THE STEREOCHEMISTRY AND VALENCE STATES OF NICKEL

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I. INTRODUCTION

A. GENERAL

The metals of the first transition series from titanium to copper are noted for the variable valence which they display in their simple salts and complex compounds. This behavior arises from the presence of an incomplete 3*d* shell of electrons; the comparative ease of removal of two or more electrons from the metal atom, together with the availability of *d* orbitals for bond formation, enables these elements to form a large number of complex compounds with various stereochemical arrangements. However, for a long time, nickel was regarded as more conservative than the other transition elements in regard to variable valence. The bivalent state was recognized in the simple salts and in many complex compounds but until quite recently the existence of higher valence states was considered uncertain (175). In nickel tetracarbonyl, known since 1888 (132), the metal was taken, at least formally, as zerovalent, but since carbonyls were often regarded as a class of compounds for which the ordinary rules of valence were not necessarily applicable, the valence of the metal remained uncertain. Thus, as recently as 1930, a formula for nickel carbonyl involving a five-membered ring consisting of four carbon atoms and a bivalent nickel atom (formula XII) was still being seriously considered (133, 183). Formulations such as this reflect the reluctance to accept the possibility of valence states other than the common one shown in the simple salts. Also, although oxides which varied in composition from Ni_2O_3 to NiO_2 were known, it was considered that these might well be peroxides rather than compounds in which the valence of nickel was greater than 2. In view of the difficulties of deciding the actual valence state of a metal in higher oxides, this caution is quite understandable. However, during the last twenty years, the valence states of 0, 1, 3, and 4 have become firmly accepted, even though some doubt still remains as to whether nickel is really univalent in the compounds having the empirical formulas $K_2Ni(CN)_3$ and NiCN. The valence state of 6 has been claimed also (68), but adequate support for this is lacking. In this review those valencies which have been definitely established will be discussed in detail and those concerning which doubt still exists will be examined. Such stereochemistry of these valence states as is known will be reviewed, with special reference to work published during the past two decades.

The reasons for the rapid development in the pure chemistry of nickel during the past twenty years are relevant to this discussion. During this period, inorganic chemistry in general, and coördination chemistry in particular, has received a great stimulus, largely due to three main developments. The first of these is the application of quantum mechanics to the study of chemical problems. Although the theoretical investigators are limited in the main to purely qualitative predictions concerning bond strength and stereochemistry, nevertheless the results have enabled chemists to understand the nature of the chemical bond and the factors which influence its strength and directional properties. Furthermore, the ability of the theoretical workers to predict what stereochemical arrangements are energetically feasible, in terms of the bond orbitals used, has led to notable advances. The fact that some controversy developed over certain predictions, e.g., with regard to the square arrangement in bivalent palladium, bivalent platinum, and certain bivalent nickel complexes, has been in itself most stimulating, since much experimental work has followed in attempts to support or disprove the theoretical predictions. Not the least valuable outcome of this work has been the light which has been thrown on the nature of the groups required for the stabilization of unusual valence states.

The second influence at work has been the application of various physical methods to inorganic chemistry. Many of these methods are not "new" in the sense of having been recently discovered, but they could be applied with a new sense of purpose following the enunciation of the relationships existing between bonding orbitals and stereochemistry as laid down by the workers in quantum mechanics; in a way, many of these methods are complementary with quantum mechanics. Thus, a magnetic moment of itself tells one nothing about the stereochemistry of nickel unless some theory relating stereochemistry with the number of unpaired electrons is acceptable. By the same token, quantum mechanics is often able to indicate that certain stereochemical arrangements only are energetically feasible but it requires some physical measurement to decide between them. The application of some of these physical techniques has encouraged the use of what were, until recently, uncommon ligands. This arises from the fact that suitable physical properties must be possessed by a molecule before certain techniques are applicable; thus, benzene-soluble non-electrolytes are desirable for measurements of electric dipole moment and the insolubility of metal-ammines has resulted in the greater use of organic arsines, phosphines, and of disubstituted sulfides for this purpose. As will be seen presently, ligands with donor atoms such as phosphorus, arsenic, and sulfur have proven of great value for the stabilization of Ni(0), Ni(III), and Ni(IV).

The third factor which has resulted in considerable advances in inorganic chemistry is the great development in fluorine chemistry. Owing to its very high electron affinity, fluorine is an ideal element for the removal of electrons from metals and hence for the preparation of metals in higher valence states. The use of elemental fluorine and bromine trifluoride has resulted in the stabilization of several higher valencies of metals of the first transition series: e.g., Co(IV) (105), Cu(III) (88), and Ni(IV) (88, 105) as the complex K_2NiF_6.

B. BOND TYPES AND STEREOCHEMISTRY

The term "stereochemistry," as generally understood, is used in reference to the arrangement of the bonds around a particular atom. Some qualification is necessary, however, because two extreme types of binding are recognized in inorganic compounds: covalent (e.g., $SnCl_4$) and electrovalent (e.g., CsF). In compounds in which the first type of binding occurs, the arrangement of the bonds around the metal atom depends upon the particular atomic orbitals of the metal atom which are used for bond formation. In the stannic chloride molecule, for example, four equivalent $5s5p^3$ orbitals of the tin atom overlap with the $2p$ orbitals of four chlorine atoms to form four σ bonds which are arranged tetrahedrally. The arrangement is dependent upon the number and nature of the atomic orbitals used; the stereochemical arrangements resulting from the various combinations of orbitals giving coördination numbers from 2 to 8 have been summarized by G. E. Kimball (102). In electrovalent compounds, however, the whole crystal is one giant molecule and the arrangement of anions about the cation is decided by the relative sizes, relative numbers, charges, and polarizabilities of the ions involved. For electrovalent compounds it is not necessary to consider the orbitals of the metal atom, except in those cases where resonance may occur between the purely ionic structure and a possible covalent structure which has the same directional properties as these resulting from the purely electrostatic model; this is, for example, quite feasible in certain octahedral and tetrahedral complexes. As used here, the term "stereochemistry" implies the arrangement around the metal atom of covalent bonds which are considered to use definite orbitals of the metal atom. For the sake of completeness, however, the crystal structures of the more common ionic lattices of bivalent nickel compounds which are known will be mentioned. Inevitably there are compounds which appear to be intermediate between these two classes. Thus, potassium ferrioxalate is a molecule in which the six iron–oxygen bonds are arranged octahedrally around the ferric atom but the magnetic moment (5.9 Bohr magnetons) clearly indicates that the five $3d$ orbitals are singly occupied and hence that none is available for covalent-bond formation with the oxygen atoms. Since the octahedral arrangement in covalent complexes of transition metals was considered to arise from the use of six $3d^24s4p^3$ orbitals, L. Pauling (153) proposed that the bonds in this molecule are essentially "ionic." The term has been criticized for various reasons, the chief objection being that the physical properties and stability of these compounds, together with the directional properties of the iron–oxygen bonds in this and in many other molecules, as in ferric tris(acetylacetone), warrants the conception that the bond is "covalent" in the simple sense in which this term is generally used. Later Pauling (157, 159) suggested that the four $4s4p^3$ bonds might resonate among the six positions, thereby giving to each bond a certain covalent character; however, this picture is not very satisfactory in view of the difference between the angles at the metal atom in a tetrahedral and in an octahedral complex.

More recently it has been proposed by H. Taube (187) that the bonds in a compound such as $K_3Fe(C_2O_4)_3$ should be regarded as covalent but using the "outer" $4d$ orbitals of the metal atom, involving the combination $4s4p^34d^2$. In $K_3Fe(CN)_6$, on the other hand, the "inner" $3d$ orbitals are used in the hybridization $3d^24s4p^3$. A similar suggestion was made by F. H. Burstall and R. S. Nyholm (27) to explain the magnetic properties of the $[Ni(dipyridyl)_3]^{++}$ and similar transition metal ions. The possibility that these "outer" $4d$ orbitals were utilized in bond formation, at least in square complexes, had been proposed some time ago by M. L. Huggins (90), who suggested that the hybridization in square cupric complexes involved $4s4p^24d$ bonds rather than $3d4s4p^2$ orbitals; by this combination the necessity for the promotion of an electron (to a $4p$ orbital) is avoided. For square complexes essentially the same idea has been advanced (170) by P. Rây and D. N. Sen, who proposed that cupric complexes of both $3d4s4p^2$ and $4s4p^24d$ types may exist. Theoretical support from calculations of overlap integrals for the use of $4d$ orbitals by metals of the first transition series for both σ- and π-bond formation has recently been obtained (43, 209). Calculations of overlap integrals have established that, at bond lengths of chemical interest, the strength of octahedral $4s4p^34d^2$ bonds, using the outer d orbitals, is greater than $4s4p^3$ bonds at the same length. Furthermore, it has been found that the more electronegative ligands should favor the use of the "outer" $4d$ orbitals, because these $4d$ orbitals project much more than do the $3d$ orbitals, thus enabling overlap at greater distances. Such bonds clearly will possess a considerable polarity, since the region of the overlap, i.e., maximum electron density, is closer to the ligand than is the case with bonds to groups of lower electronegativity. Thus the descriptions of the bonds in complexes in which no electron pairing occurs as "ionic" or "using higher level covalent bond orbitals" do not differ as much as might appear at first sight.

In this article the term "ionic" will be used to mean that, as deduced from magnetic measurements, the number of unpaired electrons in a complex is the same as in the free ion and hence that orbitals used for bond formation are *above* the $3d$ shell. In general these will be $4s4p^3$ or $4s4p^24d$ in *four*-covalent complexes and $4s4p^34d^2$ in *six*-covalent complexes. Here the term "covalent complex" will be used in reference to those complexes which show maximum electron pairing and hence which have $3d$ ("inner" d) orbitals available for bond formation. It has been known empirically for some time that electron pairing in transition complexes, and hence the use of lower $3d$ orbitals for bond formation, is favored by the *less* electronegative groups, e.g., —CN, —NO_2, —SR. Very electronegative groups like fluorine can form complexes with the first transition series, e.g., K_3FeF_6, K_3CoF_6, but electron pairing occurs in only one of these, the compound K_2NiF_6 (88, 143).

II. THE BIVALENT STATE OF NICKEL

The stereochemistry of nickel is most conveniently discussed under the various valence states; of these the common bivalent compounds will be considered first. We shall then discuss the higher and lower valence states in that order.

A. IONIC LATTICES

Although not falling strictly within the stated purview of this article, arrangements found in compounds of bivalent nickel with ionic lattices are of interest. Nickel chloride and nickel iodide both crystallize in the cadmium chloride type lattice, while nickel bromide has the cadmium iodide type of structure (204). These two structures are very similar but differ in the manner in which the layers pack together. The halogen ions are close-packed in a cubic manner in the cadmium chloride lattice but hexagonal in the cadmium iodide lattice. Nickel fluoride, however, crystallizes with a rutile structure; each nickel ion is surrounded by six equidistant fluoride ions which are arranged at the corners of an octahedron (203). Nickel oxide has a simple body-centered sodium chloride type lattice, but the sulfide possesses a peculiar 5:5 coördinated structure. The crystal structures of the anhydrous sulfate, nitrate, and other oxyanion salts do not appear to have been studied. The structures of the above salts have been discussed in detail by A. F. Wells (205). Irrespective of the anion, *hepta*- and *hexa*hydrated nickel salts are six-covalent complexes containing the $[Ni(H_2O)_6]^{++}$ cation.

In its *covalent* complexes and in complex ions, bivalent nickel is usually four- or six-covalent. In both cases the compounds may be divided into two classes on the basis of the magnetic moments.

B. FOUR-COVALENT COMPLEXES OF NICKEL

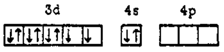
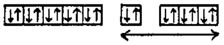
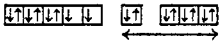
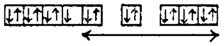
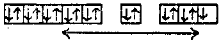
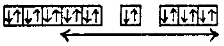
1. *Paramagnetic complexes*

Complexes in this class are generally green or blue in color, in sharp contrast with the diamagnetic complexes, which are usually red, brown, or yellow. Typical paramagnetic complexes are bis(acetylacetone) nickel and bis(triethylphosphine) nickel nitrate. The magnetic moments of these compounds vary between 3.2 and 3.4 Bohr magnetons (101), indicating two unpaired electrons.

The calculated magnetic moment for two unpaired electrons on the "spin only" formula ($\mu = \sqrt{n(n+2)}$)[1] is 2.83 Bohr magnetons; this simple formula is commonly adopted as a first approximation for elements of the first transition series. In practice, however, the moments generally exceed slightly the "spin only" value unless the atom is in an S state, i.e., has no resultant orbital angular momentum; Fe(III) and Mn(II), each with five unpaired electrons, are examples of atoms in S states. This small excess, which we shall call for convenience the "orbital increment," arises from incomplete quenching of the orbital contribution to the moment (200). This will be discussed again presently. Now, since the two electrons in paramagnetic Ni(II) complexes presumably occupy $3d$ orbitals (table 1), no $3d$ orbitals are left for bond formation. The immediately available

TABLE 1

Electronic configuration of nickel complexes

		UNPAIRED ELECTRONS	CALCULATED μ (B.M.) (SPIN ONLY)
Metallic nickel (ground state)		–	Ferromagnetic
Ni^0 (tetrahedral $4s4p^3$ bonds)*		0	Diamagnetic
Ni^{++} (free ion)		2	2.83
Ni^{II} (tetrahedral $4s4p^3$ bonds)		2	2.83
Ni^{II} (square planar $3d4s4p^2$ bonds)		0	Diamagnetic
Ni^{II} (octahedral $4s4p^34d^2$ bonds)		2	2.83
Ni^{II} (octahedral $3d^24s4p^3$ bonds)		0	Diamagnetic†
Ni^{+++} (free ion)		3	3.88
Ni^{III} (square pyramid $3d4s4p^3$ bonds)		1	1.73
Ni^{III} (square pyramid $3d^24s4p^2$ bonds)		1	1.73
Ni^{III} (octahedral $3d^24s4p^3$ bonds)		1	1.73
Ni^{++++} (free ion)		4	4.90
Ni^{IV} (octahedral $3d^24s4p^3$ bonds)		0	Diamagnetic

* Bonding orbitals shown thus: ⟷.

† Assuming that promotion of two electrons to a $5s$ orbital occurs. If the promotion were to $4d$ orbitals, paramagnetism with two unpaired electrons would be expected.

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[1] n is the number of unpaired electrons.

orbitals above the 3d level for use in a four-covalent complex are the $4s4p^3$ orbitals; assuming that these $4s4p^3$ orbitals are used, L. Pauling (151, 152) predicted that paramagnetic four-covalent complexes would be tetrahedral. This assumption has been widely accepted, but experimental support for the hypothesis has only recently been forthcoming. As recently as 1950 N. V. Sidgwick (178) pointed out that at that time no direct experimental support for the assumption was available.

