 1126.
[121] G. W. A. Fowles and C. M. Pleass, *Chem. and Ind.*, 1955, 1743.
[122] L. D. Calvert and C. M. Pleass, *J. Canad. Chem.*, 1962, **40**, 1473.

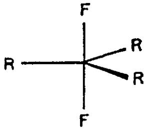
with the ligands, *e.g.*, phosphines and arsines, at axial sites.[98,99] Isoelectronic cobalt cations $Co(CO)_3L_2^+$ have been prepared but structural data are not available.[123] The geometry of dicobalt octacarbonyl has been described as two trigonal bipyramids joined at an edge;[124] however, the cobalt must be hexaco-ordinate because there is a Co–Co bond. A possibly better description of this carbonyl is two octahedra sharing a trigonal face (47).

From an analysis of the vibrational spectrum,[36–38] the state of $H_3Al[N(CH_3)_3]_2$ in solution was characterised as D_{3h} trigonal bipyramidal as was established for the crystalline state. The trichlorozinc ion in solution appears to be pentaco-ordinate with two solvent molecules in the co-ordination sphere.[125] Raman studies of these solutions suggest that the solvent molecules occupy axial positions of a trigonal bipyramid.[125] The Raman spectrum of molten SbF_3Cl_2 is relatively simple and consistent with a trigonal bipyramidal model with axial chlorine atoms.[126] N.m.r. studies unequivocally establish that SbF_3Cl_2 is associated at ~20°.[4] The conflict between these two studies may arise from the fact that the Raman analysis was effected at a higher temperature (~80°) than that by n.m.r. Alternatively, weak Raman absorptions may have gone undetected.

Electron diffraction[127] and n.m.r.[128] studies led to an initial characterisation of PF_3Cl_2 as a D_{3h} trigonal bipyramid. Later, n.m.r. unambiguously established that there are two fluorine-atom environments in PF_3Cl_2,[4,15] and arguments based on chemical shifts and coupling constants were employed to favour a C_{2v} over a C_S model. Subsequent vibrational analyses and chlorine quadrupole studies placed the C_{2v} model on a firmer basis.[20,21] Whether PF_3Cl_2 more closely approximates a trigonal bipyramid or a tetragonal pyramid has not been defined; molecular parameters are required to discern this fine point. N.m.r. data have also established C_{2v} symmetry for a long series of dialkyl-, diaryl-, and diamino-phosphorus trifluorides.[4,15] Chemical shifts[4,15] for this series and a related series of trialkylphosphorus difluorides were used to argue for near-trigonal bipyramidal geometry (48 and 49). Diphenylarsenic trifluoride, like the related phosphorus compounds, has C_{2v} symmetry and the trialkyl and

(48)





(49)

[123] W. Hieber and W. Freyer, *Chem. Ber.*, 1960, **93**, 462.

[124] J. W. Cable, R. S. Nyholm, and R. K. Sheline, *J. Amer. Chem. Soc.*, 1954, **76**, 3373.

[125] D. F. C. Morris, E. L. Short and D. N. Waters, *J. Inorg. Nuclear Chem.*, 1963, **25**, 975.

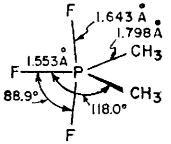
[126] K. Dehnicke and J. Weidlein, *Z. anorg. Chem.*, 1963, **323**, 267.

[127] L. O. Brockway and J. Y. Beach, *J. Amer. Chem. Soc.*, 1938, **60**, 1836.

[128] R. R. Holmes and W. P. Gallagher, *Inorg. Chem.*, 1963, **2**, 433.

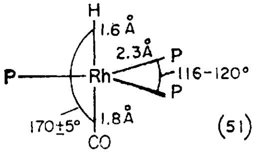
triaryl derivatives of AsF_5, SbF_5, and BiF_5 appear to have D_{3h} symmetry in the solution state.[4] Vibrational analysis of PF_2Cl_3 fairly well established D_{3h} symmetry for this compound.[20] N.m.r. results rigorously defined C_{2v} symmetry for ClF_3 in the liquid state.[19a] Infrared and Raman data similarly point to a C_{2v} model for ClF_3 and BrF_3.[40]

3. *Gaseous state.* Analyses of the microwave spectra of ClF_3[39] and BrF_3[70] established these molecules as slightly distorted trigonal bipyramids with molecular parameters of $Cl{-}F_{eq} = 1{\cdot}598$ Å, $Cl{-}F_{ax} = 1{\cdot}698$ Å, and $F_{ax}{-}Cl{-}F_{ax} = 175°$ for ClF_3, and $Br{-}F_{eq} = 1{\cdot}721$ Å, $Br{-}F_{ax} = 1{\cdot}810$ Å, and $F_{ax}{-}Br{-}F_{ax} = 172°$ for BrF_3. Electron diffraction[42] confirmed the original n.m.r.[15] characterisation of $(CH_3)_2PF_3$ as a trigonal bipyramid with equatorial methyl groups. The molecular parameters are depicted in (50).



(50)

D. $XML_2L'_2$ and XML_3L' Species (See Table 6).—1. *Solid state.* Eight single-crystal *X*-ray investigations have been made for compounds in these two classes. The triphosphine complex of rhodium carbonyl hydride, $RhH(CO)[P(C_6H_5)_3]_3$, is a near-trigonal bipyramid with phosphine ligands at equatorial positions.[52,52a] Molecular parameters are indicated in (51). The rhodium atom is located 0·36 Å above the plane of the phosphorus atoms. A pyridine complex of trimethylchlorostannane also



(51)

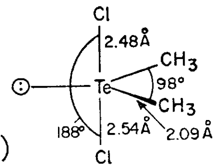
has trigonal bipyramidal geometry.[65] In this molecule, the three methyl groups are equatorial. The tin–chlorine distance is 2·42 Å.

The crystal structures of six dialkyl- and diaryl-selenium[66–68] and -tellurium dihalides[61,69] have been determined and four are schematically outlined in (52)—(55); the essential geometry of all six is trigonal bipyramidal.

Analyses of infrared spectra of $Co(CO)_3P(C_6H_5)_3Br$, $(Co(CO)_3P(C_6H_5)_3I$, and $CO(Cp)_3P(C_6H_5)_3C_6H_5$ are consistent with but do not define a C_{3v} trigonal bipyramidal structure.[129] Dipole moments for the iodide have also been cited as evidence for the C_{3v} structure[130] but these calculations are not structurally significant.

[129] W. Hieber and E. Lindner, *Chem. Ber.*, 1962, **95**, 273.

[130] A. Sacco, *Gazzetta*, 1963, **93**, 542.



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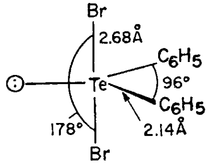

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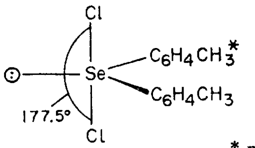

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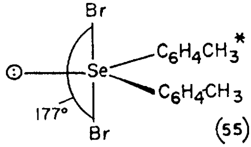
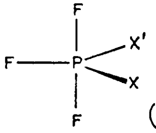


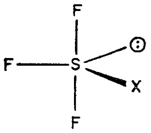
(55)

* *p*-tolyl

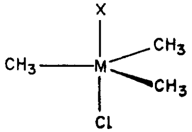
2. *Liquid and solution state.* Fluorine and proton n.m.r. data for a number of organophosphorus fluorides[4,15] have been interpreted in terms of an idealised trigonal bipyramidal model in which the fluorine atoms



(56)



(57)



(58)

occupy the two axial sites and one equatorial site (56). Similar analyses and interpretations[4] have been made for derivatives of SF_4 (57). A C_{3v} model for complexes of trialkyltin and trialkyl-lead halides has been suggested from analyses of infrared and n.m.r. data (58).[131] However, none of these studies of the solution or liquid states is definitive.

The organorhodium complexes $RhBr(1\text{-naphthyl})_2[(n\text{-}C_3H_7)_3P]_2$ and $RhBr(1\text{-naphthyl})_2[(C_2H_5)_2(C_6H_5)P]_2$ are monomeric in benzene solution and thus presumably pentaco-ordinate.[132] The authors suggest that the bulky 1-naphthyl groups shield the rhodium atom from further co-ordination to form an octahedral complex. Such a situation also apparently exists in the structures of $RuCl_2[(C_6H_5)_3P]_3$ (Section C, 1) and $Pd[(C_2H_5)_2(C_6H_5)P]_2I_2$ (Section F) in which phenyl groups effectively block the sixth co-ordination position.

3. *Gaseous state.*—No studies have been made.

E. XMLL′L″$_2$ Species.—1. *Solid state.* The iridium atom in the molecular oxygen carrier $IrO_2Cl(CO)[P(C_6H_5)_3]_2$ is in a distorted trigonal bipyramidal environment[56] if the oxygen molecule is thought of as occupying only one co-ordination position. The phosphine ligands are located at apical positions with an iridium–phosphorus distance of 2·38 Å and a P–Ir–P angle of 173°. The carbonyl group and the chlorine atom are at equatorial positions with an iridium–carbon and chlorine distance of 2·40

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[131] N. A. Matwiyoff and R. S. Drago, *Inorg. Chem.*, 1964, **3**, 337.
[132] J. Chatt and A. E. Underhill, *J. Chem. Soc.*, 1963, 2088.

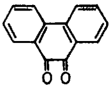
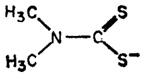
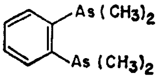
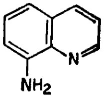
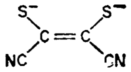
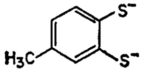
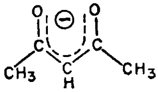
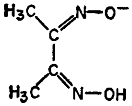
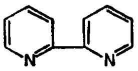
Å (average, disordered). The oxygen molecule fills the remaining equatorial position. An analogous sulphur dioxide complex, $Ir(CO)Cl(SO_2)[P(C_6H_5)_3]_2$ has been shown to have an Ir–S bond to give tetragonal pyramidal geometry[56] with sulphur at the apex. (See Note added in proof for details of this structure.)

There is a report of another apparent pentaco-ordinate structure with four kinds of ligands: $CF_3COFe(CO)(NO)[P(C_6H_5)_3]_2$. No molecular weight or spectral results have been reported.[133]

2. *Liquid state and gaseous state.* No study has been made.

F. Chelates (See Tables 7—9).—A summary of ligands and abbreviations appears in Table 2.

TABLE 2. *Chelate ligands and abbreviations*

Name	Abbreviation	Structure
9,10-Phenanthraquinone	—	
NN'-Dimethyldithiocarbamate	—	
o-Phenylenebis(dimethylarsine)	diars	
8-Aminoquinoline	—	
Maleonitriledithiolate	MNT	
Toluene-3,4-dithiolate	TDT	
Acetylacetonate	acac	
Dimethylglyoximate	DMG	
2,2'-Bipyridyl	bipy	

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[133] W. Hieber, W. Klingshirn, and W. Beck, *Chem. Ber.*, 1965, **98**, 307.

