RECENT STEREOCHEMISTRY OF THE GROUP VIII ELEMENTS

By R. S. NYHOLM, M.SC., A.R.I.C.
(UNIVERSITY COLLEGE, LONDON)

THE Group VIII elements are of special interest in the Periodic Table for the number of valencies that they display and for the ease with which they give rise to co-ordination compounds. The ammines of cobalt, platinum, and rhodium in particular have been studied for many years, but more recent work on metals other than these and with hitherto uncertain valency states suggests that a survey of the group as a whole would be profitable. Attention is directed here chiefly towards work which has been done during the last few years. This survey leads to the broad conclusion that, although many formerly doubtful valency states have been verified and the stereochemistry elucidated, yet many other problems await solution.

The properties of these elements are bound up with their special electronic arrangements. In each of the triads, Fe, Co, Ni ; Ru, Rh, Pd ; Os, Ir, Pt (referred to henceforth as the Ni, Pd, and Pt triads, respectively), the *d* orbitals are being filled, leading to a total of 18 electrons in the outermost shell. This means that *d, s,* and *p* orbitals, all of similar energy, are available for bond formation. Complex formation may thus involve the use of a mixture of *d, s,* and *p* orbitals with excellent opportunities for hybridisation, which, together with the large number of valencies of these elements, give us the greatest possibilities for stable complex formation.

Before discussing the stereochemistry of these elements in their different valency states, it is helpful to outline the more prominent chemical relationships of the group as a whole. The nickel triad differs from the other six elements in two main ways although it is very similar to them in the complexes which they form. First, iron, cobalt, and nickel form free ions much more readily than do the other elements, and as a consequence their salts differ from those of the palladium and the platinum triad. Thus the halides of Fe, Co, and Ni are true salts and give rise to simple hydrated cations, whereas the properties of the other halides are essentially those of covalent complexes. This greater tendency towards complex formation manifests itself in such ways as the formation of very stable anions and in peculiar magnetic behaviour. Secondly, although Fe, Co, and Ni show variable valency, the stability of higher-valency states increases sharply on passing from the Ni triad to the Pd and the Pt triad. Towards chlorine the maximum valency is two for all elements in the first row except iron, but it increases to four for the remainder ; and the double halides $M^{I}_2M^{IV}Cl_6$, which are so characteristic of the Pd and Pt elements, cannot be isolated with Fe, Co, and Ni. Towards oxygen, ruthenium and osmium show valencies as high as eight.

It must be emphasised that, although horizontal similarity is most evident between Fe, Co, and Ni in their simple salts, yet vertical similarity is the rule when considering complexes. A few examples will illustrate these vertical relationships. Fe, Ru, and Os in the bivalent state all form highly coloured, stable tris-*o*-phenanthroline and trisdipyridyl complexes like $[Fe(dipy)_3]Cl_2$ and give rise to the isomorphous series of cyanides $K_4M(CN)_6,3H_2O$ where M = Fe^{II}, Ru^{II}, Os^{II}. In the tervalent state, complexes of the type $K_3M^{III}(C_2O_4)_3$ ($M^{III} = Fe^{III}$, Ru^{III}) are known, but relatively few tervalent osmium compounds have been described. In the tervalent state, Co, Rh, and Ir are very much alike in their ammines, alums, and complex nitrites. However, as we shall see later, whilst bivalent cobalt gives rise to four-covalent complexes, bivalent rhodium and iridium (except in carbonyl complexes) are invariably six-covalent. Bivalent Ni, Pd, and Pt may be either four-covalent or six-covalent in their complexes, with a very marked preference for the former; in fact, six-covalent complexes of bivalent platinum and palladium are rare. Typical of the four-covalent complexes of these elements are the complex cyanides like $K_2Ni(CN)_4$; the quadrivalent state is exemplified by complex halides of the type K_2PtCl_6 and K_2PdCl_6, but the corresponding nickel compound is unknown.

In Table I are shown the valencies (and usual co-ordination numbers) of the Group VIII elements which have been established beyond any reasonable doubt. An example is given of each valency; numbers in brackets refer to co-ordination numbers which are only found very rarely. Except for occasional references, carbonyls have been omitted from this article as they have been fully discussed in an earlier Review.[1]

TABLE I

Group VIII elements: valencies and co-ordination numbers

		Co-ord. no.			Co-ord. no.			Co-ord. no.
Fe.			**Co.**			**Ni.**		
						0	$K_4Ni(CN)_4$	4
						I	$K_2Ni(CN)_3$	?
II	$[Fe(dipy)_3]Cl_2$	6, (4)	II	$CoCl_2,2py$	4, 6	II	$K_2Ni(CN)_4$	4, 6
III	$K_3Fe(CN)_6$	6, (4)	III	$[Co(NH_3)_6]Cl_3$	6	III	$NiBr_3,2PEt_3$	5
VI	$Ba(FeO_4)$	?				VI	$BaNiO_4$	?
Ru.			**Rh.**			**Pd.**		
						0	$K_4Pd(CN)_4$	4
I	RuBr,CO	?						
II	$[Ru(dipy)_3]Cl_2$	6, (4)	II	$[Rh\ py_5\ Br]Br$	6	II	$PdCl_2,2NH_3$	4, (6)
III	$K_3Ru(C_2O_4)_3$	6	III	Na_3RhCl_6	6	III	PdF_3	?
IV	$K_2[RuCl_5(OH)]$	6	IV	Cs_2RhCl_6	6	IV	K_2PdCl_6	6
V	RuF_5	?						
VI	K_2RuO_4	?	VI	K_2RhO_4	?			
VII	$KRuO_4$	?						
VIII	RuO_4	4						
Os.			**Ir.**			**Pt.**		
			I	$(IrCl)_x$	?			
II	$[Os(dipy)_3]Cl_2$	6, (4)	II	$(IrCl_2,3AsR_3)_2$	6	II	$PtCl_2,2NH_3$	4, (6)
III	$[Os(dipy)_3](ClO_4)_3$	6	III	$[Ir(NH_3)_5Cl]Cl_2$	6	III	$PtCl_3$	?
IV	$(NH_4)_2[OsCl_6]$	6	IV	$(NH_4)_2IrCl_6$	6	IV	K_2PtCl_6	6
VI	K_2OsO_4	?	VI	IrF_6	?	VI	K_2PtO_4	?
VIII	OsO_4	4						

[All of the Group VIII elements except Pd and Pt form carbonyls in which the metal atom is formally zero-valent.]

---

[1] J. S. Anderson, *Quart. Reviews*, 1947, **1**, 331.

Theoretical Basis of Stereochemistry

The modern theory of stereochemistry as applied to these elements owes much to the work of Pauling and his school. A brief summary only is given here, for many adequate reviews of the subject are available.[2, 3, 4] By making use of the directional properties of *s*, *p*, and *d* orbitals, it is possible to predict the shape of the simpler molecules. To do this a knowledge of the orbitals used for bond formation is required ; these are sometimes obvious, but with the transition elements the magnetic behaviour is often of great help.

As electrons are progressively added to an atom, the order of increasing energy in any given level is $s < p < d < f$, corresponding to azimuthal quantum numbers of 0, 1, 2, 3, respectively. In any given level a maximum of two *s*, six *p*, and ten *d* electrons may be accommodated. When electrons are added to a *p* or *d* sub-group, Hund's rule requires that the maximum number of orbitals shall be singly occupied before pairing of spins takes place ; when only five electrons are available for a *d* sub-group, for example, this means that all five spins will be parallel. Using oppositely directed arrows to indicate opposite spins, the iron atom in the ground state ($1s^22s^22p^63s^23p^63d^64s^2$) and the Fe^{++} ion ($1s^22s^22p^63s^23p^63d^6$) would be represented as in Table II. Unless far-reaching reorganisation of these levels takes place, an example of which is the ferrocyanide ion, the four electrons in the $3d$ shell of the Fe^{++} ion remain unpaired and give rise to the paramagnetic moment characteristic of the iron-group elements.

TABLE II

Electronic arrangement of iron compounds

	3*d*.					4*s*.	4*p*.		
Fe (ground state) .	↓↑	↓	↓	↓	↓	↓↑			
Fe^{++} (ion) . .	↓↑	↓	↓	↓	↓				
$Fe(CN)_6^{4-}$ (ion) .	↓↑	↓↑	↓↑	↓↑	↓↑	↓↑	↓↑	↓↑	↓↑

The shape of simple molecules can be deduced from a knowledge of the facts that *s* orbitals are spherically symmetrical whilst the three *p* orbitals are mutually perpendicular to one another. Since *s* orbitals have no directional properties, one might expect a combination of an *s* orbital with a *p* orbital to give two bonds at the maximum angle to one another, *i.e.*, 180°. Thus we find that mercuric chloride is linear since the formation of two covalent bonds from the mercury requires unpairing of the two 5*s* electrons to give a bivalent mercury atom using one 5*s* and one 5*p* orbital. Two *p* orbitals, however, give rise to a V-shaped molecule, the

---

[2] L. Pauling, " Nature of the Chemical Bond ", N.Y., 1945, 2nd edn.