The evidence in support of this hypothesis may be summarized as follows:

(*a*) *Theoretical:* Since the $4s4p^3$ orbitals are the first four empty orbitals above the filled 3d shell, it is reasonable, at first sight, to assume that these will be the ones used for bond formation in a four-covalent complex. Such a simple assumption has been proven valid for the elements of the first two rows of the Periodic Table (e.g., four-covalent nitrogen and phosphorus; four-covalent carbon and silicon; the four-covalent complexes of Zn(II), Hg(II), Cd(II), and Cu(I)). However, this argument loses much of its force when one considers the stereochemistry of four-covalent complexes of bivalent copper, for which a somewhat similar electronic arrangement occurs ($3d^9$), all five 3d orbitals being unavailable for bond formation. Yet in cupric compounds the arrangement is invariably square planar, an arrangement requiring the use of dsp^2 orbitals. For any particular transition element, quantum-mechanical calculations cannot yet be carried out with the accuracy necessary to decide whether the $3d4s4p^2$, $4s4p^24d$ square, or the $4s4p^3$ tetrahedral arrangement will have the lower energy.

(*b*) *Electric dipole moments:* K. A. Jensen (95) examined the complex $Ni(NO_3)_2 \cdot 2(C_2H_5)_3P$ and concluded that the nickel atom must be four-covalent because the compound is monomeric in freezing benzene. The high electric dipole moment (8.85 D) clearly excludes the *trans*-planar arrangement and is compatible only with a *tetrahedral* or a *cis*-planar molecule. Until recently the *trans*-arrangement was generally considered to be the thermodynamically more stable form in planar complexes; hence the *cis*-planar arrangement was regarded as improbable. However, it is known (36) that in the case of planar bivalent platinum complexes the *cis*-form is often the isomer with the greater bond energy. The equilibrium *cis* ⇄ *trans* has been studied in benzene solution. Care has to be taken when interpreting equilibria in solution, because the position of the equilibrium *cis* ⇄ *trans* in a planar complex is affected both by the relative bond energies of the two isomers and by the entropy changes involved. The expression for such equilibria

$$-RT \ln Kp = \Delta G = \Delta H - T\Delta S$$

makes this clear. Furthermore, with Pt(II) complexes the *cis*-arrangement appears to be formed most readily when the anion is most electronegative and when the ligand has a high capacity for double-bond formation. Again, since in square complexes π binding is favored for two bonds at right angles (43), the *cis*-arrangement could quite easily be the more stable for this reason.

Thus with Pt(II) it is found that the *cis*-arrangement appears to be favored by Cl > Br > I as anion and by those ligands which, whilst having a weaker capacity for σ-bond formation, may be expected to form strong π bonds, e.g., antimony, tellurium (97, 137). To sum up, the dipole moment indicates either the tetrahedral arrangement or the *cis*-planar arrangement.

(*c*) *Size of the orbital contribution to the magnetic moment:* The effect of stereochemistry upon the size of the orbital contribution to the magnetic moment of transition metal complexes has been studied by several workers during the past few years. Although the magnetic moments of complexes of the first transition series approximate to the "spin only" formula, they may sometimes exceed the calculated value by as much as 1.5 Bohr magnetons, e.g., with certain octahedral Co(II) complexes. This orbital increment is generally attributed to incomplete quenching of orbital motion by the electrical fields created by the attached atoms. If this quenching is complete a spin only value results, but where this is not so, the size of the orbital increment is an indication of the asymmetry of the field resulting from the attached atoms and hence of the stereochemistry. It has been shown (71, 160, 161, 200) that the "quenching" of the orbital contribution in octahedral nickel complexes should be greater than for those in which the attached groups are tetrahedral. A study of a large number of six-covalent complex ions of the type $[NiX_6]^{++}$, where X is H_2O, NH_3, ½en, ½dipy, ½*o*-phen (101), reveals that the magnetic moment is little affected by the nature of the above ligands and generally lies between 3.1 and 3.2 Bohr magnetons. Four-covalent complexes such as $[Ni(acetylacetone)_2]^0$ however, have magnetic moments in the vicinity of 3.3–3.4 Bohr magnetons. This appears to support the tetrahedral hypothesis, but it should be pointed out that no theoretical studies have been reported yet on the effect of a planar arrangement of surrounding atoms upon the size of the orbital contribution in a paramagnetic molecule, i.e., if the bonds were $4s4p^24d$. At present the size of the orbital contribution may be taken as suggestive of four—as against six—covalence, it does not establish definitely that the arrangement is tetrahedral rather than planar. For a more detailed discussion of this subject, with a survey of recent work, see Nyholm (142a).

(*d*) *Fine structure of the K x-ray absorption edge:* The fine structure of the *K* absorption edge is related to the stereochemistry in the following way: When electrons are excited from the *K* shell of a metal atom, they are lifted to suitable vacant orbitals on the outside of the atom. For the $[Cu(H_2O)_4]^{++}$ and $[Cu(NH_3)_4]^{++}$ ions, for example (7), two absorption maxima are observed, one of which the investigators identified as a $1s \rightarrow 4p$ transition and the other as an unresolved mixture of $1s \rightarrow 5p$, $1s \rightarrow 6p$, etc., transitions. Clearly an unequivocal assignment of the type of transition gives an indication of the *lowest* vacant orbital on the outside of the atom, provided the transition to this orbital is not forbidden by the selection rules. Then, if we have, as with Ni(II), the possibility of two types of four-covalent structure in one of which all $4p$ orbitals are filled, as in tetrahedral $4s4p^3$ complexes, and in the other a vacant $4p$ orbital is available, as in square $3d4s4p^2$ complexes, it should be possible to distinguish between them by observing the peaks in the spectrum. A peak which is attributed to a $1s \rightarrow 4p$

transition has been reported by W. W. Beeman and H. P. Hanson (74) for a series of transition metal complexes which they examined. When the four-covalent Ni(II) complexes were investigated, it was found that the diamagnetic complexes show the expected $1s \rightarrow 4p$ transition peak, but the paramagnetic complexes do not. Since in the first instance the bond orbitals are $3d4s4p^2$, a vacant $4p$ orbital is available to receive the excited electron, but in the second case the absence of a vacant $4p$ orbital is most logically explained by the assumption that all three $4p$ orbitals are being used for bond formation, i.e., for $4s4p^3$ bonds. Further work has recently been reported by G. Mitchell and W. W. Beeman (130). The absence of the peak attributed to a $1s \rightarrow 4p$ transition in bis(8-hydroxyquinoline) nickel(II) is taken as evidence for a $4s4p^3$ tetrahedral arrangement. The fact that the peak is also missing in bis(salicylaldehyde) nickel(II) dihydrate is taken as evidence for a tetrahedral arrangement here also. However, if this were an octahedral $4s4p^34d^2$ complex there would still be no vacant $4p$ orbital; hence in this case the absence of the peak is as compatible with $4s4p^34d^2$ binding as it is with $4s4p^3$ bonds. Hence it is important to establish that the nickel atom is actually four-covalent before attempting to decide the arrangement of the bonds. Work has been done on this subject by E. Vainshtein (195, 196), who found that $NiCl_2$, $NiSO_4$, and $[Ni(NH_3)_4]^{++}$ ions showed the same K absorption edges in both alcoholic and aqueous solutions. The structure of the $[Ni(CN)_4]^{--}$ ion under the same conditions was entirely different. In this case it appears that one is distinguishing between octahedral ions, e.g., $[Ni(H_2O)_6]^{++}$, and square $[Ni(CN)_4]^{--}$ ions. The evidence provided here in regard to four-covalent Ni(II) is of course indirect but can be taken as supporting the view that the paramagnetic complexes are tetrahedral.

(*e*) *The Cotton effect:* Since the reliability of conclusions as to the stereochemistry of metals on the basis of the Cotton effect has been severely questioned, no weight will be attributed to this evidence here, but a brief summary of the phenomenon is called for. The Cotton effect for metal complexes containing an optically active carbon atom is characterized by three distinct features. A substance which shows this effect has (*i*) an anomalous rotatory dispersion, (*ii*) zero rotation at a wave length in the vicinity of the maximum of the absorption band, and (*iii*) circular dichroism with maximum ellipticity in the region of zero rotation, i.e., when absorption is a maximum. P. Pfeiffer and his collaborators (164) proposed that for the Cotton effect to occur in a metal complex, the molecule must contain not only an asymmetric *carbon* atom but also a chromophoric metal atom which is asymmetric, i.e., has a tetrahedral arrangement. Since the compound bis(salicylaldehyde *d*-propylenediamine) nickel(II) shows the Cotton effect, it was concluded that the Ni(II) atom is tetrahedrally coördinated. The inactive form of this compound, however, has been shown by D. P. Mellor (119) to be diamagnetic; hence the Ni(II) atom is square coördinated. In contrast with this conclusion, H. S. French and G. Corbett (65) have concluded that the Ni(II) atom is tetrahedrally coördinated in bis(*d*-formylcamphor) nickel(II), which compound is paramagnetic. Clearly there is some anomaly here if the magnetic moment can be accepted as a reliable criterion of stereochemistry. D. P. Mellor (119) has examined this problem carefully and points out that in the second compound it is by no means certain that the band in which the Cotton effect occurs can be attributed to the nickel atom. He concludes that the appearance of the Cotton effect is more likely to be concerned with the covalent character of the metal–ligand bonds than with their stereochemistry. An indirect correlation with stereochemistry is implicit here, since strong "covalent" ($3d4s4p^2$) bonds indicate a square arrangement; nevertheless, there is no necessity for recourse to rotatory dispersion measurements to decide this, since the bond character may be ascertained as a rule simply by observation of the absorption spectra alone. More work is needed on the Cotton effect in order to establish with greater certainty its relation to other bond properties, but in the meantime it is considered unsafe to accept conclusions based thereon as reliable evidence for a tetrahedral arrangement of the bonds around a nickel atom. A. E. Martell and M. Calvin (118) also conclude that evidence so far presented does not enable one to decide with any confidence whether the Cotton effect is caused by the presence of an asymmetric metal atom or by coupling between the chromophore and the asymmetric center.

(f) X-ray crystallographic analysis: It is remarkable that until recently no x-ray crystallographic investigation of a paramagnetic four-covalent nickel complex had been carried out. Two such compounds, however, have now been examined. D. H. Curtiss, F. K. C. Lyle, and E. C. Lingafelter (46) have compared the x-ray powder diagrams of anhydrous bis(salicylaldehyde) nickel(II) with those of the corresponding bivalent zinc and copper compounds. They have shown that x-ray powder diagrams of the nickel and zinc compounds are almost identical. However, the cupric complex, which has been shown to be square planar (181), gives an entirely different powder pattern. Keeping in mind the fact that all four-covalent zinc complexes which have been investigated are tetrahedral whilst all four-covalent cupric complexes which have been studied are square planar, the above findings support the view that the nickel compound has a tetrahedral arrangement. Unfortunately the above workers were unable to obtain single crystals of the anhydrous compound, which was obtained as a powder by dehydration of the dihydrate. A similar dihydrate of nickel bis(acetylacetone), presumably octahedral, is known; from this dihydrate, crystals of the anhydrous complex may be obtained by sublimation. An x-ray examination of these crystals is being carried out by G. J. Bullen and K. Lonsdale (25); so far it has been established that the compound is not isomorphous with the corresponding cupric compound, which had been shown previously by x-ray studies to be square planar (42). The structure determination is incomplete, but the nickel atom is most probably at the center of a regular tetrahedron of oxygen atoms.

For bis(salicylaldehyde) nickel(II), M. Calvin and N. C. Melchior (30) have proposed a square planar arrangement of the bonds, because they believe that a $3d$ orbital is in some way involved in the binding. Resonance between ionic and $3d4s4p^2$ binding is envisaged, one unpaired electron being in a $3d$ and one in a $4d$ orbital. Theoretical work, however, suggests (43) that were a d orbital involved in the binding it would be a $4d$ and not a $3d$, owing to the high electronegativity of the attached groups; the problem is thus most likely to be one of distinguishing between the $4s4p^3$ and the $4s4p^24d$ combinations, since no promotion of electrons is then required.

2. Diamagnetic complexes

As previously mentioned, compounds of this class usually vary in color from yellow to red or brown. This correlation between diamagnetism and color has been examined by several workers, but several exceptions to the general rule have been observed. For example, the vermillion-colored compound, bis-(1-hydroxyacridine) nickel(II) has a moment of 3.2 Bohr magnetons (131); on the other hand, green bis(formylcamphorethylenediamine) nickel(II) is diamagnetic in the solid state (126, 210). D. P. Mellor, J. E. Mills, H. A. McKenzie, and L. N. Short (131) suggested that, since the color of the attached group itself could confuse the issue, the absorption spectrum of the complex would be a more valuable basis for comparison. From the study of the spectra of a large number of four-covalent Ni(II) compounds, and of the ligand by itself (in a suitable solvent in each case), it was found that the diamagnetic complexes usually exhibited a sharp absorption band in the vicinity of 4000 Å. This band is very intense, ϵ-values between 3,000 and 12,000 being reported. The shape of the band is also important, for, unlike the bands of most inorganic complexes, this one is very sharp and closely resembles those observed in atomic spectra. However, there are at least two exceptions to the rule that this band is diagnostic of diamagnetism; thus, the compound bis(formylcamphorethylenediamine) nickel(II), which is diamagnetic in the solid state, becomes paramagnetic when dissolved in alcohol but still shows the characteristic band near 4000 Å. (131, 210). To sum up, this sharp absorption band near 4000 Å. and/or diamagnetism may be regarded as diagnostic of a square planar arrangement as a rule but it is not an infallible guide, because at least one six-covalent Ni(II) complex is known having both of these properties (see page 283).

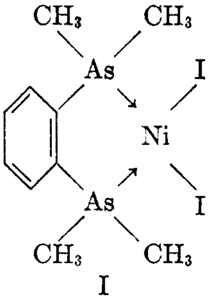
The conclusion that diamagnetic four-covalent complexes are square planar is well founded on the following pieces of self-consistent evidence:

(*a*) *Theoretical:* The diamagnetism of four-covalent Ni(II) complexes is most simply interpreted to mean that the eight $3d$ electrons of an Ni^{++} ion are forced to pair off, using four fully occupied $3d$ orbitals. This leaves one $3d$ orbital empty and when this is hybridized with the next three vacant orbitals the binding will be $3d4s4p^2$ (table 1). This results in a square planar arrangement (102). The argument was put forward by L. Pauling in 1931 (151, 152); its subsequent confirmation is one of the notable successes of quantum mechanics.