TABLE 2.—*continued.*

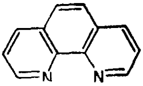
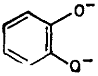
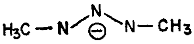
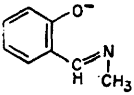
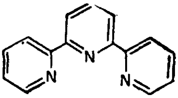
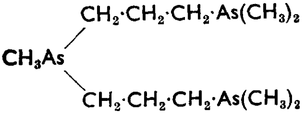
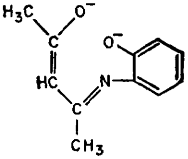
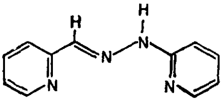
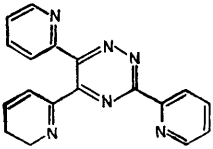
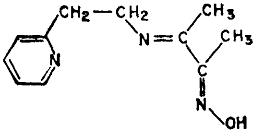
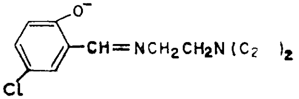
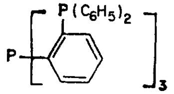
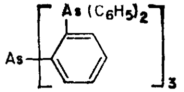
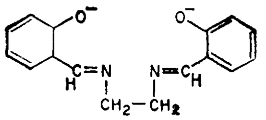
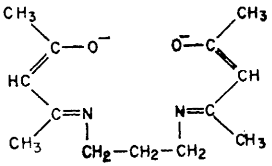
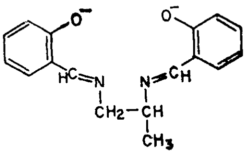
Name	Abbreviation	Structure
1,2-Bisdiphenylphosphinoethane	DPPE	$(C_6H_5)_2P{\cdot}CH_2{\cdot}CH_2{\cdot}P\ (C_6H_5)_2$
o-Phenanthroline	*o*-phen	
Catecholate	—	
1,3-Dimethyltriazene anion	dmt	
N-Methylsalicylaldiminate	sal-Me	
Terpyridine	terpy	
NNN''N''-Tetraethyldiethylenetriamine	Et_4dien	$(C_2H_5)_2N{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}N(C_2H_5)_2$
Methylbis-(3-dimethylarsinopropyl)-arsine	triars	 $CH_3As(CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}As(CH_3)_2)_2$
Acetylacetone-mono-(*o*-hydroxyanilate)	AHA	
Pyridine-2-aldehyde -2′-pyridylhydrazone	PAPHY	
3,5,6,-Tri-(2-pyridyl)-1,2,4-triazine	TPT	

TABLE 2.—*continued*

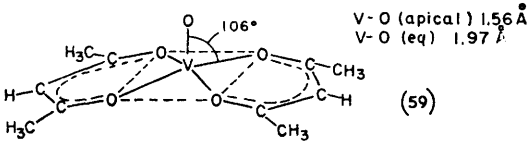
Name	Abbreviation	Structure
Diacetylmonoxime -2-(2-pyridyl)ethylamine	DAMPE	
4-Chloro-*N*-2-diethylaminoethylsalicylaldiminate	DEAS	
Tris-(*o*-diphenylphosphinophenyl)-phosphine	QP	
Tris-(*o*-diphenylarsinophenyl)arsine	QAS	
Tris-(3-dimethylarsinopropyl)phosphine	TAP	P—[—$CH_2CH_2CH_2As(CH_3)_2]_3$
NN'-Disalicylidene-ethylenediamine dianion	salicyl-en	
Bisacetylacetonatopropane-1,3-diamine dianion	acac-pn	
NN'-Disalicylidenepropane-1,2-diamine dianion	salicyl-pn	

1. *Solid state.* The adduct of tri-isopropyl phosphite with phenanthraquinone has a nearly regular trigonal bipyramidal configuration of oxygen atoms about phosphorus.[74] The isopropoxy-groups occupy one apical and two equatorial positions with phosphorus–oxygen bond lengths of 1·63 Å. The equatorial phosphorus–chelate oxygen bond length is 1·60 Å while the apical phosphorus–chelate oxygen bond is significantly longer, 1·76 Å.

The iodobis-(2,2'-bipyridyl)copper(II) cation also has a near-trigonal bipyramidal structure[75] with the iodine atom, two nitrogen atoms (from different ligands) and the copper atom coplanar. The copper–iodine bond length is 2·71 Å and all copper–nitrogen distances are 2·02 Å. There is a distortion of the two apical nitrogen atoms such that the N–Cu–N axis makes an angle of 9° with a line perpendicular to the equatorial plane.

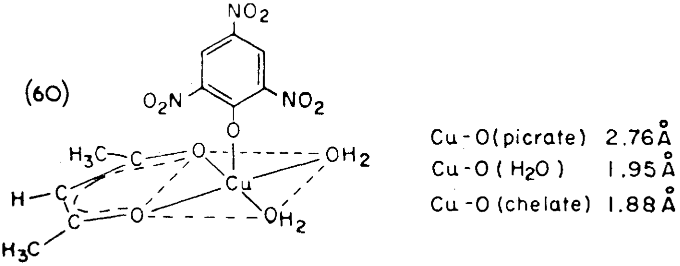
Monoaquobis(acetylacetonato)zinc(II) has been described as having a configuration intermediate between a tetragonal pyramid and trigonal bipyramid[89a, b] with all zinc–oxygen distances equal to 2·02 Å. Since the four chelate–oxygen bonds deviate only 0·1 Å from their mean plane and the zinc to water-oxygen bond is perpendicular to this plane,[89b] the structure is perhaps best described as a distorted tetragonal pyramid though the geometry cannot be precisely defined.

Bis(acetylacetonato)oxovanadium(IV) has a nearly regular tetragonal pyramidal structure (59) with the vanadium atom approximately at the centre of gravity of the pyramid.[82] Nitrosylbis[*NN*′-dimethyldithiocarbamato]cobalt(II) has a similar structure[85] with the cobalt atom displaced 0·54 Å from the plane of the four sulphur atoms towards the apical nitrosyl group. The average Co–S distance is 2·30 Å .The centre of the nitrosyl group is located at the apex of the pyramid with a Co–N distance of 1·7 Å. A preliminary report of the crystal structure of diaquoacetylacetonatocopper(II) picrate describes a tetragonal pyramidal structure (60) about the copper atom.[81] The copper atom is approximately in the same plane as the four basal oxygen atoms.



(59)

(60)



Formation of pentaco-ordinate structures by dimerisation is exhibited by the complexes bis(dimethylglyoximato)copper(II) (61) and bis(*NN*′-di-n-propyldithiocarbamato)copper(II) (62). The former is bridged through oxygen atoms[134] with a mean copper–nitrogen distance of 1·94 Å. The copper atom is displaced from the plane of the four nitrogen atoms to-

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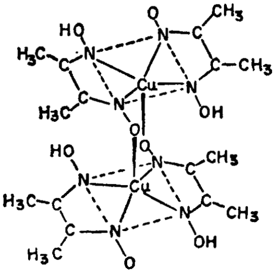
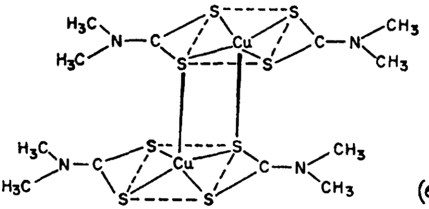
[134] E. Frasson, R. Bardi, and S. Bezzi, *Acta Cryst.*, 1959, **12**, 201.

wards an oxygen atom of a nearby molecule. The copper–oxygen distance is 2·43 Å. The dithiocarbamate[135] forms dimers through sulphur bridges



(61)

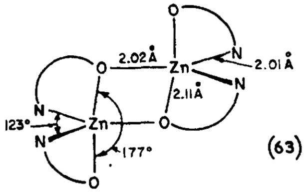
with the copper atom displaced 0·4 Å from the plane of the four sulphur atoms surrounding it towards the bridging sulphur atom.



Cu–S (basal) 2.32 Å
Cu–S (bridge) 2.71 Å

(62)

The *N*-methylsalicylaldimine complexes of manganese(II), cobalt(II), and zinc(II) are isomorphous and isostructural.[78] A crystal-structure analysis of the zinc complex[78] shows it to occur as dimers with each zinc atom in a distorted trigonal bipyramidal environment. Dimerisation is achieved *via* bridging through two oxygen atoms of the monomers as in (63). Details of the salicylaldimine ligands have been omitted for clarity. The analogous nickel(II) and copper(II) complexes are square planar when pure but when in dilute (<30%) solid solutions in the zinc lattice, they assume the trigonal bipyramidal geometry of the host zinc atoms.[136]



(63)

The peroxochromium complexes with ethylenediamine and 1,10-*o*-phenanthroline, $Cr(O)(O_2)_2(en)$ and $[Cr(O_2)_2(H_2O)(o\text{-phen})]\ H_2O$, res-

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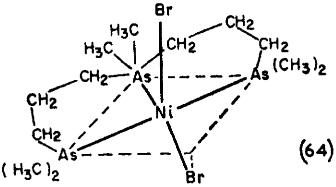
[135] A. Pignedoli and G. Peyronel, *Gazzetta*, 1962, **92**, 745.

[136] L. Sacconi, M. Ciampolini, and G. P. Speroni, *J. Amer. Chem. Soc.*, 1965, **87**, 3102.

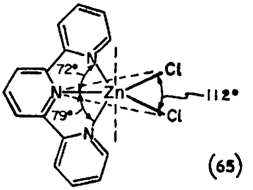
pectively, have a trigonal bipyramidal structure[79] if the O_2^{2-} ligand is considered as occupying only one bonding position. In the ethylenediamine complex, the oxide oxygen atom and one of the chelate nitrogen atoms are located at the apices. The other chelate nitrogen atom is at one of the equatorial positions with the two O_2^{2-} groups located symmetrically about the other two equatorial positions. The *o*-phenanthroline complex is similar with a water molecule and nitrogen atom at the apices and the other nitrogen atom and two O_2^{2-} groups at equatorial positions. Detailed bond lengths and angles have not yet been presented.

A triarsine complex of nickel bromide, (triars)$NiBr_2$, assumes a distorted tetragonal pyramidal structure (64) in which the nickel and arsenic atoms are very nearly coplanar with bond lengths of 2·27 Å.[86] One bromine atom is depressed 20° from this plane with a bond length of 2·37 Å and the apical bromine atom is at a distance of 2·69 Å.



(64)

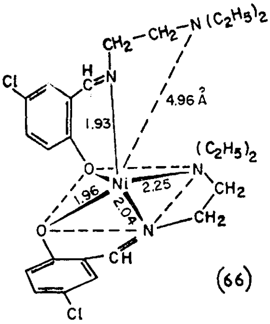
Terpyridyldichlorozinc(II) is described[77] as a distorted trigonal bipyramid (65). The distortion is imposed in part by the terpyridyl ligand which causes the apical nitrogen–zinc–equatorial nitrogen angles to decrease to 79° and 72°. The Cl–Zn–Cl angle is also reduced to 112°. The terpyridyl system is planar and this plane is perpendicular to the plane described by the zinc and chlorine atoms. Thus, C_{2v} symmetry is preserved although the



(65)

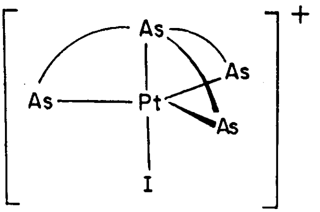
distortion from regular trigonal bipyramidal geometry is considerable. The zinc–nitrogen and zinc–chlorine distances are 2·2 and 2·29 Å, respectively. The analogous cadmium and copper compounds are isomorphous with the zinc complexes. (See Note added in proof.)

The Schiff base *N*-β-diethylamine-ethyl-5-chlorosalicylaldimine forms isomorphous[87,87a] 2:1 complexes with cobalt(II) and nickel(II) of the formula $M(DEAS)_2$. A crystal-structure determination[87,87a] of the nickel complex has shown that one of the potentially trico-ordinate ligands is actually bico-ordinate resulting in a tetragonal pyramidal configuration (66) about the nickel atom. The basal set of two nitrogen and two oxygen atoms is planar to within 0·1 Å and the nickel atom lies 0·36 Å above this plane. The shortest intermolecular non-bonded nitrogen–nickel distance is 7·81 Å.

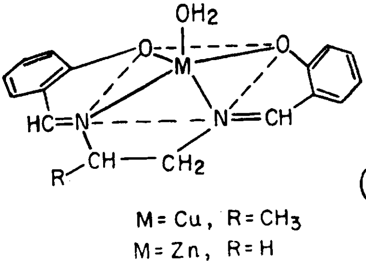


(66)

A trigonal bipyramidal configuration is adopted[76] by the ligands in an iodotetra-arsine complex [PtI(QAS)][B(C_6H_5)$_4$] (67). The central arsenic atom is located at an apex and the three remaining arsenic atoms are at equatorial positions. The iodine atom is located at the other apex. Detailed bond lengths and angles have not yet been reported but distortions from trigonal bipyramidal geometry are apparently not great.