[3] G. E. Kimball, *J. Chem. Physics*, 1940, **8**, 194.

[4] C. A. Coulson, *Quart. Reviews*, 1947, **1**, 144.

commonest example being water; here the oxygen atom ($1s^22s^22p^4$) has two singly occupied $2p$ orbitals and pairing of these with the electrons from two hydrogen atoms gives a molecule with an angle at the oxygen atom slightly greater than 90°, the widening being attributed to partial ionic character of the $2p$ bonds or some s character therein. In the same way, ammonia is a pyramidal molecule because of the use of the three $2p$ orbitals of the nitrogen atom, whilst boron trichloride is planar since the boron atom uses one $2s$ and two $2p$ orbitals for bond formation. Using symmetry theory, G. E. Kimball [3] has summarised the possibilities of stable bond formation which arise from various combinations of orbitals; the results are given in Table III. M. R. Daudel and A. Bucher [5] (approaching the problem from a different viewpoint) have confirmed several of these and have amplified the five-covalent structures by considering in more detail d orbitals in combination with the s and p.

We are specially interested in the four-, five-, and six-covalent complexes in which a mixing of s, p, and d orbitals takes place. Conditions are ideal for many possible combinations with these elements because the d sub-group and the s and p sub-groups of the next higher principal quantum number are very similar in energy. The more important combinations are the sp^3 hybridisation resulting in the tetrahedral configuration, the dsp^2 hybridisation which gives rise to planar (square) four-covalent complexes, and the d^2sp^3 hybridisation which leads to octahedral six-covalent complexes. Double-bond formation appears to increase the strength of certain of these bonds; Pauling [2] has suggested that in the case of the ferrocyanides, for example, the three remaining $3d$ electron pairs from the iron atom may be used to give double-bond character to the d^2sp^3 bonds. The recent structure determination [6] of $[Fe(CN \cdot CH_3)_6]Cl_2,3H_2O$ shows an Fe–C bond length of 1·85 A.; and since the sum of the single-bond radii for these elements is 2·00 A., this is usually taken to indicate about 50% double-bond character arising from the use of the three $3d$ electron pairs of the iron atom resonating among the six d^2sp^3 bonds. Kimball [3] has discussed the cases in which these strong π bonds might be expected. It should be mentioned, however, that the need for care in the assignment of double-bond character to short bonds has been discussed by several workers.[7, 8, 9]

Unfortunately, these theoretical methods go no further than indicating possible spatial arrangements, and as N. V. Sidgwick and H. M. Powell [10] have pointed out, "the chemist would be glad to infer the stereochemical type from some property of the molecule with which he is more familiar". It is often difficult to decide whether d, s, or p orbitals in an atom are being used for bond formation; but magnetic data are sometimes useful.

---

[5] *J. Chim. physique*, 1945, **42**, 6.
[6] H. M. Powell and G. W. R. Bartindale, *J.*, 1945, 799.
[7] A. F. Wells, *J.*, 1949, 55.
[8] G. M. Phillips, J. M. Hunter, and L. E. Sutton, *J.*, 1945, 146.
[9] H. A. Skinner and L. E. Sutton, *Trans. Faraday Soc.*, 1944, **40**, 164.
[10] *Proc. Roy. Soc.*, 1940, *A*, **176**, 153.

TABLE III

Shape of bond orbitals

Co-ord. no.	Configuration.	Arrangement.
2	sp, dp	Linear
	p^2, ds, d^2	Angular
3	sp^2, dp^2, d^2s, d^3	Trigonal plane
	dsp	Unsymm. plane
	p^3, d^2p	Trigonal pyramid
4	sp^3, d^3s	Tetrahedral
	dsp^2, d^2p^2	Tetragonal planar
	d^2sp, dp^3, d^3p	Irregular tetrahedron
	d^4	Tetragonal pyramid
5	dsp^3, d^3sp	Bipyramid
	d^2sp^2, d^4s, d^2p^3, d^4p	Tetragonal pyramid
	d^3p^2	Pentagonal plane
	d^5	Pentagonal pyramid
6	d^2sp^3	Octahedron
	d^4sp, d^5p	Trigonal prism
	d^3p^3	Trigonal anti-prism
	d^3sp^2, d^5s, d^4p^2	Mixed
7	d^3sp^3, d^5sp	ZrF_7^{3-} Structure
	d^4sp^2, d^4p^3, d^5p^2	TaF_7^{2-} Structure
8	d^4sp^3	Dodecahedron
	d^5p^3	Anti-prism
	d^5sp^2	Face-centred prism

Doubly filled orbitals contribute nothing to the spin magnetic moment, but singly filled orbitals give rise to the paramagnetic moment of $\sqrt{n(n+2)}$ Bohr magnetons (B.M.), where n is the number of unpaired electrons. This assumes that for the iron-group elements the moment may be attributed to spin only, an approximation which appears to hold for a wide range of compounds. The use of magnetic data to indicate bond type is well illustrated by the complexes of bivalent nickel. The electronic configuration of nickel in tetrahedral and planar four covalent complexes is :

	3*d*.					4*s*.	4*p*.		
Ni^{II} (Planar 4-covalent)	↓↑	↓↑	↓↑	↓↑	↓↑	↓↑	↓↑	↓↑	
Ni^{II} (Tetrahedral 4-covalent) . . .	↓↑	↓↑	↓↑	↓	↓	↓↑	↓↑	↓↑	↓↑

Thus four-covalent planar bivalent nickel complexes with dsp^2 bonds are diamagnetic but when tetrahedral complexes are formed, whether ionic or covalent using sp^3 bonds, the two unpaired electrons in the 3*d* shell will give rise to paramagnetism. This has been confirmed for a large number of nickel complexes, the magnetic moment of the tetrahedral compounds being slightly larger than 3 B.M. The predicted value is 2·83 B.M.

Magnetic data are limited in their application, for Hund's rule does not seem to apply to the palladium and the platinum triad, and rearrangement of the electrons usually takes place so as to give the minimum moment. In these two triads, the only cases where a moment greater than 1·73 B.M. (corresponding to one unpaired electron) has been observed are with the complexes of quadrivalent ruthenium. For K_2RuCl_6 the value 2·83 B.M. has been reported.[11] This is the moment expected for the d^2sp^3 octahedral configuration, but the anomalous behaviour of these elements is illustrated by the fact that the similar osmium compound, K_2OsCl_6, has a moment of only 1·3 B.M.[11] The majority of molecules with an even number of electrons are diamagnetic, owing presumably to complete quenching of both orbital and spin components by molecular or crystalline forces. D. P. Mellor[12] has reported that even complexes of Rh^{II} are diamagnetic in spite of the fact that bivalent rhodium contains an odd number of electrons. The literature has been summarised by P. W. Selwood.[85] Before the magnetic data of the Pd and the Pt triad can be of much help, the magnetic behaviour of many of the less common valency states needs further investigation.

In Table IV are shown the predicted number of unpaired electrons and magnetic moments for the planar, tetrahedral, and octahedral configurations.

Co-ordination Number Four

Although the Group VIII elements show many valencies, the number of different stereochemical types is small. The co-ordination number of 2, which is so characteristic of the univalent state of the neighbouring elements copper, silver, and gold, has not been reported except possibly for the compound RuBr,CO. Among these elements univalency is rare. There is no known example in Group VIII of the co-ordination number 3, the elements being usually 4- or 6-covalent. Recently a few 5-covalent complexes have been obtained, but the only compound in which the co-ordination number exceeds 6 is the octavalent compound OsF_8. We shall discuss the various shapes in turn and the valencies where they arise.

---

[11] W. P. Groves and S. Sugden (W. P. Groves, Ph.D. Thesis, 1941, London).

[12] *J. Proc. Roy. Soc. N.S.W.*, 1943, **77**, 145.

TABLE IV

Predicted moments for Group VIII elements in covalent complexes

		Tetrahedral ionic or sp^3 bonds.		Planar dsp^2 bonds.		Octahedral d^2sp^3 bonds.	
		Unpaired electrons.	Moment.	Unpaired electrons.	Moment.	Unpaired electrons.	Moment.
Univalent	Ni, Pd, Pt	1	1·73	—	—	—	—
Bivalent Univalent	Ni, Pd, Pt Co, Rh, Ir	2	2·83	0	Diam.	—	—
Tervalent Bivalent Univalent	Ni, Pd, Pt Co, Rh, Ir Fe, Ru, Os	3	3·88	1	1·73	—	—
Quadrivalent Tervalent Bivalent	Ni, Pd, Pt Co, Rh, Ir Fe, Ru, Os	4	4·90	2	2·83	0	Diam.
Quadrivalent Tervalent	Co, Rh, Ir Fe, Ru, Os	5	5·92	3	3·88	1	1·73
Quadrivalent	Fe, Ru, Os	4	4·90	4	4·90	2	2·83

The Planar Configuration

When there are four bonds to a metal atom (in this group), the molecule is either tetrahedral or planar. In the shaded parts of Table V are shown the valencies for which the tetrahedral and planar configurations occur. The three elements of Group Ib which form planar dsp^2 bonds have been added for comparison. The only other well-established square complex outside this table is the compound $KICl_4$,[13] the iodine atom presumably using d^2p^2 bonds.