(*b*) *Electric dipole moments:* Following his investigations of the dipole moments of the two isomers of bivalent platinum complexes of the type $[Pt(hal)_2 \cdot 2R_3P(As)]^0$ (94, 95), K. A. Jensen then examined the corresponding complexes of bivalent nickel. In the case of the Pt(II) complexes, one isomer has a dipole moment of approximately zero, when allowance for the high atom polarization is made, but for the other isomer the moment is about 10–12 Debye units. Whether the latter arises from a *cis*-planar or a tetrahedral arrangement cannot be decided from electric dipole measurements, but the zero moment can be explained only on the assumption that the compound has a *trans*-planar configuration. K. A. Jensen (96) showed that the dipole moments of $[NiCl_2 \cdot 2(C_2H_5)_3P]^0$ and $[NiBr_2 \cdot 2(C_2H_5)_3P]^0$ are zero, or nearly so, and concluded that these are all *trans*-planar. It is interesting to note that when the halogen is replaced by the more electronegative nitrate group, both the magnetic moment and the electric dipole moment indicate a change over to the tetrahedral arrangement.

(*c*) *Cis–trans isomerism:* Operating with suitable unsymmetrical chelate groups, such as benzylmethylglyoxime, several workers have reported the isolation of two forms of bivalent nickel complexes. Thus L. Tschugaeff (190–194) described two interconvertible complexes of nickel with monoethylglyoxime; later H. J. Cavell and S. Sugden (31) described two interconvertible forms of the complex of nickel with benzylmethylglyoxime. The authors endeavored to obtain *cis*- and *trans*-forms of the glyoxime complexes suitable for dipole moment measurements. Unfortunately, only one form was sufficiently soluble for accurate work and the dipole moment of this isomer was 1.6 D. This is probably the *trans*-planar form, the small "apparent" moment being most likely due to an insufficient allowance for atom polarization. More recently the isolation of two forms of bis(thiosemicarbazide) nickel(II) sulfate (96) and of nickel(II) salicylaldimine (107) has also been attributed to *cis–trans* isomerism. The greater lability of square bivalent nickel and palladium complexes in solution, as compared with those of bivalent platinum, means that identification of these isomers, even if soluble, by measurements of electric dipole moment is precluded; and the only way of establishing with certainty that they really are *cis*- and *trans*-planar isomers is by x-ray crystallography. In the past there have been many instances where the isolation of two different forms of a complex has been erroneously attributed to *cis–trans* isomerism, the best example being the case of dimethyltellurium diiodide (50, 108, 197, 198, 199). H. J. Emeleus and J. S. Anderson (57) have recently stressed the need for caution in attributing the existence of two forms of a compound to *cis–trans* planar isomerism. Although *cis–trans* isomerism *may* be the correct explanation for the isolation of two forms of a complex, the inference that the four bonds are coplanar simply because two forms of a substance can be isolated can be accepted *only* when there is adequate supporting physical evidence.

Assuming that diamagnetism establishes that the four bonds are coplanar and square, at least one Ni(II) complex has been reported (142) which must be *cis*-planar for steric reasons. When the Ni(0) complex $Ni(CO)_2 \cdot$diarsine (where diarsine = *o*-phenylenebis(dimethylarsine), the chelate group in formula I) is treated with iodine, a red compound with the formula $NiI_2 \cdot$diarsine is obtained. Since this is diamagnetic and monomeric in freezing ethylene dibromide, it undoubtedly has the structure shown on page 275.



To sum up, little firm support for a square planar arrangement of the bonds in diamagnetic Ni(II) compounds can be based on the existence of *cis–trans* isomerism. This is due to the fact that even if *cis*-isomers do exist in the solid state, they are so much more labile than the Pt(II) *cis*-isomers that they pass over to the *trans*-forms almost instantaneously in solution, thus precluding physical confirmation.

(*d*) *X-ray crystallography:* This provides abundant support for the hypothesis that diamagnetic four-covalent Ni(II) complexes are square planar. The following compounds have been shown to contain a square coördinated bivalent nickel atom: $K_2Ni(C_2O_2S_2)_2$ (from thioöxalic acid) (41); $BaNi(CN)_4 \cdot 4H_2O$ (21, 22); $Na_2Ni(CN)_4 \cdot 3H_2O$ (22); bis(*N*,*N'*-dipropyldithiocarbamate) nickel(II) (162, 163); bis(salicylaldehydeëthylenediamine) nickel(II) (the orange form as prepared by W. Klemm and K. H. Raddatz (107) was shown to be *trans*-planar (181)).

3. Factors influencing the nickel–ligand bond type

Henceforth in this article it will be assumed that the stereochemistry of a four-covalent complex of Ni(II) may be inferred from the magnetism: i.e., diamagnetic complexes are square planar and paramagnetic are tetrahedral. The weight of evidence at present fully justifies the former conclusion and provides reasonable support for the latter. Several workers have discussed the factors which decide whether the arrangement of the bonds about the Ni(II) atom in a four-covalent complex will be tetrahedral or square planar. D. P. Mellor and D. P. Craig (123) have studied a large number of compounds and have summarized the results of other investigators. Assuming that the magnetic moment of four-covalent complexes is diagnostic of stereochemistry, it is concluded that in general, as the electronegativity of the attached groups increases, so the tendency to form tetrahedral rather than square complexes increases. Thus, four oxygen atoms invariably give the tetrahedral arrangement (except in the special case of $BaNiO_2$ discussed on page 276), but four sulfur atoms often give the planar arrangement.

The stereochemistry of the Ni(II) atom is more sensitive to the groups attached to the sulfur atom than it is to those attached to the oxygen atoms. If, for example, we attach two molecules of the chelate group $CH_3S(CH_2)_2SCH_3$ to the Ni(II) atom as in $[Ni(chelate)_2]Cl_2$, the complex salt is paramagnetic (3). However, potassium nickel bis(thioöxalate) is diamagnetic (123). The ability of sulfur to effect electron pairing in these compounds is affected in two main ways; these compounds illustrate both of these. Firstly, the sulfur atom in the bis(chelate) compound is *three*-covalent, using a lone pair of electrons from the sulfur atom for the S $\rightarrow$ Ni bond, whereas in the bis(thioöxalate) complex the sulfur atom is only *two*-covalent. Secondly, the charge on the complex ion differs in the two examples and this may be of major importance in affecting the bond type; in the bis(thioöxalate) complex the extra negative charge should act so as to *reduce* the effective difference in electronegativity between the nickel and sulfur atoms and hence tend to give a less polar bond. This favors the use of lower d orbitals with electron pairing. The effect of large differences in electronegativity in favoring the use of $4s4p^3$ bond orbitals in Ni(II) complexes is understandable in the light of theoretical studies (43).

However, it is probable that double bonding is also an important factor influencing the assumption of the square arrangement. The formation of double bonds by the nickel atom enables the latter to decrease some of the negative charge which would result if two coördinate σ bonds were formed. Using $3d$ electron pairs of the Ni(II) atom, and a vacant p or d orbital of the donor atom, two strong π bonds at right angles may be formed in a square nickel complex (43). The significance of this has been discussed by J. Chatt and A. A. Williams (35) and by J. Chatt (33) in regard to bivalent platinum compounds. L. Pauling (155) was the first to propose that the $3d$ electron-pairs of the metal atoms of the first transition series could form π bonds by overlapping of these orbitals with suitable vacant orbitals of carbon in complex cyanides and metal carbonyls or with p orbitals of nitrogen in complex nitrites. The extension to the elements of the second and later row donor elements in the Periodic Table which have vacant d orbitals was envisaged by Y. Syrkin and M. Dyatkina (186) and has been discussed recently in more detail by J. Chatt (37) and others (27, 38, 208). D. P. Mellor (121, 126) has suggested that where there is definite evidence that an element can form square complexes this shape will be assumed unless: (*i*) the element is octahedrally coördinated; or (*ii*) steric effects cause bond distortions; or (*iii*) the electronegativity difference is so large as to favor "ionic" (or sp^3) bonds. To these factors should be added the effect of double bonding.

An unusual kind of square coördination is shown by the compound $BaNiO_2$. The square coördination has been established by x-ray crystallography (110, 111), but the magnetic moment (1.8 Bohr magnetons) is unusually high for this stereochemical arrangement. It is apparent that sharing of oxygen atoms between Ni(II) atoms occurs, the anion being polymeric. It is probable that the bonds in this molecule are ionic rather than $3d4s4p^2$. The square arrangement is possible in crystal coördination with ionic bonds provided the correct radius ratio of the two atoms concerned is obeyed. The argument could be advanced that the high negative charge on the anion (two negative charges to each NiO_2 unit) reduces the electronegativity difference between oxygen and nickel sufficiently to permit the formation of square $3d4s4p^2$ bonds. This is made improbable, however, by the magnetic moment. On the other hand, as suggested for Cu(II) complexes (43), the binding might involve square $4s4p^24d$ orbitals. In any case the square arrangement in $BaNiO_2$ must be considered to arise from a cause different from that operative in diamagnetic complexes.

4. Effect of extramolecular environment of the molecule (or complex ion) on the stereochemistry of the nickel atom

There is a body of evidence to show that changes in the stereochemistry of a complex ion or molecule containing Ni(II) may occur (*a*) if the compound is dissolved in certain solvents, (*b*) if different anions are used so as to change the type of lattice, or (*c*) if a change in temperature occurs. The change in stereochemistry has, in all cases, been inferred from a change in magnetic moment and/or a change in the color of a compound.

(*a*) *The effect of solvents* has been studied by J. B. Willis and D. P. Mellor (210). Several Ni(II) complexes, all of which are non-electrolytes and diamagnetic in the solid state, were dissolved in various solvents such as pyridine, chloroform, alcohol, benzene, and dioxane and the magnetic moment measured in solution. The results varied with the solvent but, in general, changes in the moment were observed most frequently when the solvent was pyridine, an effect attributed by the authors to the coördinating ability of pyridine itself. In this case the solvent could be expected to react chemically with some square complexes. Thus, the compound bis(salicylaldoxime) nickel(II) is diamagnetic both in the solid state and in benzene solution; however, in pyridine solution the magnetic moment indicates two unpaired electrons. This paramagnetism was attributed to the formation of a bis(pyridine) octahedral complex; naturally one would not expect a change in coördination number to occur in solvent benzene by this mechanism, since the latter does not act as a donor molecule towards nickel. However, the compound bis(*N*-methylsalicylaldimine) nickel(II), which is diamagnetic in the solid state, develops paramagnetism even in benzene and chloroform solutions. The magnetic moment in these solvents varies from 2.2 to 2.4 Bohr magnetons; this is less than the moment required for two unpaired electrons. The authors suggest that this indicates an equilibrium between the square diamagnetic form and the tetrahedral paramagnetic form,—an explanation which seems to be very reasonable. This is supported by the fact that W. Klemm and R. R. Raddatz (107) have reported the isolation of two forms of this compound, one of which is diamagnetic and the other paramagnetic in the solid state; the latter, which was obtained accidentally, reverted to the diamagnetic form on standing in air for a few weeks. The formation of some of the paramagnetic form in benzene and chloroform solutions suggests that the planar arrangement in the solid state owes its existence, at least in part, to the operation of *inter*molecular constraining forces; once these are diminished by solution in benzene, the molecule assumes the shape of lowest potential energy for the *isolated* molecule. This means that, although the attached groups may wish to assume a tetrahedral arrangement, the square configuration may be adopted if the crystalline forces in the solid state are large enough to outweigh the difference in energy between the two possible stereochemical arrangements. Clearly a change in the size or shape of the anion might effect such a change in these lattice forces.

Lifschitz has investigated this subject and has shown that bis(formylcamphorethylenediamine) nickel(II) is paramagnetic in methanol, nitrobenzene, or methyl cyanide solution but diamagnetic in benzene and acetone (113, 114). Again there is some correlation with the donor properties of the solvent.

(*b*) *The effect of changing the anion* is well illustrated by the diamagnetism of the pink compound $[Ni(ethylenediamine)_2][AgIBr]_2$ in the solid state (75); in contrast to this, ethylenediamine Ni(II) complexes in solution are some shade of blue to violet and display paramagnetism. As all other complexes of ethylenediamine Ni(II) salts using anions like ClO_4^- etc. are paramagnetic in the solid state, the diamagnetism here must be attributed to the constraining effect of the anion used. The anion is almost certainly linear and the packing may well be such as to force the (preferred) tetrahedral arrangement into a planar one. Such a change is feasible if the difference in energy between the two forms is small.

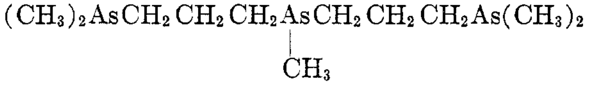
(*c*) *In four-covalent complexes increasing the temperature* should, by Le Chatelier's principle, favor a change over from the square planar to the tetrahedral arrangement. No detailed studies on such an equilibrium have yet been published, but the compound $[Ni(NO_3)_2 \cdot 2(C_2H_5)_3P]^0$ probably illustrates this phenomenon. K. A. Jensen (96) noted that whereas the solid compound is green and paramagnetic at room temperature, its alcoholic solution turns red on being cooled to the temperature of a bath of solid carbon dioxide and alcohol. The magnetic moment at this lower temperature has not been measured, but the red color suggests the formation of a square diamagnetic complex. The possible formation of $[Ni((C_2H_5)_3P)_4][NO_3]_2$ at low temperatures with the simultaneous formation of $Ni(NO_3)_2$ cannot be excluded until conductivity measurements have been carried out. Other examples of this diamagnetic–paramagnetic isomerism are discussed by Lifschitz and his collaborators (113, 114).

The differences in chemical properties between the square and tetrahedral complexes are also noteworthy. Generally speaking, the diamagnetic square compounds have little tendency to form six-covalent complexes by the addition of two ligands, whereas the tetrahedral complexes do this with ease (210). Nickel bis(acetylacetone), for example, readily acquires two molecules of water to form the paramagnetic six-covalent compound. With respect to oxidation, however, the converse is true. Provided there are strong bonds to the Ni(II) atom, the diamagnetic complexes can be oxidized without much difficulty to Ni(III) or Ni(IV) complexes, whereas no case in which a tetrahedral compound shows this behavior has been reported.