(67)



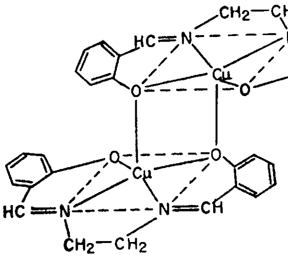
(68)

NN′-Disalicylidenepropylene-1,2-diaminecopper monohydrate and *NN′*-disalicylidene ethylenediaminezinc monohydrate have the distorted tetragonal pyramidal configuration (68). In both the copper[137] and zinc[88] compounds the chelate oxygen and nitrogen atoms are nearly coplanar with the copper atom being displaced 0·2 Å and the zinc atom 0·34 Å out of the plane towards the apical water molecule. The zinc–chelate oxygen bond lengths are 1·94 Å and the zinc–nitrogen distances are 2·08 Å with the water oxygen atom at 2·13 Å. The copper–chelate oxygen bonds are 1·94 and 1·88 Å while the Cu–N distances are 1·78 and 1·95 Å. The latter distortion may be due to steric repulsions arising from the propylenediamine ligands. The copper–water oxygen distance is 2·53 Å.

[137] F. J. Llewellyn and T. N. Waters, *J. Chem. Soc.*, 1960, 2639.

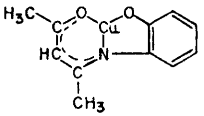
In methoxyiron(III) mesoporphyrin-IX dimethyl ester,[83] the iron atom is located 0·49 Å above the centre of the planar porphine skeleton with all iron–nitrogen distances being 2·07 Å. The tetragonal pyramidal arrangement about the iron atom is completed by an oxygen atom located at 1·84 Å along a line perpendicular to the porphine ring. A similar structure has been found for chlorohæmin[84] in which the iron atom is displaced 0·48 Å from the plane of the four nitrogen atoms. The iron–nitrogen distance in chlorohæmin is 2·06 Å and the apical iron–chlorine distance is 2·22 Å.

Anhydrous *NN′*-disalicylidene-ethylenediaminecopper is dimerised in the solid state[80] to give a tetragonal pyramidal configuration about the copper atoms as in (69). The dimerisation is achieved by bridging through a chelate oxygen atom. The copper–bridge oxygen distance is 2·41 Å while the average copper–chelate oxygen and nitrogen distances are 1·96 and 2·01 Å, respectively. The copper atoms are displaced towards the bridging oxygen atoms from the chelate atom plane.

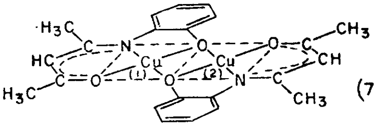


(69)

Crystals of the copper complex of acetylacetone–mono(o-hydroxyanilate) (70) are built up from dimers[138,138a] as shown in (71). The copper–bridge oxygen distances vary from 1·91 to 2·02 Å, while the average copper–nitrogen and copper–non-bridge oxygen distances are 1·99 Å and 1·90 Å, respectively. Further association occurs such that the two copper atoms are in different environments. One copper atom, Cu(1), has a distorted tetragonal pyramidal configuration with a phenolic oxygen atom of another dimer located 2·68 Å away. The other copper atom, Cu(2), has a square-planar configuration with no other atom from neighbouring molecules within 3·5 Å. The unusual properties of the solid and the copper–copper distance of 3·0 Å suggests an interaction between the copper atoms. If



(70)



(71)

[138] G. A. Barclay, C. M. Harris, B. F. Hoskins, and E. Kokot, *Proc. Chem. Soc.*, 1961, 264.

[138a] G. A. Barclay and B. F. Hoskins, *J. Chem. Soc.*, 1965, 1979.

this is considered as a sixth bond for Cu(1), then Cu(2) becomes pentaco-ordinate.

2. *Solution state.* For many chelate complexes in solution, pentaco-ordinate structures have been assigned on the basis of molecular weight and conductivity measurements (in nitrobenzene or nitromethane) in combination with other physical measurements such as electronic absorption spectra, conductimetric titrations, and magnetic susceptibilities. For example, the diarsine complexes, $[Au(diars)_2I]^{2+}$, $[Au(diars)_2]^{3+}$, and $Au(diars)_2I_2$ give clearly different electronic absorption spectra.[139] Conductimetric titrations of $[Au(diars)_2]^{3+}$ and $[Pt(diars)_2]^{2+}$ [140,140a] with I^- or Cl^- give sharp end-points corresponding to the addition of one equivalent of X^-. However, crystal-structure analysis[141] of $Pd(diars)_2I_2$ and $Pt(diars)_2I_2$ show that both contain hexaco-ordinate central atoms although the solution data are entirely consistent with a pentaco-ordinate structure. This suggests that solvent interactions may be important (*i.e.*, to give octahedral co-ordination) but there is no evidence as yet bearing upon this rather important point.

Several complexes containing nitric oxide are apparently pentaco-ordinate. The dithiocarbamate complexes $(NO)M[S_2CN(CH_3)_2]_2$ (M = Co[142], Fe[143]) are monomeric in bromoform and benzene solution respectively. An analogous vanadium complex[144] is too unstable for extensive study in solution. The cobalt compound has a tetragonal pyramidal configuration in the solid but the structure in solution is unknown. Mononitric oxide adducts of the bis-(8-aminoquinoline)cobalt(II) cation[145] and bis(acetylacetonato)cobalt(II)[146] have been isolated. Molecular weight, conductivity, and magnetic data are in agreement with pentaco-ordinate structures.

Although vanadylacetylacetone, $VO(acac)_2$, is monomeric in boiling benzene solution[147], it reacts with various amines to give the hexaco-ordinate complexes $VO(acac)_2$,amine.[147] The thermodynamics of co-ordination of a number of oxygen and nitrogen donors with $VO(acac)_2$ has been measured calorimetrically in nitrobenzene solution[148] and solvent effects on the optical and electron spin resonance spectra have also been reported.[149,150] Curiously, $VO(acac)_2$ is reported to be dimeric in molten

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[139] C. M. Harris and R. S. Nyholm, *J. Chem. Soc.*, 1957, 63.
[140] C. M. Harris, R. S. Nyholm, and D. J. Phillips, *J. Chem. Soc.*, 1960, 4379.
[140a] C. M. Harris and R. S. Nyholm, *J. Chem. Soc.*, 1956, 4375.
[141] C. M. Harris, R. S. Nyholm, and N. C. Stephenson, *Nature*, 1956, **177**, 1127.
[142] L. Cambi and A. Gagnasso, *Atti della reale accad Lincei*, 1931, (6) **13**, 404.
[143] L. Cambi and A. Gagnasso, *Atti accad Naz. Lincei*, 1931, **13**, 254.
[144] L. Malatesta, *Gazzetta*, 1941, **71**, 615.
[145] R. Nast, H. Bier, and J. Gremm, *Chem. Ber.*, 1961, **94**, 1185.
[146] R. Nast and H. Bier, *Chem. Ber.*, 1959, **92**, 1858.
[147] M. M. Jones, *J. Amer. Chem. Soc.*, 1954, **76**, 5995.
[148] R. L. Carlin and F. A. Walker, *J. Amer. Chem. Soc.*, 1965, **87**, 2128.
[149] D. Kivelson and S. K. Lee, *J. Chem. Phys.*, 1964, **41**, 1896.
[150] I. Bernal and P. H. Rieger, *Inorg. Chem.*, 1963, **2**, 256.

triphenylmethane (93°) and biphenyl (70°) but monomeric in camphor (180°C).[151]

A 1:1 adduct of bis(acetylacetonato)cobalt(II) with cyclohexylamine[152] is monomeric in chloroform solution but dimeric in carbon tetrachloride. Molecular weights in benzene solution are consistent with a monomer–dimer equilibrium. The monomer is presumably pentaco-ordinate. Spectral evidence has been presented[153] for a pentaco-ordinate pyridinebis(acetylacetonato)cobalt(II) species in the reaction of bis(acetylacetonato)cobalt(II) with pyridine in benzene solution. The complex was not isolated.

Solution n.m.r. experiments[154] indicate that dimethyl-(1,3-dimethyltriazino)tin bromide and dimethyl-(1,3-dimethyltriazino)tin iodide contain pentaco-ordinate tin.

The square-planar complexes $Co(MNT)_2^-$ and $Co(TDT)_2^-$ form 1:1 adducts with pyridine and triphenylphosphine.[155] The adducts are diamagnetic in the solid and in solution and their absorption spectra are interpreted as supporting a pentaco-ordinate structure in solution.

ortho-Quinones and α-diketones form 1:1 adducts with tertiary phosphite esters.[156] These adducts are described as having a cyclic unsaturated oxyphosphorane structure in which five oxygen atoms are co-ordinated to phosphorus. Molecular weights are consistent with this formulation. Reaction of the biacetyl adduct with additional biacetyl[157] or an aldehyde[158] leads to pentaco-ordinate cyclic saturated oxyphosphorane compounds.

Conductivities and molecular weights in nitrobenzene solution for adducts of CoI_2, $NiBr_2$, and NiI_2 with the triarsine, $CH_2As[CH_2CH_2CH_2As(CH_3)_2]_2$, are consistent with pentaco-ordinate structures for cobalt and nickel.[159] The potentially terdentate chelate diacetylmonoxime-β-pyrid-2-ylethylamine forms 1:1 complexes with $ZnCl_2$ and ZnI_2[160] which are non-electrolytes in acetonitrile solution and thus presumably pentaco-ordinate.

The nickel complex[161] $Ni(Et_4dien)Cl_2$ exists in ethanol solution as the tetraco-ordinate salt $[Ni(Et_4dien)Cl]^+Cl^-$ and in acetone as a non-ionic pentaco-ordinate complex on the basis of conductivity data and spectral measurements. Mixtures of tetra- and pentaco-ordinate complexes are apparently present in solvents such as dimethylformamide, acetonitrile, and nitromethane. However, the cobalt analogue[161] $Co(Et_4dien)Cl_2$ is a

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[151] D. P. Graddon, *Nature*, 1962, **195**, 891.

[152] J. A. Bertrand, F. A. Cotton, and W. J. Hart, *Inorg. Chem.*, 1964, 3, 1007.

[153] J. P. Fackler, *Inorg. Chem.*, 1963, 2, 266.

[154] F. E. Brinckman, H. S. Haiss, and R. A. Robb, *Inorg. Chem.*, 1965, 4, 936.

[155] C. H. Langford, E. Billig, S. I. Shupack, and H. B. Gray, *J. Amer. Chem. Soc.*, 1964, **86**, 2958.

[156] F. Ramirez and N. B. Desai, *J. Amer. Chem. Soc.*, 1963, **85**, 3252.

[157] F. Ramirez, N. Ramanathan, and N. B. Desai, *J. Amer. Chem. Soc.*, 1963, **85**, 3465.

[158] F. Ramirez, A. V. Patwardhan, N. Ramanathan, N. B. Desai, C. V. Greco, and S. R. Heller, *J. Amer. Chem. Soc.*, 1945, **87**, 543.

[159] G. A. Barclay and R. S. Nyholm, *Chem. and Ind.*, 1953, 378.

[160] E. Uhlig and D. Schneider, *Z. anorg. Chem.*, 1964, **333**, 90.

[161] H. B. Gray and Z. Dori, *J. Amer. Chem. Soc.*, 1965, **88**, 1394.

non-electrolyte in a variety of solvents and presumably pentaco-ordinate.

There is considerable evidence that the solid-state trigonal bipyramidal structure of $[Pt(QAS)I][(C_6H_5)_4B]$ (see previous section) persists in solution.[162] Molar conductivities in nitrobenzene are in agreement with the presence of a 1:1 electrolyte and, in addition, the reflectance and solution spectra (in methanol) are very similar. The latter point, though not conclusive, is certainly indicative of a preservation of structure about the platinum atom since electronic spectra are usually sensitive to change in co-ordination. The analogous palladium tetra-arsine[163] $[Pd(QAS)X]^+$, platinum tetraphosphine[164] $[Pt(QP)X]^+$, and nickel phosphine–triarsine[165] $[Ni(TAP)X]^+$ complexes are postulated as having a similar structure based on conductivity data and the similarity of their electronic spectra with those of the $[Pt(QAS)X]^+$ salts.