For criticism of the claims advanced for the square arrangement for certain other metals, see D. P. Mellor.[14]

The planar configuration was postulated in 1893 by A. Werner [15] to explain the existence of the two isomeric diammines of platinous chloride. Before this hypothesis was universally accepted, there was much controversy owing to several observations which were difficult to reconcile with the planar arrangement. The evidence for the square arrangement has been reviewed very thoroughly by Mellor [14] and will only be summarised here. Two problems need to be recognised : first, the proof of the existence of the square configuration for bivalent platinum complexes, and secondly, the establishment of the circumstances in which it is expected

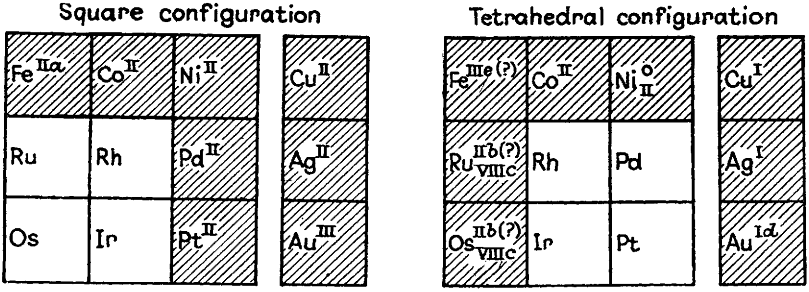
---

[13] R. Mooney, *Z. Krist.*, 1938, **98**, 377.

[14] *Chem. Reviews*, 1943, **33**, 137.

[15] *Z. anorg. Chem.*, 1893, **3**, 267.

TABLE V



Square configuration

▨ Fe^{IIa}	▨ Co^{II}	▨ Ni^{II}	▨ Cu^{II}
Ru	Rh	▨ Pd^{II}	▨ Ag^{II}
Os	Ir	▨ Pt^{II}	▨ Au^{III}

Tetrahedral configuration

▨ $Fe^{IIIe(?)}$	▨ Co^{II}	▨ Ni^{0}_{II}	▨ Cu^{I}
▨ $Ru^{IIb(?)}_{VIIIc}$	Rh	Pd	▨ Ag^{I}
▨ $Os^{IIb(?)}_{VIIIc}$	Ir	Pt	▨ Au^{Id}

(*a*) In forced configurations only.

(*b*) This valency occurs in the compounds $(pyH)_2RuCl_4$ [46] and H_2OsI_4 [47, 48] about which little is known. They are possibly some form of tetrahedron; but in their complexes Ru^{II} and Os^{II} are usually octahedral.

(*c*) The compounds OsO_4, RuO_4, and $K^+[OsO_3N]^-$.

(*d*) It has been claimed that $K[Au(CN)_2,dipy]$ is planar.[16]

(*e*) Fe_2Cl_6 in the vapour state or in non-polar organic solvents.

to arise. Here only the planar and tetrahedral shapes are considered; arguments against less likely arrangements have been given elsewhere.[14] The literature of this subject is so extensive that only a few references will be given here: for detailed references see Mellor's review.[14]

The two isomers $PtCl_2,(NH_3)_2$, which have been the subject of many chemical investigations, have been known for over 100 years. Much confusion occurs in the literature in discussing these, owing to the inconsistent use of the symbols α and β; we shall avoid these here and refer to the isomers as *cis* and *trans*. M. Peyrone's [17] reaction,

$$PtCl_4^{--} \xrightarrow{NH_3} [Pt(NH_3)Cl_3]^- \xrightarrow{NH_3} [PtCl_2(NH_3)_2]$$

leads to the *cis*-isomer, but Jorgensen's [18] reaction

$$Pt(NH_3)_4^{++} \xrightarrow{Cl^-} [Pt(NH_3)_3Cl]^+ \xrightarrow{Cl^-} [PtCl_2(NH_3)_2]$$

leads to the *trans*-isomer. The conductivity of both forms in water is small and indicates that they are non-electrolytes undergoing slow reaction with the water itself. The large number of chemical investigations lead to the definite conclusion that one isomer certainly has the *trans*-planar configuration, but for a long time many chemists considered that the other isomer was either tetrahedral or arose from structural isomerism involving 2-covalent platinum. The problem was difficult to settle, partly because the insolubility of the ammines prevented suitable accurate physical measurements, and partly because of the isolation of possible third isomers. Claims that certain bivalent platinum complexes showed optical activity also threw doubt on the planar hypothesis.[19] In addition to chemical

---

[16] H. J. Dothie, F. Llewellyn, W. Wardlaw, and A. Welch, *J.*, 1939, 426.

[17] *Annalen*, 1845, **51**, 15.

[18] S. M. Jorgensen, *J. pr. Chem.*, 1886, **33**, 489.

[19] H. Reihlen and W. Huhn, *Annalen*, 1931, **489**, 42.

investigations, the evidence for the planar arrangements includes : K. A. Jensen's[20] electric dipole moment work ; the resolution by W. H. Mills and T. H. Quibell[21] of a bivalent platinum cation which could be optically active only if the four bonds to the platinum atom were coplanar or square-pyramidal ; the isolation of a large number of geometric isomers ; certain optical properties ; the results of Raman spectral investigations ; and, finally, *X*-ray diffraction studies. The planar arrangement has been rigidly established by the detailed *X*-ray analysis of K_2PtCl_4[22] and $[Pt(NH_3)_4]Cl_2,H_2O$[23] among other platinum compounds. A survey of the mass of data shows that, with the exception of a few compounds such as pyrromethene[24] and triaminotrimethylamine[25] compounds, where the bonds must be forced out of the plane, the four bonds to a bivalent platinum atom are invariably coplanar.

It is of interest to see where else the planar arrangement should arise. L. Pauling[26] showed that 4-coplanar square complexes arise from the use of dsp^2 bonds, and magnetic data may often be used to decide whether or not these bonds are employed. Table IV shows the number of unpaired electrons expected should any given valency state assume the planar arrangement. Some elements, *e.g.*, nickel, give rise to both tetrahedral and planar complexes ; the factors leading to the change from one configuration to the other are not clear, but the relative electronegativities of the metal and the attached groups are certainly important.

Univalency.—No example is known of a planar complex of a univalent element in this group ; complexes of univalent cobalt, rhodium, and iridium, as yet unknown, would most likely show this arrangement.

Bivalency.—In addition to Pt^{II}, the square arrangement is found with Pd^{II}, Ni^{II}, Co^{II}, and Fe^{II}. Table IV shows that planar 4-covalent complexes of Pt^{II}, Pd^{II}, and Ni^{II} will be diamagnetic. In view of the marked tendency of the Pd and the Pt triad to form covalent compounds with the minimum magnetic moment, the invariable planar arrangement of the bonds around Pd^{II} and Pt^{II} is not unexpected. All complexes of palladium and platinum so far investigated have been shown to be diamagnetic.

The complexes of palladium are less stable than those of platinum and the isolation of the *cis*-isomers is more difficult. Cases where this has been achieved include the preparation of the *cis*- and *trans*-forms of palladium with benzylmethylglyoxime,[27] glycine,[28] and the diammines.[29] Bivalent nickel shows both the tetrahedral and planar arrangements, and the isola-

---

[20] *Z. anorg. Chem.*, 1936, **229**, 225.

[21] *J.*, 1935, 839.

[22] R. G. Dickinson, *J. Amer. Chem. Soc.*, 1922, **44**, 2404.

[23] E. G. Cox, *J.*, 1932, 1912.

[24] C. R. Porter, *J.*, 1938, 368.

[25] F. G. Mann and W. J. Pope, *J.*, 1926, 2675.

[26] *J. Amer. Chem. Soc.*, 1931, **53**, 1367 ; 1932, **54**, 994.

[27] F. P. Dwyer and D. P. Mellor, *ibid.*, 1938, **57**, 605.

[28] F. W. Pinkard, E. Sharrat, W. Wardlaw, and E. G. Cox, *J.*, 1934, 1012.