C. FIVE-COVALENT COMPLEXES

As shown in table 1, the formation of a square complex of Ni(II), involving the use of four $3d4s4p^2$ bond orbitals, leaves one $4p$ orbital of the nickel atom vacant. It appears feasible that this orbital might be used by one more ligand to give a five-covalent complex. This would involve the use of $3d4s4p^3$ hybrid orbitals, a combination which A. Daudel and P. Bucher concluded forms a square pyramid, the fifth bond being normal to the plane of the square (48) (*cf.* page 285). It has been suggested that this orbital is utilized to form a five-covalent complex, at least in the transition state, in order to explain the very rapid exchange of CN^- with $[Ni(CN)_4]^{--}$ ions (118). Although no solid complexes have been isolated, it was pointed out by N. V. Sidgwick (177) that the existence in solution of a complex cyanide of nickel with a coördination number greater than 4 may reasonably be inferred from the fact that an aqueous solution of $K_2Ni(CN)_4$ develops a deep red color when treated with a large excess of potassium cyanide. Sidgwick suggested that this might be a *hexa*cyanide ion; but if this were correct, and if six $3d^24s4p^3$ octahedral bonds were formed (see table 1), it would be necessary to promote two electrons to a $5s$ orbital. Such a promotion ought to lead to facile oxidation to Ni(III) and Ni(IV), forming a $[Ni(CN)_6]^{---}$ or $[Ni(CN)_6]^{--}$ ion but this has not been observed. Support for the hypothesis of Martell and Calvin (118) that the $[Ni(CN)_5]^{---}$ ion is formed in solution has recently been obtained from a spectrophotometric study of the absorption of the $[Ni(CN)_4]^{--}$ ion in the presence of varying amounts of excess cyanide ion (136). This work leads to the conclusion that a 1:1 complex ion of $[Ni(CN)_4]^{--}$ and CN^- ions is formed in solution. Further support is being sought from phase studies on the molten mixture. J. Crémoux and P. Mondain-Monval (43a) claim that on titrating $NiSO_4$ in aqueous solution with potassium cyanide a break is observed in the curve corresponding to the existence of the compound $K_4Ni(CN)_6$ in solution. They also claim that the existence of $K_4Co(CN)_6$ can be established by a similar technique. However, the work of Adamson (1) does not support the latter claim, and it therefore seems prudent to regard the existence of $K_4Ni(CN)_6$ as doubtful until more evidence in support is forthcoming.

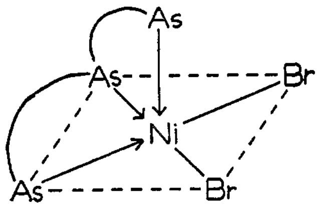
Five-covalence probably occurs in certain complexes of nickel bromide and iodide with the tritertiary arsine tridentate group shown in formula II (5), at



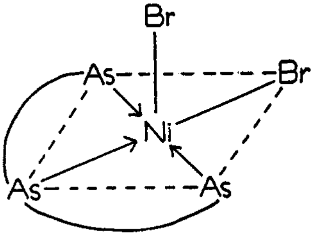
$$(CH_3)_2AsCH_2CH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{As}}CH_2CH_2CH_2As(CH_3)_2$$

II

least in solution. Complexes having the formula $NiBr_2$.triarsine and NiI_2. triarsine have been isolated; these are monomeric in nitrobenzene solution and in this solvent they are non-electrolytes, as shown by their low molecular conductivity. Assuming that all three arsenic atoms of the triarsine are coördinated to the nickel atom, the most logical conclusion is that the nickel atom is five-covalent, as shown in formula III or IV.



III



IV

Of these two possibilities III is considered the more probable in view of the fact that with other metals, e.g., univalent copper, the triarsine can attach itself at the corners of a triangular face. There remains, of course, the possibility that the triarsine is coördinated at two points only, forming a square complex. This is considered most unlikely, because (*a*) the compound does not display the reactivity and ease of oxidation in air which one would expect if one —$As(CH_3)_2$ group were free, and (*b*) the magnetic data indicate that in complexes such as $Fe(CNS)_3 \cdot$triarsine and $CoI_3 \cdot$triarsine the triarsine is attached at all three arsenic atoms to form a six-covalent complex. Furthermore, (*c*) when $NiBr_2 \cdot$triarsine is treated with bromine, the *nickel* atom and *not* one of the —$As(CH_3)_2$ groups is oxidized; the product is the Ni(III) compound $NiBr_3 \cdot$triarsine. Since the arsine groups are easily oxidized by free bromine, it follows that there are almost certainly no free —$As(CH_3)_2$ groups in the Ni(II) complex.

Support for the existence of five-covalent complexes using $3d4s4p^3$ bonds is provided by the existence of the cobaltous complex ion $[Co(CN)_5]^{---}$ in aqueous solution. It was shown by Adamson (1) that this ion has the expected unpaired electron in aqueous solution, indicating that the complex ion is monomeric (the diamagnetism of $K_3Co(CN)_5$ in the *solid* state can be attributed to dimerization with spin coupling). Furthermore, the existence of five-covalent Ni(III) in $NiBr_3 \cdot 2(C_2H_5)_3P$ (98, 99) is well established (see page 285).

All of the foregoing evidence for the possibility of five-covalent Ni(II) refers to compounds in solution and it should be pointed out that this shape need not necessarily be preserved in the solid state. The need for x-ray investigation of these compounds is therefore obvious.

D. SIX-COVALENT COMPLEXES

This is undoubtedly the most common class of nickel compounds. As with the four-covalent derivatives of Ni(II), it is again found that a subdivision into two types on the basis of magnetic susceptibility is convenient. Those of the paramagnetic type are by far the better known, few examples of the diamagnetic type having so far been reported.

1. *Paramagnetic six-covalent complexes*

A large number of compounds of the hexammine type are known, such as $[Ni(H_2O)_6]Cl_2$, $[Ni(NH_3)_6]Cl_2$, $[Ni(en)_3]Cl_2$, $[Ni(dipy)_3]Cl_2$, $[Ni(o\text{-phen})_3]Cl_2$. The ammines are not as stable as the corresponding complexes of tervalent cobalt, since they lose ammonia fairly easily, even on standing in air. Compounds of the pentammine type, $[Ni(NH_3)_5X]X$, have not been described but they probably exist in aqueous solution. In general the *hexa*-coördinated compounds are blue or green in color except when the Ni(II) atom is strongly coördinated, in which case a pink color is often observed. This occurs in the tris(dipyridyl) and tris(*o*-phenanthroline) complexes and in the compound $[Ni(NH_3)_4(NO_2)_2]^0$. There seems little doubt that the Ni(II) atom is six-covalent in the latter, since the $[Ni(NH_3)_4]^{++}$ ion is blue and the NO_2^- ion is colorless, thus suggesting that the salt-like formula $[Ni(NH_3)_4][NO_2]_2$ is improbable. Although certain of the diamagnetic six-covalent complexes are deeply colored (see page 283), there appears to be no simple correlation between color and bond type as with the four-covalent compounds. The intensity of the pink color of the dipyridyl compound is much less than that of the square diamagnetic compounds or of the compound $[Ni(diarsine)_3][ClO_4]_2$ discussed on page 283, the sharp band near 4000 Å. being noticeably absent. The stability of the nickel tris(*o*-phenanthroline) and nickel tris(dipyridyl) compounds may be associated with the possibilities for some double (π) bonding with the attached groups (27, 43) and this may explain the development of the pink color. Here the amount of double bonding is insufficient to effect electron pairing.

As with practically all six-covalent complexes which have been investigated, these compounds are octahedral. The evidence in support of this conclusion is as follows:

(*a*) *Optical resolution:* The resolution of the $[Ni(dipyridyl)_3]^{++}$ ion into *d*- and *l*-forms has been reported by several investigators (93, 135, 174). The $[Ni(o\text{-}phen)_3]^{++}$ ion has also been resolved (47). Attempts to resolve the tris(ethylenediamine) Ni(II) complex have been unsuccessful and the failure is attributed to a rapid racemization (24). This explanation is undoubtedly correct, for it has been shown (99b) that exchange of radioactive nickelous ion in water with $[Ni(en)_3]^{++}$ ions takes place very rapidly,—much faster than is the case with the corresponding dipyridyl or *o*-phenanthroline complexes.

(*b*) *X-ray crystallographic analysis:* Complete x-ray structure determinations on the following six-covalent Ni(II) complexes have established in all cases an octahedral arrangement of the attached groups: $[Ni(NH_3)_6]Cl_2$ (211), and the nitrate (212) (*cf.* 19 for the bromide, iodide, perchlorate, hexafluorophosphate, and fluosulfate of the $[Ni(NH_3)_6]^{++}$ ion); the $[Ni(H_2O)_6]^{++}$ ion in $(NH_4)_2Ni(SO_4)_2 \cdot 6H_2O$ (85) and in $[Ni(H_2O)_6][SiF_6]$ (76); the $[Ni(NO_2)_6]^{----}$ ion (58); $NiSO_4 \cdot 6H_2O$; and $NiSO_4 \cdot 7H_2O$ (8, 9). A small deviation from a regular octahedral arrangement of the attached groups has been observed in some of these complexes, particularly for the $[Ni(H_2O)_6]^{++}$ ion. This deviation takes the form of two coaxial bonds being slightly longer than the other four; P. L. Mukherjee (136a) has shown that in Tutton salts of the general formula $NiM^{\mathrm{I}}_2(SO_4)_2 \cdot 6H_2O$, the nickel atom is surrounded by an octahedron of water molecules, four of which lie nearly on the corners of a square, the nickel–oxygen distance being 1.9 Å. The other two water molecules lie on the normal through the center of the square, these two nickel–oxygen distances being 2.15 Å. This lack of symmetry is important in connection with explanations for the incomplete quenching of the orbital contribution in octahedral Ni(II) complexes. The electrical field resulting from this arrangement may be regarded as cubic with a small rhombic component (147). It is of interest to note that this asymmetry is a fairly general phenomenon for bivalent ions of the first transition series. A. D. Wadsley (202) has pointed out that a similar asymmetry occurs with certain bivalent manganese salts; similarly, the tendency for bivalent copper to acquire two slightly longer coaxial bonds normal to the plane of the four square ones has been discussed by A. F. Wells (207). A distorted octahedral arrangement also occurs in bis(glycine) nickel (II) dihydrate (182). In this molecule noticeable deviations from the normal 90° angle between adjacent bonds to the Ni(II) atom have been reported.

(*c*) *Magnetic moment:* The moments of a large number of paramagnetic six-covalent Ni(II) complexes have been reported, and in all cases these indicate that two unpaired electrons are present. A study of the effect of the electronegativity of the attached groups, and of different anions, upon the size of the moment in complexes of the type $[NiA_6]X_2$ has recently been carried out (101). It has been established that a change in electronegativity of the ligand has a small effect upon the size of the orbital contribution but that the effect of changing the anion is practically negligible. When the Ni(II) atom is surrounded by six identical groups, e.g., as in $[Ni(H_2O)_6]^{++}$ or $[Ni(NH_3)_6]^{++}$, it is found that the orbital contribution in excess of the "spin only" value of 2.83 Bohr magnetons is small, magnetic moments of the order of 3.1–3.2 Bohr magnetons being observed (101). Theory predicts (147, 200, 201) that if six groups be arranged octahedrally around an Ni^{++} ion, giving an essentially cubic field with a small rhombic component, then the orbital contribution should be smaller than for a tetrahedral arrangement. The small value of the orbital contribution in these complexes may thus be taken as consistent with an octahedral arrangement of the attached groups (see also Nyholm (142a)).

In these paramagnetic octahedral complexes the two unpaired electrons are obviously in the $3d$ shell; hence the binding is "ionic" and the use of $4s4p^34d^2$ bond orbitals is indicated. Both pictures lead to the same shape, because the arrangement of six charges around an atom so as to give the minimum electrostatic potential energy is a regular octahedron.

Although there has never been any doubt that the two unpaired electrons in complex ions like $[Ni(NH_3)_6]^{++}$ and $[Ni(H_2O)_6]^{++}$ are in the $3d$ shell (see figure 1), it has been proposed that the tris(dipyridyl) and tris(*o*-phenanthroline) ions involve $3d^24s4p^3$ bonds with promotion of two electrons to higher orbitals of the nickel atom. Thus, C. H. Johnson (99a; *cf.* Pauling (154)) suggested that the use of $3d^24s4p^3$ bonds is indicated for those octahedral complexes of the first transition series which can be resolved. However, there is no evidence to suggest that in the series H_2O < py < NH < en < dipy < *o*-phen, there is any point at which a sudden change of bond type to nickel occurs. The magnetic moment changes only slightly along this sequence and the absorption spectra indicate a steady movement of the absorption band towards the ultraviolet, the stability in water increasing in the order as shown. C. D. Russell, G. R. Cooper, and W. C. Vosburgh (171, 173) suggest that the small but perceptible change in the magnetic moment is due to increasing stability, but another possible explanation is that along this sequence the electronegativity of the attached groups is gradually decreasing and the change in magnetic moment may arise from a decrease in the orbital contribution owing to a change in the intensity of the crystalline field operating. However, this may well be saying the same thing in a different way.

The fact that the dipyridyl and *o*-phenanthroline complexes may be resolved does indicate considerable optical stability and hence strong bonds; however, the strong bonds to these chelate groups might arise from double bonding between the nickel atom and the nitrogen atom (27). Of greater significance still is the location of the two electrons if they were promoted to enable the use of $3d^24s4p^3$ bonds. In the normal process of atom building, when a $4p$ shell is filled the next two electrons go, not into $4d$ orbitals, but into a $5s$ orbital in which they are paired. Thus, the electronic configuration of the strontium atom is $1s^23s^22p^63s^23p^63d^{10}4s^24p^65s^2$ not . . . $4p^64d^2$, and it is reasonable to expect that a similar state of affairs would obtain in an octahedral Ni(II) complex when promotion of two electrons takes place. Furthermore, it follows that such a complex would be diamagnetic and should be capable of oxidation to a higher valence state of nickel, since removal of the two $5s$ electrons should be relatively easy. The fact that $[\mathrm{Ni(dipyridyl)_3}]^{++}$ ion has not been oxidized in this way suggests that no promotion, even to $4d$ orbitals, occurs. This theory finds support from the fact that a diamagnetic complex of octahedral Ni(II) has been described recently in which this promotion to $5s$ orbitals appears to take place (see page 283).

Some octahedral bivalent nickel complexes with sexadentates fall into this paramagnetic group. F. P. Dwyer, F. Lions, and D. P. Mellor (54) have prepared Ni(II) complexes of 3,6-dithia-1,8-bis(salicylideneamino)octane and of the corresponding 2-hydroxy-1-naphthylmethylene derivative. In these complexes the high electronegativity of some of the attached groups leads to paramagnetism, owing to the preference of these groups for "outer" ($4d$) orbitals for binding.

