RECENT ADVANCES IN THE STEREOCHEMISTRY OF NICKEL, PALLADIUM, AND PLATINUM

J. R. Miller

Institut für Anorganische Chemie der Universität, München, Germany

I. Introduction

In the last decade, the advent of ligand-field theory has given a tremendous impetus to the study of transition metals, and of these, nickel has been among the most studied. This element can have a variety of stereochemical configurations under various conditions, and the aim of this chapter is to summarize the position of our knowledge up to the early part of 1961. It is necessary to give such a date because the field is very active at the time of writing, and new developments are to be anticipated. Palladium and platinum have not received quite so much attention as nickel from the structural point of view; the *trans*-effect should be mentioned, however, and has been reviewed by Basolo in Volume 3 of this series.

The compounds in question are classified by oxidation state of the central metal atom. Assignment of oxidation state is normally straightforward when the formula is known, but there are cases where the choice is somewhat arbitrary. Thus bis(cyclopentadienyl)nickel, $(C_5H_5)_2Ni$, may be considered as the nickel(II) cation complexed by two cyclopentadienyl anions, or as a combination of an uncharged nickel atom with two cyclopentadienyl radicals. For the purpose of classification, such cases are treated as combinations of the oxidized metal and the reduced ligand. Nitric oxide is exceptional and its complexes are treated as those of NO^+, the odd electron being transferred to the metal, unless there is experimental evidence that such transfer does not take place.

So far as nickel is concerned, this chapter is a continuation of Nyholm's 1953 review (*192*), which is warmly recommended to the reader.

II. The Zero Oxidation State

Compounds of the elements in zero oxidation state are known for all three metals. With one exception, those of nickel contain the equivalent of four ligands coordinated to the metal, whereas palladium and platinum also form compounds of empirical formulas ML_2 and ML_3 (*162–164*).

Nickel carbonyl is by far the best-known of these compounds. All the data support a tetrahedral structure with four equivalent, linear Ni—C—O arrangements. The Raman (*3*, *52*, *61*) and infrared spectra (*8*, *53*, *135*, *136*) have been investigated and various assignments of the fundamental frequencies have been put forward on the basis of T_d symmetry (*53*, *136*, *208*). Several approximate coordinate analyses have been made using these assignments, but the spectra of isotopically substituted species have not been measured, so exact evaluations of force constants have not yet proved possible. The Ni—C and C—O stretching force constants are particularly important and the values obtained by workers using various approximations are included in Table I.

Discussion frequently arises over the charge distribution in the molecule, for, if one supposes that four coordinate bonds are formed from carbon to nickel, then the latter would have a negative charge of four electrons localized on it. This is very unlikely (*202*, *203*), and so means must be found of redistributing these electrons away from the center; the usual argument is that the electrons are donated back to the carbon monoxide groups through π-orbitals. Giacometti (*99*) has shown that there is a theoretical maximum of three bonding π-orbitals between the central atom and the ligands in a tetrahedral system, and the question here is to what extent they are used in nickel carbonyl. To this end a study of force constants is valuable, as the postulated back-donation would increase the strength (and hence the force constant) of the Ni—C bond, but would weaken the C—O bond as the donation is into antibonding π-orbitals of the carbon monoxide.

Before going on to discuss the force constants and their relationship to back-donation, a few comments must be made on the principles involved. In order to know whether a particular force constant is high or low, it is necessary to have others with which to compare it. Since the two types of bond in nickel carbonyl are on either side of a carbon atom, only force constants from other compounds with linearly bonded carbon are suitable (*34*, *194*); the compounds actually chosen contain only terminal carbon-oxygen linkages.

It has commonly been assumed that the sum of the Ni—C and C—O "bond orders" in these compounds should be four (*34*, *192*), but this is not quite justifiable. For example, in carbon dioxide the bonding to the oxygen atoms may be considered to consist of σ- and π-bonds; since there are two π-systems which are completely equivalent, there must be two degenerate bonding π-orbitals to each oxygen. With the σ-bond included, the total number of bonds to each oxygen atom is three. It follows that a total of six "directed" bonds should be associated with the carbon atom, although they are not necessarily of the same strength. This supposition is strikingly borne out by the carbon-carbon bond force constants of carbon suboxide (See Table I), which are only slightly less than that of acetylene (*246*). It thus follows that one cannot make deductions about, say, a nickel-carbon bond from measurements on the carbon-oxygen bond.

TABLE 1

FORCE CONSTANTS OF CARBONYL COMPOUNDS

Compound	$10^{-5}\, k_{CO}$ (dynes/cm)	$10^{-5}\, k_{MC}$ (dynes/cm)	Reference
CO	18.6	—	*246*
$BH_3 \cdot CO$	17.3	2.97	*47*
$Ni(CO)_4$	17.3	2.1	*136*
	16.78 16.42	2.07 2.78	*208*
	16.02	2.12	*181*
	15.89	2.52	*53*
SCO	15.7	7.2	*35*
CH_2CO	15.5	9.8	*116*
CO_2	15.24	—	*245*
C_3O_2	14.15	14.87	*245*
$Co(CO)_4^-$	13.22	3.55	*237*
$Fe(CO)_4^{2-}$	11.40	4.06	*237*

Table I shows that there is a general tendency for the C—O force constant to fall as the constant on the other side of the carbon increases. In all these compounds (except ketene) the symmetry is such that there must be two equivalent π-bonds between carbon and oxygen; decrease of the force constant is a measure of the weakening of these bonds, as compared to free carbon monoxide, by the presence of a third atom which can also form π-bonds. Table II shows that the bonds are also lengthened slightly by the process. The position of nickel carbonyl in the series shows that the back-donation is probably not very great, although this is a purely relative term. It is seen that the isoelectronic species $Co(CO)_4^-$ and $Fe(CO)_4^{2-}$ show very much greater effects, which is to be expected as one and two positive charges respectively have been removed from the nucleus.

The Ni—C force constant is not known with certainty, but all quoted values are quite small, and are of the same order as metal-carbon force constants in metal alkyls (*34*). This indicates that what effect there is does not appreciably strengthen the nickel-carbon bond. Again, the effect is much greater for the anionic isosters.

TABLE II
BOND LENGTHS IN CARBONYL COMPOUNDS

Compound	d_{CO} (Å)	d_{MC} (Å)	Reference
CO	1.13078	—	*103*
BH_3CO	1.131	1.540	*107*
$Ni(CO)_4$	1.15	1.84	*140*
	1.15	1.82	*27*
SeCO	1.159	1.709	*240*
SCO	1.16	1.56	*36*
CO_2	1.160	—	*125*
CH_2CO	1.161	1.314	*49*
HNCO	1.18	1.18	*59*
C_3O_2	1.19	1.28	*156*

The evidence for the shortening of the nickel-carbon bond by π-bonding (*202*, *203*) has been criticized on the grounds that it is possible to obtain a covalent radius for nickel only by rather dubious extrapolations (*192*, *258*). Such criticism is extended if one obtains a radius for carbon in *sp*-hybridization by subtracting an oxygen radius (0.55 Å) from the carbon-oxygen distance in nickel carbonyl. This radius (0.60 Å) added to Pauling's earlier nickel radius (*202*) gives a nickel-carbon distance of 1.86 Å, very nearly that observed. However, the nickel radius obtained by a later extrapolation (*203*) gives a distance of 1.99 Å. These inconsistencies merely demonstrate the unreliability of additivity rules for covalent radii. It is, however, clear that the carbon-oxygen distance in nickel carbonyl fits into a very similar scheme to that for the force constant, and one can again conclude that the back-donation is not very considerable.

Isoelectronic with nickel carbonyl are the anions, $Ni(CN)_4^{4-}$ and $Pd(CN)_4^{4-}$, which are obtained as their potassium salts by reduction of the corresponding cyanides of oxidation state +2 with potassium in liquid ammonia (*32*, *65*, *186*). The infrared spectrum of the nickel complex has been reported (*67*) to show only one band at 1985 cm^{-1}, in the triple-bond region, which agrees with the expected tetrahedral structure (but is also compatible with other configurations). The lowness of the frequency corresponds to the greater degree of back-donation in species of low oxidation state and high negative charge.

There are other nickel(O) complexes derived from this cyanide, such as $K_2[Ni(CN)_2(CO)_2]$ (*190*), $K_2[Ni(CN)_3(NO)]$ (*185*), and $K_4[Ni(HC_2)_4]$ (*191*). The second of these is monomeric in solution and diamagnetic (*184*), and its infrared spectrum (*114*) has bands at 2133 cm^{-1}, 2118 cm^{-1}, and 1780 cm^{-1}; by comparison with $Co(CO)_3(NO)$, for which a coordinate analysis in C_{3v} symmetry has recently been given (*156*), these bands may be assigned to symmetrical and asymmetrical C—N and to N—O stretching vibrations respectively. The corresponding frequencies for $Co(CO)_3(NO)$ are 2108 cm^{-1}, 2047 cm^{-1}, and 1822 cm^{-1}. The N—O frequency is typical of that of coordinated NO^+ (*141*).

There are many complexes of nickel(O) with phosphines, but only tetra(trifluorophosphine)nickel has been studied structurally. Its Raman spectrum (*262, 263*) has been explained on the basis of T_d symmetry, three polarized bands being readily assigned to totally symmetric Ni—P stretching, P—F stretching, and P—F "umbrella" vibrations. The force constants are very interesting; that for Ni—P stretching is 2.71×10^5 dynes/cm, somewhat greater than the corresponding constant for nickel carbonyl. The P—F stretching constant is higher than that in free trifluorophosphine, which is difficult to explain on back-donation theory unless the FPF bond angles are altered. Such a change might similarly account for the PF_3 "umbrella" force constant being lower than in the free ligand; this is difficult to understand, as such a motion is expected to be strongly inhibited by coordination to a fourth atom. It is of obvious interest to see what happens in the cases of trichloro- and tribromo-phosphine.

Very little has been published on the structural properties of other phosphine complexes of nickel(O), but tetra(methyldichlorophosphine)-nickel is worthy of mention because it may be prepared by the direct action of the ligand on nickel metal (*210*).

Two interesting compounds of formulas $(Ph_3P)_2Ni(NO)_2$ and $(Ph_3O_3P)_2$-$Ni(NO)_2$ have recently been reported (*113*): they are obtained by the action of nitric oxide on the corresponding dicarbonyls. The first is diamagnetic, monomeric in benzene, and has a dipole moment of 4.26 Debye units. A single, unresolvable band in the infrared spectrum at 1745 cm^{-1} is shifted to 1706 cm^{-1} on substitution of ^{15}NO, and it can be clearly assigned to a nitrogen-oxygen stretching vibration of the NO^+ type (*141*). The presence of two such groups in a nonsymmetric molecule is incompatible with the appearance of only one such band, and the authors concluded that the NO groups must be coordinated in entirely different ways. There are several possibilities; the most reasonable seem to be those where the second group coordinates as the anion NO^-, through either oxygen or nitrogen, or even as a π-complex. In this way the oxidation state of the nickel remains zero.

The carbonyl groups in nickel carbonyl may be replaced by isonitriles as well as by phosphines etc. (*162*); in general all the carbonyl groups are replaced in the direct reaction, but a compound $(MeNC)_3Ni(CO)$ has been obtained. Cotton and Zingales have measured the infrared spectra of a few of these compounds in the triple-bond region (*46*), and some interesting facts emerge. The frequencies are shown in Table III and it is clear that the tetra-isonitriles show two N—C stretching frequencies. The authors interpret this as due to slight departures from strict T_d symmetry by bending at the nitrogen atoms. Such bending is caused by the decrease in N—C "bond order" due to the back-donation, with a subsequent tendency toward sp^2 hybridization of the nitrogen atom. Cotton and Zingales rightly point out that if one could attach a second atom to the nitrilic carbon atom without changing the N—C force constant, the observed N—C frequency would be higher than in the free ligand. The fact that it is lower is evidence of a definite amount of back-donation. The band at 1923 cm^{-1} in the spectrum of $(MeNC)_3Ni(CO)$ is assigned to the carbonyl group, the other two to N—C vibrations. This fits in with C_{3v} symmetry, and one cannot decide on these grounds alone whether the methyl isocyanide groups are bent at the nitrogen atoms or not. The C—O frequency is very low and can be associated with a considerable degree of back-donation to the carbonyl group, at the expense of the nitrile groups, which now show a mean frequency only slightly lower than that of the free ligand.

TABLE III
INFRARED SPECTRA OF SOME ISONITRILE COMPLEXES[a]

Compound	Wavenumbers	Free ligand in $CHCl_3$	Free ligand in C_7H_{16}
$(p\text{-}Me\cdot C_6H_4NC)_4Ni$	2065, 2033	2136	2132
$(C_6H_5NC)_4Ni$	2050, 1990	2136	2134
$(p\text{-}Cl\cdot C_6H_4NC)_4Ni$	2049, 2008	2136	2132
$(CH_3NC)_3(CO)Ni$ (Nujol)	2183, 2128, 1923	2142	2168

[a] Cotton and Zingales (*46*).

Compounds of palladium and platinum in zero oxidation state are no longer rare, but there is little or no structural information available. The best ligands seem to be isonitriles, tertiary phosphines, and tertiary arsines (*162–164*); compounds of platinum(O) with ammonia and ethylenediamine have been reported, but are very unstable (*253, 254*). The striking point of interest is that many of these complexes have only two or three ligands per metal atom. Those with four do not seem to be particularly stable, and $(Ph_3P)_4Pd$, for example, dissociates in solution to give $(Ph_3P)_3Pd$ (*163*). The structures of these "coordinatively unsaturated" compounds may be polymeric, but if they are not their general structural chemistry would be extremely interesting.* Bis(acrylonitrile)nickel appears to be the only known case of such unsaturation for nickel. This compound can take up one or two molecules of triphenylphosphine (*229, 230*), and its infrared spectrum indicates that only the vinyl grouping is involved in the bonding, and not the cyanide group (*96*). The same conclusion holds for the triphenylphosphine adducts. Bis(acrolein)nickel can also take up triphenylphosphine, but here the infrared data indicate that in the first complex both the vinyl double bond and the carbonyl group are involved, whereas in the adducts the carbonyl group is "liberated."

Cyclopentadienyl nickel nitrosyl, $(C_5H_5)Ni(NO)$, is an interesting case of nickel(O) in which the nickel is coordinated by the ions $C_5H_5^-$ and NO^+. It has an "open sandwich" type of structure (*21, 48*); its stability may be compared with that of other compounds of this type. For example, benzene chromium tricarbonyl is noticeably more stable than either chromium hexacarbonyl or dibenzene chromium, and may indeed be prepared by heating these two together (*80*). The bands appearing in the microwave spectrum indicate that the Ni—N—O linkage is strictly linear (*48*), and the molecule thus has C_{5v} symmetry. The nickel-carbon distance is not known accurately, but is certainly less than that in nickelocene. The structure may be correlated with the tetrahedral configuration if one considers the cyclopentadienyl anion to coordinate three electron pairs and the nitrosyl cation one. The latter idea agrees with the N—O frequency of 1833 cm^{-1} (*141, 207*).

In summary, it can be seen that the structural chemistry of the zerovalent complexes has to date been dominated by investigations on nickel carbonyl. Preliminary studies on other compounds indicate that the tetrahedral structure may not be the only possibility, and thorough investigation of the "unsaturated" species is likely to develop. Back-donation may be examined by study of force constants, in favorable cases merely of observed frequencies, and it would be interesting to see more cases of competition for back-donation, as in $(MeNC)_3Ni(CO)$.

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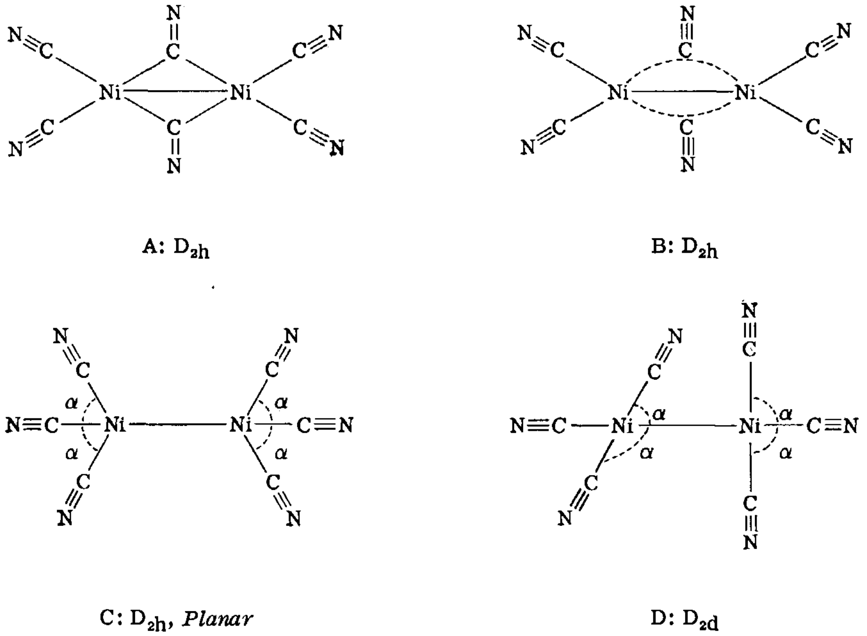
* It has recently been shown (*38a*) that the triphenylphosphine complexes of platinum are in all probability complex hydrides of platinum(II), with general formula $[(Ph_3P)_xPtH_2]$ where $x = 2, 3$, or 4. As these materials have always been used in the preparation of other "platinum(0)" complexes, it is now doubtful whether such complexes have in fact ever been obtained since it is possible that they are all hydrides.