[29] A. Grunberg and V. M. Shul'man, *Compt. rend. Acad. Sci. U.R.S.S.*, 1933, **136**, 143 ; F. G. Mann, D. Crowfoot, D. Gattiker, and N. Wooster, *J.*, 1935, 1642.

tion of *cis*-planar complexes is difficult, as with palladium. The circumstances in which nickel gives tetrahedral complexes are discussed later. With cobalt, the magnetic data [30, 31] indicate the planar arrangement for many of the internal complexes. Planar complexes should contain one unpaired electron, and the tetrahedral, three. It is interesting to compare the non-ionic trialkylphosphine complexes of bivalent Pt, Pd, Ni, and Co which have the general formula $M^{II}X_2,2PR_3$. Platinum [20] forms very stable complexes which may be isolated in *cis*- and *trans*-forms; these are sufficiently stable to permit of physical measurement without ready isomerisation. From palladium,[32] only the *trans*-planar isomer has been obtained, the groups being more labile than with platinum. Nickel [33] forms both planar and tetrahedral complexes; the chloride and bromide complexes with triethylphosphine are diamagnetic with a zero dipole moment, and are thus the *trans*-planar derivatives. However, the nitrate, $Ni(NO_3)_2,2PEt_3$, has a dipole moment of 8·85 D. and a magnetic moment of 3·05 B.M., showing that it is tetrahedral. Finally, with cobalt [34] the only complexes obtained, even of the chloride or bromide, are strongly paramagnetic with a large dipole moment; $CoCl_2,2PEt_3$ has a dipole moment of 8·7 D. and a magnetic moment of 3·5 B.M., which are consistent with the tetrahedral arrangement. From bivalent iron, no trialkylphosphine complex could be obtained; even with other co-ordinating groups, square complexes are formed from this element only in forced configurations. Thus the tendency to form square complexes decreases in the order $Pt > Pd > Ni > Co > Fe$. It will be noticed that when compounds of the type MX_2Y_2 are obtained as square complexes in only one form it is usual to assume that these are the *trans*-forms. This is not always true for platinum; the only form of the complex $PtCl_2,2TeR_2$ so far isolated is the *cis*-isomer.[35] It is found also that the stability of *cis*-isomers increases in the sequence $PtI_2X_2 < PtBr_2X_2 < PtCl_2X_2$.

No square complexes have been obtained from bivalent Ru, Os, Rh, or Ir.

Tervalency.—The claim by G. Grube and G. Fromm [36] that *cis*- and *trans*-planar isomerism of a tervalent ruthenium compound has been observed in solution must be treated with reserve. These workers attributed the green and yellow colours of aqueous solutions of $RuCl_3$, prepared by different methods, to *cis-trans*-isomerism in the cation of $[Ru(H_2O)_2Cl_2]^+Cl^-$. Their claim rests largely on colour differences and on the fact that electrical conductivity shows only one ionised chlorine in each case; however, the colour differences may well arise from *cis-trans*-isomerism in an octahedral complex ion.

---

[30] D. P. Mellor and D. P. Craig, *J. Proc. Roy. Soc. N.S.W.*, 1940, **74**, 495; E. D. Barkworth and S. Sugden, *Nature*, 1937, **139**, 374; L. Cambi and L. Malatesta, *Gazzetta*, 1939, **69**, 547.

[31] D. P. Mellor and C. D. Coryell, *J. Amer. Chem. Soc.*, 1938, **60**, 1768.

[32] F. G. Mann and D. Purdie, *J.*, 1935, 1549.

[33] K. A. Jensen, *Z. anorg. Chem.*, 1936, **229**, 265.

[34] *Idem, ibid.*, p. 282.

[35] *Idem, ibid.*, 1937, **231**, 365.

[36] *Z. Electrochem.*, 1940, **46**, 661.

The Tetrahedral Configuration

This configuration has been assumed rather than proven in many cases, and with the bivalent complexes of cobalt and nickel, for example, it is assumed wherever the dipole moment and magnetic data exclude the planar arrangement. There appears to be no case of an optical resolution of a tetrahedral element in Group VIII. Of the few compounds whose structures have been fully determined, one should mention Cs_3CoCl_5 (by *X*-ray [37]) and $Ni(CO)_4$ (by electron diffraction [38, 39]).

Zero-valent and Univalent State.—Although the carbonyls are a group of compounds wherein the metal atom is formally zero-valent, special interest attaches to the isolation of the first salt-like substances in which the metal atom shows zero-valency. By reduction of the bivalent cyanide of nickel and palladium with potassium in liquid ammonia, the complexes $K_4Ni(CN)_4$ [40] and $K_4Pd(CN)_4$ [41] have been isolated. Both are yellow solids and are strong reducing agents which gradually decompose water with the evolution of hydrogen. The palladium compound is less stable than its nickel analogue, and no corresponding platinum compound has been described. These compounds are electronically similar to $Ni(CO)_4$, and, since the metal atoms have completed 3*d* shells, the filling of the next sp^3 orbitals will presumably lead to the tetrahedral configuration. The red colour of reduced solutions of $K_2Ni(CN)_4$ is due to the presence of the intermediate compound $K_2Ni(CN)_3$, a derivative of univalent nickel. This substance absorbs carbon monoxide and nitric oxide to give, respectively, $K_2Ni(CN)_3CO$ and $K_2Ni(CN)_3NO$, in which the nickel is presumably 4-covalent. The red solution of $K_2Ni(CN)_3$ is diamagnetic,[42] which is unusual, since univalent nickel contains an odd number of electrons. It has been suggested that an Ni–Ni bond may explain the diamagnetism, but an explanation in terms of two bridging cyano-groups [81] is possible ; in any case the anion is almost certainly polymerised to the 4-covalent state. The simple cyanide NiCN is known but has been little studied.

The Bivalent State.—The complexes of bivalent nickel, and to a lesser extent, bivalent cobalt, have been the subject of much investigation because these elements also show the planar configuration. The tetrahedral configuration may be distinguished from the planar configuration by magnetic, dipole-moment, and *X*-ray diffraction measurements. Of these, the first is the most widely used. With bivalent nickel there is as yet no certain method for predicting whether a group will give rise to the planar or the tetrahedral configuration. The shape may be correlated fairly closely with the electronegativity of the attached groups and with the colour or, better still, the absorption spectrum of the complex. The tendency to form the

---

[37] H. M. Powell and A. F. Wells, *J.*, 1935, 359.

[38] L. O. Brockway and P. C. Cross, *J. Chem. Physics*, 1935, **3**, 828.

[39] C. R. Bailey and R. R. Gordon, *ibid.*, 1938, **6**, 225.

[40] J. W. Eastes and W. M. Burgess, *J. Amer. Chem. Soc.*, 1942, **64**, 118.

[41] J. T. Burbage and W. C. Fernelius, *ibid.*, 1943, **65**, 1484.

[42] D. P. Mellor and D. P. Craig, unpublished.

tetrahedral configuration increases as the difference in electronegativity between the nickel atom and the attached groups increases. Thus all complexes in which nickel is attached to four oxygen atoms are tetrahedral,[43] whilst with four sulphur atoms the complexes show the diamagnetism characteristic of the planar arrangement. The correlation with colour is of wider applicability. It has been known for some time that the diamagnetic complexes of nickel range from red through reddish-brown to a yellow colour, whilst the paramagnetic tetrahedral complexes are usually blue or green.[44] As the colour of the co-ordinating group itself may cause confusion, Mellor and his co-workers [45] investigated the absorption spectra of a large number of internal nickel complexes and the chelate groups from which these were obtained. It was found that the absorption spectrum of paramagnetic complexes differs only very little from that of the chelate itself. However, diamagnetic complexes usually showed a new absorption band of considerable intensity near 4000 A. In a few cases this nickel band was partly obscured by bands due to the chelate group itself, but it seems to be almost invariably the rule that planar nickel complexes show this strong absorption band near 4000 A. There are only two known exceptions to this rule, namely, the 8-mercaptoquinoline–nickel complex and the bisformylcamphor–ethylenediamine compound, both of which are paramagnetic but show the characteristic absorption band at 4000 A.

The many attempts to obtain tetrahedral complexes of other elements in Group VIII have met with little success, for the elements Fe, Ru, Os, Rh, and Ir have a marked preference for the 6-covalent state. The absence of the tetrahedral configuration with these elements is a reflection of their tendency to form covalent bonds and of their complexes to have the minimum magnetic moment.

Some apparently 4-covalent complexes of the formula $R^I_2[RuCl_4]$ (R = pyridinium or other organic bases) have been described by L. W. N. Godward and W. Wardlaw.[46] These compounds are diamagnetic, and hence from Table IV are apparently not planar. The compounds H_2OsI_4 [47] and K_2OsI_4 [48] have not been investigated recently, but may be similar. The diamagnetism may indicate d^2sp orbitals for which an irregular tetrahedron is expected, but no other physical measurements are available.

Higher Valencies.—The tetrahedral configuration for the oxide OsO_4 [49] is indicated from electron-diffraction measurements, and this structure is supported by the *X*-ray investigation of $K^+[OsO_3N]^-$. F. M. Jaeger and J. E. Zanstra [50] claimed that this compound is tetrahedral. RuO_4 is no

[43] D. P. Mellor and D. P. Craig, *J. Proc. Roy. Soc. N.S.W.*, 1940, **74**, 475.