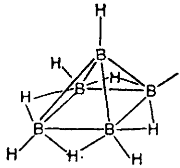
Several nitric oxide adducts of various phenyl substituted *NN'*-disalicylidene-ethylenediaminecobalt complexes have been described[166] and on the basis of conductivities and molecular weights obtained in nitrobenzene are described as containing pentaco-ordinate cobalt. From the similarity of these compounds to the zinc and copper monohydrates of similar ligands (previous section) tetragonal pyramidal geometry seems reasonable though this is purely speculative.

A similar situation exists for bisacetylacetonatopropylenediamino-oxovanadium(IV) which has been partially resolved into optical enantiomers.[167,167a]

F. Pentaco-ordination in Molecular Polyhedra and in Periodic Lattices (See Table 10).

—There are a number of molecular aggregates in which certain atoms attain a co-ordination number of five. Such structures are particularly common in electron-deficient molecules like the boron hydrides in which multicentre bonding is extant. An excellent example of pentaco-ordinate boron is the apical boron atom in B_5H_9 (72) which is bonded to four boron atoms and one hydrogen atom.[168]

Pentaco-ordinate boron atoms are found in many structures[168a] includ-



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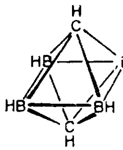

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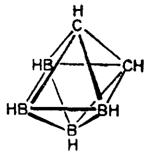

(74)

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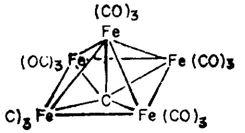
[162] J. A. Brewster, C. A. Savage, and L. M. Venanzi, *J. Chem. Soc.*, 1961, 3699.
[163] C. A. Savage and L. M. Venanzi, *J. Chem. Soc.*, 1962, 1548.
[164] J. G. Hartley, L. M. Venznai, and D. C. Goodall, *J. Chem. Soc.*, 1963, 3930.
[165] G. S. Benner, W. E. Hatfield, and D. W. Meek, *Inorg. Chem.*, 1964, **3**, 1544.
[166] A. Earnshaw, P. C. Hewlett, and L. F. Larkworthy, *Nature*, 1963, **199**, 483.
[167] K. Ramaiah, F. E. Anderson, and D. F. Martin, *Inorg. Chem.*, 1964, **3**, 296.
[167a] K. Ramaiah and D. F. Martin, *J. Inorg. Nuclear Chem.*, 1965, **27**, 1663.
[168] W. J. Dulmadge and W. N. Lipscomb, *Acta Cryst.*, 1952, **5**, 260.
[168a] W. N. Lipscomb, "Boron Hydrides", W. A. Benjamin, Inc., New York, 1963.

ing B_9H_{15}, B_8Cl_8, $B_9H_{14}^-$, $B_3C_2H_5$, $B_{10}H_{16}$, and $B_{10}H_{10}^{2-}$. In all these, the essential pentaco-ordinate geometry is a tetragonal pyramid. This is primarily a reflection of the structure as a whole, rather than any tendency of an individual boron atom to assume such geometry. Trigonal bipyramidal co-ordination is impossible for an atom that is part of a regular polyhedron and not very likely for an atom that is part of a polyhedron. The 6,9 boron atoms in the $B_{10}H_{14}^{2-}$ structures, *i.e.*, $B_{10}H_{12}$,2base are pentaco-ordinate and the geometry of these atoms can be considered as a distorted trigonal bipyramid or distorted tegragonal pyramid.[168a,169] Any distinction between the two descriptions is meaningless since the angles should be very sensitive to the spatial requirements of the base ligand.

Carboranes are polyhedra comprised of boron and carbon atoms. The carbon atoms are pentaco-ordinate in certain of these carboranes, *e.g.*, the two isomers (73) and (74) of $B_4C_2H_6$.[168a] Although none have been described, polyhedra with pentaco-ordinate beryllium or nitrogen atoms should be possible in polyhedral structures. In fact, any element which can form tetrahedral structures is inherently capable of pentaco-ordination in polyhedral aggregates.

The co-ordination number of five for carbon is also exhibited[170] in the compound $Fe_5(CO)_{15}C$ (75). The central carbon atom is located slightly *below* the plane of the basal iron atoms. The average carbon–basal iron atom distance is 1·89 Å and the carbon–apical iron atom distance is 1·96 Å.

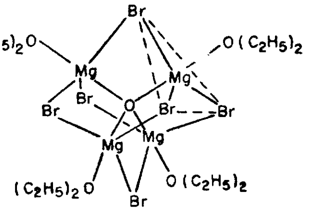


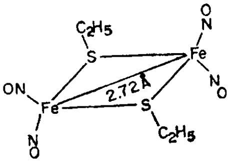
(75)

The black isomer of an acetylene–iron carbonyl complex, $Fe_3(CO)_8$-$(C_6H_5C_2C_6H_5)$, contains four carbon atoms (from the acetylenes) which are also in tetragonal pyramidal configurations.[171]

An unusual structure (76) is that of $Mg_4Br_6O[(C_2H_5)_2O]_4$ which contains pentaco-ordinate magnesium in a nearly regular trigonal bipyra-

(76)





(77)

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[169] D. E. Sands and A. Zalkin, *Acta Cryst.*, 1962, **15**, 410.

[170] E. H. Braye, L. F. Dahl, W. Hübel, and D. L. Wampler, *J. Amer. Chem. Soc.*, 1962, **84**, 4633.

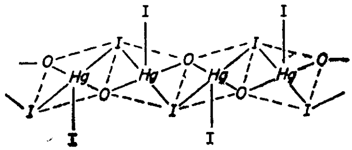
[171] R. P. Dodge and V. Schomaker, *J. Organometallic Chem.*, 1965, 3, 274.

midal configuration.[90] The $(C_2H_5)_2O$–Mg–O angle is 180° and the Br–Mg–Br angles are approximately 120°. Bond distances are: Mg–Br 2·6 Å; Mg–O (central) 1·95 Å; Mg–O (ethereal) 2·11 Å.

In Roussin's red ethyl ester, $[(NO)_2Fe(SC_2H_5)]_2$, the iron and sulphur atoms are coplanar (77) and the arrangement of nitrogen and sulphur about each iron atom is nearly tetrahedral.[172] The short iron–iron distance suggests a strong interaction between them and this is consistent with the observed diamagnetism. The point at which a "strong interaction" becomes a bond is a matter of semantics but it seems reasonable to consider the iron atoms as forming five bonds. Similar structures have been postulated for the related $[Fe(MR_2)(NO)_2]_2$ (M = P, As; R = CH_3)[173] and $[Fe(CO)_3NH]_2$[174] which would contain bridging MR_2 and NH groups respectively.

Copper(II) formate is not a discrete unimolecular salt but a polymeric array of copper atoms with bridging formate groups.[175] The co-ordination number of the copper is five with a distorted tetragonal pyramid of four oxygen atoms at a distance of 1·95 Å and an axial oxygen atom at 2·40 Å. Geometry here is primarily determined by the lattice, *i.e.*, a square-planar copper(II) complex with a weak intermolecular interaction on the d_{z^2} axis.

The complex compound Hg_2O_2NaI[176] has a polymeric structure in which the mercury atom is pentaco-ordinate with a distorted tetragonal pyramidal structure (78). The mercury–iodine distances are 3·33 Å and the mercury–oxygen distances are 2·03 Å. The mercury atom is in the centre of the plane formed by two oxygen and two iodine atoms.



(78)

Vanadium pentoxide assumes a layer structure[177] in which each vanadium forms bonds to five oxygen atoms arranged in a distorted trigonal bipyramid. The bipyramids are joined in two directions by sharing corners. The vanadium–oxygen bond distances range from 1·54 Å to 2·02 Å. A sixth oxygen atom (from the next layer) is located at a distance of 2·81 Å suggesting an interaction between layers to give an octahedral configuration about the vanadium atom.

A crystal-structure determination of germanium difluoride[178] shows it to be a fluorine-bridged chain polymer with the parallel chains cross-

[172] J. T. Thomas, J. H. Robertson, and E. G. Cox, *Acta Cryst.*, 1958, **11**, 599.

[173] R. G. Hayter and L. F. Williams, *Inorg. Chem.*, 1964, **3**, 717.

[174] W. Hieber and H. Beutner, *Z. anorg. Chem.*, 1962, **317**, 63.

[175] G. A. Barclay and C. H. L. Kennard, *J. Chem. Soc.*, 1961, 3289.

[176] K. Aurivillius, *Acta Chem. Scand.*, 1960, **14**, 2196.

[177] A. Byström, K. A. Wilhelmi, and O. Brotzen, *Acta Chem. Scand.*, 1950, **4**, 1119.

[178] J. Trotter, M. Akhtar, and N. Bartlett, *J. Chem. Soc.* (*A*), 1966, 30.

linked by weak fluorine bridges. Each germanium atom is in a distorted trigonal bipyramidal environment with apical fluorine atoms at distances of 2·09 and 2·57 Å. The F_{ax}–Ge–F_{ax} angle is 163°. Two equatorial fluorine atoms are located at 1·79 and 1·91 Å with a F_{eq}–Ge–F_{eq} angle of 91·6°. The third equatorial position is presumably occupied by a non-bonding electron pair.

A red form of *trans*-di-iodobis(dimethylphenylphosphine)palladium(II) has been shown[179] to consist of planar $[(CH_3)_2(C_6H_5)P]_2PdI_2$ groups joined through iodine bridges to give a polymeric array of distorted tetragonal pyramids about each palladium atom. Bond lengths are: Pd–P, 2·34 Å (avg.), Pd–I (basal), 2·63 Å (avg.); Pd–I (axial bridge), 3·28 Å. The formation of a fifth long bond to palladium *via* a bridging atom is quite similar to that found for a variety of copper compounds described in Section F. The authors note that the sixth bonding position of palladium may be filled by a hydrogen on the *β*-carbon of a phenyl ring on one of the phosphine ligands. The calculated distance for the assumed Pd–H interaction is 2·8 Å.

IV. Tabulation of Established and Potential Pentaco-ordinate Structures.

TABLE 3. ML_5 *Species.*

Species	d^x	Proposed structure*	Phys. state†	Technique‡	Ref.
PF_5	d^0	TBP	l, g	IR, R	20, 20*a*
		TBP	g	ED	20*b*
PCl_5	d^0	$PCl_4^+PCl_6^-$	c	*X*	13
		TBP	g	ED	180
PBr_5	d^0	$PBr_4^+Br^-$	c	*X*	181
$P(OC_2H_5)_5$	d^0				182
$P(C_6H_5)_5$	d^0	TBP	c	*X*	44
VF_5	d^0		g	IR	183
NbF_5	d^0	OT	c	*X*	1
		Assoc.	l	V	5
				NMR	184
$NbCl_5$	d^0	OD	c	*X*	185
		Dimer	sln	MW	186
		TBP	g	ED	187
$NbBr_5$	d^0	TBP	g	ED	187
TaF_5	d^0	OT	c	*X*	1
		Assoc.	l	V	5
				NMR	184
$TaCl_5$	d^0	OD	c	*X*	188
$TaBr_5$	d^0	TBP	g	ED	187
CrF_5	d^1				189
MoF_5	d^1	OT	c	*X*	190

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[179] N. A. Bailey, J. M. Jenkins, R. Mason, and B. L. Shaw, *Chem. Comm.*, 1965, 237.