III. Oxidation State +1

The compounds discussed in this section are restricted to nickel, as the existence of palladium(I) or platinum(I) compounds has not been established. Since nickel(I) contains nine *d*-electrons, analogies with copper(II) might be expected, but these do not arise; there are, however, certain similarities with cobalt(O), particularly in the tendency to dimerization.

The best-known of the nickel(I) complexes is the cyanide, $K_4[Ni_2(CN)_6]$, first isolated by Bellucci (*19*, *20*), and later by Nast and Pfab (*188*). The salt is diamagnetic in solution and in the solid state (*168*, *244*), and the anion has been shown to be binuclear in solution by a cryoscopic method (*189*). There is little doubt that the anion is binuclear in the solid as well, for it is impossible to account for the diamagnetism without invoking direct nickel-nickel interaction.



A: D_{2h}

B: D_{2h}

C: D_{2h}, *Planar*

D: D_{2d}

FIG. 1. Possible structures of the $[Ni_2(CN)_6]^{4-}$ ion.

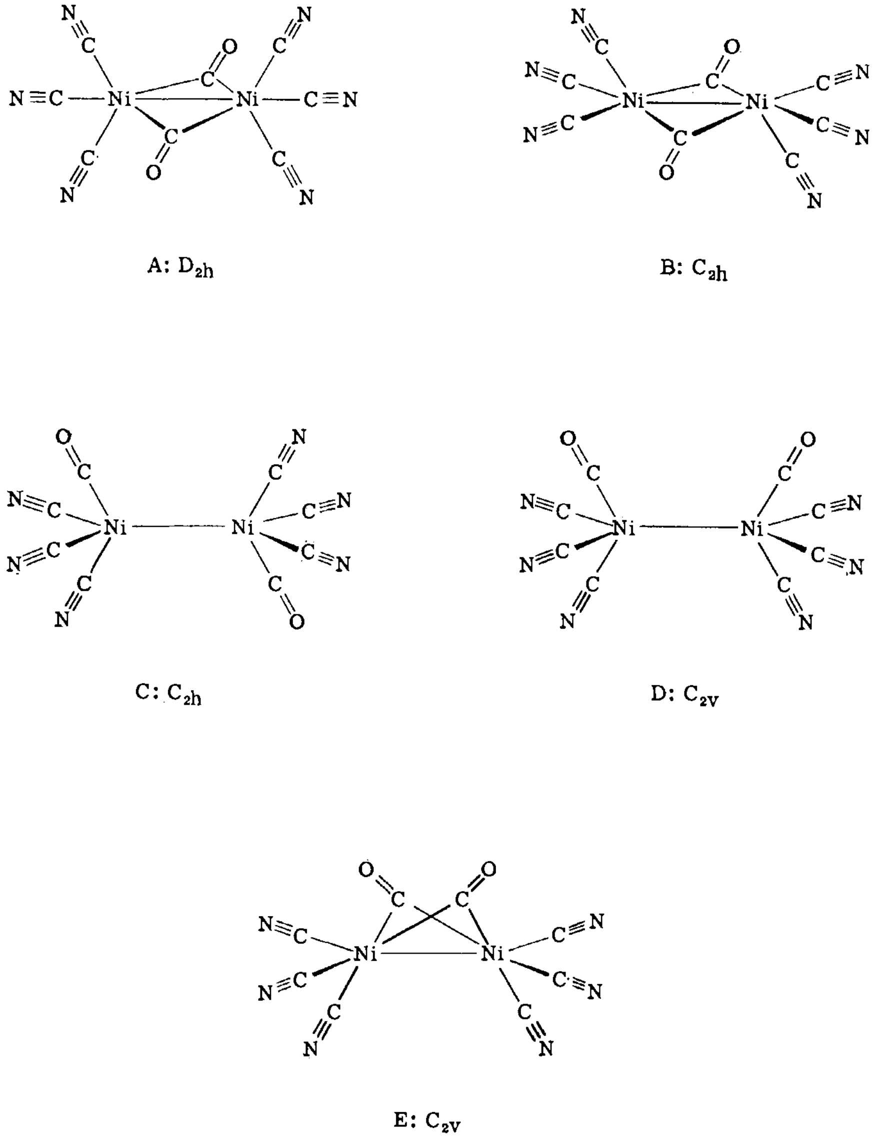
In a preliminary X-ray investigation, Nast and Pfab (*188*) were able to say that the anion is flat and binuclear; they suggested the structure shown in Fig. 1A. Later, however, the same authors (*206*) found that the structure was more complicated than they had previously imagined. The anions are stacked in layers with a certain degree of randomness. It is fairly certain that the anions have centers of symmetry, and the nickel-nickel distance has been estimated at 2.6 Å. In view of the awkward unit cell of this particular salt, it would be worthwhile to investigate the structures of other compounds with other cations replacing potassium.

The Raman spectrum has been measured (*226*), but the authors report that their solutions were yellow (this substance is usually deep red), and the one frequency observed was only two wavenumbers different from that of $K_2Ni(CN)_4$. It must be concluded that the solution had oxidized. The infrared spectrum has also proved difficult to obtain because of the presence of $K_2Ni(CN)_4$, but El-Sayed and Sheline (*66*) report three bands in the triple-bond region, at 2128 cm^{-1}, 2079 cm^{-1}, and 2055 cm^{-1}. The presence of three such frequencies can be made to agree with a variety of structures; the above authors accepted Nast and Pfab's suggested geometry, with two cyanide bridges (*188*), and devised structure B of Fig. 1. Carbon-nitrogen triple-bond character must be preserved throughout as the three observed frequencies are too high for anything else. The bridging bonds are formed by using the lone-pair orbitals of the carbon atoms as the centers of two three-center bonds, dsp^2 "hybrids" from the nickel atoms being the other components. The carbon-nitrogen bonds are thus undisturbed. Griffith and Wilkinson (*114*) have pointed out that the X-ray evidence for bridging is very far from conclusive, and regard the infrared evidence as excluding this possibility. If it is accepted that there are three, and only three, infrared active vibrations, then D_{2h} or D_{2d} symmetry is indicated; these are represented as C and D respectively in Fig. 1. The angles α are not necessarily 90°, but must be equal. Structure C would be favored by the layer lattice and the probable presence of a symmetry-center (*206*), structure D by electrostatic repulsion between cyanide groups. Ethane-like structures are excluded as they would have only two CN stretching frequencies.

The hexacyano-dinickelate(I) ion is coordinatively unsaturated and its solutions can absorb two molecules of carbon monoxide to give the salt $K_4[Ni_2(CN)_6(CO)_2]$ (*186, 190*). This is diamagnetic and the anion is binuclear in solution (*184*); thus the above formulation is generally accepted. Its structure is of particular interest as it is isoelectronic with dicobalt octacarbonyl, for which several structures have been suggested on the basis of vibrational spectra (*33, 91*), and of its reaction with acetylenes (*178*). It is normally assumed that the two carbon monoxide groups are not on the same nickel atom and that if bridges are formed the carbon monoxide groups are responsible for them. Using nujol mulls with rock-salt optics, Griffith *et al.* (*110*) have resolved four bands in the infrared spectrum at 2135 cm^{-1}, 2055 cm^{-1}, 1983 cm^{-1}, and 1905 cm^{-1}. These values correspond to those of dicobalt octacarbonyl (*33*) at 2070 cm^{-1}, 2043 cm^{-1}, 2025 cm^{-1}, and 1858 cm^{-1} and it is tempting to assign the two molecules to the same point group. However, the use of lithium fluoride optics has revealed seven bands in the spectrum of dicobalt octacarbonyl (*24*), at 2070, 2060, 2044, 2032, 2024, 1869, and 1860 cm^{-1}. The newly observed bands are underlined. It remains to be seen whether further bands can be located in the spectrum of $K_4[Ni_2(CN)_6(CO)_2]$. Before discussing the possible symmetries, the number of possible arrangements may be reduced a little by attempting to decide whether bridges are formed or not. In neither of these substances can the lowest frequencies be unconditionally assigned to bridging carbonyl groups, as much lower ones have been observed where bridging is impossible, as in $Co(CO)_4^-$ and in $Fe(CO)_4^{2-}$ (*237*). However, the grouping of the bands in the spectrum of $Co_2(CO)_8$ suggests that two of the carbonyl groups are bound in a way different from that of the others, and all structures so far suggested for this substance do contain bridges (*33, 91, 178*); they belong to point groups D_{2h}, C_{2h}, and C_{2v}. Only the last is feasible, as the first two would have only four infrared active C—O stretching vibrations. Some conceivable structures for the $[Ni_2(CN)_6(CO)_2]^{4-}$ ion are shown in Fig. 2; A, B, and C would have four infrared active C—O vibrations. Griffith *et al.* (*110*) prefer C as they consider the lowest frequency (1905 cm^{-1}) to be too high for bridging. The grouping of the four bands observed to date (they are fairly evenly distributed) certainly does not support the idea that any group is bonded in a significantly different way from the others. Structure D is the *cis* equivalent of C and has lower symmetry; seven vibrations should be infrared active in the triple bond region. Structure E is included as an analogy with structures suggested by Mills *et al.* (*178, 248*) for dicobalt octacarbonyl and for bis(cyclopentadienylnickel carbonyl) on the basis of their reactions with acetylenes. It has C_{2v} symmetry and predicts seven infrared bands, five due to cyanide groups, two to carbonyl groups; it does, however, contain bridges, and this makes it less likely than C or D. It will be interesting to see if the differences in structure between the isoelectronic $Co_2(CO)_8$ and $[Ni_2(CN)_6(CO)_2]^{4-}$, as deduced from infrared spectra, can be reconciled with the normally close similarities between isoelectronic species.

Another member of this series is bis(cyclopentadienylnickel carbonyl), $(C_5H_5NiCO)_2$; it is dimeric, diamagnetic, and must, therefore, contain a nickel-nickel bond (*79*). The dipole moment, quoted (*79*) as 0 ± 0.38 Debye unit, indicates that the molecule must be very nearly centro-symmetric in benzene. The infrared spectrum, however, shows two carbonyl stretching frequencies in the solid state and in solution, but the vapor at 100°C shows only one band (*173, 199*). The wave-numbers are shown in Table IV.

The observed frequencies are influenced by the solvent, and the splitting appears to increase with the polar nature of the solvent. It may be that the "free" molecule indeed has a center of symmetry but is slightly distorted



A: D_{2h}

B: C_{2h}

C: C_{2h}

D: C_{2v}

E: C_{2v}

Fig. 2. Possible structures of the $[Ni_2(CN)_6(CO)_2]^{4-}$ ion.

in solution, thereby allowing the second C—O frequency to become active. It is suggested that the splitting of this band in the solid state is due to the presence of two different molecular sites in the crystal; this has also been put forward to explain a similar excess of carbon-oxygen bands in the infrared spectrum of crystalline $[C_5H_5Fe(CO)_2]_2$, which is known to have

TABLE IV

Carbonyl Stretching Frequencies of Bis(cyclopentadienyl-nickel Carbonyl)

Phase	(cm^{-1})		Splitting (cm^{-1})	Prism
	Strong	Very strong		
Solid (KBr)	1873	1828	45	NaCl
C_6H_6 solution	1891	1844	47	LiF
$CHCl_3$ solution	1892	1845	47	LiF
CS_2 solution	1893	1850	43	LiF
CCl_4 solution	1893	1850	43	LiF
C_6H_{12} solution	1895	1854	39	LiF
Vapor (100°C)	—	1860	—	NaCl

a center of symmetry (*45, 176*). Therefore it may be assumed that the structure is a centro-symmetric one.

The values observed for the carbon-oxygen frequency are intermediate between those found for bridging groups and those normally found for terminal groups. It has been suggested on the basis of preliminary X-ray

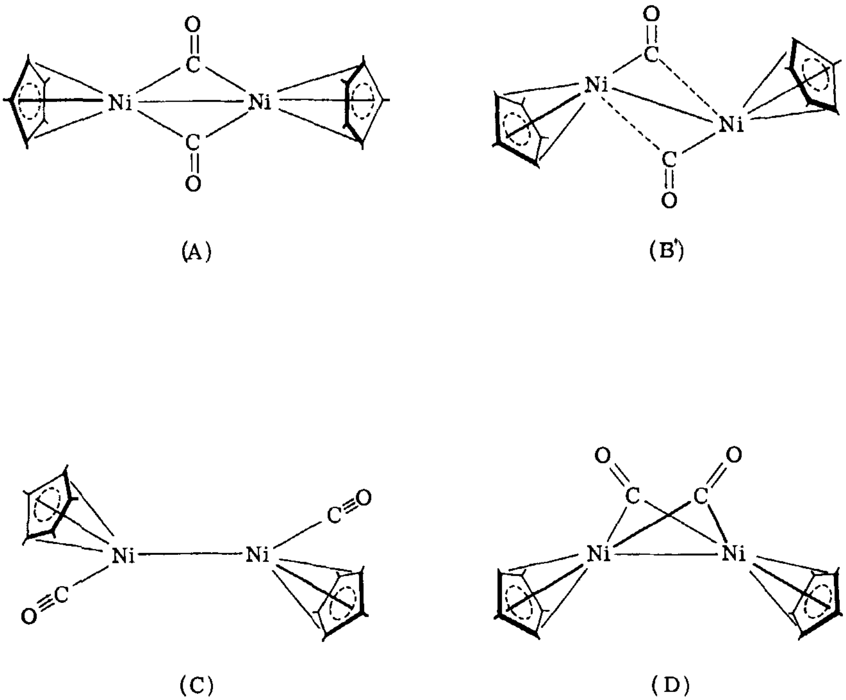


Fig. 3. Possible structures of $(C_5H_5)_2Ni_2(CO)_2$.

work (*199*) that there are in fact two bridging carbonyl groups, but that each group is associated more closely with one nickel atom than with the other. This is shown in Fig. 3B, drawings A and C showing respectively the "fully bridged" and nonbridged possibilities. This partial bridging offers a reasonable explanation of the intermediate frequency and is still compatible with a zero dipole moment.

The nonsymmetrical structure suggested by Tilney-Bassett and Mills (*247*, *248*) must be mentioned in connection with the acetylene derivatives of this compound. The structure is shown in Fig. 3D, and the argument is as follows. The carbonyl groups are replaceable by one molecule of acetylene, a reaction quite analogous to the displacement of the two "bridging" groups of dicobalt octacarbonyl by an acetylene. The structure of diphenylacetylene dicobalt hexacarbonyl (*235*) is based on a tetrahedron of two carbon and two cobalt atoms, the other groups being attached as shown in Fig. 4. It is very reasonable to accept similar structures for acetylene bis(cyclopentadienylnickel) compounds. If the acetylene molecule is now replaced by two carbonyl groups, structure D of Fig. 3 is obtained. This is a very interesting suggestion and is worth further investigation, but the structure so obtained for the parent compound is very difficult to reconcile with the zero dipole moment.

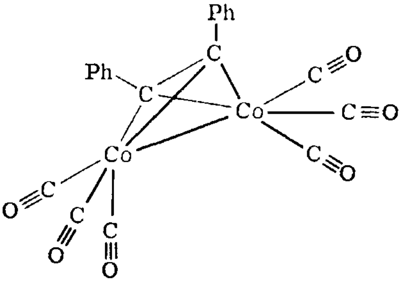


FIG. 4. Structure of $(C_6H_5)_2C_2Co_2(CO)_6$.

If bis(cyclopentadienylnickel carbonyl) is heated above 130°C, some carbon monoxide is lost and the tri-nuclear tris(cyclopentadienylnickel) dicarbonyl is formed (*79*). The dipole moment is zero, and the infrared spectrum shows typical π-cyclopentadienyl bands and only one carbon-oxygen vibration, at 1742 cm^{-1}. These facts are consistent with a symmetric structure, which has been confirmed by X-ray analysis (*177*, *199*); the structure is shown in Fig. 5. The nature of the bonding round the carbonyl groups is of particular interest; it may be noted that the four bonds round the carbon atoms are arranged with O—C—Ni and Ni—C—Ni angles of about 135° and 76° respectively. The carbon-oxygen distance is comparatively large and the stretching frequency abnormally low, but the unusual hybridization may account for this rather than an unusual amount of "back-coordination." The substance has an odd number of electrons and the magnetic moment of 1.79 B.M. (*79*) shows the maximum degree of spin-pairing. The results of an electron spin resonance investigation should prove very interesting.