[44] L. Pauling, *op. cit.*, p. 119.

[45] H. A. Mckenzie, D. P. Mellor, J. E. Mills, and L. N. Short, *J. Proc. Roy. Soc. N.S.W.*, 1944, **78**, 70.

[46] *J.*, 1938, 1422.

[47] E. P. Alvarez, *Chem. News*, 1905, **91**, 172.

[48] N. A. Orloff, *Chem.-Ztg.*, 1907, **31**, 1063.

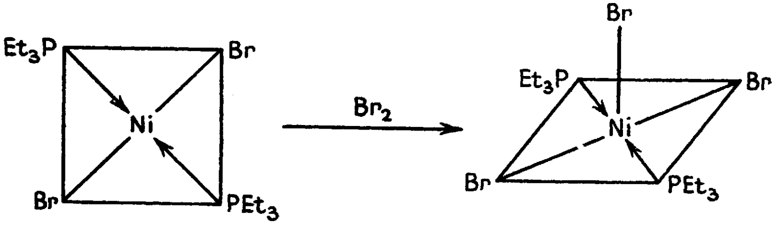
[49] L. O. Brockway, *Roy. Mod. Physics*, 1936, **8**, 260.

[50] *Proc. Acad. Sci. Amst*, 1932, **35**, 610, 787.

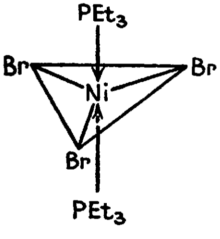
doubt similar to OsO_4. Osmium also shows a valency of eight in the fluoride OsF_8, which is one of the few cases where an element is 8-covalent. If the bonds used in this molecule are d^5sp^2 a face-centred prismatic structure has been predicted.[3]

Co-ordination Number Five

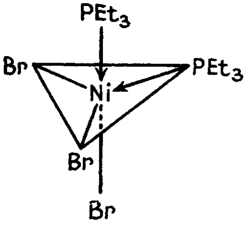
Apart from the carbonyl $Fe(CO)_5$, this co-ordination number had not been reported until recently in Group VIII. However, several compounds have now been obtained for which this unusual co-ordination number is claimed. When investigating the complexes of bivalent nickel with tertiary phosphines, Jensen [33] observed that oxidation of the *trans*-planar form of bistriethylphosphinedibromonickel (I) with bromine gave a compound $NiBr_3,2PEt_3$. This is a typical covalent complex, being soluble in benzene in which it is monomeric, and it is therefore apparently not a binuclear derivative of octahedrally co-ordinated nickel. Further data on this compound are now available; [51] the magnetic moment of 1·72—1·90 B.M. indicates the presence of one unpaired electron, presumably in the 3*d* shell, and suggests the use of dsp^3 bonds in the nickel atom. Jensen claims that this also excludes the bridged structure, since he expects that such a bridged compound would be diamagnetic.[52] Kimball [3] predicted that the use of dsp^3 bonds should lead to a trigonal bipyramid (III), but Daudel and Bucher [5] have suggested that, in addition, the tetragonal pyramid (II) would arise if the *d* electron has a lower quantum number than the *s* and *p*. A choice between these is possible from a determination of the dipole moment. Structure (II) should have the dipole of a



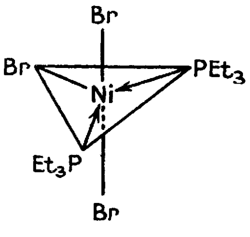
(I.) (II.)



(IIIA.)



(IIIB.)



(IIIC.)

---

[51] K. A. Jensen, *Acta Chem. Scand.*, in the press.

[52] *Idem*, unpublished.

single Ni–Br bond, about 2—3 Debye units; (IIIA) would be zero, and (IIIB) and (IIIC), by comparison with *cis*-compounds like $PtBr_2,2PEt_3$, should have a moment of the order of 7—10 D.

The experimental value of 2·5 D. is consistent with the tetragonal pyramid (II) and with Daudel and Bucher's prediction for the use of $3d4s4p^3$ bonds. Since the compound is very unstable, *X*-ray confirmation of the structure would be difficult, and the isolation of more stable compounds is desirable. A similar 5-covalent complex is obtained by the action of bromine on bisdimethylglyoximenickel.

The preparation of corresponding 5-covalent complexes of other metals has been attempted. The planar bivalent complexes of palladium and platinum with arsines and phosphines, when treated with halogens, give rise to octahedral quadrivalent complexes only. Tervalent compounds of palladium and platinum are uncommon; the compound $PtCl_3,2NH_3$ is probably a dimer containing one bi- and one quadri-valent platinum atom. A 5-covalent complex of tervalent cobalt [52] has been obtained by oxidising $CoCl_2,2PEt_3$. The product, $CoCl_3,2PEt_3$, contains the two unpaired electrons required for dsp^3 bonds. The original cobaltous complex contains three unpaired electrons and is tetrahedral; one of these unpaired 3*d* electrons becomes paired in the cobaltic compound to change the hybridisation from sp^3 to dsp^3. The unusual character of this cobaltic compound is emphasised by the fact that octahedral Co^{III} complexes are invariably diamagnetic.

It is of interest to note that the tetragonal pyramid has been suggested [10] for the compound IF_5, but electron-diffraction studies of this compound were inconclusive.[86]

Co-ordination Number Six

This is the commonest co-ordination number which the Group VIII elements display, and has been the subject of extensive investigation with these elements, particularly in their higher valency states. The octahedral distribution, arising from the use of d^2sp^3 bonds, has been well established by studies of geometric isomerism, optical resolution, and *X*-ray diffraction; recent investigations have been more concerned with establishing the relative positions of the six groups in certain geometric isomers and with elements showing 6-covalency in valencies which were formerly rather doubtful.

Univalency.—There is no known case in which a univalent metal is octahedrally co-ordinated.

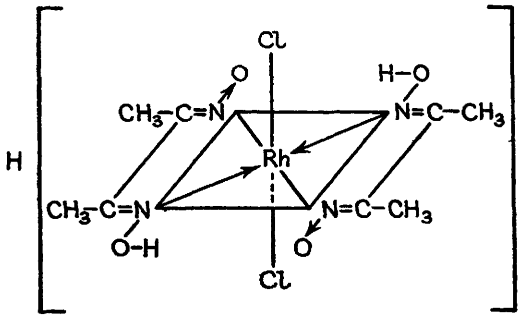
Bivalency.—In this valency one might expect to find both 4- and 6-covalent complexes, and for many of the elements this is so, but usually there is a marked preference for one or the other. Bivalent Fe, Ru, and Os are almost invariably octahedral in their complexes, and the complexes of these elements with dipyridyl or *o*-phenanthroline are sufficiently stable to permit resolution into optically active isomers. In their octahedral complexes, bivalent Fe, Ru, and Os are isoelectronic with tervalent Co, Rh, and Ir and with quadrivalent Ni, Pd, and Pt. With the exception of

Ni^{IV}, and to a lesser extent Pd^{IV}, this series gives rise to some of the most stable octahedral complexes in Group VIII, all of which are diamagnetic when covalent.

Of special interest is a comparison of the complexes of bivalent cobalt, rhodium, and iridium ; stable complexes of the last two in this valency state have only recently been obtained. Bivalent cobalt gives octahedral complexes which are oxidised very readily to derivatives of tervalent cobalt, but in addition it forms both tetrahedral and planar 4-covalent complexes. One might expect that Rh^{II} and Ir^{II} would form 4-covalent complexes from a consideration of the relative behaviour of bivalent nickel, palladium, and platinum. However, it is found that bivalent rhodium and iridium form exclusively 6-covalent complexes, and are thus more like ruthenium and osmium to the left rather than cobalt or the elements to the right.

Complexes of bivalent rhodium and iridium have been obtained with a variety of ligands (*i.e.*, co-ordinating groups ; *e.g.*, NH_3) such as pyridine, tertiary arsines, and dimethylglyoxime,[53] but in every case the metal is 6-covalent. Even the most favourable conditions for their formation have failed to give any 4-covalent complexes. In all cases the bivalent rhodium complexes were obtained by reducing the corresponding tervalent complex. It can be shown from the potentials Rh/Rh^{III} ($c + 0{\cdot}8$ v.) and Rh^{II}/Rh^{III} ($c + 0{\cdot}1$ v.) that the Rh^{++} ion is thermodynamically unstable, like the cuprous ion, in solution. A dark red solution of bivalent rhodium quickly forms a deposit of metallic rhodium and a solution of the lighter-coloured rhodic salt. Hence, to keep rhodous complexes in contact with water, they need either to be very insoluble or to dissociate only to a very small extent.