TABLE 3.—*continued.*

Species	d^x	Proposed structure*	Phys. state†	Technique‡	Ref.
$MoCl_5$	d^1	OD	c	*X*	2
		TBP	g	ED	191
WCl_5	d^1				192
$Mo(CN)_5^-$	d^2				193
TcF_5	d^2				189*c*
ReF_5	d^2				1
$ReCl_5$	d^2				194
$ReBr_5$	d^2				195
MnF_5^-	d^3				196
RuF_5	d^3	OT	c	*X*	197
IrF_5	d^4	OT	c	*X*	198
$MnCl_5^{2-}$	d^4				199
MnF_5^{3-}	d^5				200
$Co(CN)_5^{3-}$	d^7				9
$Co(CNCH_3)_5^{2+}$	d^7				10
$Cr(CO)_5^{2-}$	d^8				201
$Mo(CO)_5^{2-}$	d^8				201
$W(CO)_5^{2-}$	d^8				201
$Mn(CO)_5^-$	d^8	D_{3h}, TBP	sln	IR	202
$Tc(CO)_5^-$	d^8				203
$Re(CO)_5^-$	d^8				204
$Fe(PF)_3)_5$	d^8				205*a*, *b*
$Fe(CO)_5$	d^8	TBP	c	*X*	53
		TBP	g, l	IR, R	54
		TBP	g	ED	206
$Co(CNCH_3)_5^+$	d^8	TBP	c	*X*	51
$Ni(CN)_5^{3-}$	d^8	TP	sln	IR	91
$Pt(SnCl_3)_5^{3-}$	d^8	TBP	c	*X*	55
$CuCl_5^{3-}$	d^9	TBP	c	*X*	57
AsF_5	d^{10}	TBP	g, l	IR, R	58
$As(CH_3)_5$	d^{10}				207
$As(C_6H_5)_5$	d^{10}	TBP	c	*X*	44
SbF_5	d^{10}	OD	l	FNMR	3
$SbCl_5$	d^{10}	TBP	c	*X*	59
		TBP	g	ED	180
$Sb(CH_3)_5$	d^{10}				207
$Sb(C_6H_5)_5$	d^{10}	TP	c	*X*	34
BiF_5	d^{10}				208

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* TBP, trigonal bipyramid; OT, octahedral tetramer; Assoc., associated; OD, octahedral dimer; TP, tetragonal pyramid; P, polymer; Dissoc., dissociated in solution; D, dimer; M, monomeric.

† c, crystal; g, gas; l, liquid; sln, solution; m, melt.

‡ *X*, *X*-Ray diffraction; IR, infrared spectroscopy; R, Raman spectroscopy; ED, electron diffraction; V, viscosity; MW, molecular weight; NMR, nuclear magnetic resonance spectroscopy; FNMR, nuclear magnetic resonance spectroscopy with use of fluorine-19; M, microwave spectroscopy; DM, dipole moment.

TABLE 4. XML_4 *Species*

Species	d^x	Proposed structure*	Phys. state†	Technique‡	Ref.
SF_4	d^0	C_{2v}, TBP	l	FNMR	19*b*
				IR, R	47, 46
		C_{2v}, TBP	g	ED, M	45
OSF_4	d^0	C_{2v}, TBP	l, g	IR, R	48, 49
				ED	50
$CF_3N{=}SF_4$	d^0	C_{2v}, TBP	l	FNMR	4
$FPCl_4$	d^0	C_{3v}, TBP	l, g	IR, R	20
$(C_2H_5)_2NPF_4$	d^0	C_{2v}, TBP	l	FNMR	4
$(CH_3)_2NPF_4$	d^0				95
CF_3PF_4	d^0				15
CF_3PCl_4	d^0	C_{2v}, TBP	g, l	IR, R	43
CH_3PF_4	d^0	C_{2v}, TBP	g	ED	42
RPF_4 ($R{=}CH_3$, C_2H_5, n-C_4H_9, C_6H_5)	d^0	C_{2v}, TBP	l, sln	FNMR§	15
$SiF_4{\cdot}N(CH_3)_3$	d^0				108, 109
$SiCl_4{\cdot}N(CH_3)_3$	d^0				105, 106
$TiCl_4{\cdot}N(CH_3)_3$	d^0				104
$MoOF_4$	d^0				209, 210
WOF_4	d^0				210, 211
$ReOF_4$	d^1				210
$ReOCl_4$	d^1				212
$OsOCl_4$	d^2				213
$Cl_4OsOOsCl_4$	d^3				214
$ReBr_4O^-$	d^3				94
$[ClRe(OCOR)_2]_2$	d^4	C_{4v}, TP	c	§	215
$PtOF_4$	d^4				216
$\{[(C_6H_5)_2CH_3AsO]_4$-$MnClO_4\}^+$	d^5	TP	c	*X*	93, 73

TABLE 4.—*continued.*

Species	d^x	Proposed structure*	Phys. state†	Technique‡	Ref.
$\{[(C_6H_5)_2CH_3AsO]_4\text{-}FeClO_4\}^+$	d^6	TP	c	*X*	93, 73
$R_3PMn(CO)_4$	d^7	C_{3v}, TBP	c	IR	102
$\{[(C_6H_5)_2CH_3AsO]_4\text{-}CoClO_4\}^+$	d^7	TP	c	*X*	93, 73
$R_3PMn(CO)_4^-$	d^8	C_{3v}, TBP	c	IR	101
$NOMn(CO)_4$	d^8	C_{3v}, TBP	sln	IR	100
$RNCFe(CO)_4$	d^8	C_{3v}, TBP	sln	IR	98
$R_3PFe(CO)_4$	d^8	C_{3v}, TBP	sln	IR	98
$[(CH_3)_2N]_3PFe(CO)_4$	d^8				217
$(C_6H_5)_3AsFe(CO)_4$	d^8	C_{3v}, TBP	c, sln	IR	99
$(C_6H_5)_3SbFe(CO)_4$	d^8	C_{3v}, TBP	c, sln	IR	99
$F_3PFe(CO)_4$	d^8				205*b*
$HFe(CO)_4^-$	d^8	C_{3v}, TBP	sln	R	97
$HCo(CO)_4$	d^8	C_{3v}	sln	IR	96
$CH_3Co(CO)_4$	d^8				218
$(CO)_5Mn\text{-}Co(CO)_4$	d^8				219
$(CO)_5Re\text{-}Co(CO)_4$	d^8				220
$IrBr_4NO_2^{2-}$	d^8				221
$\{[(C_6H_5)_2CH_3AsO]_4\text{-}NiClO_4\}^+$	d^8	TP	c	*X*	93, 73
$\{Pt[(C_6H_5)_3Sb]_4NO_3\}^+$	d^8				222
$\{[(C_6H_5)_2CH_3AsO]_4\text{-}CuClO_4\}^+$	d^9	TP	c	*X*	93, 73
$\{[(C_6H_5)_2CH_3AsO]_4\text{-}ZnClO_4\}^+$	d^{10}	TP	c	*X*	93, 73
SeF_4	d^{10}	C_{2v}, TBP	sln, g	FNMR	19*b*
				ED	113
$SeCl_4$	d^{10}				110, 111
TeF_4	d^{10}				223
$TeCl_4$	d^{10}	C_{2v}, TBP	g	ED	114
		$TeCl_3^+Cl^-$	sln	R	110, 111
$C_6H_5AsF_4$	d^{10}				4
$Sb_2F_7^-$	d^{10}	$F_3SbFSbF_3^-$	c	*X*	92
$SbFCl_4$	d^{10}	C_{3v}	sln	R	224
$GeF_4\cdot N(CH_3)_3$	d^{10}				108, 109
$SnF_4\cdot N(CH_3)_3$	d^{10}				108, 109
$GeCl_4\cdot N(CH_3)_3$	d^{10}				105, 106
$SnCl_4\cdot N(CH_3)_3$	d^{10}				105, 106
$SnCl_4\cdot$donor¶	d^{10}	C_{2v}	l, sln	R	103

*†‡ See footnotes to Table 3.

§ Speculative.

¶ Donor = alcohols, ethers, nitriles, and $POCl_3$.

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TABLE 5. X_2ML_3 *Species.*

Compound	d^x	Proposed structure*	Phys. state†	Technique‡	Ref.
ClF_3	d^0	C_{2v}, TBP	c, l, sln, g	X, M, IR, R, NMR	39, 40, 41, 19*a*, 70
Cl_2PF_3	d^0	C_{2v}, TBP	l, g	NMR IR, R	4, 20
Br_2PF_3	d^0	C_{2v}, TBP	sln	NMR	4, 225
Cl_3PF_2	d^0	D_{3h}, TBP	l	IR, R	20
$[(C_2H_5)_2N]_2PF_3$	d^0	C_{2v}, TBP	sln, l	NMR	4
R_2PF_3	d^0	C_{2v}, TBP	sln, l	NMR	4
$(CH_3)_2PF_3$	d^0	C_{2v}, TBP	g	ED	42
$(C_6H_5)_2PF_3$	d^0	C_{2v}, TBP	sln, l	NMR	4
$(CF_3)_3PF_2$	d^0	D_{3h}, TBP	sln, l	NMR	4
$(C_2F_5)_2PF_3$	d^0	D_{3h}, TBP	sln, l	NMR	4
R_3PF_2	d^0	D_{3h}, TBP	l, sln	NMR	4
$(C_6H_5)_3PF_2$	d^0	D_{3h}, TBP	l, sln	NMR	4
$H_3Al[N(CH_3)_3]_2$	d^0	D_{3h}, TBP	sln, c	IR, R, X	36-38, 35
$H_3Al[N(n\text{-}C_3H_7)_3]_2$	d^0				226
ReO_2F_3	d^0				210, 227
OsO_3F_2	d^0				228
$Cl_3Ti[N(CH_3)_3]_2$	d^1				104
$Cl_3V[N(CH_3)_3]_2$	d^2	§			121, 122
$H_3Re[P(C_6H_5)_3]_2$	d^4				229
$RuCl_2[P(C_6H_5)_3]_3$	d^6	C_{2v}, TP	c	X	72
$CoCl_3[P(C_2H_5)_3]_2$	d^6	D_{3h}, TBP	sln	DM	120
$CoBr_3[P(C_2H_5)_3]_2$	d^6				120
$Re(CO)_3[P(C_6H_5)_3]_2$	d^7				230
$Ir(CO)_2Br_3^-$	d^7				231
$NiCl_3[P(C_2H_5)_3]_2$	d^7				120
$NiBr_3[P(C_2H_5)_3]_2$	d^7				120
$Fe(CO)_3\{P[N(CH_3)_2]_3\}_2$	d^8	D_{3h}, TBP	c	IR	217
$Fe(CO)_3(PF_3)_2$	d^8				205*b*
$Fe(CO)_3[P(C_6H_5)_3]_2$	d^8	D_{3h}, TBP	sln	IR	98
$Fe(CO)_3[As(C_6H_5)_3]_2$	d^8	D_{3h}, TBP	sln, c	IR	99
$Fe(CO)_3[Sb(C_6H_5)_3]_2$	d^8	D_{3h}, TBP	sln, c	IR	99
$Fe(CO)_3(CNR)_2$	d^8	D_{3h}, TBP	sln	IR	98
$Co(CO)_3L_2^+$ L = $P(C_6H_5)_3$, $P(C_2H_5)_3$, $P(C_6H_{11})_3$, $P(OC_6H_5)_3$, $As(C_6H_5)_3$, $Sb(C_6H_5)_3$	d^8				123