The only apparently mononuclear complex of nickel(I) so far discovered is $K_3Ni(CN)_4$ (*187*). It is an extremely reactive substance obtained by reduction of $K_2Ni(CN)_4$ in strongly alkaline solution; it has a magnetic moment of 1.73 B.M., which is the value expected for one unpaired electron. This compound may be compared with the complex acetylides prepared by Nast (*183*), which have empirical formulas $K_3Ni(C_2R)_4$ (R = H, CH_3, or C_6H_5), They are diamagnetic, however, and must therefore be formulated as binuclear, i.e., $K_6[Ni_2(C_2R)_8]$. The fact that acetylides and cyanide have very similar properties as ligands (*183*) indicates that the factors governing the dimerization of nickel(I) complexes must be very subtle indeed.

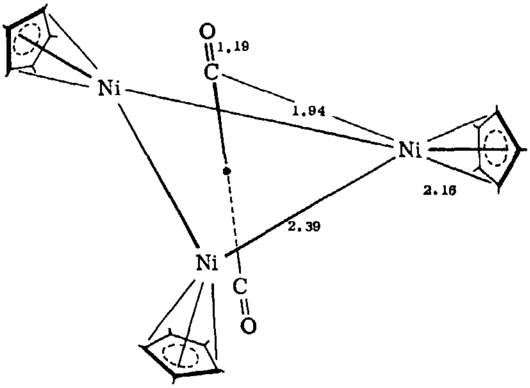


FIG. 5. Structure of $(C_5H_5)_3Ni_3(CO)_2$.

In general, nickel(I) complexes are binuclear and diamagnetic, with a total of eight ligands, although one with only six is also known. The types of ligand so far known to stabilize this oxidation state are all capable of accepting back-donation into empty antibonding orbitals. In only one case is the structure known with certainty, and this substance does not belong to the usual dimer class. Of particular interest are the possibility of bridge formation in dicarbonyl species, and the general question of the basic stereochemistry round each nickel atom; in different suggested structures this is variously based on square-planes, trigonal bi-pyramids, square pyramids, and octahedra.

IV. Oxidation State +2

A. GENERAL

It is in this oxidation state that the most striking advances have been made in the stereochemistry of these elements. The search for tetrahedral nickel(II) complexes, eventually successful in its original aim, has allowed certain other discoveries to be made which have opened up new ideas in stereochemistry. The subject is very closely connected with ligand-field theory, and the essentials of this theory are summarized here as they apply to d^8-systems. For the reader who is unfamiliar with ligand-field theory, more complete accounts can be found in several review articles (*10, 22, 64, 109, 137, 180, 193, 196, 197*).

Most of the stereochemical arrangements found in these complexes are based on the octahedron or on the tetrahedron, and may be derived from these configurations by a suitable distortion. Both basic systems have cubic symmetry and *d*-orbital energies are split into a triplet and a doublet. The group-theoretical notation will be used for their description.*

In an octahedral field the triplet t_{2g} lies lower in energy than the doublet e_g, and the electron configuration of the lowest level may be written $(t_{2g})^6(e_g)^2$. There is only one way of arranging the electrons in this configuration, and it is therefore nondegenerate and not liable to Jahn-Teller distortions (*131*). Thus, when the six ligands are identical, one may expect the complexes to be quite regular. The two e_g electrons are spin-parallel, and, since there is no resultant orbital angular momentum once the degeneracy of the *d*-orbitals is lifted, magnetic moments should be close to the spin-only value of 2.83 B.M. However, the first excited triplet level ($^3T_{2g}$, see Fig. 6) has essentially the configuration $(t_{2g})^5(e_g)^3$; there are three possible ways of arranging the five t_{2g} electrons and the d_{yz} and d_{zx} orbitals retain their rotation properties with respect to the *z*-axis. This level, therefore, has orbital angular momentum (*75*), and the spin-orbit coupling of nickel(II) is large enough to allow mixing of this level with the lowest level to produce the true ground state. The effective result is that the orbital angular momentum is not completely "quenched" by the ligand field, and moments normally found for octahedral nickel(II) complexes are in the range 3.0–3.3 B.M.

Measurements of visible and ultraviolet spectra have become of great importance in the study of nickel(II) complexes, as the spectra of octahedral complexes have been very thoroughly assigned. The basic principles for the interpretation of ligand-field spectra have been laid down by Orgel

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* Orbital triplet: $d_{xy}, d_{yz}, d_{zx} \equiv d_\epsilon \equiv \gamma_5$. In octahedral field t_{2g}, in tetrahedral t_2.
Orbital doublet: $d_{x^2-y^2}, d_{z^2} \equiv d_\gamma \equiv \gamma_3$. In octahedral field e_g, in tetrahedral *e*.

(*195*), and a simplified diagram showing the splittings of the free-ion electronic states by an octahedral field is shown in Fig. 6. Splitting of the states ^1G and ^1S are not shown, as they are much less important in the spectra than the triplet states. Transitions are from the $^3A_{2g}$ ground state to higher triplet states. All transitions are symmetry-forbidden, but become weakly allowed when the center of symmetry is removed by vibrational and other distortions; the molar extinction coefficients are normally in the range 1–50 for triplet-triplet transitions, and less than one for the spin-forbidden triplet-singlet transitions, unless such a transition happens to be close to a triplet-triplet transition, when it may "borrow" intensity. It can be seen from Fig. 6 that there are in all four triplet states and thus three bands may be expected in the spectrum. The frequency of the first (lowest energy) is approximately equal to Δ, the ligand-field splitting of the t_{2g} and e_g orbital sets. The other two are related (*26*) in a complicated fashion to Δ and to an interelectron repulsion parameter, *B*. It has been found that many complexes fit this scheme quite closely; those complexes which do not are thought to be distorted (*26*). Strong tetragonal distortion may cause the first band to split into two components.

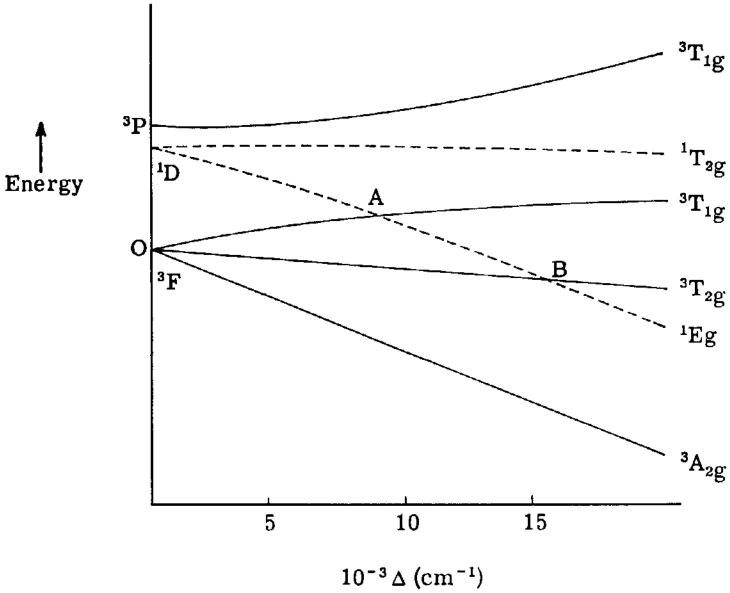

FIG. 6. Orgel diagram for Ni^{2+} in octahedral field.

In a tetrahedral field, the *d*-orbitals are split into a lower doublet (*e*) and an upper triplet (t_2), giving the lowest configuration as $(e)^4(t_2)^4$. The

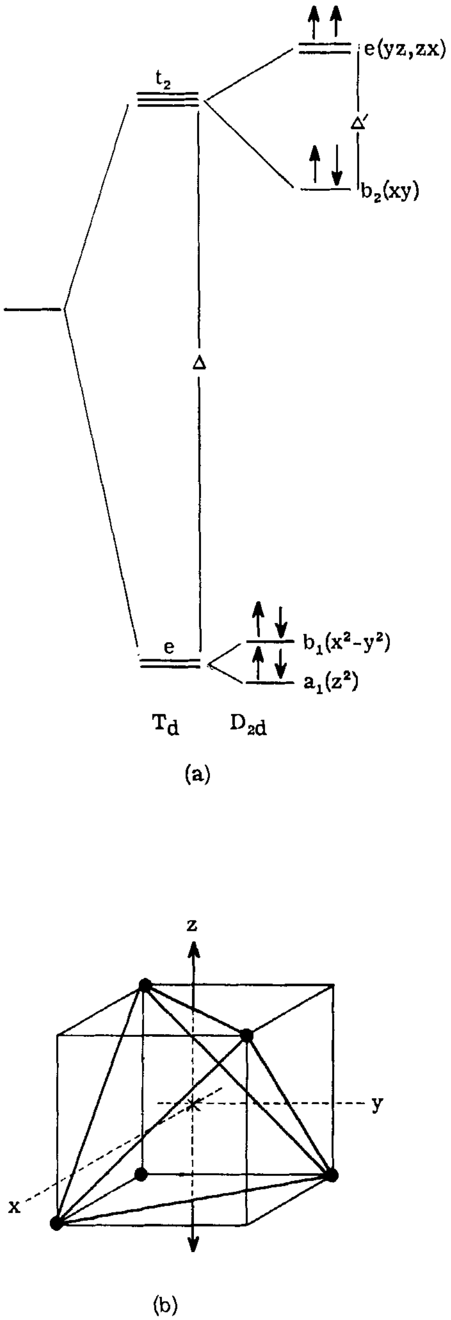

Fig. 7. Tetragonal distortion of a tetrahedral complex.

presence of four electrons in the t_2-orbitals means that there is threefold degeneracy here, which has two important consequences.

There is an odd electron partially distributed between the d_{yz} and d_{zx} orbitals, which still retain their degeneracy and their rotational properties with respect to the z-axis. The orbital angular momentum is thus not quenched by the ligand-field, and values of the magnetic moment as high as 4.1 B.M. are possible. The moment should be temperature dependent, and at low temperatures should drop rapidly towards zero, as the lowest state due to spin-orbit coupling is in fact "nonmagnetic" (*74*, *75*).

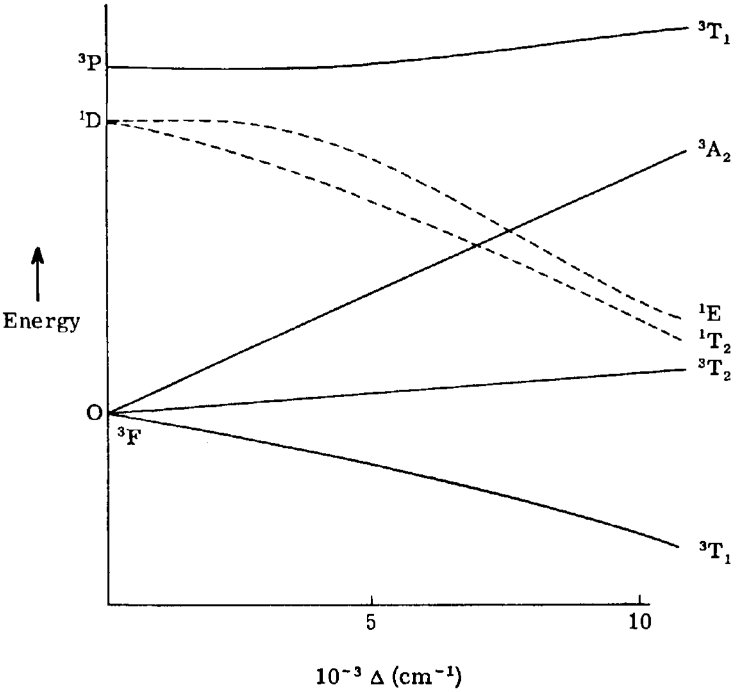

Fig. 8. Orgel diagram for Ni^{2+} in tetrahedral field.

According to the Jahn-Teller theorem (*131*), the system may become more stable by distorting to remove the degeneracy of the orbital triplet. It is only necessary to split one orbital from the other two, and, if the "center of gravity" of the three orbitals is considered to remain at the same level, stabilization may be achieved by a distortion which depresses, say, the d_{xy} orbital and raises the other two. This is shown in Fig. 7(a). The tetragonal elongation shown in Fig. 7(b) is just such a distortion. If this distortion were strong, the orbital angular momentum of the regular tetrahedral system would be quenched, and lower magnetic moments would be expected.

It has been shown, however, that the orbital degeneracy of the $^3T_1(F)$ state would be lifted by spin-orbit coupling (*142*). In this case there is no longer any need for Jahn-Teller distortion, and when the four ligands are identical the tetrahedral complexes may be quite regular.

The Orgel diagram for tetrahedral nickel(II), shown in Fig. 8, is similar to that for the octahedral case, but the levels are inverted. The lowest level, $^3T_1(F)$, has the same symmetry properties as the higher level $^3T_1(P)$, and the two influence each other; therefore, since all transitions are from $^3T_1(F)$, no transition corresponds to the splitting Δ. To a first approximation the transition energies should be given by 0.8 Δ, 1.8 Δ, and $(^3P - {}^3F) + 0.6\ \Delta$ (*120*). Δ is much smaller than in the octahedral case and the first transition, to $^3T_2$, lies in the far infrared and has not been observed.

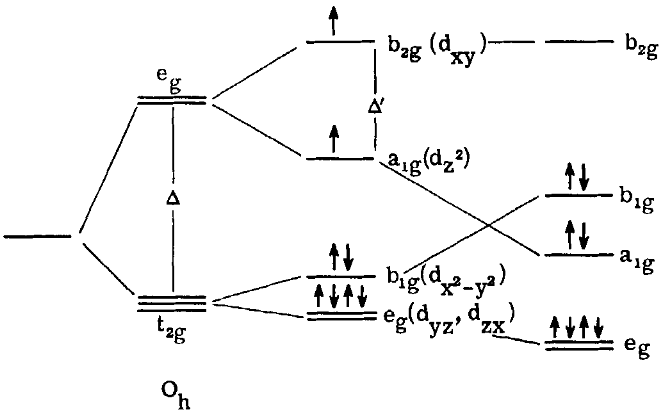

FIG. 9. Tetragonal distortion of an octahedral complex.

In the point-group T_d, *p*-orbitals transform in the same way as d_{xy}, d_{yz}, and d_{zx}, owing to the absence of a center of symmetry. This has the important consequence that all six orbitals are mixed together and the electronic transitions have some *d-p* character; they are therefore not forbidden and have higher intensities than the nearly pure *d-d* transitions of octahedral complexes.

The well known square-planar complexes of these metals are best considered as the limit of tetragonal distortion of octahedral complexes. If the ligands on the *z*-axis of an octahedral complex are moved away from the metal, the orbital energies move roughly as shown in Fig. 9. The complex will remain paramagnetic until Δ' is larger than the energy required to pair two electrons; when the distortion is greater the complex becomes diamagnetic with the eight electrons in the four low-lying *d*-orbitals. It is important to note that there is no sharp change in the orbital-scheme, or in the nature of the bonding, at the magnetic change-over. The early tetragonal distortion is observable in the spectra of certain complexes as a splitting of the first band, which is no longer a simple $t_{2g} \rightarrow e_g$ transition (*26*).

It must be emphasized that square-planar complexes cannot be treated quantitatively on a purely electrostatic basis, as allowance must be made for covalent bonding. Nickel(II) forms square-planar complexes only with particularly strong ligands which have the ability to form π-bonds. The four σ-bonds are formed by combining ligand orbitals with $nd_{x^2-y^2}$, $(n + 1)s$, $(n + 1)p_x$ and $(n + 1)p_y$ orbitals of the metal. The $(n + 1)p_z$ orbital may be used in the π-bonding, but generally remains an unoccupied nonbonding orbital; it is important in the formation of diamagnetic, penta-coordinated complexes which are described later.

B. TETRAHEDRAL COMPLEXES OF NICKEL(II)

The development of this class of compound has had a comparatively long history, but only in recent years has reasonable verification of its existence been achieved.

The absence of X-ray crystal structure determinations for the compounds is very marked; in their absence, the basic criteria for the assignment of a tetrahedral configuration to a nickel(II) complex used to be paramagnetism and tetra-coordination. The number of cases in which the latter criterion was assumed, or completely overlooked, is surprisingly large. One of the most frequent mistakes was to neglect the presence of water in a compound as a possible ligand. For example, bis(salicylaldehyde)nickel dihydrate was always referred to simply as bis(salicylaldehyde)nickel, and was for many years considered as tetra-coordinated and tetrahedral on account of its paramagnetism (*250*). The nickel in this complex is now known to be effectively octahedral, with coplanar salicylaldehyde groups and two water molecules in *trans*-positions (*148*). Removal of the water molecules gives a product isomorphous with its zinc analogue (*55*); this has been cited as evidence in favor of a tetrahedral configuration. However, the spectrum shows that the coordination of the nickel is octahedral; the substance is polymerized (*151*, *174*), probably in a fashion similar to bis(acetylacetone)nickel (*30*, *31*, *108*).