The behaviour towards dimethylglyoxime illustrates the tenacity with which the 6-fold co-ordination is retained. This substance forms a strong acid (IV) with tervalent rhodium chloride, but attempts to reduce this fail to give a 4-covalent complex. Unstable rhodous complexes containing three dimethylglyoxime groups are formed in the absence of chloride ion. As dimethylglyoxime usually tends to occupy only 4 positions around a metal atom, the reluctance to form 4-covalent complexes is emphasised.



(IV.)

---

[53] F. P. J. Dwyer and R. S. Nyholm, *J. Proc. Roy. Soc. N.S.W.*, 1941, **75**, 127 ; 1942, **76**, 133 ; 1942, **76**, 275 ; 1944, **78**, 266.

The behaviour towards pyridine is shown below:

$$\begin{tikzcd}
{[\mathrm{Rh\ py_6}]\mathrm{Br_3}} \arrow[r, "\mathrm{H_3PO_2}", "\text{at } 100^\circ"'] & {[\mathrm{Rh\ py_6}]\mathrm{Br_2}} \arrow[r, "\mathrm{HBr}", "\text{at } 0^\circ"'] & {[\mathrm{Rh\ py_5\ Br}]\mathrm{Br}} \arrow[dl, "\text{Reflux with aqueous HBr}"] \\
{[\mathrm{Rh\ py_3\ Br_2}]_2} & {[\mathrm{Rh\ py_4\ Br_2}]^0} \arrow[l, "\text{Reflux with}", "\text{alcoholic HBr}"'] &
\end{tikzcd}$$

Further refluxing with hydrobromic acid gives pyridinium salts containing rhodium in the anion.

The complexes of bivalent iridium [54] are similar to those of bivalent rhodium but in general are less stable.

An example of the ability of bivalent nickel to show both 4- and 6-covalency is given by the substance of empirical formula $Ni(CN)_2,NH_3,C_6H_6$. The molecule of benzene is held very tenaciously, and thus caused much speculation as to the type of supposed bond between the hydrocarbon and the nickel atom. A complete *X*-ray diffraction study of this substance by H. M. Powell and J. R. Rayner [55] has shown that it contains equal numbers of octahedral and 4-covalent planar nickel atoms with the benzene imprisoned in the lattice. It belongs to a class of molecular compounds to which the general name of " clathrate " compounds has been given. It is noteworthy that the magnetic moment of this compound had been shown to be consistent with half of the nickel atoms being bound with square covalent bonds and half with ionic bonds.[56] The structure of the compound is shown in Fig. 1 and consists of sheets of polymerised $Ni(CN)_2$ with two NH_3 groups on alternate Ni atoms, one of the NH_3 groups being above the other and below the plane. Undoubtedly many other structures in which the element appears to have an unusual co-ordination number will prove on *X*-ray examination to retain the usual co-ordination number by polymerisation.

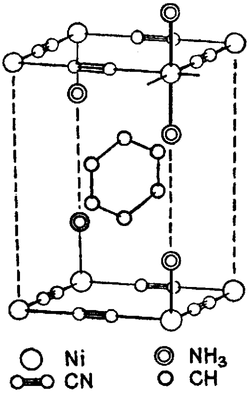


FIG. 1

(*Reproduced by kind permission from* Nature, 1949, **163**, 566.)

Although bivalent nickel forms quite stable octahedral complexes, those of bivalent palladium and platinum are rare; this is unusual, for one might expect the tendency to form complexes with the higher co-ordination number to increase with increasing atomic weight. All octahedral bivalent nickel complexes have a magnetic moment corresponding to two unpaired electrons, but of the other two elements, only the complex salt $[Pt(NH_3)_4(CH_3{\cdot}CN)_2]Cl_2$ appears to have been measured and it is diamag-

---

[54] F. P. J. Dwyer and R. S. Nyholm, *J. Proc. Roy. Soc. N.S.W.*,1943, **77**, 116.

[55] *Nature*, 1949, **163**, 566.

[56] D. P. Mellor and D. P. Craig, unpublished.

netic. Although the compound $[Ni(NH_3)_6]Cl_2$ is probably ionic, the very stable red $[Ni(dipy)_3]Cl_2$ complex, which has been resolved, seems to be covalent. If the usual $3d^24s4p^3$ bonds are used for bonding in the latter, it becomes necessary to promote two electrons, presumably to the $5s$ and $5p$ levels, and the fact that these compounds are not readily oxidised to form quadrivalent nickel has been considered a drawback to Pauling's theory. The difficulty of preparing octahedral complexes of bivalent palladium and platinum seems to be due to the absence of available orbitals. A square complex of Pt^{II}, for example, has only one unfilled $6p$ orbital, and the formation of an octahedral bivalent complex using $5d^26s6p^3$ bonds necessitates the promotion of two electrons from the $5d$ shell. The diamagnetism of platinum compounds indicates that this is unlikely ; R. F. Asmussen [57] has avoided this difficulty by the suggestion that two of the NH_3 groups in the compound $[Pt(NH_3)_4(CH_3{\cdot}CN)_2]Cl_2$ are bound by " ion-dipole " bonds. One would expect the stability of compounds formulated in this manner to be less than that of truly covalent complexes.

The Tervalent State.—Complexes of the elements in this valency state are almost invariably octahedral, and those of Fe, Ru, Os ; Co, Rh, and Ir have been studied with many different co-ordinating groups. Although tervalent cobalt, rhodium, and iridium form ammines of marked stability, those of the other three elements are less well defined. K. Gleu and his co-workers [67] have studied the ammines of ruthenium, but those of osmium warrant further investigation. The elements Ru, Os, Rh, and Ir form 6-covalent non-ionic complexes with tertiary arsines of the general formula $M^{III}(Hal)_3,3AsR_3$,[58] which are soluble in organic solvents in which they are monomeric, indicating that the metals are 6-covalent. Ferric chloride forms unstable complexes which are probably polynuclear.[59] Little is known of the tervalent compounds of palladium and platinum, but the only complex of tervalent nickel investigated so far is 5-covalent. As mentioned previously, not many well-defined complexes of tervalent osmium have been described and its chemistry needs further study.

Several *X*-ray structure determinations have been carried out on these octahedral complexes. In the main, these investigations have confirmed the structures previously assigned on chemical grounds. However, the *X*-ray examination of the silver derivative of Erdmann's salt has given a surprise. When this salt, $(NH_4)[Co(NH_3)_2(NO_2)_4]$, is treated with oxalic acid, two *cis*-NO_2 groups are replaced by the oxalate group, forming $(NH_4)[Co(NH_3)_2(NO_2)_2(C_2O_4)]$. If the two NH_3 groups are originally *trans*, only a single optically inactive derivative is expected. However, if the two NH_3 groups are originally *cis*, two geometric isomers are expected, one of which should be capable of optical activity. Since the latter was observed, Erdmann's salt was believed to be the *cis*-diammine. The *X*-ray

---

[57] " Magnetokemiske Undersgelser Over Unorganiske Kompleksforbindelser", Copenhagen, 1944 (Doctorial Thesis), p. 243.

[58] F. P. Dwyer and R. S. Nyholm, *J. Proc. Roy. Soc. N.S.W.*, 1946, **80**, 217 ; 1947, **81**, 272 ; 1942, **76**, 140 ; 1945, **79**, 121.

[59] R. S. Nyholm, *ibid.*, 1944, **78**, 229.

study of the silver salt, $Ag[Co(NH_3)_2(NO_2)_4]$, by A. F. Wells[60] has shown that this is definitely the *trans*-diammine. The reason for this difference is not clear, but the migration of groups during chemical reactions seems the most likely explanation. This result is a reminder of the need for caution in interpreting the results of some chemical reactions.

The Quadrivalent State.—Well-defined quadrivalent compounds of the last six elements exist, but little is known of the quadrivalent state for iron, cobalt, and nickel, which elements form very few compounds wherein the valency of the element exceeds three.

The best-known quadrivalent compounds are the double chlorides of formula $M^{I}_2M^{IV}Cl_6$. The isolation of the compound Cs_2RhCl_6[61] completes the series for the palladium and the platinum triad. This compound, obtained as a green powder by oxidising Cs_3RhCl_6 with ceric nitrate, is isomorphous with $(NH_4)_2PtCl_6$, the Rh–Cl distance being 2·3 A. The corresponding osmium compound, K_2OsCl_6, is isomorphous with K_2PtCl_6.

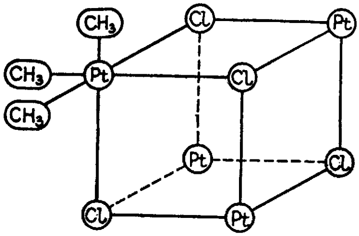


FIG. 2

The complexes of quadrivalent platinum with ammonia and with many other co-ordinating agents have been studied in very great detail. Palladium forms similar compounds, but they are reduced very easily to the bivalent state and decompose on standing. The octahedral ammines of quadrivalent iridium have been well studied, but those of ruthenium and osmium need further investigation.