TABLE 5.—*continued.*

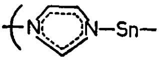
Compound	d^x	Proposed structure*	Phys. state†	Technique‡	Ref.
$NiX_2[PH(C_6H_5)_2]_3$(X = Cl, Br, I)	d^8	Dissoc.			232
$Ni(C{\equiv}CC_6H_5)_2[PC_6H_5(C_2H_5)_2]_3$	d^8	Dissoc.			233
$Pd(C_{14}H_{13}P)_3Br_2$	d^8	TP	c	*X*	71
$(CH_3)_3AsF_2$	d^{10}	D_{3h}, TBP	sln	NMR	4
$(C_6H_5)_3AsF_2$	d^{10}	D_{3h}, TBP	sln	NMR	4
$(C_6H_5)_2AsF_3$	d^{10}	C_{2v}, TBP	sln, l	NMR	4
$(CH_3)_2AsF_3$	d^{10}	Assoc.		NMR	4
$(CH_3)_3SbF_2$	d^{10}	D_{3h}, TBP	sln, c	NMR, IR	4, 115
$(CH_3)_3SbCl_2$	d^{10}	D_{3h}, TBP	c	IR, *X*	115, 60
$(CH_3)_3SbBr_2$	d^{10}	D_{3h}, TBP	c	IR, *X*	115, 60
$(CH_3)_3SbI_2$	d^{10}	D_{3h}, TBP	c	IR, *X*	115, 61
$(CH_3)_3Sb(OH)_2$	d^{10}	D_{3h}, TBP	c	IR	115
$(C_2H_5)_3SbF_2$	d^{10}	D_{3h}, TBP	c	IR	115
$(C_2H_5)_3SbCl_2$	d^{10}	D_{3h}, TBP	c	IR	115
$(C_2H_5)_3SbBr_2$	d^{10}	D_{3h}, TBP	c	IR	115
$(C_2H_5)_3SbI_2$	d^{10}	D_{3h}, TBP	c	IR	115
$(C_6H_5)_3SbF_2$	d^{10}	D_{3h}, TBP	sln	NMR	4
$(C_6H_5)_3SbCl_2$	d^{10}	D_{3h}, TBP	c	*X*	62
$(CH_3)_2SbCl_3$	d^{10}				234
$(C_6H_5)_2SbCl_3$	d^{10}	C_{2v}, TBP	c	*X*	63
$(ClCH{=}CH)_3SbCl_2$	d^{10}	TBP	c	*X*	64
Cl_2SbF_3	d^{10}	Assoc.		NMR	4
Cl_2SbF_3	d^{10}	D_{3h}, TBP	m	R	126
$(C_6H_5)_3Sb(OCOCH_3)_2$	d^{10}				235
$(C_6H_5)_3BiF_2$	d^{10}	D_{3h}, TBP	sln	NMR	4
$(C_6H_5)_3BiCl_2$	d^{10}				236
$(C_6H_5)_3BiBr_2$	d^{10}				236
$(C_6H_5)_3BiI_2$	d^{10}				237
$(C_6H_5)_3Bi(OH)_2$	d^{10}				238
BrF_3	d^{10}	C_{2v}, TBP	l, g	IR, R, M	40, 70
$(CH_3)_3Sn(NH_3)_2{}^+$	d^{10}	D_{3h}, TBP	c	IR	118
$-F-Sn(CH_3)_3-$	d^{10}	P, D_{3h}, TBP	c	*X*	6
$-OC(H)O-Sn(CH_3)_3-$	d^{10}	P, D_{3h}, TBP	c	IR, *X*	8
$-HO-Sn(CH_3)_3-$	d^{10}	P, D_{3h}, TBP	c	IR, *X*	116, 7
$-HO-Sn(CH_3)_3-$	d^{10}	D	sln	IR	116
$-OC(CH_3)OSn(CH_3)_3-$	d^{10}	P	c	IR	8
$-OC(CH_3)OSn(n-C_3H_7)_3-$	d^{10}	P, D_{3h}, TBP	c	IR	8
$-OC(H)OSn(C_2H_5)_3-$	d^{10}	P, D_{3h}, TBP	c, sln	IR	8
$-OC(H)OSn(n-C_3H_7)_3-$	d^{10}	P, D_{3h}, TBP	c, sln	IR	8
 $(n-C_4H_9)_3-$	d^{10}	P	c, sln	*X*, IR	117

TABLE 5.—*continued.*

Compound	d^x	Proposed structure*	Phys. state†	Technique‡	Ref.
$ZnX_3(solvent)_2^-$	d^{10}	D_{3h}, TBP	sln	R	125
$TlX_3[OS(CH_3)_2]_2$ ($X=Cl^-, Br^-, I^-$)	d^{10}				239
$TlX_3[OP(C_6H_5)_3]_2$ ($X=Cl^-, Br^-, I^-$)	d^{10}				239
$TlX_3(C_5H_5N)_2$ ($X = Cl^-, Br^-, I^-$)	d^{10}				239

* The abbreviation MW stands for microwave.
*†‡ See footnotes to Table 3.
§ Solid isomorphous with $Cl_3Ti(NMe_3)_2$

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TABLE 6. XML_2L_2' *and* XML_3L' *Species.*

Species	d^x	Proposed structure*	State†	Technique‡	Ref.
$PF_3(H)C_6H_5$	d^0	TBP	l–sln		4
$PF_3C_6H_5[N(CH_3)_2]$	d^0	TBP	l–sln		4
$PF_3C_6H_5[N(C_2H_5)_2]$	d^0	TBP	l–sln		4
$PF_3C_2H_5[N(C_2H_5)_2]$	d^0	TBP	l–sln		4
$PF_3CH_3(C_6H_5)$	d^0	TBP	l–sln		4
$PF_3(Cl)C_6H_5$	d^0	TBP	sln		4
SF_3CF_3	d^0	TBP	l-sln		4
$SF_3(n\text{-}C_3F_7)$	d^0	TBP	l–sln		4
$SF_3C_6H_5$	d^0	TBP	l–sln		4
$SF_2(n\text{-}C_3F_7)_2$	d^0	TBP	l–sln		4
$SF_2(n\text{-}C_3F_7)CF_3$	d^0	TBP	l–sln		4
$SF_3N(CH_3)_2$	d^0	TBP	l–sln		240
$ReNCl_2[P(C_6H_5)_3]_2$	d^2				241
$ReNBr_2[P(C_6H_5)_3]_2$	d^2				241
$ReNI_2[P(C_6H_5)_3]_2$	d^2				241
$Re(NO)_2[P(C_6H_5)_3]_2I$	d^6				242
$RhBr(1\text{-naphthyl})_2\text{-}[(n\text{-}C_3H_9)_3P]_2$	d^6				132
$RhBr(1\text{-naphthyl})_2[(C_6H_5)\text{-}(C_2H_5)_2P]_2$	d^6				132
$Ir(CO)(Amine)_2Br_2$	d^7				243

TABLE 6.—*continued.*

Species	d^x	Proposed structure*	State†	Technique‡	Ref.
$Mn(CO)_3NO[P(C_6H_5)_3]$	d^8	M	sln		244
$Rh(NO)Cl_2[P(C_6H_5)_3]_2$	d^8				245
$Rh(NO)Cl_2[As(C_6H_5)_3]_2$	d^8				245
$Rh(NO)Cl_2[Sb(C_6H_5)_3]_2$	d^8				245
$Co(CO)_3P(C_6H_5)_3Br$	d^8	TBP, C_{3v}	c	IR	129
$Co(CO)_3P(C_6H_5)_3I$	d^8	TBP, C_{3v},-TP	c, sln	IR, DM	129, 130
$Co(CO)_3P(C_6H_5)_3C_6H_5$	d^8	TBP, C_{3v}	c	IR	129
$IrX(NO)_2[P(C_6H_5)_3]_2$	d^8				246
$RhH(CO)[P(C_6H_5)_3]_3$	d^8	TBP	c	*X*	52, 52*a*
$IrH(CO)[P(C_6H_5)_3]_3$	d^8				247
$SbFCl(C_6H_5)_3$	d^{10}	TBP, C_{3v}	sln	NMR	4
$Sn_4(C_2H_5)_8Cl_4O_2$	d^{10}				248
$Sn_4(C_2H_5)_8Br_4O_2$	d^{10}				248
$Sn_4(n\text{-}C_4H_9)_8Cl_4O_2$	d^{10}				248
$Sn_4(n\text{-}C_4H_9)_8Br_4O_2$	d^{10}				248
$Sn_4(CH_3)_8Cl_4O_2$	d^{10}				248
$(CH_3)_3SnCl\cdot(NC_5H_5)$	d^{10}	TBP, C_{3v}	c	*X*	65
$(CH_3)_3SnCl\cdot OS(CH_2)_4$	d^{10}	TBP, C_{3v}	sln	IR, NMR	131
$(C_2H_5)_3SnCl\cdot OS(CH_2)_4$	d^{10}	TBP, C_{3v}	sln	IR, NMR	131
$(C_2H_5)_3PbCl\cdot OS(CH_2)_4$	d^{10}	TBP, C_{3v}	sln	IR, NMR	131
$TeCl_2(CH_3)_2$	d^{10}	TBP, C_{2v}	c	*X*	61
$TeBr_2(C_6H_5)_2$	d^{10}	TBP, C_{2v}	c	*X*	69
$(C_6H_5)_2SeCl_2$	d^{10}	TBP	c	*X*	66
$(C_6H_5)_2SeBr_2$	d^{10}	TBP	c	*X*	67
$(p\text{-}CH_3C_6H_4)_2SeCl_2$	d^{10}	TBP	c	*X*	68
$(p\text{-}CH_3C_6H_4)_2SeBr_2$	d^{10}	TBP	c	*X*	68

*†‡ See footnotes to Table 3.

[240] Br. G. C. Demitras, R. A. Kent, and A. G. MacDiarmid, *Chem. and Ind.*, 1964, 1712. [241] J. Chatt, J. D. Garforth, N. P. Johnson, and G. A. Rowe, *J. Chem. Soc.*, 1964, 1012. [242] M. Freni, D. Giusto, and V. Valenti, *Gazzetta*, 1964, **94**, 797. [243] M. Angoletta, *Gazzetta*, 1959, **89**, 2359. [244] R. F. Lambert and J. D. Johnston, *Chem. and Ind.*, 1960, 1267. [245] W. Hieber and K. Heinicke, *Z. anorg. Chem.*, 1962, **316**, 321. [246] M. Angoletta and G. Caglio, *Gazzetta*, 1963, **93**, 1584. [247] S. S. Bath and L. Vaska, *J. Amer. Chem. Soc.*, 1963, **85**, 3500. [248] D. L. Alleston, A. G. Davies, M. Hancock, and R. F. M. White, *J. Chem. Soc.*, 1963, 5469.

TABLE 7. *Species containing bidentate chelates*

Species§	d^x	Proposed structure*	State†	Technique‡	Ref.
$(i\text{-}C_3H_7O)_3P$(phenanthraquinone)	d^0	TBP	c	*X*	74
$(RO)_3P$(*o*-quinone)	d^0				156
$(RO)_3P$(diketone)	d^0				157, 158

TABLE 7.—*continued.*

Species§	d^x	Proposed structure*	State†	Technique‡	Ref.
$[Si(C_6H_5)_3(bipy)]^+$	d^0				249
$RSi(catecholate)_2$	d^0				250
$Cr(O)(O_2)(en)$	d^0	TBP	c	*X*	79
$VO(acac)_2$	d^1	TP	c	*X*	82
$[Cr(O_2)(H_2O)(o\text{-phen})]H_2O$	d^2	TBP	c	*X*	79
$NOV(S_2CNR_2)_2$	d^4				144
$[Mn(diars)Cl_2H_2O]^+$	d^4				251
$[Mn(sal\text{-}Me)_2]_2$	d^5	TBP	c	*X*	78
$[Co(8\text{-aminoquinoline})NO]^{++}$	d^6				145
$[Co(MNT)_2{\cdot}L]^-$ $L = C_5H_5N, (C_6H_5)_3P$	d^6				155
$[Co(TDT)_2{\cdot}L]^-$ $L = C_5H_5N, (C_6H_5)_3P$	d^6				155
$Mn(CO)(DPPE)_2$	d^7				252
$Mn(CO)_3(DPPE)$	d^7				252
$NOFe(S_2CNR_2)_2$	d^7				143
$Fe(CO)_2(diars)I$	d^7				253
$Co(DPPE)_2X^+$	d^7				254
$[Co(sal\text{-}Me)_2]_2$	d^7	TBP	c	*X*	78
$Co(acac)_2{\cdot}py$	d^7				153
$Co(acac)_2{\cdot}cyclohexylamine$	d^7				152
$Ni(diars)Br_3$	d^7				255
$Ni[(CH_3)_2PCH_2CH_2P(CH_3)_2]Br_3$	d^7				256
$Fe(CO)_3(diars)$	d^8				253
$Fe(CO)(diars)_2$	d^8				253
$NOCo(S_2CNR_2)_2$	d^8	TP	c	*X*	85
$NOCo(S_2CNR_2)_2$	d^8				142
$NOCo(acac)_2$	d^8				146
$Co(DPPE)_2H$	d^8				257
$[Ni(diars)_2X]^+$	d^8				140
$[Pd(diars)_2X]^+$	d^8				140*a*
$[Pd(DPPE)_2X]^+$	d^8				222
$[Pt(diars)_2X]^+$	d^8				140
$[Pt(DPPE)_2X]^+$	d^8				222
$[Au(diars)_2I]^{++}$	d^8				139
$[Cu(S_2CNR_2)_2]_2$	d^9	TP	c	*X*	135
$Cu(acac)(H_2O)_2(picrate)$	d^9	TP	c	*X*	81
$[Cu(DMG)_2]_2$	d^9	TP	c	*X*	134
$[Cu(bipy)_2I]^+$	d^9	TBP	c	*X*	75
$[Cu(bipy)_2ClO_4]^+$	d^9				258
$[Cu(bipy)_2X]^+$	d^9				259
$[Cu(o\text{-phen})_2X]^+$	d^9				259
$Cu(acac)_2(4\text{-methylpyridine})$	d^9				260

TABLE 7.—*continued.*

Species§	d^x	Proposed structure*	State†	Technique‡	Ref.
$Zn(acac)_2{\cdot}H_2O$	d^{10}	TBP	c	*X*	**89**
$[Zn(sal\text{-}Me)_2]_2$	d^{10}	TBP	c	*X*	**78**
$Tl(bipy)X_3$	d^{10}				265
TlX_3(o-phen)	d^{10}				239, 265
$(CH_3)_3Sn[SCSN(CH_3)_2]$	d^{10}				261

*†‡ See footnotes to Table 3.