Ligand-field theory predicted (*10*, *22*) that tetrahedral nickel(II) complexes should be unstable with respect to octahedral ones, at least so long as the two extra ligands were available. This arises because, if one accepts the *d*-orbital "center of gravity" as an energy-zero (a point which should be raised more often), the crystal-field stabilization of an octahedral complex works out to be 0.84 Δ greater than that of a tetrahedral complex with the same ligands. [Δ is the orbital splitting in the octahedral case, and is approximately $\frac{9}{4}$ that of a tetrahedral complex with similar ligands (*9*).] This energy difference would be of the order 20–40 kcal/mole for common ligands. Other factors governing the relative stabilities of complexes, such as entropies, solvation energies, lattice energies, etc. must not be forgotten, but nevertheless the difference in ligand-field stabilization has an important role.

After the emergence of ligand-field theory several supposedly tetrahedral nickel(II) complexes were reexamined and without exception were found to be not tetrahedral. The structure of Jensen's compound, $(Et_3P)_2Ni(NO_3)_2$, is still unknown (*5, 100, 132*), and the possibility of its being tetrahedral remains, but the formation of nitrate bridges in the solid seems more likely to the author. The fact that it is monomeric in solution does not exclude the possibility of solvent coordination, or of the nitrate ion being bidentate as in copper nitrate (*252*). Some of the configurations established by the reexaminations mentioned above are surprising and are discussed in other sections.

The first definitive case of nickel(II) in a tetrahedral environment was in the spinel $NiCr_2O_4$ (*215*); the octahedral sites in the oxide lattice are preferentially occupied by chromium(III) ions, leaving only tetrahedral sites for the nickel(II) ions.

Nickel(II) ions exist in tetrahedral environments in certain chloride and nitrate melts, and also in mixed crystals based on oxide or chloride lattices (*25, 115, 138, 228, 241*). These homogeneous mixtures are usually deep blue, in contrast to the yellow mixed halides, of formula $MNiX_3$, in which it has been shown that the nickel is octahedrally coordinated (*4, 6*). The magnetic properties of these mixtures do not seem to have been investigated, but the spectra are well-known. Spinel, $MgAl_2O_4$, in which a small percentage of the magnesium atoms have been replaced by nickel, shows twin peaks at 15,700 cm^{-1} and 16,700 cm^{-1} (*228*); up to 25% nickel may be incorporated into the Cs_2ZnCl_4 lattice and here the main peaks are at 14,200 cm^{-1} and 15,300 cm^{-1} (*115*). Similar bands appear in the melts, with extinction coefficients of about 170. Other, weaker bands which appear are sometimes due to octahedral species, and should not at present be used for diagnostic purposes.

The $[NiCl_4]^{2-}$ anion may be readily obtained in salt form with large cations. Gill and Nyholm (*101, 102*) prepared a set of such salts with the triphenylmethylarsonium and tetra-ethylammonium cations and several transition metals. The triphenylmethylarsonium salts with divalent metals, formula $[Ph_3MeAs]_2[MCl_4]$, are isomorphous, except for the copper salt; the crystals have the cubic space group $P2_13$ with four metal atoms in a unit cell. This in itself is evidence that the anions are tetrahedral. The high magnetic moments of the nickel compounds provide further support. (See Table V).

The formation of a deep blue color in a solution of a nickel halide in various organic solvents is quite common, but, in the absence of other ligands, it is due to only a small amount of a tetrahedral anion; qualitative spectra obtained from these solutions are unreliable. The solutions are in general very complicated as a result of competition between solvent molecules and halide ions for the coordination sites. Certain results with solvents such as dimethyl formamide and dimethyl sulfoxide (*28, 98, 167*) indicate that any or all of the species $[NiX_nS_{6-n}]^{2-n}$ may be present, where X =

TABLE V

MAGNETIC MOMENTS OF TETRAHEDRAL NICKEL(II) COMPLEXES

Compound	μ_{eff} B.M.	Reference
$[Ph_3MeAs]_2[NiCl_4]$	3.89	*101*
$[Ph_3MeAs]_2[NiCl_4]$	4.1 (solution)	*101*
$[Et_4N]_2[NiCl_4]$	3.87	*101*
$[Me_3PhCH_2N]_2[NiCl_4]$	4.45	*98*
$[Ni(DMSO)_6][NiCl_4]$[c]	“3.65”[a] 3.92[b]	*42*
$[Ni(TpO)_6][NiCl_4]$[d]	“3.69”[a]	*84*
$[Et_4N][NiBr_4]$	3.79	*101*
$[Ni(TpO)_6][NiBr_4]$[d]	“3.77”[a]	*84*
$[Ph_3MeAs]_2[NiI_4]$	3.49	*101*
$[Et_4N][Ph_3P \cdot NiBr_3]$	3.68	*41*
$[Bu_4N][Ph_3P \cdot NiI_3]$	3.46	*41*
$(Ph_3P)_2NiCl_2$	3.40 3.07	*41* *251*
$(Ph_3P)_2NiBr_2$	3.25 2.92	*41* *251*
$(Ph_3P)_2NiI_2$	3.27	*41*
$(Ph_3PO)_2NiCl_2$	3.7	*44*
$(Ph_3PO)_2NiBr_2$	3.98	*44*
$(Ph_3PO)_2NiI_2$	3.84	*44*
$(Et_3PO)_2NiBr_2$[e]	3.40	*129*
$[(C_6H_{11})_3PO]_2Ni(NO_3)_2$[e]	3.26	*129*
$[(C_6H_{11})_3PO]_2NiCl_2$[e]	3.65	*129*
$Ni(NO)(OH)_3$	2.97	*111*
$[Ni(NO)(NH_3)_2(OH)](OH)_2$	2.9	*112*

[a] Figures in quotation marks refer to moments not corrected for the moment of the cation.

[b] Calculated after allowing for moment of cation.

[c] DMSO = dimethyl sulfoxide.

[d] TpO = tetrahydrothiophen oxide.

[e] No other evidence that they are tetrahedral.

halide, S = solvent. The addition of a large excess of halide ion improves the spectra but they remain unreliable.

Furlani and Morpurgo (*98*) have, however, obtained very good spectra of the complex anions in nitromethane; addition of a small excess of halide was necessary in most cases. Their results are summarized in Table VI, together with the assignment in a regular tetrahedral field. The symbols used may be understood by reference to the Orgel diagram of Fig. 8.

TABLE VI
SPECTRA OF TETRAHEDRAL ANIONS IN NITROMETHANE (*98*)

$[NiCl_4]^{2-}$		$[NiBr_4]^{2-}$			
cm^{-1}	ϵ_{mol}	cm^{-1}	ϵ_{mol}	Assignment	Calculated ($\Delta = 3700\ cm^{-1}$)
7,380	19	7,000	30	$^3T_1 \rightarrow {}^3A_2$	6,800
11,620	4.2	10,720	1.2	$^3T_1 \rightarrow {}^1T_2$	11,160
				$^3T_1 \rightarrow {}^1E$	11,880
14,240	210	13,260	267	$^3T_1 \rightarrow {}^3T_1(P)$	14,800
15,250	204	14,200	271	$^3T_1 \rightarrow {}^1T_2$	17,740
~16,000	~120	—	—		
~20,000	~1.1	18,200	9.0	$^3T_1 \rightarrow {}^1A_1$ ^1E $^1T_1$	19,000– 20,500
		21,400	0.8		

The principal frequencies in the spectrum are given approximately by 0.8 Δ, 1.8 Δ, and 0.6 Δ + (^3P − ^3F). (^3P − ^3F) depends on the interelectron repulsion parameters; in the gaseous ion it is equal to 16,900 cm^{-1} (*4*), but decreases on complex formation owing to delocalization of electrons over the ligands (*4*, *26*). The first transition lies in the far infrared and has not yet been observed.

The authors (*98*) have put forward three possibilities for the splitting of the "characteristic" band at about 14,500 cm^{-1}. If a transition to a singlet state lies close to the triplet transition, the former can "borrow" intensity. Such a singlet could be $^1T_2(D)$. This effect would, however, be very dependent on Δ, and should disappear when the main transition is no longer near a cross-point on the Orgel diagram; it is therefore not consistent with the fact that the splitting remains fairly constant at about 1000 cm^{-1} in the range 15,200 cm^{-1} (Ni^{2+} in spinel) to 13,700 cm^{-1} (in $NiBr_4^{2-}$).

Liehr has shown (*142*) that the orbital degeneracy of the ground state in a tetrahedral nickel(II) complex may be lifted by spin-orbit coupling. This means that these complexes may not be liable to Jahn-Teller distortion as has been thought for some time. Such coupling would also have the effect of splitting all transitions into several components, the exact number depending on the multiplicity and selection rules in each case. Thus spin-orbit coupling offers a very reasonable explanation of this splitting.

The third possibility is that the complex is distorted; the authors state that this would be expected on purely electrostatic grounds. A tetragonal distortion splits all states into two, except for $^3A_2$ which cannot be split; the $^3T_2$ and $^3T_1(P)$ transitions would therefore be split into two.

It has recently been shown that alkyl sulfoxides are good solvents for transition metal halides, and many adducts can be isolated (*42, 84, 167, 227, 231*). Nickel perchlorate takes up six dimethyl sulfoxide ligands, but the chloride apparently only three. It has been shown from the reflectance spectrum and from the high magnetic moment (*42*) that this compound should be formulated as $[Ni(DMSO)_6][NiCl_4]$, in which the anion is tetrahedral. Infrared spectra (*43, 127*) show that the dimethyl sulfoxide coordination is through oxygen. Similar compounds are found with tetrahydrothiophenoxide (*84*).

Phosphorus compounds yield a comparatively large number of tetrahedral nickel complexes. The first compounds of this class to be reported were $(Ph_3P)_2NiCl_2$ and $(Ph_3P)_2NiBr_2$ (*251*). X-ray evidence indicates the coordination of the metal in the chloride to be tetrahedral in the solid state; in solution they are monomeric and nonconducting, but this is not necessarily relevant as solvent participation in the coordination sphere cannot be excluded. The magnetic moments are not much greater than the spin-only value, and a regular tetrahedral configuration must be excluded. Cotton (*41*) has found that the visible spectra agree with distorted tetrahedral structures.

More regular complexes with triphenylphosphine are obtained in compounds like $Et_4N[Ph_3P{\cdot}NiBr_3]$, made by heating equimolar proportions of tetra-ethylammonium bromide, triphenylphosphine, and nickel bromide in butanol (*41*). The conductivities of these substances in suitable solvents are typical of 1:1 electrolytes, and the high magnetic moments and absorption spectra point very strongly to the tetrahedral configuration.

Phosphine oxides give a variety of complexes with nickel(II) and with other transition metals. A yellow complex, $[(Ph_3PO)_4Ni][ClO_4]_2$, was thought to contain a tetrahedral cation (*14*) on account of the high magnetic moment of 3.51 B.M., but the absorption spectrum does not agree with such a supposition; the cation has now been assigned a distorted planar shape (*40*). This compound is described to illustrate the danger of relying on a relatively high magnetic moment alone to decide on a tetrahedral configuration.

Several compounds of general formula $(R_3PO)_2NiX_2$ (R = Alkyl or aryl, X = Cl, Br, or I) are known (*44, 129*), and the triphenyl complexes are without doubt tetrahedral (*44*). The field round the nickel atom in

$(Ph_3PO)_2NiBr_2$ is very nearly regular. Arsine oxides form similar complexes (*106*).

Griffith *et al.* (*111*, *112*) have shown that the blue compounds obtained by the interaction of nitric oxide and nickel carbonyl in the presence of water or an alcohol (*68*) have the general formula $Ni(NO)(OR)_3$, and are probably tetrahedral. The N—O stretching frequency of 1828 cm^{-1} in $Ni(NO)(OH)_3$ indicates coordination of NO^+; the spectra show absorption at 15,500 cm^{-1}, in agreement with other such complexes, but the magnetic moment of $Ni(NO)(OH)_3$ is only 2.97 B.M., which indicates considerable distortion.

It can be concluded that tetrahedral nickel(II) complexes may be recognized by four-coordination, a fairly characteristic spectrum, and, if nearly regular, a magnetic moment in excess of 3.6 B.M. Some attempt should be made to confirm four-coordination, but this may be difficult without the help of X-ray diffraction. It is not sufficient to note that the complex has an unexpectedly deep blue colour (*147*), or even that the spectrum is intense, because there may be a charge-transfer band in the visible region; the spectra usually show two fairly sharp maxima close together and a weaker band at about half the frequency. A high magnetic moment indicates that the effective field is nearly regular, but the distorted complexes show moments only slightly above the spin-only value. X-ray analysis apart, there is no single criterion to distinguish a tetrahedral complex, but a combination of spectrum and magnetic moment is effective.

C. SQUARE-PLANAR COMPLEXES

1. *General*

Square-planar complexes of platinum(II) and palladium(II) have been known for a long time; the comparatively simple unit cells of compounds such as K_2PdCl_4, K_2PtCl_4, and $Pd(NH_3)_4Cl_2H_2O$ led to early elucidation of the structures (*257*) and they all contain square-planar ions. The simple halides $PdCl_2$ and $PtCl_2$ (*71*) consist of chains in which the metal is bonded from the corners of a square. Nickel chloride, on the other hand, has a layer lattice in which the nickel is octahedrally coordinated, and in the halide complexes the coordination is tetrahedral, as described in Section IV,B.

The tetracyano-complexes of all three metals are square-planar and very similar, corresponding salts being isomorphous. Coordinate analyses have recently been given in D_{4h} symmetry for the nickel (*154*) and for the platinum complexes (*243*).

Nickel cyanide itself is soluble in ammonia solutions, which will then absorb certain molecules like benzene and aniline. Crystalline products are obtainable of general formula [$Ni(CN)_2 \cdot NH_3 \cdot X$], where X is, say, benzene. The benzene derivative has a comparatively simple tetragonal unit cell (*212*). It consists of layers of coplanar [$Ni(CN)_4$] squares linked together by [$Ni(NH_3)_2$] groups, attached through cyanide nitrogen atoms. The layers are stacked together so that the ammonia groups stick out of the planes and help to form "boxes"; the benzene molecules lie in these boxes, with their planes at right angles to the nickel-cyanide layers. The aniline derivative is very similar (*211*), but there is a certain degree of randomness depending on which direction the aniline adopts. When the substituent is removed, the product takes up water very readily, but, although the structure remains essentially the same, it becomes strongly distorted (*213*). Pyridine is not taken up in the same way as benzene or aniline, but replaces the ammonia to give [$Ni(CN)_2 \cdot C_5H_5N$]. It is believed that here the layers are pushed so far apart that clathrate formation cannot occur, at least with benzene (*211*). It would be worth investigating whether larger molecules, such as naphthalene, can be absorbed.

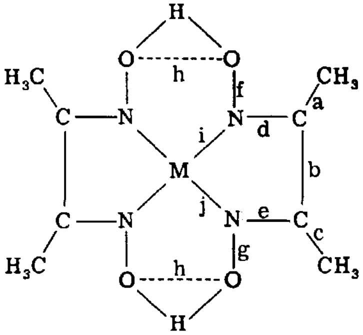

FIG. 10. The ligand skeleton in dimethylglyoxime complexes.

References		a	b	c	d	e	f	g	h	i	j
(*260*)	Ni	1.50	1.54	1.53	1.30	1.29	1.36	1.35	2.40	1.85	1.85
(*260*)	Pd	1.55	1.47	1.54	1.31	1.31	1.37	1.33	2.59	1.93	1.99
(*200*)	Pt	1.46	1.57	1.47	1.27	1.38	1.31	1.24	3.03	1.93	1.95

The structures of a large number of square-planar organic chelates of nickel, palladium and copper have been wholly or partially determined; details may be found in the references given. These chelates have been generally of two types, (1) *cis*- and *trans*-complexes based on salicylaldimine (*51*, *72*, *88*, *148*, *149*, *169*, *170*, *198*, *233*, *234*, *238*) and (2) complexes of *vic*-dioximes (*85–87*, *105*, *200*, *201*, *260*). In the first type, the donor atoms are two nitrogens and two oxygens, and the *trans*-configuration is preferred; a *cis*-configuration may be forced by the requirements of the ligand, as in bis(salicylidene)ethylendi-imine complexes. There is a general tendency for these complexes to stack in a way similar to that of naphthalene and other condensed aromatic hydrocarbons (*214*), with interplanar spacings of about 3.4 Å.