Quadrivalent platinum forms some interesting organo-metal compounds in which the bonds were originally believed to be tetrahedral.[68] Recent electron-diffraction studies of the compounds tetramethylplatinum $[Pt(CH_3)_4]_4$ and trimethylplatinum chloride $[Pt(CH_3)_3Cl]_4$ show that these substances are tetramers[62] in which the platinum atom is octahedrally co-ordinated, a result more consistent with the observed diamagnetism. Molecular-weight determinations on $[(CH_3)_3PtCl]_4$, although not very accurate owing to low solubility, also support the four-fold association.[63] The basic structure of $[Pt(CH_3)_3Cl]_4$ is shown in Fig. 2; the three CH_3 groups which are attached to each metal atom are omitted from all but one Pt atom for the sake of clarity. The co-ordination number of 6 for the Pt^{IV} atom is attained by making use of the donor properties of two other chlorine atoms. In polymerising to the extent necessary to reach the stable co-ordination number, this compound is similar to the tetramer $[CuI,AsEt_3]_4$, in which the copper atom attains a co-ordination number of 4 by making use of iodine bridges.[64] The Pt–Cl–Pt angle has been estimated

---

[60] *Z. Krist.*, 1936, **94**, 447.

[61] F. P. Dwyer and R. S. Nyholm, *Nature*, 1947, **160**, 502; *J. Proc. Roy. Soc. N.S.W.*, 1947, **81**, 267.

[62] R. E. Rundle and J. H. Sturdivant, *J. Amer. Chem. Soc.*, 1947, **69**, 1561.

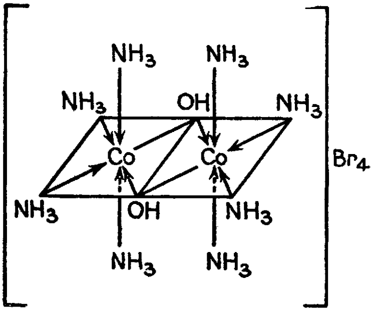
[63] R. C. Menzies and H. Overton, *J.*, 1933, 1290.

[64] F. G. Mann, D. Purdie, and A. F. Wells, *J.*, 1936, 1503.

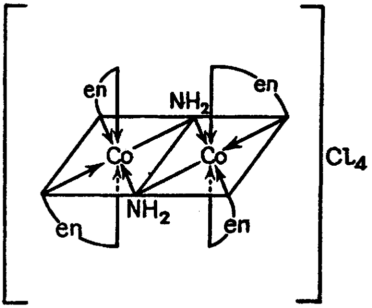
at 99°. Tetramethylplatinum is also found to be a tetramer, and in this case the polymerisation to the octahedral configuration is reflected in the physical properties, for whilst $[Pt(CH_3)_4]_4$ is a crystalline solid, other compounds of the type $M(CH_3)_4$ are low-boiling liquids. The structure is basically the same as that of trimethylplatinum chloride, except that each chlorine atom is replaced by a CH_3 group. The conclusion that carbon violates the octet rule and becomes 6-covalent seems at first sight inescapable, but it has been suggested that the electron pair involved in bond formation from the CH_3 group resonates between all three Pt atoms. Unfortunately, interatomic distances involving carbon atoms had to be assumed, but it is significant that the Pt–C distance is at least greater than the sum of the Pt^{IV} and C^{IV} bond radii. The problem involved in formulating this compound is similar to that encountered with the alkylaluminium dimers, *e.g.*, $[Al(CH_3)_3]_2$. For these compounds, structures involving " protonated bonds " have been suggested by L. O. Brockway and N. R. Davidson [65] similar to those of K. S. Pitzer [66] for the boron hydrides, but as the determination of the position of a proton is still very difficult, these formulations are still largely speculative.

Polynuclear Complexes

Complexes in which many bridging groups connect two similar metal atoms have been known for a long time, Werner having described complexes of cobalt and chromium in which such diverse groups as —OH, $—NO_2$, $—O_2$, —O—, $—O{\cdot}SO_2—$ (sulphato), and $—O{\cdot}C(CH_3){=}O—$ (acetato) acted as bridges between two metal atoms. Examples of such complexes are (V) and (VI). No special problems are involved in formulating these compounds, since in all cases the ability of the groups to donate electrons is well established. More recently, much attention has been paid to the



(V.)



(VI.)

(en = Ethylenediamine.)

---

[65] *J. Amer. Chem. Soc.*, 1941, **63**, 3287.

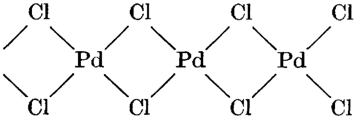
[66] *Ibid.*, 1945, **67**, 1126.

[67] *Z. anorg. Chem.*, 1936, **227**, 237 ; 1938, **235**, 201 ; 1938, **237**, 187, 197, 326, 335, 360.

[68] E. G. Cox and K. Webster, *Z. Krist.*, 1935, **90**, 561.

complexes in which two halogen atoms act as a bridge between two metal atoms. These are of special interest, since the formation of co-ordinate links by halogen atoms other than in bridged compounds is very rare; examples include the ions Br_3^- and I_3^-. A comprehensive review of the occurrence of these bridges is given by F. G. Mann.[69] Since that report further work on their chemical behaviour and structure has been done. The halogen bridged complexes of the Group VIII elements are especially suitable for investigation because the stability of the co-ordination compound in various solvents enables the use of reactions which are not so convenient with other bridge-forming elements like Al, Hg, Cd, etc.

Examples of halogen bridges in simple halides of Group VIII elements include $PdCl_2$ and Fe_2Cl_6. Palladous chloride consists of chains of the type (VII) of indefinite length.[70] The shape of the ferric chloride molecule



(VII.)

has not been settled. In the solid state the anhydrous compound forms a layer lattice [71] in which each iron atom is surrounded octahedrally by six chlorine atoms. However, the compound sublimes readily and below 700° K. exists in the vapour state as double molecules. It is also dimeric in solvents which do not co-ordinate with the iron atom; in pyridine, however, the molecular weight indicates that the monomer is present, presumably as the result of the reaction $Fe_2Cl_6 + 2py \longrightarrow 2py{\rightarrow}FeCl_3$. Magnetic measurements [72] show that the vapour is strongly paramagnetic. It has been customary to regard the bonds in such a molecule as ionic, but L. Pauling [73] has suggested that magnetic measurements may distinguish, not necessarily between ionic and covalent bonds, but often between weak covalent and strong covalent bonds, the former using unstable orbitals at higher levels, leaving singly occupied orbitals at lower levels. The physical properties of the ferric chloride, such as volatility and solubility in organic solvents, are more consistent with the idea of essentially covalent bonds, and the formula generally accepted involves a halogen bridge between two 4-covalent ferric atoms. If the bonds used are $4s4p^3$, a slightly distorted tetrahedral configuration for each iron atom as with Al_2Cl_6 is expected.

Compounds of every element in Group VIII except cobalt and nickel have been reported in which halogen bridges have been postulated to retain the usual 4- or 6-co-ordination. The structures of very few of these have been established with certainty, but the palladium compounds have been

---

[69] *Ann. Reports*, 1938, **35**, 148.

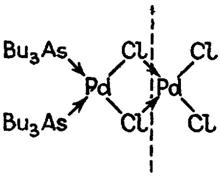
[70] A. F. Wells, *Z. Krist.*, 1938, **100**, 189.

[71] N. Wooster, *ibid.*, 1932, **83**, 35.

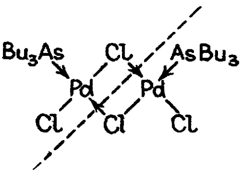
[72] A. Lallemand, *Ann. Physik*, 1935, **3**, 97.

[73] *J.*, 1948, 1461.

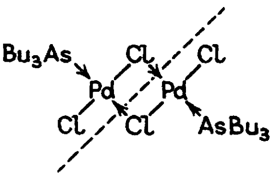
very thoroughly investigated by Mann and his co-workers.[74, 75] Their study was confined chiefly to the arsine and phosphine complexes of the general formula $[PdX_2,A]_2$, where X = Cl, Br, I, CNS, NO_2, and A = PR_3 or AsR_3 ; these are more suitable than the ammine complexes for investigation, because the latter are insoluble in suitable organic solvents, and furthermore the ammines have a great tendency to form salt-like substances. These palladium compounds are formed readily and allow of easy replacement of groups, but this behaviour means that care is necessary in interpreting results, since rearrangements may occur ; some earlier work gave apparently contradictory results for this reason. The complex $[PdCl_2,AsR_3]_2$ (or its phosphine analogue) might be expected to occur as one or all of three geometric isomers, (VIII), (IX), and (X), since the compound is known to be dimeric in solution.



(VIII.)



(IX.)



(X.)