2. Diamagnetic six-covalent complexes

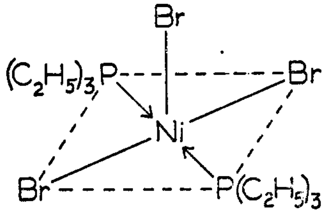
Only one definite compound of this class has been described (140). When air is bubbled for a long time into a hot alcoholic solution of the red, diamagnetic complex $[\mathrm{Ni(diarsine)_2}]\mathrm{Cl_2}$, a Ni(III) compound, $[\mathrm{NiCl_2(diarsine)_2}]\mathrm{Cl}$, discussed under Ni(III), is precipitated. However, after removal of the latter the solution is still intensely red and on addition of perchloric acid a deep red compound of the formula $[\mathrm{Ni(diarsine)_3}][\mathrm{ClO_4}]_2$ is precipitated. The substance differs from the square complex $[\mathrm{Ni(diarsine)_2}][\mathrm{ClO_4}]_2$, among other properties, by its much greater stability to water and more intense absorption spectrum. It is clearly an octahedral tris(chelate) complex analogous to the corresponding cobaltous complex $[\mathrm{Co(diarsine)_3}][\mathrm{ClO_4}]_2$ (27). The nickel compound is diamagnetic and hence presumably utilizes $3d^24s4p^3$ orbitals, as discussed in the preceding paragraph. The postulated promotion of the two electrons to higher orbitals is supported by the fact that the complex may be oxidized by chlorine to a higher valence state of nickel. As might be expected, highly charged ions such as $[\mathrm{Ni(diarsine)_3}]^{++++}$ are unstable; hence loss of one molecule of the chelate group takes place readily to give the Ni(III) complex ion containing two halogen atoms. The optical resolution of the $[\mathrm{Ni(diarsine)_3}]^{++}$ ion is being studied (27) with a view to confirming the postulated octahedral arrangement. The latter rests at the moment on the analysis and chemical properties of this compound. There are at least two other known compounds which probably fall into this class—the green form of $NiI_2 \cdot (diarsine)_2$ (64) and the purple compound $[Ni(triarsine)_2][ClO_4]_2$ (4); the triarsine in the latter is shown in formula II (page 279). The former is prepared by treating an aqueous solution of the red salt $[Ni(diarsine)_2]Cl_2$ with excess potassium iodide. A green diamagnetic precipitate is obtained which has the above formula. This compound is soluble in chloroform but the solution slowly deposits a brown compound having the same empirical formula; the brown form may be obtained instantly by treating the green compound with alcohol or acetone. The brown substance is undoubtedly the salt $[Ni(diarsine)_2]I_2$, whereas the solubility of the green form in chloroform supports the view that it is the non-electrolyte $[NiI_2(diarsine)_2]^0$. The purple compound, $[Ni(triarsine)_2][ClO_4]_2$, is diamagnetic; its conductivity in nitrobenzene indicates that three ions are formed in this solvent. Obviously it could be either a square compound of Ni(II) with one —$As(CH_3)_2$ group of each triarsine not coördinated or a six-covalent complex. Four-covalence is considered improbable for the reasons discussed in Section II,C. By way of comparison, the magnetic moment of the corresponding Co(II) compound is <2.02 Bohr magnetons; this is the usual value observed for octahedral $3d^24s4p^3$ Co(II) complexes with a small orbital contribution (64b) (see table 1). On the other hand, square-coördinated four-covalent Co(II) complexes generally have moments in the range 2.1–2.9 Bohr magnetons, because in these complexes the unpaired electron is in a $3d$ rather than a $5s$ orbital and the orbital contribution is much less fully quenched. The compound $[Ni(triarsine)_2][ClO_4]_2$ may be oxidized, presumably to a higher valence state of nickel, but the product of oxidation is unstable and decomposes quickly, probably owing to intramolecular oxidation and reduction.

III. THE TERVALENT STATE OF NICKEL

Although there had been earlier reports of compounds containing tervalent nickel, it is only during the past ten years that this valence state has become generally accepted. The reason for this is now plain. Unless one uses fluorine for the oxidation, in which case quadrivalent nickel complexes are formed, the preparation of complexes of nickel in higher valence states usually involves the oxidation of a square Ni(II) compound. The groups which form square Ni(II) complexes are those of low electronegativity, and usually these are able to form double bonds with the metal atom. Examples include P(III) in tertiary phosphines, As(III) in tertiary arsines, and S(II) in thiols; N(III) can also be effective, but usually structures involving the —N= group are necessary. This enables the nitrogen atom, by suitable bond rearrangement, to form double bonds with the nickel atom. The ligands containing these groups are usually quite strong reducing agents; hence when a complex containing them is oxidized, there is always the possibility that the ligand itself, rather than the metal, undergoes oxidation; indeed, this does occur unless strong metal–ligand bonds are present. Much of the controversy in the past has centered around this problem. Fortunately there is, in the case of Ni(III), one simple confirmatory test for the valence state. As may be seen from table 1, the Ni^{+++} ion will contain three unpaired electrons if Hund's rules are obeyed. Thus, provided there is only one nickel atom present per molecule, "ionic" Ni(III) complexes will contain three unpaired electrons. If electron pairing *does* take place, then one unpaired electron must always be present, since the total number is uneven. (The proviso of only one nickel atom per molecule is mentioned, because metal–metal spin coupling is feasible in certain polymeric compounds.) Of the two possibilities one would normally expect to find only one unpaired electron, because the ligands which stabilize Ni(III) are just those which favor electron pairing. Furthermore, as the valence of a metal increases, so does its tendency to form complexes with electron-pairing increase (*cf.* Co(III) with Co(II)). It is unfortunate that the magnetic criterion was not used more frequently in earlier investigations. The complexes of Ni(III) will be discussed here, but higher oxides in which the valence of nickel might be three will be considered under quadrivalent nickel.

A. FIVE-COVALENT COMPLEXES

The first clearly defined Ni(III) compound was described by K. A. Jensen (96). When the red, planar compound $[NiBr_2 \cdot 2(C_2H_5)_3P]^0$ (bis(triethylphosphine) dibromo nickel(II)) was treated with bromine a violet substance having the formula $NiBr_3 \cdot 2(C_2H_5)_3P$ was obtained. This was shown to be monomeric in freezing benzene; this is most readily explained by assuming that the nickel atom is five-covalent. Later (98) it was shown that the compound is paramagnetic, containing one unpaired electron per nickel atom (μ = 1.7–1.9 Bohr magnetons); this supports the tervalency assigned to the nickel atom. From the electric dipole moment (2.5 D) it was concluded that the bipyramidal structure could be excluded and the square pyramid arrangement shown in formula V was proposed. Support for this structure was adduced on theoretical grounds also. As may be seen from table 1, the most probable bonding orbitals are $3d4s4p^3$ if the unpaired electron is still in the $3d$ shell. For an arrangement such as this, involving a d orbital having a principal quantum number one *less* than that of the s and p electrons, A. Daudel and P. Bucher (48) have shown that a square pyramid is to be expected. Kimball (102) gives only the bipyramid for the combination dsp^3, but in his analysis no attempt was made to distinguish between "upper" and "lower" d orbitals in the hybridization. The square pyramid arrangement could also arise if the bonding orbitals were $3d^24s4p^2$, the unpaired electron being promoted. There appears to be no easy way of distinguishing between these possibilities. The instability of the compound makes x-ray de-

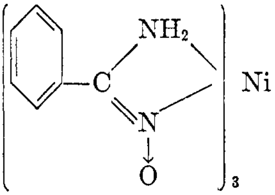


V

terminations of structure difficult. This is unfortunate, because the high atomic polarization of this type of compound introduces an arbitrary factor into the calculated dipole moment and a consequent element of uncertainty concerning the stereochemistry. In this instance, however, there seems little doubt that the square pyramid structure is correct.

Several other complexes which are formed by oxidizing square Ni(II) complexes with halogens probably have the same shape. A good deal of work has been done on the oxidation of Ni(II)glyoxime complexes, but the conclusions of the various workers are conflicting. F. Feigl (59) suggested that the red solution obtained by treating bis(dimethylglyoxime) nickel(II) with oxidizing agents in the presence of ammonia contained Ni(III) or Ni(IV), but A. Okac and M. Polster (146) disagreed with this conclusion. These workers asserted that the oxime rather than the Ni(II) atom is oxidized and claim that the red precipitate which is formed on neutralization of the oxidized solution is obtained only when lead dioxide is used as the oxidizing agent. Furthermore, they claim that the precipitate always contains some lead. Earlier, K. A. Hofmann and E. Ehrhardt (86) claimed to have isolated a complex Ni(III) salt of formoxime, *viz.*, $Na_3[Ni(CH_2NO)_6]$, but K. A. Jensen (209) reported that the compound is diamagnetic. This could mean that the compound contains both Ni(II) and Ni(IV), but the nickel is clearly not tervalent.

One of the earliest claims for the isolation of six-covalent Ni(III) is that of J. V. Dubsky and M. Kuras (51). These workers claimed that oxidation by air in aqueous solution of the complex formed between benzamidoxime and nickel salts yielded a deep purple Ni(III) complex apparently having the following formula:

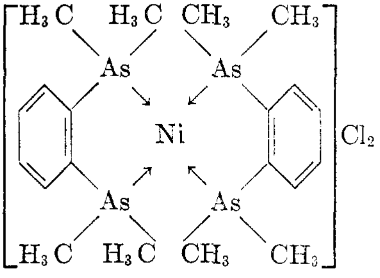


It was also reported that hydrogen peroxide gave the same product but that the oxidation to Ni(III) took place more rapidly. As pointed out earlier (*vide* table 1) Ni(III) complexes should be paramagnetic irrespective of their stereochemistry. L. Malatesta (116) repeated the preparation of this benzamidoxime compound and showed that it is diamagnetic. If the analysis is correct, this can be explained either (*a*) by assuming that the ligand itself has undergone oxidation or (*b*) by postulating that the complex contains square diamagnetic Ni(II) and diamagnetic octahedral Ni(IV) in equal amounts. K. A. Jensen (209) considers that the second explanation is probable in many cases, but a more thorough investigation of this compound is required before any conclusion can be arrived at.

Although the reaction between nickel(II) oxime complexes and oxidizing agents, e.g., bromine, has been used as the basis for the analytical determination of nickel (60, 172), the nature of the highly colored oxidation product has not been finally settled. In particular, a magnetochemical study of the oxidized solutions is desirable. This might at least establish whether Ni(III) is present; however, the magnetic moment does not distinguish between octahedral Ni(IV) and square Ni(II) because both are diamagnetic. When a Ni(II) oxime complex is oxidized in the solid state with an anhydrous oxidant, the formation of a Ni(III) complex is more feasible, since hydrolysis is precluded. Such oxidations have been studied by K. A. Jensen (209); a tribromide of bis(dimethylglyoxime) nickel(II) has been prepared which has a magnetic moment corresponding to one unpaired electron. K. A. Jensen concludes that the nickel is tervalent. L. Edelman (56) has also studied the oxidation of Ni(II) glyoxime compounds with halogens under anhydrous conditions. A dark brown monobromide and monoiodide of Ni(II) α-benzildioxime was isolated but no magnetic moments were reported. K. A. Jensen (209) states that the monobromide is diamagnetic, but the paramagnetism characteristic of Ni(III) has also been observed (149). This disagreement could arise from the fact that the properties of this compound seem to depend on the method of preparation. It is being investigated further. On heating, these bromides revert to the original red Ni(II) complexes.

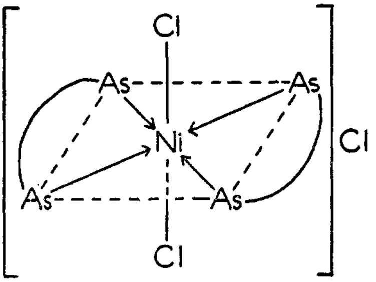
B. SIX-COVALENT COMPLEXES

Using as the ligand the strongly coördinating ditertiary arsine chelate group, *o*-phenylene(bisdimethylarsine), (*cf.* formula I, page 275) a series of stable Ni(III) complexes has been described recently (140) in which the metal atom is apparently octahedrally coördinated. Treatment of nickel chloride in alcoholic solution with the diarsine yields the red diamagnetic Ni(II) complex shown in formula VI; this is thus square planar. When this compound is treated with suitable oxidants, a greenish brown compound is precipitated having the empirical formula $NiCl_3 \cdot 2$diarsine. Air in the presence of hydrochloric acid is more suitable than chlorine for the oxidation; otherwise some Ni(IV) or decomposition products may be formed. This compound is formulated as the octahedral *salt*



VI

$[Ni^{III}Cl_2(diarsine)_2]Cl$ (formula VII) on the basis of its physical properties and chemical reactions.



VII

These may be summarized as follows: (*a*) the compound is soluble in water, in which its molecular conductivity (before slow decomposition occurs) is that usually observed for a uni-univalent electrolyte; (*b*) hydrochloric acid precipitates the complex from aqueous solution, indicating that at least some of the chlorine is ionized; (*c*) sulfur dioxide causes the green solution to turn red and the solution then contains the $[Ni(diarsine)_2]^{++}$ ion. This indicates reduction either of a higher valence state of nickel or of an oxidation product of the ditertiary arsine; (*d*) potentiometric oxidation of the $[Ni(diarsine)_2]^{++}$ ion requires one equivalent of an oxidant (ceric sulfate), indicating a valence change of one; (*e*) argentometric titration in cold alcohol causes loss of all chlorine, but a definite inflection after one chlorine atom has been precipitated indicates that one chlorine is more reactive than the other two; (*f*) chemical derivatives may be prepared in which the ClO_4^- or $\frac{1}{2}PtCl_6^{--}$ groups replace only one of the chlorine atoms, showing that one of these only is ionized; (*g*) the paramagnetic susceptibility of the compound, and of the perchlorate derivative, indicates one unpaired electron per nickel atom (μ = 1.9 Bohr magnetons); (*h*) similar oxidation by air of the corresponding Fe(II) and Co(II) complexes of this ditertiary arsine also yields compounds of Fe(III) and Co(III) of the type $[M^{III}Cl_2(diarsine)_2]Cl$.

It is concluded, therefore, that the nickel atom is tervalent. The corresponding bromide, $[NiBr_2(diarsine)_2]Br$, and thiocyanate, $[Ni(CNS)_2(diarsine)_2]CNS$, have been prepared and the magnetic moments again indicate tervalent nickel. It is not known whether the two halogen atoms are *cis* or *trans* in these octahedral complexes, but they are probably *trans*.