In certain cases, very strong intramolecular hydrogen bonds are formed. Nickel (*105*, *260*), palladium (*201*, *260*), and platinum (*200*) dimethylglyoxime complexes are isomorphous, but there are differences in the detailed bond lengths found. The skeleton is shown in Fig. 10 with the distances concerned. The O—O distances are 2.40 Å, 2.62 Å, and 3.03 Å respectively. The O—H frequency in the infrared spectrum of the nickel compound is at 1775 cm^{-1} (*219*), about half of that for a free hydroxyl group. This decrease is so marked and the distance between oxygen atoms so short that a fully symmetrical hydrogen bond has been suggested.* In bis(ethylmethylglyoxime)nickel, the length of this bond is even shorter, 2.33 Å (*86*). Fairly strong hydrogen bonding is also believed to be present in the nickel and palladium salicylaldoxime complexes (*169*, *234*), in this case between an oxime and a ligand (phenolic) oxygen.

Bis(N-methylsalicylaldimine)nickel exists in at least three forms. The orthorhombic α- and the monoclinic β-forms are diamagnetic. The third form is amorphous, highly insoluble and paramagnetic (*117*, *224*); it is believed to be polymeric and to contain effectively octahedrally coordinated nickel. In the β-form, the four nickel-ligand bonds are coplanar, but the rest of the molecule is twisted out of this plane slightly (*88*). In the α-form the molecules are planar and the metal atoms are stacked directly on top of each other to form a chain parallel to the *c*-axis (*72*, *170*). Such a structure is analogous to that of the dimethylglyoxime complexes of nickel, palladium, and platinum, and is discussed in the next section.

Bis(N-methylsalicylaldimine)copper exists in orthorhombic α- and γ-forms and in a monoclinic β-form. The α- and β-forms are isomorphous with the nickel compounds (*170*). Only the α-form is known for the palladium chelate.

2. Direct Stacking and Metal-Metal Interactions

It has been mentioned that the dimethylglyoxime complexes of nickel, palladium, and platinum, and the N-methylsalicylaldimine complexes of

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* Blinc and Hadži (*23a*) have shown that this frequency, which lies at about 1650–1820 cm^{-1} in a series of *vic*-dioxime complexes, is more probably the in-plane O-H deformation frequency, and that the O-H stretching frequency lies in the range 2340–2380 cm^{-1}; they find the out-of-plane O-H vibration between 860 and 930 cm^{-1}. It seems likely that the hydrogen atoms do not lie directly between oxygen atoms, but it is still uncertain whether they are symmetrically disposed with respect to the oxygen atoms or not.

nickel, copper, and palladium (α-forms), contain flat molecules which are stacked in columns with the metal atoms directly over each other. In the dimethylglyoxime complexes, alternate molecules are twisted through 90°, thus accommodating the rather bulky methyl groups and allowing a comparatively close approach of metal atoms. In the N-methylsalicylaldimine complexes both methyl groups and benzene rings must be accommodated, and the approach of metal atoms is not quite so close. The metal-metal distances are shown in Table VII, together with such distances in a selection of salts isomorphous with Magnus's green salt, $\mathrm{Pt(NH_3)_4{\cdot}PtCl_4}$, which show very similar crystal structures to the chelates (*7, 50*).

TABLE VII

METAL-METAL DISTANCES IN SOME COMPOUNDS OF COLUMNAR STRUCTURE

Compound	M-M distance (Å)	Color or Dichroism	References
$\mathrm{Ni(DH)_2}$[a]	3.25 ± .005	Abnormal	*105, 260, 265*
$\mathrm{Pd(DH)_2}$[a]	3.26 ± 0.01	—	*201, 260*
$\mathrm{Pt(DH)_2}$[a]	3.23 ± 0.01	Abnormal	*200, 265*
α-$\mathrm{Ni(MeS)_2}$	3.30, 3.27(5)	"Normal"	*72, 170*
α-$\mathrm{Cu(MeS)_2}$	3.33, 3.31	—	*149, 170*
α-$\mathrm{Pd(MeS)_2}$	3.28(5)[c]	—	*170*
$\mathrm{Pt(NH_3)_4{\cdot}PtCl_4}$	3.23, 3.24(5)	Abnormal	*7, 171, 264*
$\mathrm{Pd(NH_3)_4{\cdot}PtCl_4}$	3.25	Normal	*171*
$\mathrm{Cu(NH_3)_4{\cdot}PtCl_4}$	3.23, 3.22	Normal	*29, 171*
$\mathrm{Pt(MeNH_2)_4{\cdot}PtCl_4}$	3.25	Abnormal	*171, 266*
$\mathrm{Pd(NH_3)_4{\cdot}PdCl_4}$	3.25	Normal	*171*
$\mathrm{Pt(NH_3)_4{\cdot}Pt(SCN)_4}$	3.35	"Normal"	*172*

[a] $\mathrm{DH_2}$ = dimethylglyoxime.

[b] MeSH = N-methylsalicylaldimine.

[c] Assumed to be $c/2$.

In order to account for the insolubility and analytical specificity of the nickel and palladium dimethylglyoxime derivatives, Godycki and Rundle (*105*) suggested that there is a bonding interaction between the metal atoms along the chains; this would be of a strength sufficient to increase the lattice energy and to depress the solubility, as compared to the copper derivative. Such a comparison can at best be very crude, for the copper complex has subsequently been shown to have an entirely different structure (*85*), and the solvation energies are not necessarily comparable. There is, however, other evidence for some sort of interaction between the metal atoms.

Banks and Barnum (*13*) have found that the visible spectra of a series of these nickel and palladium *vic*-dioxime complexes always show a band in the solid state which is not present in solution spectra. This difference may be due to a solvent effect or to metal-metal interaction in the solid; the latter is more likely as the solvents used were not of the type to produce strong axial perturbations (see Section IV,D,*1*), at least in these particular compounds. The crystal spectrum of bis(dimethylglyoxime)nickel (*265*) shows that the band is more strongly polarized in the z-direction than in the xy-plane; there may be two components, one excited only by radiation polarized in the z-direction, the other only in the xy-plane, but this must be regarded as uncertain at present. The appearance of a band polarized more strongly perpendicular to a molecular plane, and at the same or a lower frequency, than in the plane has been termed "abnormal dichroism," and is evidence for interaction between planes (*264*).

The frequencies of the solid-state bands fall as the metal-metal distance decreases (*13*); the same effect may be brought about by the application of high pressure (*268*), which is presumably a way of decreasing the metal-metal distance. In two compounds, minima have been found in the frequency-pressure relationship, and it is reasonable to suppose that such minima would be more generally found were the pressure high enough. The initial drop in frequency must be caused either by an increase in the energy of the ground state (i.e., less stable), by a decrease in the energy of the excited state, or by a combination of the two. The rise in frequency after the minimum may be due to a reversal of the above, or to a change in the nature of the absorption. It is apparent that a definite assignment of the band must be made before one is able to distinguish the above possibilities, and unfortunately there is no general agreement about this. D_{4h} (square-planar) symmetry is commonly assumed for the ligand-field, but D_{2h} would probably be more accurate, as in the case of bis(N-methylsalicylaldimine)-nickel (*72*). Banks and Barnum have assumed that the solid-state transition is a "vibronically-allowed" one from the d_{z^2}-orbital to the d_{xy} (a_{1g}* and b_{2g}* in D_{4h} symmetry, as shown in Fig. 11), but Zahner and Drickamer assume it to be a fully allowed transition to the p_z-orbital (a_{2u} in D_{4h} symmetry), from any of the occupied "sink orbitals" (*268*). The latter authors suggested that the frequency first falls with increasing pressure owing to the lowering of the energy of the p_z-orbital under the influence of metal *cations* on the z-axis; the frequency then rises as the influence of d_{z^2} electrons on the neighboring molecule becomes more important. Any interaction of this type, it should be noted, would have no effect on the ground state, and would be neither bonding nor antibonding.

Miller (*172*) has argued that, in the crystal, the d_{z^2}-orbitals and p_z-orbitals should be smeared out into bands as shown in Fig. 11. This is supported by the broadening of the band in the visible by increase of pressure (*268*). By assuming Banks and Barnum's assignment of the band in the visible, it would be concluded that the d_{z^2}-orbitals were not only smeared out, but also raised in energy. This would be an antibonding effect, and in such a case one could not explain the formation of the structure on the basis of a metal-metal bond (*105*).

However, in the bands formed by the d_{z^2} and p_z-orbitals, there are orbitals with the same symmetry properties. The higher energy ones from

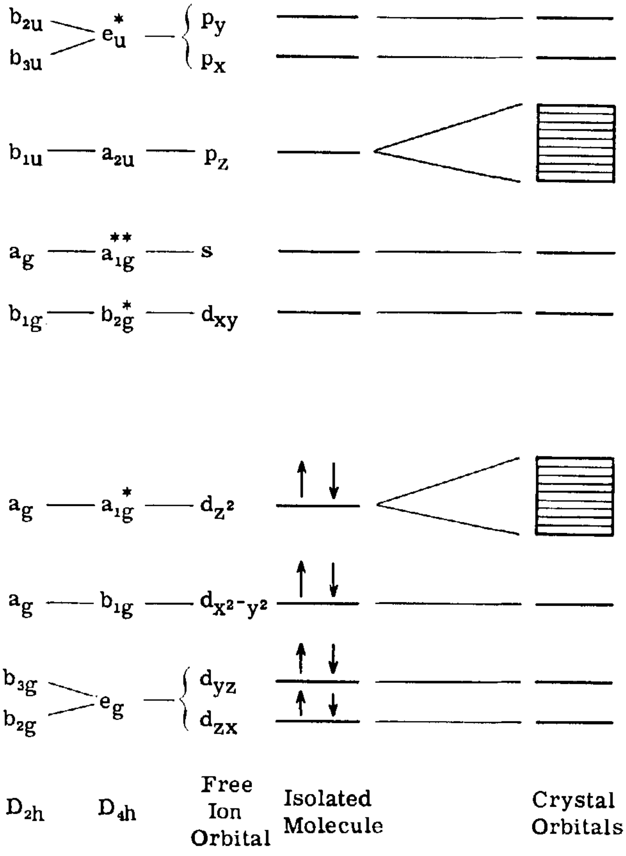


FIG. 11. Metal-metal interaction in square-planar complexes. Axes are taken between the ligands.

p_z could be mixed into the ground state to produce a lower energy, i.e., a bond. This corresponds to the configurational interaction suggested by Rundle (*217*). If the transition is from d_{z^2} to p_z, then there are two opposing effects. The action of like orbitals on each other will narrow the gap between the top of the d_{z^2} band and the bottom of the p_z band, thus lowering the frequency. Configurational interaction would on the other hand enlarge the gap. A balance of these two factors might explain the minimum in the frequency-pressure curve.

However, discussion of this type is very speculative and one can readily develop theories for the few facts known. It is important that the crystal spectrum should be more closely studied to determine at least the symmetry of the field. That the solid state band is polarized along the z-direction means that, whatever the symmetry, the excited state (the ground state is fully symmetric) must be represented in the same way as z, i.e., B_{1u} in D_{2h}, or A_{2u} in D_{4h}. This can arise directly if the transition is to the p_z-orbital, but can also arise from symmetrical transitions coupled to unsymmetrical vibrations. When this transition has been given an assignment, it will then be somewhat simpler to consider the causes of its movement with variations in the metal-metal distance.

The crystal of Magnus's green salt, $Pt(NH_3)_4 \cdot PtCl_4$, contains chains of alternate anions and cations stacked flat on top of each other to form a tetragonal unit cell (*7*, *50*). The abnormal color is due to shifts towards the red in the spectrum of the anion (*264*); the crystals exhibit abnormal dichroism. On going from K_2PtCl_4 to Magnus's green salt, the perpendicular absorption (polarized along the z-axis) shifts from 29,300 cm^{-1} to 22,670 cm^{-1}, the parallel (in-plane polarized) absorption from 27,700 cm^{-1} to 24,700 cm^{-1}. It is very reasonable to assign the perpendicular band to a $^1A_{1g} \rightarrow {^1A_{2u}}$ transition, an electron being promoted to a $6p_z$-orbital.

The decrease in the frequency of this band in Magnus's green salt may in part be explained by the presence of cations on the z-axis, but this is not sufficient because such a shift should be largely independent of the nature of the cation. It has recently been shown that the tetrammine-copper and palladium(II) chloroplatinites are very nearly isodimensional with Magnus's green salt, but that the colors of these salts are in no way abnormal (*171*, *172*); there can therefore be no large shifts in the visible region of the spectrum. It has further been shown that an abnormal color, in compounds of the same structure, is specific to compounds containing platinum in both anion and cation. It has therefore been suggested (*172*) that the transition is from an occupied orbital (probably $5d_{z^2}$) of the anion to the empty $6p_z$-orbital of the cation. These orbitals are probably in any case influenced in the same way as in the dimethylglyoximates, but it is reasonable that the $6p_z$-orbital of the cation should have a lower energy than that of the anion. It is also possible that the nonsymmetrical $4f$- and $5f$-orbitals may be used by platinum.

Rundle and others (*7*, *105*, *217*) have suggested that the interaction between the metal atoms in these compounds is bonding, and that it is largely responsible for the uptake of the structure. So far as the analogues of Magnus's green salt are concerned, it has been shown that the structure is electrostatically very favorable (*172*), and that it is adopted by many compounds whose colors show no signs of shifts in their spectra. It is concluded that what interaction there is does not play an important role in the bonding, and arises only when electrostatic factors have already determined a suitable structure.

To be consistent, the same conclusion should be drawn for the dimethyloxime complexes. The difficulty here is to answer the question as to why other flat, uncharged, molecules do not stack in a similar fashion. It is believed that in fact they would do so were it not for factors such as mutual repulsion of π-electrons, as in condensed hydrocarbons (*214*). An examination of the bond lengths shown in Fig. 10 indicates that in the dimethylglyoxime complexes the π-bonding is not nearly so extensive as commonly imagined. Similarly, it is known that aromatic donor-acceptor complexes, e.g., quinhydrone, stack in a fashion very similar to the dimethylglyoxime complexes (*166a*), and also show abnormal dichroism (*182*).

D. THE RELATIONSHIP BETWEEN OCTAHEDRAL AND SQUARE-PLANAR COMPLEXES

It has already been shown in Section IV,A that square-planar complexes may be derived from octahedral ones by an infinite tetragonal distortion. There are many complexes which can be classified neither as octahedral nor as square-planar, and belong somewhere in the range of tetragonal distortion; they may be either diamagnetic or paramagnetic, or the two forms may exist in equilibrium. Under suitable conditions the complete range may be studied, and the present state of our knowledge is here described and discussed.

1. *Solution Paramagnetism of Nickel(II) Complexes*

It is now well known that many diamagnetic, square-planar nickel(II) chelates develop temperature-dependent paramagnetic moments in solution. The subject was last reviewed by Sacconi (*221*) in 1959, but later developments make a further summary worthwhile.

The first observation of an "abnormal" magnetic moment, in the sense intended here, was made by French *et al.* (*90*), who found that the normally diamagnetic bis(formylcamphor)ethylenedi-imine nickel(II) had a magnetic moment of 1.9 B.M. in methanol. They suggested that a fraction of the complex molecules were "fully paramagnetic" in the solution, an idea which is still universally accepted. Willis and Mellor (*261*) developed this theme and found that the phenomenon covered a wide range of nickel chelates and also of solvents. The moments developed were larger in pyridine than in "inert" solvents like benzene or chloroform, and the moments in pyridine often corresponded to complete conversion into paramagnetic species. They postulated the formation of octahedral di-pyridine adducts, or at least equilibria of the form:

$$\underset{\text{Diamagnetic}}{[\text{Chelate}]} + 2C_5H_5N \rightleftharpoons \underset{\text{Paramagnetic}}{[\text{Chelate}\cdot(C_5H_5N)_2]}$$

lying well to the right. The smaller paramagnetism in other solvents was regarded as due to equilibria between square-planar and paramagnetic, tetrahedral species. Calvin and Melchior (*37*), however, suggested the existence of paramagnetic, square-planar species, an idea not far removed from current theories.

The formation of solvent adducts was confirmed by the isolation of several paramagnetic di-pyridine adducts (*17*, *39*); these were more readily formed by *trans*-planar chelates, such as those of salicylaldoxime and N-methyl-salicylaldimine. Basolo and Matoush (*17*) found that there is no correlation between the paramagnetism of a given chelate and the base-strengths of the solvents benzene and its alkyl homologues. They counted this against the idea that solvent adducts were formed in all solvents, but it must be pointed out that the base-strength is a measure of the coordinating power of the solvent towards a proton; such factors as steric hindrance here play no part, but they would be of considerable importance in coordination to a large chelate molecule.

Clark and Odell have found (*39*) that the susceptibility varies with temperature in a way that can be explained very well on the basis of temperature-dependent equilibria between diamagnetic and paramagnetic forms. This is valid equally for pyridine and for "inert" solvents. Thermodynamic quantities calculated from these measurements show that the paramagnetic forms have the lower enthalpies, and that there are relatively large increases of entropy on going from the paramagnetic to the diamagnetic forms.