(1) The dipole moment expected for these three structures are 12–14, 7–8, and 0 D., respectively. The value found experimentally is 2·34 for the tributylphosphine compound and 2·52 for the tributylarsine analogue. These figures, whilst suggesting a preponderance of (X) in solution, indicate that (IX) and possibly even (VIII) may be present also.

(2) Treatment with a suitable amine (NH_2R), *e.g.*, *p*-toluidine, produces two moles of the monomer $PdCl_2,AsBu_3,NH_2R$ only ; this suggests that diagonal splitting along the dotted line of (IX) or (X) occurs, since both of these would give the same product. Failure to obtain any of the compound $PtCl_2,2NH_2R$, which is only very slightly soluble and thus could not escape isolation, appears to eliminate (VIII) entirely, unless rearrangement occurred during the reaction.

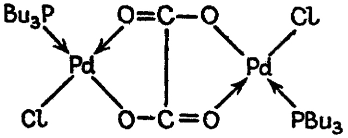
(3) When the tributylphosphine compound reacts with 2 : 2′-dipyridyl, two products are isolated, $PdCl_2,2AsBu_3$ and dipy$PdCl_2$. This was originally believed to support structure (VIII), which was presumed to react by vertical splitting along the dotted line. Similar evidence was provided by ethylenediamine. However, it was found that the palladium complex (XI), in which the oxalato-group bridges the metal atoms, gave a similar reaction, $PdCl_2,2PBu_3$ and dipy $Pd(COO)_2$ being formed. Since *X*-ray diffraction studies had shown that the bridged oxalato-compound has a centre of symmetry and thus definitely has one chlorine atom on each palladium atom, one concludes that migration of PBu_3 molecules had occurred. This reaction emphasises that in the case of palladium, reactions based on

---

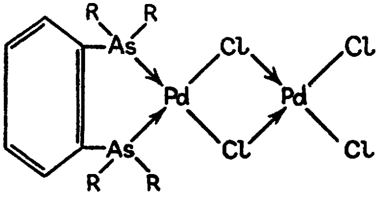
[74] F. G. Mann and D. Purdie, *J.*, 1936, 873.

[75] J. Chatt and F. G. Mann, *J.*, 1939, 1622 ; *J.*, 1938, 1649.

the use of *cis*-chelating groups need to be interpreted with care ; a chelate group, such as dipyridyl, must of necessity occupy two *cis*-positions because of its dimensions, and when such a strong co-ordinating bidentate compound is used, eviction of a *cis*-PBu_3 group and rearrangement of the two Cl atoms is a necessary consequence.



(XI.)



(XII.)

(4) Further evidence against structure (VIII) has been provided by attempts to isolate a complex (XII) by using a *cis*-chelating diarsine as the co-ordinating group.[76] This chelate co-ordinates very strongly with bivalent palladium, forming a completely strainless ring, but no bridged complex could be obtained. Although negative evidence, the fact that no bridged complex can be obtained in which both arsine groups are attached to the same palladium atom must be considered as good evidence against their existence. The complete *X*-ray analysis of the compound $[PdBr_2,As(CH_3)_3]_2$ shows that in the solid state the *trans*-symmetric structure (X) is present.[77] All Pd–Br distances in the bridge are equal and the angles between the bonds are almost 90°.

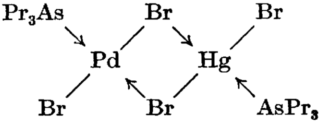
Bivalent platinum gives bridged complexes similar to those of palladium ; compounds of the formula $[PtCl_2,A]_2$ have been reported [87] where $A = SR_2$, PPr_3, PCl_3, $P(OCH_3)_3$, CO, C_2H_4, etc. They are not as easy to obtain as the corresponding palladium complexes, but once formed they appear to be quite stable.[78] Since platinous complexes exhibit geometric isomerism more often than any other planar element, it might be possible to isolate isomers of types (IX) and (X) from the platinum complexes.

Bivalent rhodium forms some bridged complexes of the general formula $[RhX_2,3AsR_3]_2$, where X = Cl, Br, I. These provide examples of bridging between 6-covalent metals atoms. Molecular-weight determinations show that they are dimeric,[79] but their structure has not yet been investigated in detail. Iridium forms similar complexes to those of rhodium but they are less stable.[54] A few bridged complexes between dissimilar metal atoms are known. They are much less stable than complexes between two metal atoms of the same kind, and highly specific factors appear to be involved in their formation. The palladium–mercury complex with tripropylarsine (XIII) is an example of this type of complex.[80] Although it has been

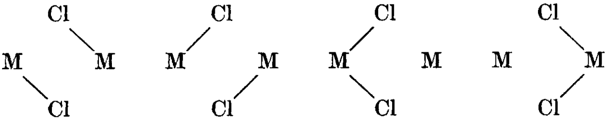
---

[76] J. Chatt and F. G. Mann, *J.*, 1939, 2086.
[77] F. G. Mann and A. F. Wells, *ibid.*, p. 702.
[78] J. Chatt, private communication.
[79] F. P. Dwyer and R. S. Nyholm, *J. Proc. Roy. Soc. N.S.W.*, 1941, **75**, 127.
[80] F. G. Mann and D. Purdie, *J.*, 1940, 1230.

customary to formulate these bridges in such a way as to involve one covalent and one so-called co-ordinate link from each halogen atom in the bridge, K. A. Jensen and R. W. Asmussen[81] have recently suggested resonance among the structures (XIV)—(XVII). They have pointed out the reluctance of the halogen atom in alkyl halides, for example, to form co-ordinate links, and have directed attention to the deep colour of most of these bridged complexes; furthermore, the diamagnetism of certain compounds like $Fe_2(CO)_9$ can be explained on their hypothesis without the need for postulating metal–metal bonds. Many other observations will need to be taken into account in a more complete picture of these compounds. They have been reported chiefly in lower valency states, although a few of metals of higher valency states exist, *e.g.*, $[Pt(CH_3)_3\ py\ I]_2$.[82] They occur only where the metal–halogen bond is essentially covalent. Facts relating to the specificity of the metal and the relative strength of the bridges when different halogens are involved do not yet permit of reliable generalisations.



(XIII.)



(XIV.) (XV.) (XVI.) (XVII.)

Summary and Outlook

The approach to inorganic chemistry has been much influenced during the past few years by certain factors which indicate the probable direction of future development. The orientation of four and six bonds around a metal atom was correctly predicted more than 50 years ago, and for a long time workers were concerned mainly with establishing which particular configurations occur for a given element. Inorganic chemistry, however, received for many decades much less interest than its importance warrants.

The development of the *X*-ray diffraction method of examining substances has led to an entirely new structural chemistry of the solid state.[83] Since most of these structure determinations take some time, it is natural that so far attention has been directed very largely to key substances; compounds of the elements in less common valency states have been

---

[81] *Z. anorg. Chem.*, 1944, **252**, 234.

[82] C. S. Gibson, R. V. G. Ewens, and M. E. Foss, *Nature*, 1948, **162**, 692.

[83] A. F. Wells, " Structural Inorganic Chemistry ", Oxford, 1945.

generally ignored. In Group VIII, for example, bond lengths for the bivalent and tervalent states of many elements have never been measured. Many other radii have been obtained by extrapolation procedures which are open to doubt. More determinations in this group are needed, particularly with complexes of unusual co-ordination numbers.

The application of quantum mechanics has enabled us to understand why molecules take up certain shapes, but the complexity of the molecules limits us to qualitative predictions at present. One of the most promising of recent developments is the attempt by Y. K. Syrkin[84] to correlate reactivity with bond type. Starting with the square complexes of bivalent platinum, an explanation of the relative reactivity of the chlorine atoms in *trans*-diamminoplatinous chloride as compared with the *cis*-compound has been advanced.

Knowledge is gradually being accumulated on the stability of complexes as a function of the metal and the valency state, and the nature of the ligand attached. Further work is necessary to enable us to correlate the strength of attachment of a group and the metal, its valency, and the stereochemical type. For this purpose a more detailed investigation of some of the less common valency states is required. It is hoped that this review, whilst indicating the developments which have taken place recently, will emphasise the scope for further investigation.

The Reviewer wishes to acknowledge helpful criticism by Professor C. K. Ingold, F.R.S., and valuable discussion with Dr. D. P. Craig, Dr. F. P. Dwyer, Dr. P. B. D. de la Mare, and Dr. J. Chatt. He also wishes to acknowledge the award by the University of London of an Imperial Chemical Industries Fellowship during the tenure of which this Review was written.

---

[84] *Bull. Acad. Sci. U.R.S.S.*, Classe Sci. chim., 1948, 69.

[85] P. W. Selwood, " Magnetochemistry ", 1943, Interscience, N.Y.

[86] H. Braune and P. Pinnow, *Z. physikal. Chem.*, 1937, *B*, **35**, 239.

[87] J. W. Mellor, " Comprehensive Treatise of Inorganic Chemistry ", Vol. XVI, p. 361.