The bonding orbitals used in these compounds and the location of the unpaired electron are of great interest. It seems most probable that the bonding is $3d^24s4p^3$ with promotion of the single unpaired electron to a 5*s* orbital. This formulation is supported by the fact that the chloro and bromo complexes may be oxidized further to Ni(IV) compounds, and also by the fact that the magnetic moment is not much in excess of the spin only value for one unpaired electron (1.73 Bohr magnetons). For octahedral complexes containing only one unpaired 3*d* electron the moment is usually considerably greater than 2.0 Bohr magnetons, owing to an appreciable unquenched orbital contribution. Thus, in the isoelectronic sequence Cr(I), Mn(II), and Fe(III) the magnetic moments of the "covalent" octahedral complexes (all of which contain one unpaired 3*d* electron) are greater than 2.0 Bohr magnetons, e.g., [Cr(dipyridyl)$_3$]ClO$_4$, μ = 2.0–2.1 Bohr magnetons (78); for the [Mn(CN)$_6$]$^{----}$ ion, mean μ = 2.11 Bohr magnetons (67); for the [Fe(dipydridyl)$_3$]$^{+++}$ ion, μ = 2.3–2.4 Bohr magnetons (27). However, an *s*-electron should have no orbital contribution and hence a μ of 1.7–1.8 Bohr magnetons. The value of 1.9 Bohr magnetons for the above Ni(III) complexes might well reduce to nearer 1.7 Bohr magnetons if the θ correction in the Curie–Weiss equation, magnetic susceptibility $= C/T + \theta$, were measured. At least the low orbital contribution supports the promotion hypothesis (*cf.* 64b).

K. A. Jensen and B. Nygaard (99) have postulated that Ni(III) complexes are formed as intermediates in the spontaneous oxidation of mono-, di- and triaminoguanidine Ni(II) compounds by air. This spontaneous exothermic absorption of atmospheric oxygen illustrates the remarkable ease with which some of the square Ni(II) compounds may be oxidized; it also shows that the oxidation of [Ni(diarsine)$_2$]$^{++}$ by air in hot solution is not as unusual as it at first seems to be.

It is of interest to compare the relative ease with which square complexes of bivalent iron, cobalt, and nickel tend to reach the six-covalent state. In the case of iron the square arrangement is observed only when special steric requirements operate which force the four bonds into one plane, e.g., as in the ferrous porphyrin complexes. These tend to become six-covalent fairly easily; thus, the ferrous hemoglobin complex combines with carbon monoxide or oxygen readily to form six-covalent derivatives.

Square cobaltous complexes are well known for the ease with which they undergo oxidation (124). Also, the tendency for some of the square complexes of Co(II) with quadridentate groups to increase the coördination number is well illustrated by the "oxygen-carrier" complexes investigated by M. Calvin, R. H. Bailes, and W. K. Wilmarth (29) and also by C. H. Barkelew and M. Calvin (6). The bis(salicylaldehydeëthylenediamine) cobalt (II) complex absorbs atmospheric oxygen so rapidly that the magnetic moment must be measured in the absence of air; in the presence of oxygen it slowly falls from that required for one unpaired electron until it reaches zero, a value usually characteristic of tervalent cobalt. Nickel undergoes oxidation much less readily than Co(II) and unless the Ni(II)–ligand bonds are very strong the net result is oxidation of the ligand itself instead of the metal, even though the formation of Ni(III) compounds may be the first step in this process. In the search for different kinds of Ni(III) complexes this point needs to be kept in mind; if (*i*) use is made of a ligand whose coördinating groups are of low electronegativity, in order to form square $3d4s4p^2$ complexes, and (*ii*) the metal–ligand bonds are sufficiently strong, it should be possible to isolate many more compounds of nickel in this valence state.

Finally it has been suggested that certain naturally occurring ores of nickel contain the metal in the tervalent state. Arsenical nickel glance, NiAsS, has a pyrites type of structure in which the nickel atom is octahedrally coöordinated

(206). L. Pauling (155) assumed that the nickel is tervalent but pointed out that the orbital used by the expected unpaired electron was unknown. P. Rây and D. N. Sen (169) determined the magnetic moment of a specimen of this substance and obtained a value of μ = 1.85 Bohr magnetons. However, analysis of the specimen used showed that about one-third of the nickel atoms had been replaced by iron and cobalt atoms; this makes the interpretation of the moment more difficult. If both the substituting metal atoms also occur in the tervalent state, and if the binding uses $3d^24s4p^3$ bond orbitals, the number of unpaired electrons expected for these will be: Fe(III), one; Co(III), nil. Hence unless the problem is affected by partial metallic character, the conclusion that the nickel atom is tervalent most satisfactorily accounts for the observed moment. In kupfernickel or red nickel ore (NiAs), which crystallizes in the nickel arsenide structure, each nickel atom is again octahedrally coördinated (206) and μ = 0.7 Bohr magneton. This is interpreted by P. Rây and D. N. Sen to mean that the binding in the crystal is largely metallic; hence chemical valence does not arise and the nickel atom is not tervalent.

IV. THE QUADRIVALENT STATE OF NICKEL

By analogy with palladium and platinum, both of which give rise to quadrivalent octahedral complexes, diamagnetic compounds of this valence state for nickel might be expected. The failure to obtain such complexes until recently was generally explained by the fact that for the vertical triads of Group VIII (Fe, Ru, Os; Co, Rh, Ir; Ni, Pd, Pt) the higher valence states become progressively less stable as the atomic number of the metal decreases. Nevertheless, the number of quadrivalent nickel complexes which have now been described establishes that, given the right conditions, this valence state may be stabilized fairly easily. In general, a higher valence state may be stabilized either by the use of a very electronegative group with a high electron affinity and hence oxidizing power, e.g., fluorine, or by coördinating the metal with a suitable coördinating agent which changes the oxidation–reduction potential by forming strong covalent bonds with the element. Both methods may be used to obtain Ni(IV).

The valence state of nickel in its higher oxides has not yet been settled. When nickel salts are treated with chlorine in alkaline solution a black, hydrated oxide is precipitated, the formula of which varies from $NiO_2 \cdot xH_2O$ to $NiO \cdot xH_2O$. The importance of these compounds as depolarizers in the iron–nickel accumulator has led to a considerable amount of work in order to determine their structures and the valence state of the nickel atom. It has been claimed by several workers that these higher oxides are stable only if hydrated and that no anhydrous oxide containing more oxygen than in NiO exists (91, 115, 189). G. F. Huttig and A. Peter (91) concluded from the similarity of behavior of the hydrated Ni_2O_3 oxide and the compound $Co_2O_3 \cdot H_2O$, when they are heated, that the nickel was tervalent. However, compounds can be prepared in which the ratio of oxygen to nickel is nearly as high as 2.0 (13, 14, 20). R. W. Cairns and E. Ott (28) concluded from a study of the *K* edge of the x-ray absorption spectrum that the nickel atom is tervalent in the hydrated higher oxide. N. V. Sidgwick (179) has summarized the experimental work; he suggested that a hydrated Ni(III) oxide definitely exists but maintained that any oxygen in excess of this is held in the form of peroxide links. J. W. Mellor (127), on the other hand, concluded that there is no definite oxide between hydrated NiO and NiO_2 and considers that $Ni_2O_3 \cdot xH_2O$ is a mixture of these two. This is the opinion also of E. E. Vainshtein (196). From an examination of the K absorption edge x-ray lines of Ni, $NiSO_4$, NiO, Ni_2O_3, NiS, and Ni_3S_4, it was concluded that NiO and NiO_2 are the only true oxides, Ni_2O_3 being a mixture. This is based on the assumption that if a compound has its exact stoichiometric composition the K_{α_1} and K_{α_2} lines are symmetrical. Any asymmetry is ascribed to the presence of nickel in more than one valence state. This K_α line asymmetry occurs in the case of Ni_2O_3; hence it is concluded that both Ni(II) and Ni(IV) are present. From their study of the iron–nickel accumulator Von O. Glemser and J. Einerhand (66) claim that NiO_2 exists in the charged cell and that this reverts to Ni(III) on discharge. Unfortunately, magnetic data are not helpful in this problem because of the high magnetic concentration of the nickel. In any case paramagnetism could arise from unpaired electrons on the oxygen atoms if these were present in peroxide structures. It is concluded that the valence of the metal atom in these higher oxides cannot be considered as settled.

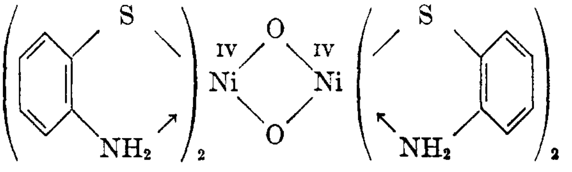
Until recently there was uncertainty also in regard to the valence state of nickel in the alkali nickelates. These are made by fusing NiO with potassium hydroxide in the presence of an oxidizing agent such as potassium nitrate or potassium chlorate. Green melts are obtained to which various formulas such as K_2NiO_4 (see later) have been assigned (67, 68, 69, 70). These compounds have been further investigated by J. J. Lander and L. A. Wooten (110, 111); from both magnetic measurements and x-ray diffraction studies on the compound of formula $BaNiO_3$, which was obtained as a black powder, it was concluded that the nickel atom in the compound is quadrivalent. The nickel atom is octahedrally coördinated and the use of $3d^24s4p^3$ bonds is inferred from the magnetic moment, which corresponds to 0.8 unpaired electron; although the authors attributed this to partial ionic character in the bonds, it seems more likely to be due to impurities.

As long ago as 1907, R. Hall (73) reported the isolation of quadrivalent nickel as a complex heteropolymolybdate of the formula $3BaO \cdot NiO_2 \cdot 9MoO_3 \cdot 12H_2O$. This compound is purple in color and is a strong oxidizing agent. Recently it has been shown (165) that the compound is diamagnetic, a result which supports the view that the nickel atom is quadrivalent. The isolation of a dark purple periodate of the formula $Na(K)NiIO_6 \cdot xH_2O$ has also been reported by P. Rây and C. Sarma (167, 168). The small magnetic moment of this compound (1.1–1.3 Bohr magnetons) is attributed to a small amount of dissociation and it is claimed that the nickel atom is octahedrally coördinated to six oxygen atoms, some of which are shared between nickel atoms. No x-ray measurements are available in support of this proposed structure.

The higher valence state of the transition metals may often be stabilized as the simple or complex fluorides. Recently quadrivalent cobalt as the black K_3CoF_7 and tervalent copper as green K_3CuF_6 have been reported (105). A red complex nickel fluoride, K_2NiF_6 (18, 105), has also been prepared. This substance is diamagnetic (88, 143). The diamagnetism clearly indicates the use of $3d^24s4p^3$ octahedral bonds, as in table 1. This result is rather unexpected, since the isoelectronic K_3CoF_6 is found to contain the four unpaired electrons expected for the free Co^{+++} (129). However, with Co(III) very electronegative groups are necessary in order to maintain the maximum multipicity, as illustrated by the fact that even the $[Co(H_2O)_6]^{+++}$ ion is diamagnetic (2, 188). In the complex Ni(IV) fluoride, nickel shows marked similarity to the corresponding platinum compound, K_2PtF_6, which is also diamagnetic (122, 143). This is in keeping with the generalization that iron, cobalt, and nickel resemble the elements of higher atomic weight in Group VIII most in the compounds in which *"covalent"* bonds are formed but resemble one another in simple salts or in complexes in which the bonds are *"ionic."*

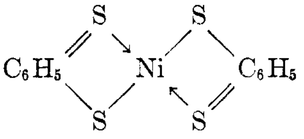
In the foregoing Ni(IV) complexes stabilization is effected by using very electronegative ligands (fluorine, oxygen), but, provided certain conditions are satisfied, this stabilization is possible with attached groups of low electronegativity. As discussed on page 266, the use of $3d^24s4p^3$ bond orbitals involving the use of "inner" *d* orbitals is favored by groups of low electronegativity. However, as with Ni(III) it is essential that very strong bonds be formed between the ligand and the nickel atom, because any tendency towards dissociation will result in oxidation of the ligand itself. The coördination of groups which are reducing agents with metals in high oxidation states may often be effected provided the method of preparation is indirect, i.e., by the oxidation of a complex of the metal in its lower valence state. Thus, complexes of Pt(IV) may be obtained with tertiary phosphines, e.g., $PtCl_4 \cdot 2(C_2H_5)_3P$ (32), or with tertiary arsines (139), e.g., $PtX_4 \cdot 2(C_2H_5)_3As$ (where X = Cl, Br, and I), in spite of the fact that the ligands are very powerful reducing agents in the free state. The preparation is effected by oxidation of the square platinous compounds. In the case of Ni(IV) it is necessary to use chelate groups in place of the simple trialkylphosphines or trialkylarsines, since with these oxidation to the tervalent state only may be effected. Thus, if the Ni(III) complex $[NiCl_2(\text{diarsine})_2]Cl$ is suitably oxidized, e.g., with concentrated nitric acid, a deep blue compound of the formula $[NiCl_2(\text{diarsine})_2][ClO_4]_2$ may be prepared (141). This compound has the expected oxidizing action of Ni(IV) and may be reduced to the original Ni(III) complex by treatment with sulfur dioxide or other reducing agents. The conclusion that the Ni(III) atom, rather than the chelate group, has been oxidized is supported by the fact that the blue oxidation product is diamagnetic, as expected of Ni(IV). When the susceptibility is corrected for diamagnetism, a magnetic moment of about 0.7 Bohr magneton is obtained. This small residual moment is not unusual, being observed even with Co(III) complexes; it probably arises partly from traces of impurity formed by decomposition and partly from the uncertainty of the diamagnetic correction. The drastic method of preparation might be expected to result in some decomposition. Oxidation with chlorine is undesirable, since the Ni(III) complex must be dissolved in water and this leaves the way open for dissociation and consequent partial oxidation of the tertiary arsine groups. A corresponding bromo complex, $[NiBr_2(diarsine)_2][ClO_4]_2$, has been prepared also. These complexes are undoubtedly octahedrally coördinated, but the arrangement of the two cationic halogen atoms is unknown; they are presumably *trans* but x-ray examination is needed to establish this. The remarkable stabilization of the higher valence states effected by this chelate group is reflected in the oxidation potentials. These have been estimated as +0.7 v. for the system $[Ni^{II}(diarsine)_2]^{++}/[Ni^{III}Cl_2(diarsine)_2]^{+}$ (140) and +1.1 v. for the system $[Ni^{III}Cl_2(diarsine)_2]^{+}/[Ni^{IV}Cl_2(diarsine)_2]^{++}$ (141).

W. Hieber and R. Bruck (83) have described a series of Ni(IV) complexes with chelate groups such as *o*-mercaptoaniline (*o*-aminothiophenol) and with other thio acids. With *o*-aminothiophenol a deep blue binuclear complex was isolated which is formulated with an oxygen bridge between the two nickel atoms as shown in formula VIII.