In the last few years the phenomenon has been extensively studied by Sacconi and his colleagues, who have investigated the physical properties of a series of bis(N-alkylsalicylaldimine)nickel compounds; the alkyl chains have always been unbranched. Measurements of atom polarizations (*221a*, *225*) and of dipole moments (*225*) indicate that there are no tetrahedral species in these solutions; the dipole moments of both diamagnetic and of paramagnetic species are almost certainly zero, and so the *trans*-planar configuration (D_{2h} symmetry) is common to both forms. The retention of D_{2h} symmetry in the paramagnetic form does not exclude the possibility of solvent coordination on the z-axis.

The magnetic moments and atom polarizations of these complexes are dependent on solvent, temperature, and length of the alkyl chain. For a particular solvent and temperature, the variations of both magnetic moment and of atom polarization show rather characteristic zig-zags when plotted against the number of carbon atoms in the chain; the highest values of both quantities are always found for the methyl derivative (*225*). The zig-zag pattern corresponds to that found for the base-strengths of the primary aliphatic amines.

The chelates described above also develop paramagnetism when they are melted; the temperature variation of the magnetic moments and the spectra show distinct similarities to the solution properties (*222*, *223*), indicating that the mechanism for the formation of paramagnetic species is very similar in both cases.

Bis(N-methylsalicylaldimine)nickel may be converted into a buff-colored paramagnetic isomer by heating the normal β-form at about 200°C. (*117*, *224*). The properties of this isomer indicate that it is polymeric, and the nickel atom probably achieves effectively octahedral coordination by sharing of oxygen atoms. This discovery is highly suggestive that the magnetic moments of the melts, and also of the solutions, are due to polymerization, or at least to some form of association. Viscosity measurements of the melts (*222*) show a reciprocal dependence on temperature, indicating that there is no association. In sharp contrast to this, many cases of association in solution have recently been found; in particular, bis(N-methylsalicylaldimine)nickel has been shown by both spectroscopic and by cryoscopic methods to associate in fairly strong benzene solution (*73*). The association is particularly strong when the alkyl group in a N-alkylsalicylaldimine complex is branched or aromatic, and the solution magnetic moments are correspondingly high (*126*).

From the facts so far described it is clear that in solutions and melts of these nickel(II) chelates there are equilibria between diamagnetic and paramagnetic species. In some cases this is clearly due to the formation of octahedral solvent adducts, although it has been shown (*73*) that even in pyridine association may also be a cause of paramagnetism. The quantum-mechanical description of this equilibrium is that singlet (diamagnetic) and triplet (paramagnetic) states, separated by an energy ΔE, are both occupied according to the Maxwell-Boltzmann distribution law. Assuming that the singlet lies lowest for ΔE positive, then the following relationship may easily be derived (*11*):

$$\mu_{\mathrm{eff}} = g\sqrt{\frac{6}{3 + e^{\Delta E/RT}}}\ \mathrm{B.M.}$$

g is the Landé splitting factor, and, if the possibility of the paramagnetic form being regularly tetrahedral is excluded, may be taken as about 2.2. From the known values of μ_{eff} under various conditions, ΔE may be calculated. Clark and Odell's results (*39*) give negative values at low temperatures showing the triplet to lie lowest (at 198°C. and below). The values found are usually quite small, between 0 and 4 kcal/mole. There is a steady increase with temperature up to about 120°C, after which the value remains almost constant (*232*). This behavior is reflected by a minimum in μ_{eff} at about 120°C, in both solutions and melts.

The theory needed to explain why normally diamagnetic compounds should develop singlet and triplet states of very nearly equal energy has been developed by Maki (*159–161*); Ballhausen and Liehr have come to similar conclusions on much simpler grounds (*11*). Maki (*159*) has used purely electrostatic models to determine the splittings of the states of a nickel(II) ion in different symmetries. The results obtained have been tested by attempting to assign the near infrared and visible spectra of suitable complexes with them (*160, 161*).

In D_{4h} symmetry (square-planar, with or without ligands on the z-axis), the ^3F, ^1D, ^3P, and ^1G states of the free ion split into 5, 4, 3, and 7 components respectively. Many of the components have the same transformation properties and can mix. When there are no ligands on the z-axis, a singlet, $^1A_{1g}$, becomes the lowest level as the field strength increases; the next highest triplet is $^3B_{2g}$. These correspond approximately to the electron configurations shown in Fig. 12, the axes being taken between the ligands.

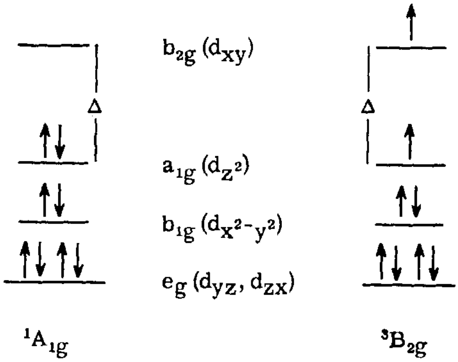


FIG. 12. Electron configurations in D_{4h} symmetry.

The singlet state will lie the lower only when Δ is greater than the energy necessary to pair two spins in the d_{z^2}-orbital. This has been estimated at 15,000 cm^{-1}, or 43 kcal/mole (*11*). When there are no ligands on the z-axis, Δ is determined by the field due to the four in-plane ligands. Under such conditions one finds that all complexes are diamagnetic. However, Δ is reduced by ligands, or negative charge, on the z-axis because the energy of the d_{z^2}-orbital is raised, and at some stage the singlet and triplet states will change their order. The weaker the in-plane field, the smaller is the axial perturbation needed to produce paramagnetism.

In D_{2h} symmetry (*trans*-planar), the system is very similar except that more states of the same transformation properties are produced by the field, and there is more mixing. A larger in-plane field is necessary to give a singlet ground state than in the D_{4h} case, and there are three triplets of fairly low energy, their exact order depending on the field. This system is more susceptible to z-axial perturbations than the D_{4h} case, i.e., a triplet ground state is more readily obtained; this difference increases markedly with the departure from D_{4h} symmetry.

The C_{2v}, or *cis*-planar, case is very similar to D_{4h} and the parameters used for the different ligand atom fields may be replaced by a single mean value.

The assignments of the spectra of suitable nickel(II) complexes on the grounds of the theory roughly described (*160, 161*) are on the whole impressively accurate, but in certain cases errors of over 30% may mean either that the purely electrostatic picture is not good enough, or that adjustment of the parameters would improve the agreement. Measurements of crystal spectra (*72*) have shown some of Maki's assignments to be unlikely.

From these arguments it may be concluded that a low-lying triplet state may be induced in a planar complex either by axial perturbation or by weakening of the in-plane field, or by both effects acting simultaneously. Weakening of the in-plane field is likely in *trans*-planar complexes where the two types of ligand are very different.

"Axial perturbation" may be taken to indicate the presence of negative charge on the z-axis, which means that there must be atoms there. From the chemist's point of view it is interesting to know what sort of atoms lie on the axis, and whether they should be regarded as coordinated to the metal or not. Maki (*161*) proposed that, in solutions of these nickel chelates, all molecules are equally solvated, and that the difference between pyridine and "inert" solvents is only one of degree. In the melts there must then be some sort of molecular interaction, which does not have more than a minimal effect on the viscosity (*222*); the melts can be regarded as "auto-solutions" (*221*).

It has now been shown that solution paramagnetism can very often be correlated with association (*69, 73, 108, 126*), the axial perturbation being produced by other solute molecules. This effect takes place simultaneously with the solvation (*73*), but very little is so far known about the relative degrees of solvation and of association, or about the relative powers of the two effects to produce a low-lying triplet. Where association is responsible for the paramagnetism, the susceptibility should be strongly concentration-dependent, the exact relationship depending on the number of molecules associated together. As an example of the balance of factors, Clark and Odell (*39*) found that the magnetic moment of bis(salicylidene)-phenylenedi-imine nickel in dioxane falls from 2.16 B.M. to 2.02 B.M. as the concentration decreases from $1.89 \times 10^{-2}\,M$ to $0.68 \times 10^{-2}\,M$. The size of the moment indicates that roughly one half of the molecules are in the triplet state. The concentration-dependence found indicates association, but the variation of the moment in the concentration-range given is far too small for this to be the only cause of paramagnetism.

There are, then, three effects which can produce a low-lying triplet state in a solution of a planar complex:

(1) The process of solution, neglecting the effect of axial solvation, may weaken the in-plane metal-ligand bonds. *Trans*-planar complexes are probably the most sensitive in this respect.

(2) Axial solvation has the effect of raising the energy of the d_{z^2}-orbital, thus lowering the lowest triplet state.

(3) Association of complexes could produce the same effect as (2), and, if ligand atoms are shared, would probably also weaken the in-plane bonding.

The variation of ΔE, the energy of the triplet state above the singlet, with complex, solvent, and temperature, may be qualitatively explained in terms of the above three effects. It has already been described how ΔE can be calculated from the magnetic moment, and that it is negative at low temperatures (*39*), and increases steadily, reaching a nearly constant, positive value at about 120°C (*221*, *222*).

A complex with a particularly strong in-plane field clearly favors a large positive value of ΔE. Similarly, solvents with high dipole moments or high coordinating ability will favor low values of ΔE. Increase of temperature would have various effects, tending to increase or decrease ΔE. It would loosen metal-ligand bonds and decrease the in-plane field; ΔE would thus decrease. It would also diminish the tendency of solvent dipoles to orient themselves on the z-axis, with consequent increase of ΔE; it would similarly decrease the tendency towards association, again increasing ΔE. The distribution between singlet and triplet states is dependent on the relationship of ΔE and temperature, and, depending on whether ΔE is positive or negative, increase of temperature will favor an increase or a decrease of the magnetic moment respectively.

The observed behavior of ΔE (*221*, *222*) is such that, starting from a completely paramagnetic state (ΔE negative), increasing temperature at first loosens the attachment of solvent molecules and lessens association more than it weakens the in-plane bonds. At about 120°C., the weakening of the in-plane field becomes more important, and may even cause a slight drop in ΔE. Such conclusions are extremely reasonable, and offer a good qualitative explanation of the variation of ΔE, and of μ_{eff}, with temperature. Too little is, however, known about the quantitative aspects, particularly in the relative importance of solvation and of polymerization.

2. Tetragonal Distortions of Octahedral Complexes

a. Paramagnetic Compounds. By tetragonal distortion is meant that distortion which reduces the effective symmetry of the ligand field from O_h to D_{4h}. When all the ligands in a mixed nickel(II) complex are electrically very similar, e.g., water and ammonia, the ligand field remains essentially regular, and the splitting Δ has a weighted mean value (*25, 136a, 137a*). When the ligands are identical, quite regular octahedral complexes are expected, but are sometimes not formed. Thus the "hexacyanonickelate" anion is so strongly distorted that it is effectively only four-coordinated; a pentacyano-complex is formed in solutions containing a large excess of cyanide ion and is diamagnetic like the tetracyanide (see Section IV,E). Nyholm (*192*) has described certain diamagnetic complexes of nickel(II), such as $[\mathrm{Ni(diarsine)_3}](\mathrm{ClO_4})_2$, which are regarded as hexacoordinated. A possible explanation for this behavior is that an exceptionally strong ligand field may somehow produce a singlet (^1E_g) ground state which would show strong Jahn-Teller distortion.

In certain cases, distortion may be imposed by the crystal structure. Nickel and palladium(II) fluorides have the rutile structure (*16, 18, 239*); in the nickel salt the fluoride octahedron is slightly flattened, whereas in palladium(II) fluoride, it is elongated. The metal-fluorine distances are shown in Table VIII. The fluoride is, incidentally, the only paramagnetic palladium(II) compound known. The magnetic moment of 1.84 B.M. at room temperature is low probably because of antiferromagnetism (*16*). In the mixed fluoride K_2NiF_4, the fluoride ions are not equivalent (*216a*) as those in the *xy*-plane are shared between two nickel atoms, whereas those on the *z*-axis are close to only one nickel atom. It follows that the ligand-field round the nickel may not necessarily be distorted if the fluoride ions concerned have different perturbing powers. In the cubic perovskite struc-

TABLE VIII
METAL-FLUORIDE DISTANCES

Substance	Structure	M-F_z (Å)	M-F_{xy} (Å)	Reference
NiF_2	Rutile	1.99	2.02	*18, 239*
PdF_2	Rutile	2.171	2.155	*16*
$KNiF_3$	Perovskite (Cubic)	2.01	2.01	*139a*
K_2NiF_4	Tetragonal	1.975	2.000	*12*

ture all anion positions are equivalent, and in $KNiF_3$ the nickel is regularly surrounded (*139a*).

In nickel(II) complexes, tetragonal distortion occurs when two ligands in *trans*-positions are very different from the other four. Such a situation commonly arises with four nitrogen atoms at the corners of a square and two halogen atoms or pseudo-halogen groups on the *z*-axis. The compounds *trans*-$[Ni(C_5H_5N)_4X_2]$, where X = Cl, Br, NCS, have nickel-nitrogen (pyridine) distances of 2.00 Å, and nickel-halogen (nitrogen in the case of thiocyanate) distances of 2.39 Å, 2.58 Å, and 2.00 Å respectively (*209*). In themselves, these distances are no reflection of tetragonal distortion, because of the varying field-strengths of the axial ligands. The spectra form a very much more sensitive test. When the distortion is strong, the first band ($^3A_{2g} \rightarrow {}^3T_{2g}$ in octahedral symmetry) may split into two components, due to the splitting of the $^3T_{2g}$ state into ^3E_g and $^3B_{1g}$ components (*x*- and *y*-axes chosen between ligands.) The first band in the spectrum of *trans*-$[Ni(C_5H_5N)_4Cl_2]$ has been shown to have two components at 8500 cm^{-1} and 10,900 cm^{-1} (*26*). The thiocyanate does not show splitting, but detailed examination of the bands observed shows that there is slight distortion of the field (*26*).

Maki (*159*, *160*) has assigned the spectra of bis(*o*-phenylenediamine)-nickel chloride and of bis(N,N′-diphenylethylenediamine)nickel chloride in octahedral, tetrahedral, and tetragonal symmetries. The first two gave no agreement with the observed spectrum, and the last gave better quantitative agreement when the presence of an axial charge was allowed for. The hydrochloride of bis(dimethylglyoxime)nickel is almost certainly another member of this group of compounds (*231a*), but it is not easy to say how big any tetragonal distortion is, because all the ligand-field bands are not observable, being hidden under charge-transfer bands (*26*). The first band is not split, and so any distortion is probably slight.

The structures of the anhydrous and hydrated forms of bis(acetylacetone)nickel, and of bis(salicylaldehyde)nickel have been topics of discussion for many years. The details are not fully known, but it is clear that all four species should be classified, so far as the nickel atoms are concerned, as tetragonally distorted octahedral complexes. The spectra of the anhydrous acetylacetonate in benzene (*136a*), and of the dihydrate in solution and as powder (*160*), are practically identical, and have been assigned in tetragonal symmetry (*159*, *160*). It is impossible to account for the observed spectrum with tetrahedral symmetry. It has been known for some time that the anhydrous compound consists of trimers in the solid state (*30*), and it has been shown more recently that the units are held together by sharing of oxygen atoms, at the corners of rather distorted octahedra (*31*). Nickel-oxygen distances are "normal," 2.00 Å, if the oxygen is not shared, and about 2.18 Å when the oxygen atom is shared. The nickel atoms are collinear and only 2.89 Å apart; magnetic interactions might be expected, but such an investigation has not yet been reported. The substance remains trimeric in benzene, but is broken up by donor solvents, with which it forms mono- and di-adducts (*108*). The similarity of the spectrum in benzene to that of the dihydrate means either that the ligand-fields in the two substances are accidentally very similar, or that in the dihydrate the trimeric form persists and the water is merely crystal water.

Bis(salicylaldehyde)nickel dihydrate is a *trans*-planar chelate with the two water molceules coordinated to the nickel from positions on the z-axis (*148*). Maki has given a detailed assignment (*159*, *160*) of the powder spectrum in D_{2h} symmetry; the agreement between observed and calculated frequencies is on the whole good, but the error in the first band is 25–30%. Ferguson has examined the crystal spectrum (*72*) and has put forward alternative assignments for certain bands. The spectrum of the anhydrous compound (*174*) is different from that of the dihydrate, and almost identical with that of the anhydrous acetylacetonate in benzene. The general properties of this substance support the belief that it is polymeric (*151*, *174*), in a way analogous to that of the acetylacetonate. Maki attempted to obtain this substance by treating a dimethylformamide solution of anhydrous nickel chloride with salicylaldehyde. The spectrum of this solution has been assigned on the basis of D_{2h} symmetry, but is very different from the powder spectrum of the anhydrous compound (*174*). This may be accounted for if one considers dimethylformamide as a donor-solvent; its tendency to coordinate is quite strong (*28*, *98*, *175*).

The diamagnetic-paramagnetic isomerism between yellow and blue forms of complex salts of nickel with C-substituted ethylenediamines, christened "the tale of the blue and the yellow," by Ballhausen and Liehr (*11*), has provoked controversy for some time.