§ The group X represents a uninegative anion such as Cl^-, Br^-, NO_3^-, SCN^-, etc. See Table 2 for a list of chelate ligands and abbreviations.

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TABLE 8. *Species containing terdentate chelates.*

Species§	d^x	Proposed structure*	State†	Technique‡	Ref.
$Co(triars)Br_2$	d^7				159
$Co(DEAS)_2$	d^7	TP	c	*X*	87, 87*a*
$Co(Et_4dien)Cl_2$	d^7				161
$Ni(triars)Br_2$	d^8	TP	c	*X*	86
$Ni(triars)X_2$	d^8				159, 262
$Ni(DEAS)_2$	d^8	TP	c	*X*	87, 87*a*
$Ni(Et_4dien)Cl_2$	d^8				161
$Cu(terpy)Cl_2$	d^9	TBP	c	*X*	77
$[Cu(AHA)]_4$	d^9	TP	c	*X*	138, 138*a*
$Cu(PAPHY)X_2$	d^9				266
Cu(PAPY)(acac)	d^9				266
$Cu(TPT)X_2$	d^9				267
$Zn(TPT)Cl_2$	d^{10}				267
$Zn(DAMPE)X_2$	d^{10}				160
$Zn(terpy)Cl_2$	d^{10}	TBP	c	*X*	77
$Cd(terpy)Cl_2$	d^{10}				77
$Sn(CH_3)_2(dmt)Br$	d^{10}				154
$Sn(CH_3)_2(dmt)I$	d^{10}				154

*†‡ See Table 3

§ See Table 7.

[266] J. F. Geldard and F. Lions, *Inorg. Chem.*, **1965**, **4**, 414. [267] J. F. Geldard, *Inorg. Chem.*, 1965, 4, 417.

TABLE 9. *Species containing quadridentate chelates.*

Species§	d^x	Proposed structure*	State†	Technique‡	Ref.
VO(acac-pn)	d^1				167, 167*a*
chlorohemin	d^5	TP	c	*X*	84
methoxyiron(III) meso-porphyrin-IX-dimethyl ester	d^5	TP	c	*X*	83
Co(salicyl-en)NO	d^8				166
$[Ni(QP)X]^+$	d^8				263
$Ni(QAS)X]^+$	d^8				263
$[Ni(TAP)X]^+$	d^8				165
$[Pd(QP)X]^+$	d^8				164
$[Pd(QAS)X]^+$	d^8				163, 264
$[Pt(QAS)I]^+$	d^8	TBP	c	*X*	76
$[Pt(QAS)X]^+$	d^8				162, 264
$[Pt(QP)X]^+$	d^8				164
Cu(salicyl-pn)H_2O	d^9	TP	c	*X*	137
$[Cu(salicyl\text{-}en)]_2$	d^9	TP	c	*X*	80
Zn(salicyl-en)H_2O	d^{10}	TP	c	*X*	88

*†‡ See Table 3.
§ See Table 7.

TABLE 10. *Molecular polyhedra and periodic lattices.*

Species	d^x	Proposed structure*	Ref.
B_5H_9†	d^0	TP(B)	168
$Fe_3(CO)_8(C_6H_5C_2C_6H_5)_2$	d^0	TP (C)	171
$Fe_5(CO)_{15}C$	d^0	TP (C)	170
$Mg_4Br_6O[(C_2H_5)_2O]_4$	d^0	TBP (Mg)	90
V_2O_5	d^0	TBP (V)	177
$[(NO)_2Fe(SC_2H_5)]_2$	d^6	(Fe)	172
$[Fe(MR_2)(NO)_2]_2$ (M = P, As)	d^6	(Fe)	173
$[Fe(CO)_3(NH)]_2$	d^6	(Fe)	174
$[(CH_3)_2(C_6H_5)P]_2PdI_2$	d^8	TP (Pd)	179
$Cu(HCOO)_2$	d^9	TP (Cu)	175
Hg_2O_2NaI	d^{10}	TP (Hg)	176
GeF_2	d^{10}	TBP (Ge)	178

* The pentaco-ordinate atom is shown in parentheses. TP, Tetragonal pyramid; TBP, trigonal bipyramid. All were examined in the crystalline state by *X*-ray methods except those of refs. 173 and 174.

† There is a very large number of polyhedral boranes which have at least one pentaco-ordinate boron atom; see ref. 168*a*.

TABLE 11. *Additions to Tables* 3—10.

Compound§	d^x	Proposed structure*	State†	Technique‡	Ref.
ML_5 *Species*					
RhF_5	d^2	OT	c	X	269
$(R_2C{=}CR)_5Sb$ $(R = H, CH_3)$	d^{10}				287
XML_4 *Species*					
Cl_3CPF_4	d^0	TBP	sln	PhNMR, FNMR	273
$Tc_2Cl_8{}^{3-}$	d^3	TP	c	X	284
$Re_2Cl_8{}^{2-}$	d^4	TP	c	X	283
$Cu(NH_3)_4SO_4,H_2O$	d^9	TP	c	X	270
$HCo(PF_3)_4$	d^8				288
$ICo(PF_3)_4$	d^8				289
$HRh(PF_3)_4$	d^8	TP	sln	PNMR	274
$(C_6H_5)_3PAuCo(CO)_4$	d^{10}	TBP, C_{3v}	c	X	271
$(R'_2C{=}CR)_4SbI$ $(R', R = H, CH_3)$	d^{10}				287
X_2ML_3 *Species*					
$[(C_6H_5)_3P]_2Ru(CO)_3$	d^8	TBP	sln	IR	277
$(R_2C{=}CR)_3Sb(C_6H_5)_2$ $(R = H, CH_3)$	d^{10}				290
$(R_2C{=}CR)_2Sb(C_6H_5)_3$ $(R = H, CH_3)$	d^{10}				290
$(CH_3)_3Sn(SCN)_2$	d^{10}				301
$(CH_3)_2SnCl_3{}^-$	d^{10}	TBP	c	X	275
XML_2L_2' *and* XML_3L' *Species*					
$Cl_3CPF_2X_2$	d^0	TBP	sln	FNMR, PhNMR	273
$XCo(CO)_2(PR_3)_2$ $(R = C_6H_5, OC_6H_5)$	d^8				291
$CH_3Co(CO)_2[P(C_6H_5)_3]_2$	d^8				291
$XCo(CO)_3P(OC_6H_5)_3$	d^8				292
$HCo(PF_3)_3(CO)$	d^8				293
Species containing chelate ligands					
$P(OR)_3$(diphenylpropanetrione)	d^0				294
$P(OR)_3$(phenylglyoxal)	d^0				294
$VO(MNT)_2{}^{2-}$	d^1				295
VO(1-phenyl-1,3-butanedionate)$_2$	d^1	TP	c	X	279
$[Mo(OOCCH_3)_2]_2$	d^4	TP	c	X	285
$(C_5H_5N)Co$(N-*o,o'*-xylidylsalicylideneiminate)$_2$	d^7				296
$Co(DEAS)_2$	d^7	TP	c	X	281
$Co(NO)(diars)_2{}^{2+}$	d^7				297

TABLE 11.—*continued*

Compounds§	d^x	Proposed structure*	State*	Technique‡	Ref.
$\{$Ni[tris-(*o*-methylthiophenyl)phosphine)]X$\}^+$	d^8				282
$\{$Ni[tris(*o*-methylthiophenyl)phosphine]L$\}^{2+}$ [L = C_5H_5N, $(C_6H_5)_3P$, $CH_3(C_6H_5)_2P$]	d^8				282
Cu(sal-Me)$_2$(C_5H_5N)	d^9	TP	c	*X*	278
$(C_6H_5)_3$Sn(8-quinolinate)	d^{10}				298
$(C_6H_5)_3$Sn(*N*-nitroaminomethane)	d^{10}				299
$(C_6H_5)_3SnClO_4$	d^{10}				300
$(C_6H_5)_3SnNO_3$	d^{10}				300

*†‡ See Table 3; PhNMR, PNMR stand for ^{31}P and proton nuclear magnetic resonance, respectively.

§ For chelate ligand abbreviations, see Table 2. X represents Cl^-, Br^-, or I^-.

[268] S. G. Shore, V. P. Petro, J. Howatson, Paper presented at the 150th American Chemical Society Meeting, Atlantic City, New Jersey, August, 1965. [269] J. H. Holloway, P. R. Rao, and N. Bartlett, *Chem. Comm.*, 1965, 306. [270] F. Mazzi, *Acta Cryst.*, 1955, **8**, 137. [271] B. T. Kilbourn, T. L. Blundell, and H. M. Powell, *Chem. Comm.*, 1965, 444. [272] R. R. Holmes and R. P. Carter, jun., *J. Chem. Phys.*, 1965, **43**, 1650. [273] J. F. Nixon, *J. Inorg. Nuclear Chem.*, 1965, **27**, 1281. [274] Th. Kruck, W. Lang and N. Derner, *Z. Naturforsch.*, 1965, **20b**, 705. [275] F. W. B. Einstein and B. R. Penfold, to be published. [276] R. R. Holmes and R. P. Carter, jun., *J. Chem. Phys.*, 1965, **34**, 1645. [277] J. P. Collman and W. R. Roper, *J. Amer. Chem. Soc.*, 1965, **87**, 4008. [278] D. Hall, S. V. Sheat, and T. N. Waters, *Chem. and Ind.*, 1965, 1428. [279] P. K. Hon, R. L. Belford, and C. E. Pfluger, *J. Chem. Phys.*, 1965, **43**, 1323. [280] L. Sacconi, P. Nannelli, N. Nardi, and U. Campigli, *Inorg. Chem.*, 1965, **4**, 943. [281] L. Sacconi, M. Ciampolini, and G. P. Speroni, *Inorg. Chem.*, 1965, **4**, 1116. [282] G. Dyer and D. W. Meek, *Inorg. Chem.*, 1965, **4**, 1398. [283] F. A. Cotton and C. B. Harris, *Inorg. Chem.*, 1965, **4**, 330. [284] F. A. Cotton and W. K. Bratton, *J. Amer. Chem. Soc.*, 1965, **87**, 921. [285] D. Lawton and R. Mason, *J. Amer. Chem. Soc.*, 1965, **87**, 922. [286] J. A. Ibers, *Ann. Rev. Phys. Chem.*, 1965, **16**, 375. [287] A. N. Nesmeyanov, A. E. Borisov, and N. V. Novikova, *Bull. Acad. Sci. U.S.S.R., Chem. Sci.*, 1964, 1116. [288] Th. Kruck, W. Lang, and A. Engelmann, *Angew. Chem. Internat. Edn.*, 1965, **4**, 148. [289] Th. Kruck, W. Lang, and A. Prasch, *Angew. Chem. Internat. Edn.*, 1965, **4**, 706. [290] A. N. Nesmeyanov, A. E. Borisov, and N. V. Novikova, *Bull. Acad. Sci. U.S.S.R., Chem. Sci.*, 1964, 1112. [291] W. Hieber and H. Duchatsch, *Chem. Ber.*, 1965, **98**, 2933. [292] W. Hieber and H. Duchatsch, *Chem. Ber.*, 1965, **98**, 2530. [293] Th. Kruck and W. Lang, *Chem. Ber.*, 1965, **98**, 3060. [294] F. Ramirez, A. V. Patwardhan, and C. P. Smith, *J. Org. Chem.*, 1965, **30**, 2575. [295] N. M. Atherton, J. Locke, and J. A. McCleverty, *Chem. and Ind.*, 1965, 1300. [296] S. Yamada and H. Nishikawa, *Bull. Chem. Soc. Japan*, 1965, **38**, 683. [297] R. D. Feltham and R. S. Nyholm, *Inorg. Chem.*, 1965, **4**, 1334. [298] M. Wada, K. Kawakami, and R. Okawara, *J. Organometallic Chem.*, 1965, **4**, 159. [299] L. J. Winters and D. T. Hill, *Inorg. Chem.*, 1965, **4**, 1433. [300] H. C. Clark and R. G. Goel, *Inorg. Chem.*, 1965, **4**, 1428. [301] A. Cassol, R. Portanova, and R. Barbieri, *J. Inorg. Nuclear Chem.*, 1965, **27**, 2275.