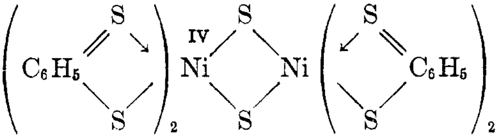


VIII

Similar binuclear complexes have been isolated using thiobenzoic acid, C_6H_5CSSH, which reacts readily with bivalent nickel to form the Ni(II) compound shown in formula IXa. Treatment of this with sulfide ions in alkaline solution in the presence of air as the oxidizing agent finally yields a deep violet complex of Ni(IV) (formula IXb). In this instance the two sulfur atoms form the bridge between the two Ni(IV) atoms. In the absence of oxidizing agents, but in the presence of groups which can stabilize zerovalent nickel, disproportionation of the Ni(II) complex (IXa) will occur, producing Ni(0) as $Ni(CO)_4$ and Ni(IV) as the bridged complex shown in formula IXb. H. J. Emeleus and



IXa

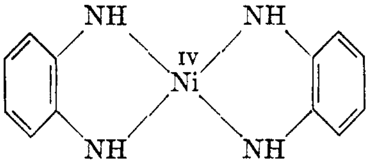


IXb

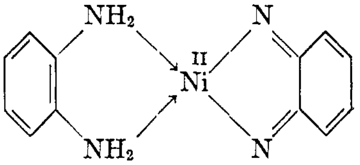
J. S. Anderson (57) point out that this disproportionation of Ni(II) complexes also occurs with simple square compounds such as nickel (II) bis(dimethylglyoxime). When treated with carbon monoxide, $Ni(CO)_4$ and an Ni(IV) complex is produced. The latter is promptly reduced by the excess carbon monoxide to form the original Ni(II) complex. Since this now reacts again, it follows that yields of 100 per cent of $Ni(CO)_4$ are theoretically possible. In practice, yields of up to 90 per cent of the calculated amount of nickel carbonyl have been obtained.

It is most probable that Ni(IV) complexes of oximes can be prepared but, as discussed under Ni(III) above, the valence state of 4 in oxime complexes cannot yet be regarded as unambiguously established.

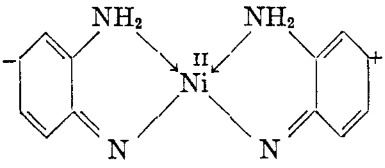
The problem of deciding for certain the valence state of the nickel atom in oxidized complexes is illustrated by the deep purple compound of nickel and *o*-phenylenediamine which is formed by oxidation by air in ammoniacal solution; this was first studied by F. Feigl and M. Furth (61).



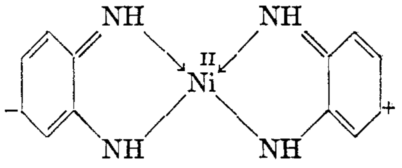
Xa



Xb



Xc



Xd

The compound has marked oxidizing properties and liberates two equivalents of iodine from iodides in acid solution. F. Feigl proposed that the complex had the structure shown in formula Xa, the nickel atom being quadrivalent. However, this formula is difficult to accept for several reasons. If the metal atom is quadrivalent, one would expect six- rather than four-covalence; also, no evidence in support of the proposed type of structure was advanced. It has recently been shown (64) that the compound is a non-electrolyte in acetone solution and that it is diamagnetic. The latter makes formula Xa untenable, because, according to Pauling's theory, square Ni(IV) should contain two unpaired electrons. The molecular weight of the compound is unknown, but if the nickel atom is four-covalent, it is more likely that the metal is bivalent. Any of the formulations shown in formulas Xb, Xc, and Xd, all involving Ni(II), could explain the oxidizing power of the complex whilst presenting a more probable kind of nickel–nitrogen bond. Infrared measurements (64) indicate that no amino groups are present, thereby excluding formulas Xb and Xc. The intense purple color may be correlated with the conjugation of double bonds. It is possible, however, that the compound is polymeric, dissolving only in those solvents which break the structure. There is little doubt that the too ready postulation of rather improbable structures involving higher valence states led to an even greater reluctance than usual in many quarters to accept the possibility that nickel was ever ter- or quadrivalent at all.

Valence states of nickel greater than four

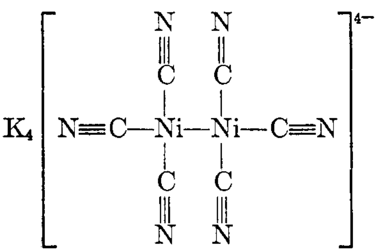
Several rather doubtful claims have been made for the isolation of nickel compounds in which the valence state of the metal atom is greater than 4 (127).

D. K. Goralevitsch (68, 69, 70) reported the preparation of a green Ni(VI) compound of the formula K_2NiO_4, which he obtained by fusing nickel oxide with a mixture of potassium hydroxide and either potassium nitrate or potassium chlorate. J. J. Lander and W. Wooten (110, 111), however, found that although they could isolate a Ni(IV) complex from such a melt, no evidence for Ni(IV) was obtained. In the absence of any supporting physical evidence for the valence state of 6, the claim of Goralevitsch must be regarded as unproven. Nevertheless, the chemistry of both platinum and iron indicates that Ni(VI) is not improbable. A valence state of 6 for platinum in PtO_3 seems to be quite satisfactorily established (180); also iron is known to be hexavalent in the red compound K_2FeO_4. The valence state in the latter has been confirmed by magnetic susceptibility measurements, which indicate the two unpaired electrons expected for Fe(VI) (89).

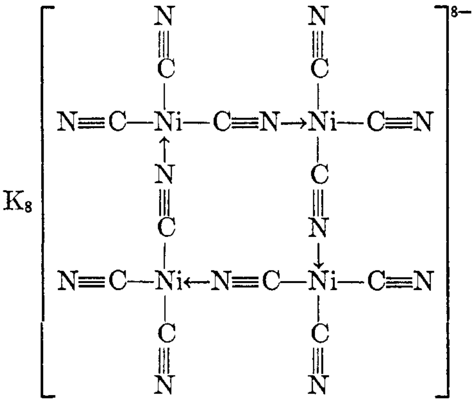
V. THE UNIVALENT STATE OF NICKEL

This is the only valence state of nickel from 0 to 4 about which there still is any real uncertainty. When an aqueous solution of $K_2Ni(CN)_4$ is reduced with sodium or potassium amalgam a red color develops and a red crystalline compound may be isolated having the empirical formula $K_2Ni(CN)_3$ (11, 12, 15, 16). I. Bellucci and R. M. Corelli (15, 16) observed that on treatment of the red solution with sulfuric acid the orange monocyanide, NiCN, could be isolated. It has been shown (125) that the potassium salt is diamagnetic in aqueous solution; this indicates the absence of the unpaired electron expected for Ni(I).

The fact that $K_2Ni(CN)_3$ is diamagnetic in the solid state need not prove anything about the valence state of the nickel, because $K_2Co(CN)_5$, which has the expected one unpaired electron in aqueous solution, is diamagnetic in the solid state (1); this probably arises from interatomic spin coupling consequent upon the arrangement of the atoms in the crystal as in cupric acetate (17). Mellor and Craig (125) suggest that the anion is dimeric and propose the structure shown in formula XIa.



XIa



XIb

Here the nickel atom is effectively bivalent, since a nickel–nickel bond is present in the anion. The tetrameric structure shown in formula XIb is also a possibility but seems less likely, partly owing to the large negative charge on the anion, but more especially because it does not account for the diamagnetism. There are precedents for such a metal–metal bond as is suggested in formula IXa,—notably the mercurous ion, Hg_2^{++}. The μ-dicyano bridged structure proposed by P. Rây and H. Sahu (166) cannot be considered likely for steric reasons. The cyano group normally forms colinear bonds and not the angular bonds required in a μ-dicyano bridged structure. It is thus important to isolate monomeric complexes to establish that the nickel atom is monovalent. A solution of $K_2Ni(CN)_3$ in water absorbs up to one molecule of carbon monoxide per nickel atom; the red color disappears and the complex in solution is presumed to be $K_2Ni(CN)_3CO$, but no solid compound has been isolated (117). The magnetic moment of this compound has not been reported. It is of considerable interest because, if the substance is diamagnetic, the cyanocarbonyl anion must be polymeric in order to have an even number of electrons. If the polymerization shown in formula XIa really does occur, then the nickel atom is bivalent as in mercurous salts. In the absence of further experimental work on this valence state it must be regarded as existing, at least formally, in both $K_2Ni(CN)_3$ and $(NiCN)_x$. Although there are obvious difficulties, an x-ray crystal structure of $K_2Ni(CN)_3$ is badly needed and a more thorough investigation of the magnetic properties of the carbonyl derivatives of the compound may prove of considerable value.[2]

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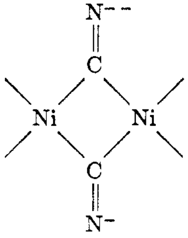
[2] *Footnote added in proof:* Some important work on this subject has just become available. R. Nast and W. Pfab (136b) have prepared crystals of $K_2Ni(CN)_3$ and have studied their structure by x-ray crystallography. They find that the anion is dimeric, i.e., $[Ni_2(CN)_6]^{----}$, the two nickel atoms being connected by two bridging cyanide groups. The binding to the cyanide groups is unusual, in that it involves three bonds to the carbon atoms:



The bridging cyanide groups thus function in the same way as the bridging carbon monoxide groups in $Fe_2(CO)_9$. Both nickel atoms are square coördinated, and they are considered to be bivalent. It is claimed that the electron deficiency is compensated for by resonance between $=N^-$ and $=N^{--}$ in the cyanide bridge. Without further support this explanation appears to provide a less satisfactory explanation for the diamagnetism than a metal–metal interaction. The compound $K_2Ni(CN)_3CO$ has also been isolated in the solid state by R. Nast and H. Roos (136d) (see also R. Nast and T. Von Krakkay (136c)). This compound is diamagnetic, and it is concluded that the anion is again dimeric. It is thus isoelectronic with dicobalt octacarbonyl, in which some kind of metal–metal interaction is assumed to occur in order to account for the diamagnetism.

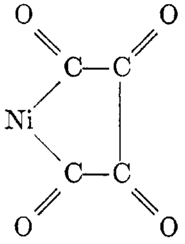
C. L. Deasy (49) has proposed alternative structures for the compound $K_2Ni(CN)_3$ based on the assumptions (*a*) that the Ni(I) atom is three-covalent and (*b*) that there is an unpaired electron in the compound. Since (*b*) is incorrect and (*a*) has not been established, the structures proposed cannot be accepted.

VI. The Zerovalent State of Nickel

All zerovalent complexes of nickel are four-covalent, the best known being nickel tetracarbonyl, $Ni(CO)_4$. The study of zerovalent complexes of nickel has recently been taken up by several investigators, and the results are likely to have an important effect upon the development of ideas concerning the nature of the so-called coördinate bond. The structure and properties of nickel carbonyl have such a marked relevance to other Ni(0) complexes that this compound will be discussed first.

A. NICKEL CARBONYL

Nickel carbonyl was first described by R. L. Mond, C. Langer, and F. Quincke in 1890 (132); it is easily prepared by the action of carbon monoxide upon finely divided nickel at temperatures below 100°C. However, it is only during the last decade that its structure was finally settled. R. L. Mond, C. Langer, and F. Quincke originally proposed the ring structure shown in formula XII, largely in an attempt to retain the usual valence state of 2 for nickel. Measurements of the parachor were regarded as support for this formulation (183), but as soon as more direct methods for structure determination were applied it became apparent that all four carbonyl groups were attached separately to the metal atom, which was thus four-covalent. The next question was whether the four bonds were planar or tetrahedral. From measurements of the electric dipole moment L. E. Sutton, R. G. New, and J. B. Bentley (184, 185) concluded that the four carbonyl groups were attached through the carbon and not through the oxygen atom. If the latter were true, the Ni—O—C bonds would be bent and, like $C(OC_2H_5)_4$, the $Ni(CO)_4$ molecule would then have a finite dipole moment. After allowing for atom polarization this dipole moment is zero; this is in harmony with the view that the three Ni—C—O atoms are colinear in all four cases. However, the dipole moment does not distinguish between a planar and a tetrahedral configuration. The latter was shown to be correct both by electron diffraction measurements (23) and also from a study of the infrared and Raman spectra.



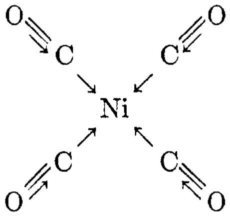
XII

B. L. Crawford and P. C. Cross, Jr., (44) carried out an investigation of the infrared spectrum and a quantitative vibrational analysis of the molecule and found that no satisfactory assignment of the frequencies could be made if it were assumed that the molecule was square planar. However, a satisfactory assignment could be made for a tetrahedral molecule only if it could be shown that the earlier Raman polarization data of A. B. F. Duncan and J. W. Murray (53) were in error. On reëxamining the Raman spectra, B. L. Crawford and W. Horowitz (45) showed that one of the lines previously reported as partially polarized was actually depolarized; the rest of the data were shown to be consistent only with the tetrahedral molecule.

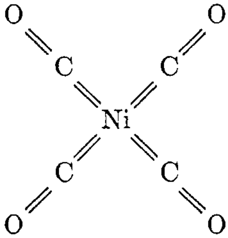
Further support for the tetrahedral arrangement comes from theoretical arguments based on the magnetic susceptibility. It was shown by A. E. Oxley (148) and W. Klemm, H. Jacobi, and W. Tilk (106) that the compound is diamagnetic; this is interpreted most simply to mean that the ten electrons of the nickel atom occupy the five $3d$ orbitals to give the configuration $3d^{10}$ (table 1). If it be assumed that the next available four orbitals are used for bond formation ($4s4p^3$), then the molecule should be tetrahedral. It is probably safer to say, however, that the magnetic data and theoretical conclusions based thereon are consistent with other experimental findings than to regard them as strong evidence for the tetrahedral arrangement. As pointed out earlier, the use of $4s4p^24d$ *square* bonding orbitals is also consistent with the diamagnetism, although in this instance the low electronegativity of the attached groups makes the square arrangement most improbable. In cases such as this the magnetic data must be interpreted with caution.

Recently an x-ray crystallographic analysis of solid nickel carbonyl has been carried out (109). The tetrahedral arrangement of the four bonds about the nickel atom has been confirmed; the Ni—C—O atoms have been shown to be colinear. The nickel–carbon and carbon–oxygen bond lengths have been found to be 1.84 Å. and 1.15 Å., respectively.