Originally discovered by Lifschitz and his colleagues (*144*–*146*), and by others (*104*, *124*), these compounds are of general formula $Ni(Sen)_2X_2$, where Sen = substituted ethylenediamine, X = monovalent anion. They exist in blue and in yellow forms and may nor may not contain water. The forms are converted into each other under a variety of conditions; heating in general favors the yellow form, but the only regular feature is that the blue compounds are paramagnetic, the yellow ones diamagnetic. No crystal structures seem to have been investigated. Furlani (*97*) has shown that the spectra of some of the blue compounds are readily interpreted on the basis of tetragonally distorted octahedral fields. This is supported by theoretical work (*11*, *120*). Such a structure means that the anions take part in the coordination to the nickel. In the case of bis(phenylethylenediamine)nickel perchlorate, one must therefore accept that the perchlorate ion is here acting as a ligand. The spectra of the yellow compounds are compatible with a tetragonal structure in which a singlet state lies lowest (*120*). Ballhausen and Liehr (*120*) suggest that the ease of convertibility may arise because only a very small change in the distance of the anion from the metal is needed. It would clearly be of interest to know whether the two isomers of any of the compounds have the same crystal form. If the magnetic change depends only on the anion-metal distance, then one would expect favorable cases to show "abnormal" magnetic moments as described in Section IV,D,*1*. This has not been directly observed in the solid state, but the spectrum of the green solution of bis(stilbenediamine)nickel formate in alcohol shows it to be a mixture of blue and yellow forms (*97*); one presumes the magnetic moment would show a value between zero and 3.2 B.M.

The compounds described in this section are a very limited selection of those belonging to this class. It has been shown that one of the basic requirements for tetragonal distortion is that two ligands should be of an essentially different nature from the other four. X-ray crystal structure determinations of course confirm that a complex is *trans*-octahedral, but the metal ligand bond-lengths are not very helpful in determining whether the ligand-field has octahedral or tetragonal symmetry. For this purpose the visible spectrum is useful if the distortion is relatively large; small distortions are probably best detected by electron spin resonance.

b. Hexa-coordinated Diamagnetic Complexes. Nyholm (*192*) has reported and discussed certain nickel(II) complexes with chelating tertiary arsines which are hexa-coordinated and yet diamagnetic. In these compounds the arsenic ligands should in principle be equivalent, but the only reasonable explanation of the diamagnetism is that the degeneracy of the antibonding e_g-orbitals is removed, the splitting being sufficient to allow the two electrons concerned to become paired in the lower-lying of the two component orbitals. This degeneracy can be removed only by distortion.

However, most of this section will be concerned with apparently hexa-coordinated complexes of palladium(II) and of platinum(II). Most of the evidence for the existence of such complexes comes from spectroscopic and conductivity studies on solutions, but there is a certain amount of crystallographic information available.

The most remarkable compounds of this type have the general formula $Pt(NH_3)_4(RCN)_2X_2$, where R = CH_3 or C_6H_5, X = halogen. The structure of $Pt(NH_3)_4(CH_3CN)_2Cl_2(H_2O)$ shows the presence of the cation $[Pt(NH_3)_4(CH_3CN)_2]^{2+}$, whose form (*119b*) is shown in Fig. 13. The acetonitrile groups are antiparallel to each other, and, if x- and y-axes are taken along the platinum-ammonia directions, lie over the xy-direction. The perpendicular acetonitrile-platinum distance is about 3 Å. This compound, and also $[Pt(NH_3)_4(C_6H_5CN)_2]I_2$, show no infrared absorptions in the 2000 cm^{-1}

region, and so the effect of the bonding must be to reduce considerably the carbon-nitrogen bond order. The bonding of the nitrile groups may be explained as follows. Occupied bonding π-orbitals of the nitrile groups form a centro-symmetrical combination which interacts with the $5d_{z^2}$- and $6s$-orbitals of the metal, and an unsymmetrical combination which reacts with the $6p_z$-orbital. The corresponding unoccupied antibonding π-orbitals similarly give combinations which can react with the $5d_{zx}$- and $6p_x$-orbitals of the metal, the latter probably not being of great importance when the distance of the nitrile groups from the metal is borne in mind. The most important contributions to the bonding then come from σ-interactions with fully-symmetric metal orbitals ($5d_{z^2}$, $6s$, and possibly $6d_{z^2}$) and from the back-donation from $5d_{zx}$ of the metal into empty antibonding π-orbitals of the ligands. The true symmetry of the ion is C_{2h}, but a suitable assumption for molecular-orbital treatments would be D_{2h}; the carbon and nitrogen atoms forming the "triple" bonds are treated as equivalent. The above considerations not only offer some explanation of the bonding, but also explain why the acetonitrile molecules are held above one diagonal of the platinum-ammonia square (*119b*).

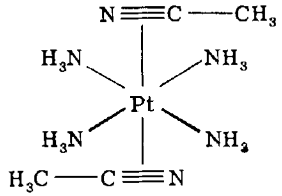


FIG. 13. Structure of the $[(CH_3CN)_2(NH_3)_4Pt]^{2+}$ ion.

Other crystallographic work has shown that the compounds of general formula $[M(DA)_2I_2]$, where M = Ni, Pd, or Pt, and DA = *o*-phenylenebis(dimethylarsine) are isomorphous (*119a*); in particular, the palladium compound has a tetragonally distorted octahedral structure with four arsenic atoms 2.38 Å from the metal at the corners of a square, and two iodine atoms on the *z*-axis, at a distance of 3.52 Å. It would be of interest to know how much this second distance is altered in the nickel and platinum compounds. They are formally analogous to the paramagnetic bis(*o*-phenylenediamine)nickel chloride, described in Section IV,D,*2*,*a*; the diamagnetism of $[Ni(DA)_2I_2]$ may be taken to mean that the in-plane field of the arsenic atoms is much stronger than that of the nitrogen atoms in the *o*-phenylenediamine analogue.

These bis(diarsine) complexes show remarkable behavior in solution. When the anion is perchlorate, they are 2:1 electrolytes in solvents such as nitrobenzene (*118b*, *119*), and the formation of solvated cations $[M(DA)_2]^{2+}$

is the only explanation. With halogens, thiocyanate, and nitrite however, the solutions are those of 1:1 electrolytes, and the compounds have therefore been formulated as $[M(DA)_2X]X$. The "free" anion may be replaced by perchlorate, the products still being 1:1 electrolytes. It is very tempting to assume that these cations are penta-coordinated, but the possibility of solvent-coordination cannot be excluded. (The solid complexes are discussed in Section IV,E).

The effects of solvation on the square-planar tetrachloropalladite ion have been investigated by spectrophotometric methods (*118a*). Pronounced blue shifts are found when the salts go into solution, the shift increasing in the order nitrobenzene < nitromethane < acetone < acetonitrile < water. This information indicates the solvation to be strongest with water, but gives no absolute value, nor can one tell how many solvent molecules are involved. It is reasonable to suppose that two molecules are used equally to solvate the anion, which is supported by the formation of a hexa-bromopalladite anion in nitrobenzene when excess of bromide is added (*118*).

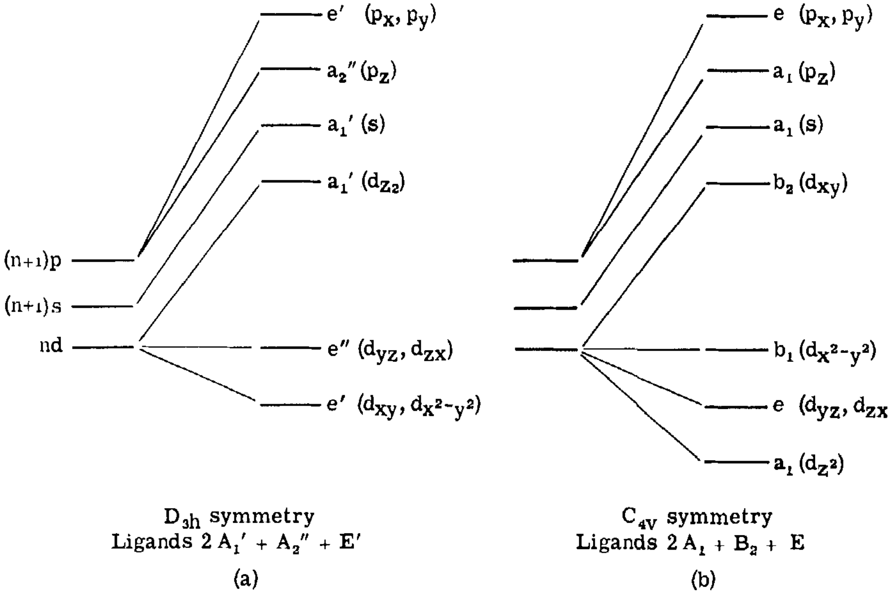
Corresponding platinum-containing ions show no shifts in their solution spectra, even when dissolved in strong hydrochloric acid (*118*); thus the solvation here has a minimal effect on the ligand field.

When the apparently penta-coordinated diarsine complexes just described are dissolved in solvents more "polar" than nitrobenzene, they tend to dissociate into halide ions and bivalent cations, thus becoming 2:1 electrolytes (*119*). The effect is most marked with the platinum compounds. It has been shown that solvation effects might be less with platinum than with palladium, and so, other things in the equilibria being equal, it can also be concluded that the bonding of further ligands by a square-planar complex is much weaker with platinum than with palladium. Square-planar nickel complexes are of course the most ready to take up further ligands.

E. PENTA-COORDINATED COMPLEXES

On the general principle that in molecule formation all of the orbitals of suitable energy should be used, it might be expected that penta-coordinated complexes of d^8-systems would be very common. There is a total of nine metal orbitals available; the eight electrons of the metal will fill four of them and five remain to interact with ligand lone-pair orbitals. Two of the most likely configurations would be a square pyramid (C_{4v}) and a trigonal bipyramid (D_{3h}). The groupings of the metal orbitals are shown in Fig. 14 for these symmetries. The scheme in C_{4v} symmetry is somewhat similar to that in D_{4h} symmetry, but the lower symmetry brings p_z-orbitals into the same representation as s and d_{z^2}, and they can now interact with each other. The symmetry does not demand that the metal atom should lie in the base-plane, and it has indeed been found that the metal is slightly out of this plane in certain compounds of this structure (*85*, *157*).

When a large excess of cyanide ion is added to a solution of the $Ni(CN)_4^{2-}$ anion, a deep red color develops, disappearing again on dilution. The solution remains diamagnetic. As long ago as 1923, Job and Samuel (*133*) suggested, on spectrophotometric grounds, that a hexacyano-complex was formed with no intermediate stages. Nyholm (*192*) has discussed the subject and found the evidence for a hexacyanide very doubtful; he has further quoted evidence for a pentacyanide but no hexacyanide. More recently a thorough infrared and ultraviolet spectrophotometric investigation has confirmed the existence of only a pentacyanide (*154*). Evidence for a hexacyanide based on the catalysis of proton relaxation (*23*) must be regarded as doubtful. Nothing at all is known about the structure of this ion, and in making speculations the possibility of water occupying the sixth coordination site should not be neglected.



D_{3h} symmetry
Ligands $2A_1' + A_2'' + E'$
(a)

C_{4v} symmetry
Ligands $2A_1 + B_2 + E$
(b)

FIG. 14. Orbital splittings in penta-coordinated complexes.

The tertiary triarsine complexes* of nickel(II) halides have been more thoroughly investigated. They have formulas $[Ni(TA)X_2]$, and are not dissociated in solution (*15*, *192*). The fact that oxidation affects the metal but not the arsenic must mean that all arsenic atoms are coordinated to the

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* Triarsine = TA = $Me_2As(CH_2)_3 \cdot As(Me) \cdot (CH_2)_3AsMe_2$.

metal, for the free ligand is readily oxidized. The possibility of solvation of course remains. However, a recent crystal-structure determination of the bromide (*157*) has shown that the nickel is indeed penta-coordinated. The structure (see Fig. 15) is based on a square-pyramid with a bromine atom on the axis, but the second bromine is depressed 20° below the base plane. The nickel atom is raised very slightly above the plane of the arsenic atoms, towards the axial bromine.

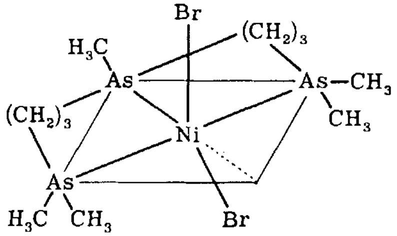


FIG. 15. Structure of (Triarsine)$NiBr_2$.

The corresponding palladium compound (*157*) must be formulated as $[Pd(TA)Br]^+Br^-$. The cation is essentially square-planar, but the bromine atom is displaced 10° out of the arsenic-palladium plane. Such a distortion is very unusual for palladium, and may be due to a steric effect of the alkyl chains in the arsine ligand. This might similarly account for the distortion of the nickel complex from a square pyramidal shape.

Of the diarsine complexes partly described in Section IV,D,*2*,*b*, the perchlorates, $[M(DA)_2X]ClO_4$, are isomorphous (*119a*). Full details of the structure have not been published, but it seems very likely that the cations contain essentially penta-coordinated metal atoms.

A structure based on the trigonal bi-pyramid has been reported (*158*) for the compound tris(*o*-diphenylarsinophenyl)arsine-iodo-platinum(II) tetraphenylborate, $[Pt(QAS)_4I](BPh_4)$. The arsine ligand (QAS) contains four arsenic atoms and has essentially trigonal symmetry. The platinum atom is displaced slightly out of the equatorial plane towards the iodine atom; bond lengths are not given but are "approximately those that would be expected for single bonds to platinum."

Effectively penta-coordinated complexes are found among the π-complexes of these metals with unsaturated hydrocarbon derivatives; these are described in Section IV,F.

In general, penta-coordinated complexes are rather rare. So far as nickel, palladium, and platinum are concerned, it seems that such complexes may be formed as intermediates when square-planar complexes accept further ligands in their tendency to become hexa-coordinated. The type of chelate used so far has been restricted to rather complicated arsine derivatives, and it would be interesting to see what differences donor atoms

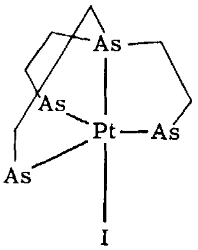


FIG. 16. Structure of penta-coordinated platinum complex.

such as nitrogen, phosphorus, and sulfur show when they are used in similar ligands.

F. π-COMPLEXES

This section is intended to cover those complexes which contain unsaturated hydrocarbon groups coordinated sideways to the metal atom through their π-orbital systems. The substances are rather arbitrarily divided according to whether the ligand is classed as uncharged or anionic.

1. Uncharged Ligands

The typical members of this group are the ethylene complexes, $[C_2H_4{\cdot}PtCl_2]_2$ and $K[C_2H_4{\cdot}PtCl_3]$, discovered by Zeise (*269, 270*) one hundred and thirty years ago. Structure determinations of several of these compounds make it quite clear that the ethylene molecule is bonded to the metal such that the carbon-carbon bond is symmetrically placed at right angles to the plane formed by the metal and other ligand atoms (*2, 57, 263a, 263b*). The only exception seems to be in the dimer $[\text{Styrene}{\cdot}PdCl_2]_2$, where the double bond is somewhat twisted away from the metal, possibly because of steric hindrance of the bulky phenyl groups (*125a*). In these dimeric substances, the molecules contain halogen bridges and the ethylene molecules are arranged *trans* to each other (*57, 125a*). The structure of ethylene dichloro-methylamine platinum(II) is shown in Fig. 17 as an example (*2*).

Unfortunately it is difficult to resolve the X-ray diffraction of the carbon atoms in these compounds from that of the heavy elements present, and in no case are the metal-carbon or carbon-carbon distances known with sufficient accuracy to enable pronouncements about the carbon-carbon bond order to be made. In this respect the infrared spectra ought to be helpful, but there is considerable controversy over the assignment of absorption at about 1500 cm^{-1}. Russian authors (*7b*) have assigned this to a CH_2-deformation mode, but the British school favors an assignment to carbon-carbon stretching, on the grounds that it appears even in complexes where there are no ethylenic CH_2 groups (*1*, *37a*, *209a*). The Russians (*7b*) in general conclude that the bonding of the ethylene involves formation of a three-membered ring analogous to ethylene oxide or cyclopropane. This involves complete reduction of the carbon-carbon bond to a single bond, and also means that the platinum would be oxidized to the +4 state. The British school use a molecular orbital approach, involving the σ-donation of a filled π-orbital to the metal, balanced by back-donation into the antibonding π-orbital of the ethylene.

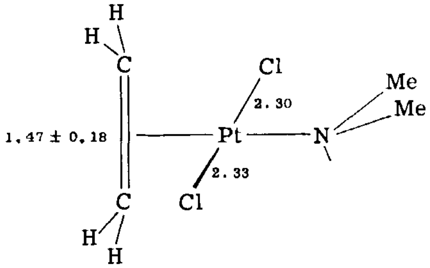


FIG. 17. Structure of *trans*-[$(Me_2NH)(C_2H_4)PtCl_2$].