Note Added, December 1965.—The following examples of pentaco-ordination were found after the completion of the original manuscript. (For references, see footnotes to Table 9.)

Cryoscopy have shown that phosphorus pentachloride is dimeric in carbon tetrachloride solution but monomeric in benzene.[268] Vibrational spectra[268] of both solutions are consistent with a trigonal-bipyramidal configuration. Rhodium pentafluoride has been found[269] to be isomorphous with the analogous ruthenium, osmium, and iridium compounds. The structural unit in RhF_5 is presumably a fluorine-bridged tetramer as in RuF_5 to give hexaco-ordinate rhodium atoms.

In crystalline tetramminecopper sulphate monohydrate, $Cu(NH_3)_4SO_4,H_2O$, the copper atoms are in a tetragonal-pyramidal configuration.[270] The four nitrogen atoms are coplanar with a copper–nitrogen distance of 2·05 Å. An oxygen atom of an apical water molecule is located at a distance of 2·59 Å. A second (bridging) water molecule located at a distance of 3·37 Å from the copper completes a distorted octahedron if this is considered to be a bonding distance.

An *X*-ray structural analysis has shown triphenylphosphinegold cobalt tetracarbonyl, $(C_6H_5)_3PAuCo(CO)_4$, to have a trigonal-bipyramidal configuration with the gold atom at an apical position.[271] The three equatorial carbonyl groups are displaced towards the gold atom. Complete bond angles and distances have not yet been reported.

A crystal structure analysis[283] of the $Re_2Cl_8^{2-}$ anion has shown the rhenium atoms to be in a tetragonal-pyramidal configuration with the two $ReCl_4$ groups joined by a Re–Re bond 2·24 Å long. Each rhenium atom is displaced from the plane of the co-ordinated chlorine atoms towards the other rhenium atom. The rhenium–chlorine distances are 2·29 Å (avg.) and the chlorine atoms are in an eclipsed configuration. The $Tc_2Cl_8^{3-}$ anion has been shown[284] to be virtually isostructural with the rhenium analogue. The Tc–Tc bond length is 2·13 Å and the Tc–Cl bond lengths are 2·35 Å. Multiple bonding in the Re–Re and Tc–Tc bonds has been postulated.[283,284]

Some dielectric constant measurements of the phosphorus compounds PCl_4F, PCl_3F_2, and PCl_2F_3 have recently been reported[272,276] for the gas, liquid, and solution states.

A crystal structure analysis has shown that the compound $[(CH_3)_2SnCl(terpy)]^+[(CH_3)_2SnCl_3]^-$ contains hexaco-ordinate tin in the cation and pentaco-ordinate trigonal-bipyramidal tin in the anion.[275] The methyl groups in the anion are located at equatorial positions with a tin–carbon distance of 2·19 Å (avg.). The apical chlorine–tin distance is 2·54 Å and the equatorial chlorine–tin distance is 2·35 Å. The compound is distorted from a regular trigonal bipyramid such that the C–Sn–C angle is 139°.

The monomeric ruthenium complexes $[(C_6H_5)_3P]_2Ru(CO)_3$ and $[(C_6H_5)_3As]_2Ru(CO)_3$ exhibit only one infrared carbonyl stretching frequency.[277] This is consistent with, but does not establish, a trigonal-bipyramidal configuration with the carbonyl groups at equatorial positions.

A crystal structure determination[278] of the monopyridine adduct of bis-(*N*-methylsalicylaldiminato)copper(II) has shown the copper atom to be in a tetragonal-pyramidal environment. The pyridine nitrogen atom is located at the apex with a copper–nitrogen distance of 2·31 Å. The copper atom is displaced 0·21 Å from the plane of the chelate-oxygen and nitrogen atoms towards the apex. The copper–oxygen and copper–chelate nitrogen bond distances are 2·00 Å and 1·89 Å, respectively.

Vanadyl bis(1-phenylbutane-1,3-dione) has been shown by a crystal-structure analysis[279] to be a distorted tetragonal pyramid with the vanadyl oxygen atom at the apex at a distance of 1·612 Å. The vanadium–chelate oxygen distances vary from 1·95 Å to 1·98 Å with the vanadium atom displaced from the plane of the chelate oxygen atoms towards the vanadyl oxygen atom. The phenyl groups are in a *cis* configuration.

Magnetic and spectral data of solutions of the 3-chloro-, 5-chloro-, and 3,4-benzo-substituted bis-(*N*-β-diethylamine-ethylsalicylaldiminato)-nickel(II) complexes have been interpreted[280] in terms of an equilibrium involving tetra-, penta, and hexa-co-ordinate nickel complexes. The complex bis-(*N*-β-diethylamine-ethyl-5-chlorosalicylaldiminato)cobalt(II) is isomorphous[281] with the analogous nickel compound[87,87a] and therefore presumably has a similar tetragonal-pyramidal configuration. Other analogous ring substituted cobalt complexes may have pentaco-ordinate structures in the solid or solution state.[281]

The quadridentate ligand tris-(*o*-methylthiophenyl)phosphine (TSP) forms complexes with nickel(II) of the type [Ni(TSP)X]+.[282] An analysis of electronic spectra of these complexes has been used to establish trigonal bipyramidal geometry. Salts of the formula $[Ni(TSP)L](ClO_4)_2$ [L = $(C_6H_5)_3P$, C_5H_5N, or $CH_3(C_6H_5)_2P$] have also been obtained and have similarly been postulated[282] as trigonal bipyramids on the basis of their electronic spectra. Crystallographic studies of these compounds are necessary to confirm the structural speculation.

Molybdenum(II) acetate has been shown[285] by an *X*-ray structural analysis to be dimeric with the two molybdenum atoms bridged by the four acetate groups. The Mo–O bond lengths are 2·10 Å with the four oxygen atoms about each molybdenum composing a slightly distorted square planar configuration. A tetragonal pyramid is formed about each molybdenum by an Mo–Mo bond 2·11 Å in length. Multiple bonding between the molybdenum atoms has been postulated.[285]

A recently published review[286] describes some pentaco-ordinate structures determined by *X*-ray analysis.

Note added in Proof.

The following examples of penta-co-ordinate structures have been recently confirmed by *X*-ray structural analyses.

The pentachlorostannate anion, $SnCl_5^-$, has been found to have a nearly regular trigonal bipyramidal structure[302] with all Sn-Cl distances equal within experimental error. The results of a recent electron diffraction study[303] of iron pentacarbonyl show the axial Fe-C bonds to be *shorter*

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than the equatorial Fe-C bonds by 0·045 Å. A recalculation[303] of bond lengths from the published *X*-ray data[304] also suggested that the axial bonds in $Fe(CO)_5$ are shorter. These electron diffraction results have, however, been criticised[305] as being incapable of detecting a difference of 0·045 Å in bond length. In addition, an earlier recalculation[53] of the *X*-ray data[304] had shown that the axial bonds are either slightly longer or the same length as the equatorial bonds but *not* shorter. This result is more likely and is in accord with the structural results of other trigonal bipyramidal ML_5 complexes (See Section IIIA).

Triphenylbismuth dichloride has a trigonal bipyramidal configuration[306] with the chlorine atoms in axial positions. Bond lengths are Bi-Cl 2·6 Å and Bi-C 2·24 Å.

The detailed structural results[307] for the iridium complex, $IrCl(SO_2)[P(C_6H_5)_3]_2$, confirm the preliminary assignment[56] of tetragonal pyramidal geometry about the iridium atom (See Section III E 1). The CO, Cl, and two trans P atoms occupy basal positions and the iridium atom lies 0·21 Å above this plane towards the apical sulphur atom of the SO_2 group. The basal bond distances are normal with Ir-P 2·34 Å, Ir-Cl 2·37 Å, and Ir-C 1·96 Å. The Ir-S distance of 2·49 Å is rather long and the plane of the SO_2 group is tipped 32° with respect to the Ir-S vector.

Potassium di-*o*-phenylenedioxyarsenate(III), $K[As(C_6H_4O_2)_2]$, has the four oxygen atoms arranged at the corners of the base of a distorted tetragonal pyramid[308] at distances of 1·81 to 2·01 Å. It is assumed that a lone pair of electrons occupies the fifth, apical position.

The β form of $Co(PAPHY)Cl_2$ has essentially square pyramidal geometry.[309] The cobalt is 0·39 Å above the basal plane containing the tridentate (PAPHY) ligand and one chlorine atom. The second chlorine atom is in the apical position.

A cobalt complex of 2,2′,2″-terpyridyl, $Co(terpy)Cl_2$, is isomorphous with the corresponding zinc compound[309] and the latter has recently been shown[310] to be better described as a slightly distorted tetragonal pyramid with an apical chlorine atom rather than as the originally described[77] distorted trigonal bipyramid (See p. 256).

Bivalent transition metal ions from Mn to Zn form apparently five co-ordinate complexes[311] with the tetradentate ligand tris-(2-dimethylaminoethyl)amine, Me_6tren, of the type $[M(Me_6tren)X]X$ (X = Cl, Br, I, NO_3, ClO_4). The cobalt complex, $[Co(Me_6tren)Br]Br$, has been shown[312] to have a trigonal bipyramidal configuration with the co-ordinated

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bromine at an apical position. The three dimethylamino-groups lie at the corners of the equatorial plane. The analogous chromium complex has been shown[312] to be isomorphous with the cobalt complex.

Two additional examples of the formation of penta-co-ordinate tetragonal pyramidal complexes of Cu(II) by association in the solid state are found in the $CuCl_3^-$ ion and for the *cis*-modification of bis(D-α-alaninato) copper(II). The salt $(CH_3)_2NH_2CuCl_3$ exists[313] as isolated $Cu_2Cl_6^{2-}$ dimers which are tied together into infinite chains by Cu-Cl bridges 2·73 Å in length. The other Cu-Cl distances vary from 2·25 to 2·35 Å. The net result is a distorted tetragonal pyramidal arrangement around each copper atom. The closest approach to the sixth, octahedral position is by a methyl group at 3·78 Å. The stereochemistry of the alaninato complex[314] is also a distorted square pyramid with carboxyl-oxygen atoms bridging copper atoms in a polymeric structure. This bridging oxygen atom is at an apical position with a Cu-O distance of 2·37 Å. The base of the pyramid has two Cu-N distances of 1·98 Å and two Cu-O distances of 1·93 Å. The copper atom is displaced 0·1 Å from the basal plane towards the bridging oxygen atom.

In the cobalt complex, $[(CF_3)_2C_2S_2]_2Co$, five-co-ordination is achieved by dimerisation through sulphur atoms[315] to give a distorted tetragonal pyramidal arrangement about each cobalt atom. The Co-S (apical, bridge) distance is 2·38 Å and the Co-S (basal) distance is 2·16 Å. The cobalt atom is displaced 0·37 Å toward the apical sulphur atom. A Co-Co distance of 2·78 Å suggests an interaction between them to give formally six-co-ordinate cobalt.

An aluminosiloxane complex $[(CH_3)_2Si]_4Al_4Br_5O_6$, contains one five-co-ordinate aluminium atom bonded to four oxygen atoms and one bromine atom.[316] The other two aluminium atoms are tetrahedrally co-ordinated. The stereochemistry about the unique aluminium atom is intermediate between a trigonal bipyramid and tetragonal pyramid.

The additional examples of pentaco-ordination are summarised in Table 11.

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