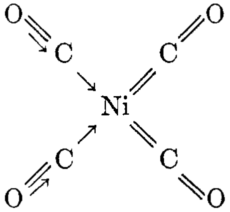
The actual bond lengths in nickel carbonyl have led to important theoretical deductions. From electron diffraction measurements the nickel–carbon and carbon–oxygen bond distances are respectively 1.82 Å. and 1.15 Å., almost identical with the values obtained by x-ray crystallography. The expected bond length for a nickel–carbon single bond is estimated at 2.00 Å. (156), whilst the bond lengths for $C{=}O$ (double) and $C\equiv O$ (triple), as in carbon monoxide, are respectively 1.22 Å. and 1.13 Å. On the basis of this it has been concluded that there is a good deal of double-bond character in the nickel–carbon bond, the carbon–oxygen bond being intermediate in character between a double and a triple bond. This conclusion was supported also by measurements of the carbon–oxygen stretching force constant in nickel carbonyl, for which the value 15.89×10^5 has been reported by C. R. Bailey and R. R. Gordon (4). The force constant for a carbon–oxygen double bond in formaldehyde is 12.1×10^5 dynes/cm., whilst that for a carbon–oxygen triple bond (in carbon monoxide) is 18.6×10^5 dynes/cm. (79). From this it was concluded that the carbon–oxygen bond in nickel carbonyl is intermediate between a double and a triple bond; also it was inferred from the infrared data that the nickel–carbon bond has some double-bond character. As will be seen presently (144), however, R. S. Nyholm and L. N. Short conclude that the nickel–carbon bond has almost 100 per cent double-bond character. A. F. Wells (207) has questioned the assignment of double-bond character to certain bonds on the basis of bond shortening alone, pointing out that for many metal complexes the "calculated" single-bond lengths in certain valence states have been estimated by rather doubtful extrapolation procedures, e.g., the nickel–carbon bond length in the zerovalent nickel compounds, and further that changes in bond length owing to polarity alone are important. However, in this instance the weight of other evidence strongly supports the conclusion that in nickel carbonyl there is double-bond character in the nickel–carbon bond. This is also supported on other theoretical grounds. If the single bond structure (formula XIIIa) is assigned to nickel carbonyl, it is apparent that a formal charge of −4 units is thrown onto the nickel atom; if allowance is made for the relative electronegativities of nickel (estimated) and carbon, this value is reduced to something between −2 and −3. Now it has been pointed out by L. Pauling (156) that the acceptance of such a large negative charge by an electropositive metallic atom is most improbable if there is some mechanism whereby it can be delocalized. Furthermore, L. Pauling (156, 158) proposes that, in general, the charge on an atom is usually fairly close to zero and in any case lies between +1 and −1 units. The formation of double (π) bonds between the nickel atom and the carbon atom using 3*d* electron pairs of the metal would enable the delocalization of negative charge from the nickel atom and at the same time give rise to the postulated double-bond character. L. Pauling (158) concluded that bond-length data and the electrical neutrality principle were best satisfied by the structure shown in formula XIIIb, though the force constant data supported that shown in formula XIIIc.



XIIIa



XIIIb



XIIIc

C. A. Coulson (40) also regards formula XIIIb as the best single representation of the structure of nickel carbonyl. However, he agrees that force constant data for the nickel–carbon bond are more compatible with a single bond. A reëxamination of the infrared data (144), however, reveals that the carbon–oxygen bond should be regarded as a double bond rather than a triple bond; hence the nickel–carbon bond is almost purely a double bond also. This conclusion arises from the fact that in comparing the carbon–oxygen bond stretching force constant in nickel carbonyl with carbon–oxygen bonds, it is important to choose compounds in which the bond hybridization is the same in all cases (here, *sp* linear hybrids). Thus, ketene ($CH_2{=}C{=}O$) is a more appropriate compound for comparison than, for example, formaldehyde, in which the bond hybridization is sp^2. When the effect of σ-bond hybridization is allowed for, it is concluded that the carbon–oxygen bonds in nickel carbonyl are almost certainly double bonds only. Hence all four nickel–carbon bonds are double bonds also. Finally, it has been pointed out that theoretical support for double bonding to transition metals is provided from calculations of overlap integrals (43). It has also been noted (142) that those ligands which replace CO from nickel carbonyl are just those for which double bonds between the nickel atom and the ligand donor atom may be written.

B. SUBSTITUTED NICKEL CARBONYL COMPOUNDS

A considerable number of zerovalent nickel complexes are known in which one or more carbonyl groups have been replaced by other ligands. In general these are formed by the direct reaction of the substituting ligand with nickel carbonyl in benzene or alcoholic solution or by treating a suitable complex of the ligand (e.g., the zinc chloride complex) with nickel carbonyl directly. Typical reactions are discussed by F. Hein (77) and many examples of substituted nickel carbonyls are listed by J. W. Copenhaver and M. H. Bigelow (39).

Monosubstituted derivatives are illustrated by $(C_6H_5)_3AsNi(CO)_3$, $(C_6H_5)_3PNi(CO)_3$, and $(C_6H_5)_3SbNi(CO)_3$.

Disubstituted derivatives, which are more common owing to the ease with which certain chelate groups such as dipyridyl, *o*-phenanthroline, and *o*-phenylenebis(dimethylarsine) ("diarsine") will react, are illustrated by the compounds $\{(C_6H_5)_3P\}_2Ni(CO)_2$, dipy$Ni(CO)_2$, *o*-phen$Ni(CO)_2$, and diarsine$Ni(CO)_2$.

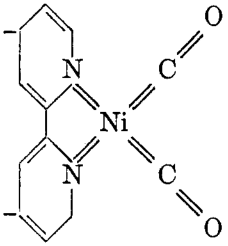
Trisubstituted complexes are more difficult to obtain using the ligands shown above, but they may be prepared by using alkyl and aryl isocyanides as donors. W. Hieber and E. Bockly (81, 82) have prepared, for example, $(CH_3N{\equiv}C)_3NiCO$.

Tetrasubstituted compounds are of special interest and the isolation of several compounds of this type with rather unusual ligands has been reported. Phenyl isocyanide replaces all four carbonyl groups directly to yield $Ni(C{=}NC_6H_5)_4$ (81, 82). J. Chatt and A. A. Williams (35) found also that whereas no reaction between finely divided nickel and phosphorus trifluoride occurs, the replacement of three carbonyl groups may be effected easily by refluxing for some time in an inert atmosphere. J. W. Irvine and G. Wilkinson (92) were able to replace all four carbonyl groups by treating the nickel carbonyl with a large amount of phosphorus trichloride, the excess of the latter being subsequently removed by distillation. $Ni(PCl_3)_4$ is a pale yellow crystalline solid which decomposes above

120°C. on heating; it is monomeric in freezing benzene and is diamagnetic like $Ni(CO)_4$. (The corresponding phosphorus tribromide compound has also been prepared.) Since the compound forms single hexagonal crystals, an x-ray crystallographic study is awaited with considerable interest. Surprisingly, the compound is stable in air and is unreactive to water at room temperature over a period of some days. The compound $Ni(PF_3)_4$ has been prepared by G. Wilkinson (208) both by treating $Ni(PBr_3)_4$ with fluorine and by the action of phosphorus trifluoride on $Ni(PCl_3)_4$ or $Ni(PBr_3)_4$. $Ni(PF_3)_4$ is a liquid (b.p., 70.7°C.; f.p., −55°C.) which is less reactive than the chloride or bromide. It may even be steam distilled with slight decomposition.

The phosphorus trihalide derivatives of zerovalent nickel are most significant in regard to theories concerning double bonding. It has been shown by J. Chatt and A. A. Williams (35) that whereas phosphorus trifluoride shows no tendency to coördinate with boron trifluoride, complexes of the type $PtCl_2 \cdot 2PF_3$ may be prepared readily. Since boron trichloride is a strong electron acceptor, its failure to form a complex with phosphorus trifluoride can only mean that the lone electron-pair of the phosphorus atom normally used for a σ bond is not readily available for bond formation, presumably owing to the strong inductive effect of the three fluorine atoms. The coördination with Pt(II), however, can be interpreted if it be assumed that a major factor in the binding is the formation of a π bond arising from the use, by a $5d$ electron pair of the platinum atom, of a vacant $3d$ orbital of the phosphorus atom. Paradoxically, the formation of this π bond should result in a strengthening of the σ bond, because the acceptance by the phosphorus atom of a d electron pair from the platinum atom should result in a loosening of the hold on the $3s$ lone pair of the phosphorus atom, which are thereby made more readily available for σ-bond formation. The fact that Ni(0) complexes may be formed with phosphorus trifluoride and trichloride is taken as strong evidence in support of the double-bond hypothesis; in such compounds as these the formation of π bonds must be regarded as making a major contribution to the strength of the bond.

Some infrared studies on the compound diarsine$Ni(CO)_2$ (144) are also significant. In an attempt to understand why only two carbonyl groups may be replaced instead of all four, the stretching force constants of the carbon–oxygen bonds in $Ni(CO)_4$ and in diarsine$Ni(CO)_2$, were compared. The change in the carbon–oxygen force constant from $Ni(CO)_4$ (15.89×10^5) to diarsine$Ni(CO)_2$ (15.7×10^5) is very small. It indicates that there is a very small *decrease* in the amount of triple-bond character in the carbon–oxygen bond as compared with that in $Ni(CO)_4$ and hence that there is a very small *increase* in the double-bond character of the nickel–carbon bond in diarsine$Ni(CO)_2$, as compared with that in $Ni(CO)_4$. If the assumption is made that in both compounds the charge on the nickel atom is approximately the same, and hence that the nickel atom forms the same number of double bonds in both cases, then we may conclude that there is slightly less double-bond character in the nickel–arsenic bond than there is in the nickel–carbon bond. The difference, however, is almost negligible. It thus appears that since the nickel–carbon bonds in both complexes are of the same kind, the difficulty of removing the remaining two carbonyl groups from diarsine$Ni(CO)_2$ arises not from any pronounced increase in bond strength of the Ni—CO bond in diarsine$Ni(CO)_2$ as compared with that in $Ni(CO)_4$, but from some difficulties in the mechanism. It is of interest to compare the force constant of the carbon–oxygen bond in dipyridyl$Ni(CO)_2$, 14.4×10^5, with the two values quoted above. In this instance the decrease in bond order of the carbon–oxygen bond is more appreciable and we may infer that a correspondingly marked increase in the nickel–carbon bond order has occurred. Hence, since a higher percentage of the permitted number of π bonds figures in the nickel–carbon bonds in this molecule than in the two preceding ones, we may conclude that the double-bond character of the nickel–nitrogen bond in the dipyridyl complex is less than that of the nickel–arsenic bond in the diarsine complex. This is not unexpected, since in the case of the dipyridyl complex a vacant orbital for the *d* electron of the nickel atom can be made available on the nitrogen atom only by invoking structures such as those shown in formula XIV. No such delocalization of charge around the benzene ring is necessary with the diarsine however, because the arsenic atom already has available a vacant 5*d* orbital for the reception of the 3*d* electrons of the nickel atom.



XIV

Finally, reference should be made to the unique salt of zerovalent nickel, $K_4Ni(CN)_4$ (55). This is formed by the reduction of the red salt of empirical formula $K_2Ni(CN)_3$ with potassium or calcium (55) in liquid ammonia. This reddish yellow solid is a powerful reducing agent which evolves hydrogen from water and decomposes rapidly in air. It is clearly isoelectronic with $Ni(CO)_4$, the four cyanide ions replacing the four carbonyl groups; the four potassium ions merely confer electrical neutrality on the compound. In view of the fact that CO and CN^- are isoelectronic, it is probable that the cyanide groups are attached to the nickel atom in the same way as is the carbonyl, i.e., through the carbon atom. This view is supported by the fact that the complexes of Ni(0) with isocyanides involve a nickel–carbon and not a nickel–nitrogen bond. The determination of the structure of the compound $K_4Ni(CN)_4$ by x-ray diffraction studies is difficult owing to its instability; if this difficulty can be surmounted it should be possible to distinguish between an Ni—C—N and an Ni—N—C link. The binding should affect the colinearity of the Ni—C—N atoms. Ni—C—N should be linear but Ni—N—C would probably be V-shaped.

Now that so many stable compounds of zerovalent nickel are available, it is

TABLE 2

Valence states of nickel and data regarding nickel complexes

VALENCE STATE	COÖRDINATION NO.	SHAPE	EXAMPLES	BOND ORBITALS	MAGNETIC MOMENT	
					Experimental	Calculated
					Bohr magnetons	*Bohr magnetons*
0............	4	Tetrahedral	$Ni(CO)_4$; $(C_6H_5)_3P \cdot Ni(CO)_3$ $Ni((C_6H_5)_3P)_2(CO)_2$; $Ni(dipy)(CO)_2$ $Ni(CH_3NC)_3CO$; $Ni(C_6H_5NC)_4$; $Ni(PF_3)_4$; $K_4Ni(CN)_4$	$4s4p^3$	0	0
1 (?).........	4 (?)	Square planar (?)	$K_2Ni(CN)_3$; $K_2Ni(CN)_3CO$	?	0	1.73
2............	4	Square planar	$NiCl_2((C_2H_5)_3P)_2$; $Ni(DMG)_2$*	$3d4s4p^2$	0	0
	4	Tetrahedral	$Ni(NO_3)_2((C_2H_5)_3P)_2$; Ni(ac-ac)$_2$†	$4s4p^3$	3.3	2.83
	5	Square pyramid (?)	$[Ni(CN)_5]^{---}$, $[NiBr_2\text{triarsine}]^0$	$3d4s4p^3$	0	0
	6	Octahedral	$[Ni(NH_3)_6]Cl_2$; $[Ni(NO_2)_6]^{----}$	$4s4p^34d^2$	3.1	2.83
		Octahedral	$[Ni(\text{diarsine})_3][ClO_4]_2$	$3d^24s4p^3$	0	0
3............	5	Square pyramid	$[Ni(BMG)_2]Br$‡; $[NiBr_3((C_2H_5)_3P)_2]^0$	$3d^24s4p^2$ or $3d4s4p^3$	1.9	1.73
	6	Octahedral	$[NiCl_2(\text{diarsine})_2]ClO_4$	$3d^24s4p^3$	1.9	1.73
4............	6	Octahedral	K_2NiF_6; $BaNiO_3$ $[NiCl_2(\text{diarsine})_2][ClO_4]_2$	$3d^24s4p^3$	0	0

* DMG = dimethylglyoxime *less* one proton.

† ac-ac = acetylacetone *less* one proton.

‡ BMG = benzil dioxime *less* one proton.

to be hoped that many structure determinations will be carried out. The structures of the phosphorus trihalide complexes in particular invite attention, but the partly substituted compounds such as $(C_6H_5)_3PNi(CO)_3$ and diarsine$Ni(CO)_2$ offer excellent material for the study of the effect of successive replacement of CO upon the lengths of the nickel–carbon bonds in the remaining carbonyl groups.

VII. Summary and Conclusions

A summary is given in table 2 of the valence states discussed and their relevant stereochemical data. This table makes clear at a glance the rapid recent development in this subject during recent years. At the same time, the obvious need for further work on the so-called univalent state of nickel is emphasized. Further work on the oxides of nickel and upon the alleged valence states greater than 4 is also essential.

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