It has been shown (*213a*) that the protons in $[C_2H_4PtCl_2]_2$ powder show rather large resonance shifts, which is taken to indicate that the hydrogen atoms lean back away from the metal atom. This could support the three-membered ring theory, but would also be caused by back-donation into the antibonding π-orbital. It seems to the author that the two theories are not basically different, but are convenient models which represent the same thing. Even ethylene oxide can be treated as a π-complex, involving donation from an ethylene molecule to an oxygen atom, balanced by back-donation in the usual way.

Of very great current interest is the appearance of cyclobutadiene as a ligand. Longuet-Higgins and Orgel (*150*) predicted that this unknown (and probably very unstable) hydrocarbon might be stabilized by coordination to a metal atom; the nickel family seemed to them more likely than most. The first compound of this type reported was (tetramethylcyclobutadiene)-nickel chloride (*54*), a comparatively stable, red, diamagnetic compound. A preliminary crystal structure determination (*62*) indicates that it is a dimer in the solid state, with two chlorine bridges, and a four-membered ring attached symmetrically to each nickel atom. If the ring is considered to be a bidentate ligand, the nickel is here penta-coordinated. Several materials are now known with tetraphenylcyclobutadiene attached to nickel, palladium, and iron, (*58, 89, 128, 165*) and with cyclobutadiene itself attached to silver (*7a, 94*).

The structure of tetraphenylcyclobutadiene iron tricarbonyl (*58*) shows the four-membered ring to be square within the limits of the errors. By comparing the infrared spectra of these substances, Fritz (*93*) has given a preliminary assignment of the observed frequencies; from the general similarity it is probable that in all cases the ring is planar and square.

2. Anionic Ligands

The "parent" member of this class is bis(cyclopentadienyl)nickel, usually referred to as nickelocene. It behaves in many ways like an ordinary octahedral nickel(II) complex, and has a magnetic moment of 2.88 B.M. (*78, 259*). It is isomorphous with ferrocene (*205*), which has the now well-known "sandwich" structure of D_{5d} symmetry (rings "staggered"). The *b*- and *c*-axes of the monoclinic unit cell are slightly longer than for ferrocene, and this is interpreted as indicating longer nickel-carbon distances. Electron diffraction studies (*204*) give a nickel-carbon distance of 2.18 Å.

The infrared spectrum (*95, 149a, 259*) of nickelocene is extremely similar to that of ferrocene; what differences there are confirm the view that the metal-ring bonding in the nickel compound is weaker, and the carbon-carbon bonding in the ring slightly stronger, than in ferrocene.

Many theoretical treatments of the bonding in sandwich compounds have been given (*63, 130, 143, 166, 179, 216, 267*); in D_{5d} symmetry, the metal orbitals split into groups a_{1g} ($4s$ and $3d_{z^2}$), a_{2u} ($4p_z$), e_{1g} ($3d_{yz}$ and $3d_{zx}$), e_{1u} ($4p_x$ and $4p_y$), and e_{2g} ($3d_{xy}$ and $3d_{x^2-y^2}$). These orbitals can interact with combinations of the ring π-orbitals having the same transformation properties. The interaction with $4p$-orbitals is usually neglected in these treatments. Dunitz and Orgel's treatment is summarized (*63*). The stable molecular orbitals of the system are a_{1g} and a_{2u}, mostly concerned with the ligands, and a bonding, doubly-degenerate e_{1g}-orbital, covering the whole molecule. The last-mentioned is largely responsible for the stability. The remaining four "ligand electrons" are placed in the nonbonding e_{1u}-orbitals (see Fig. 18). Of the metal orbitals e_{2g} are affected only slightly; $3d_{z^2}$ is only slightly affected but can interact with $4s$ and the ligand a_{1g} combination, and its position is somewhat uncertain. These orbitals can accommodate six electrons, and are virtually nonbonding. The next orbitals to be occupied would be the singlet a_{1g}^{**} ($4s$) or the doublet e_{1g}^{*}, which is an antibonding set. As the compound is paramagnetic, the two remaining electrons cannot lie in the a_{1g}^{**} singlet, and the a_{1g}^{**}-orbital must lie above or at about the same energy as the e_{1g}^{*} pair.

Orgel has pointed out (*197*) that this orbital scheme is essentially the same as that produced by trigonal distortion of an octahedral complex ($O_h \rightarrow D_{3d}$ symmetry); it is thus reasonable to regard the cyclopentadienyl anion, benzene etc. as trigonal donors of three electron pairs.

When cyclopentadiene and nickel carbonyl are gently heated together, a red, diamagnetic compound of formula $C_{10}H_{12}Ni$ is obtained (*81*). It was originally thought to be bis(cyclopentadiene)nickel(0), but is now known to be cyclopentadienyl cyclopentenylnickel(II), as a result of proton magnetic resonance studies (*60*, *83*, *134*). The spectra show four peaks, whose intensities are in the ratio 5:1:2:4. The first one, with a τ-value of 4.8 ppm, is typical of the coordinated cyclopentadienyl group, and the others are assigned to seven protons of the other ring. Four of these are aliphatic, and the other three "allylic," of which two are equivalent. The structure thus deduced is shown in Fig. 19. The compound is equivalent to nickelocene with one of the rings reduced, and it may in fact be prepared in this way (*60*).

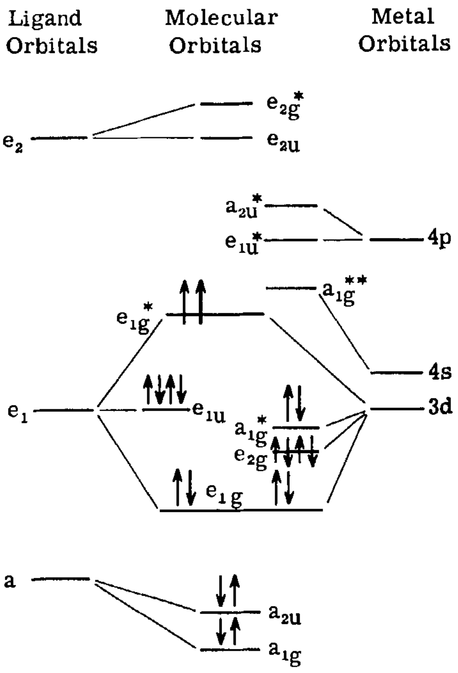


FIG. 18. Molecular orbitals in nickelocene.

The palladium analogue of this compound is not yet known, but the

TABLE IX

PROTON CHEMICAL SHIFTS OF π-ALLYL DERIVATIVES (τ-SCALE)

Compound	Mc/sec	Aromatic	Allylic[a] A	Allylic[a] B	Allylic[a] C	Aliphatic	Ref.
$[(\alpha\text{-Me-}C_3H_4)NiBr]_2$	60	—	5.56	7.48 7.61	8.63[b] 8.85	9.57 9.68	*139*
$[(\alpha\text{-Me-}C_3H_4)PdCl]_2$	60	—	3.96	5.38 5.43	6.50	8.00	*56*
$[(\beta\text{-}BrC_3H_4)PdCl]_2$	60	—	—	5.23	6.33	—	*38*
$[(C_3H_5)PdCl]_2$	60	—	3.88	5.25	6.29	—	*56*
$[(C_3H_5)PdCl]_2$	60	—	3.89	5.30 5.35	6.19 6.40	—	*152*
$[(C_6H_9)PdCl]_2$	56.4	—	4.49	—	4.78	8.20	*134*
$(C_3H_5)(Ph_3P)NiCl$	60	(2.88)	3.97	6.12	6.95	—	*123*
$(\beta\text{-Me-}C_3H_4)(Ph_3P)NiCl$	60	(3.02)	—	6.34	6.88	7.33	*123*
$(C_3H_5)Ni(C_5H_5)$	60	4.21	6.30?	6.88 6.94	8.02[b] 8.23	—	*152*
$(C_3H_5)Ni(C_5H_5)$	40	4.21		6.78	8.12	—	*139*
$(C_3H_5)Pd(C_5H_5)$	60	3.50	4.32	5.59 5.68	6.90 6.72	—	*152*
$(C_3H_5)Pt(C_5H_5)$	40	4.25	—	6.40 6.43	7.97[b]	—	*232a*
$(C_5H_7)Ni(C_5H_5)$	40	4.75	4.87	—	6.04	8.93	*83*
$(C_5H_7)Ni(C_5H_5)$	56.4	4.79	4.95	—	6.12	8.92	*134*
$(C_5H_7)Ni(C_5H_5)$		4.78		5.03		8.51–9.24	*60*
$(C_6H_9)Pd(C_5H_5)$	56.4	4.22	5.04	—	5.18	8.56	*134*
(in acetone)	40	4.16	4.91	—	7.53	8.51	*83*

[a] The protons are labeled as in Fig. 20.

[b] These large shifts may mean that the terminal carbon atoms are much nearer to the metal than is the central atom.

compound cyclopentadienyl cyclohexenyl palladium(II) is similar (*82*, *83*, *134*, *232a*), consisting of a symmetrical cyclopentadienyl ring on one side of the metal, and an allyl group bridged by three methylenes on the other.

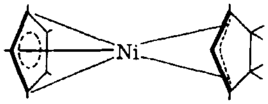


FIG. 19. Structure of $(C_5H_7)Ni(C_5H_5)$.

Many compounds are now known which contain simple allyl residues bonded sideways to a metal. Table IX is a summary of the proton resonances for the series. The coupling constants in general are more characteristic than the chemical shifts of allyl groups bonded in this way (*139*), but the scattered data are not complete enough to permit a summary of this aspect, so far as the nickel family is concerned.

Palladium appears to be especially suitable for forming these complexes. As an example, allyl alcohol reacts with palladium(II) chloride (*236*) to give bis(allylpalladium chloride), $[(C_3H_5)PdCl]_2$. Its nmr spectrum shows three peaks (*56*), in the ratio 1:2:2, indicating the structure shown in Fig. 20. The exact location of the allyl groups with respect to the metal is not yet known, but there is no doubt about the π-configuration. A σ-configuration is obtained when the allyl-halogen complexes are dissolved in dimethyl sulfoxide (*38*), probably because the solvent coordinates to the metal, partially replacing the allyl group. This is most easily imagined if the π-allyl group is considered as a bidentate ligand, the σ-allyl group as monodentate.

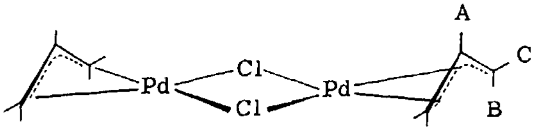


FIG. 20. Structure of $[(C_3H_5)PdCl]_2$.

Several nickel derivatives of the type $[ANiX]_2$ (A = allyl, X = halogen) are known, but they are very much less stable to air than the palladium compounds (*76*, *77*). The small dipole-moment of bis(allylnickel bromide) may mean that the nickel-bromine bridges are not coplanar (*76*).

The allyl group itself may also be attached to a cyclopentadienyl-metal residue, giving compounds of the type $(C_3H_5)M(C_5H_5)$. These are known for nickel (*77*, *152*), palladium (*232*), and platinum (*232a*). The palladium and platinum compounds are remarkably stable; the nickel derivative is liquid at room temperature, and decomposes very readily in oxygen.

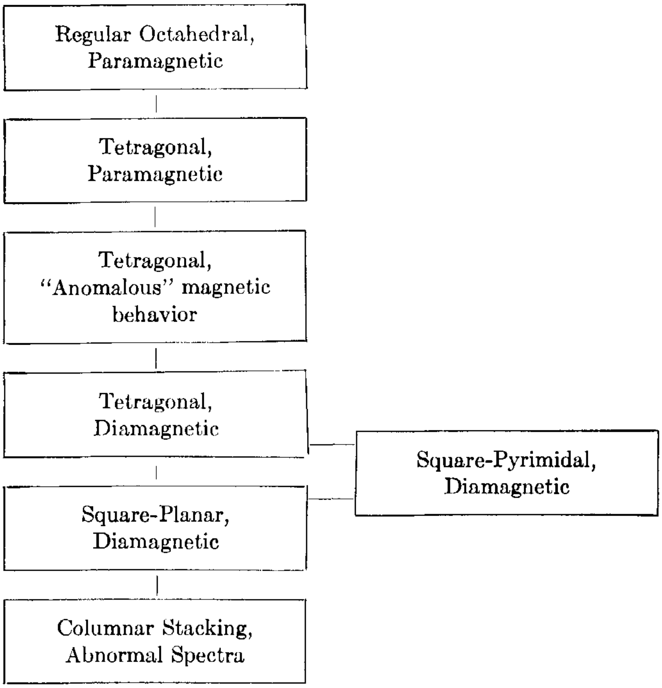
The infrared spectra of these allyl, cyclopentenyl etc. derivatives show certain characteristics in common, and Fritz (*92*) has put forward a preliminary assignment of the main frequencies of bis(allylpalladium chloride). A strong, sharp band between 500 cm^{-1} and 600 cm^{-1} is found in all the systems studied, and is assigned to the allylic C—C—C bending vibration; it may be used for diagnostic purposes.

The bonding of the three allylic carbon atoms to the metal in these compounds may be regarded in terms of a bidentate ligand. In the dimeric allyl-metal halides, this is consistent with the normal tetra-coordination, and in the cyclopentadienyl-allyl compounds it is interesting to note that the metal atoms are effectively penta-coordinated. Diamagnetism is preserved throughout.

In the light of the existence of the above compounds it is possible to make a few remarks on the "nonexistence" of bis(cyclopentadienyl)palladium (and also the platinum compound). The compounds $(C_3H_5)Pd(C_5H_5)$ and $(C_6H_9)Pd(C_5H_5)$ are both stable entities, and there is no reason to doubt that the cyclopentenyl derivative, $(C_5H_7)Pd(C_5H_5)$, would also prove to be stable. There is then no inherent difficulty in attaching groups of this type to palladium. If the compound above were dehydrogenated, $(C_5H_5)_2Pd$ would result, in principle at least. It can be shown geometrically, that, if the new cyclopentadienyl ring is regular, and if the three carbon atoms originally bonded to the metal are equidistant from the metal, then the "new" double bond must be in a coordinating position. By analogy with nickelocene this would involve unpairing of two electrons and their promotion to antibonding orbitals. This is almost unknown in the chemistry of palladium(II); the postulated material could either decompose, oxidize to $(C_5H_5)_2Pd^{2+}$, or distort. The hexa-coordinated palladium(II) complexes already described are distorted tetragonally. In symmetrical cyclopentadienyl complexes, the distortion is effectively trigonal, a distortion which does not remove the degeneracy of the e_{1g} antibonding orbitals. In this case, then, distortion is unlikely to remove the paramagnetism. Decomposition or oxidation remain as the most likely possibilities.

G. SUMMARY

The information in the preceding sections shows that there is a generally close relationship between the different symmetries found in complexes, and that suitable distortion may very often be invoked to describe the changes taking place on going from one type of complex to another. The relationship between octahedral and square-planar complexes is particularly close, with tetrahedral and trigonal-bipyramidal structures occurring only under special conditions. Excluding these configurations, the relationship between the others may be represented diagrammatically:



Platinum(II) compounds are to be found only towards the bottom of this scheme, palladium(II) reaches further up, its fluoride belonging to the tetragonal, paramagnetic class. Nickel(II) complexes cover the whole range of behavior, and may in addition be tetrahedral.

V. Some Platinum(IV) Compounds

Platinum(IV) has six "valency" electrons, and a regular octahedral configuration is to be expected in its compounds, as is indeed found to be the case (*257*). The need for six ligands while the oxidation state is only four leads to some very unusual structures.

Trimethylplatinum chloride and tetramethylplatinum are structurally very similar; they form cubic unit cells of sides 10.55 Å and 10.145 Å respectively, with eight formula units in the cell (*220*). The platinum and chlorine positions in trimethylplatinum chloride show that the true molecule is a tetramer of the form shown in Fig. 21. The general structural similarity of the tetramethyl indicates a similar type of molecule with methyl bridges replacing chlorine atoms. No comment is offered here on the bonding of these methyl bridges, but its very unusual nature gives an insight into the very strong tendency of platinum(IV) to adopt an octahedral configuration. The tetramethyl remains tetrameric in benzene solution (*218*), from which it crystallizes with two molecules of benzene (to four platinum atoms). The benzene is not coordinated in any way, the crystals containing the original tetramers and benzene of crystallization (*218*).

The complex $(CH_3)_6Pt_2en_3I_2$ (en = ethylenediamine) contains the centro-symmetric cation $[en(CH_3)_3Pt\text{-}en\text{-}Pt(CH_3)_3en]^{2+}$, in which there is only one ethylenediamine bridge; methyl groups are arranged in *cis*-positions, and the platinum atoms are 7.79 Å apart (*249*).

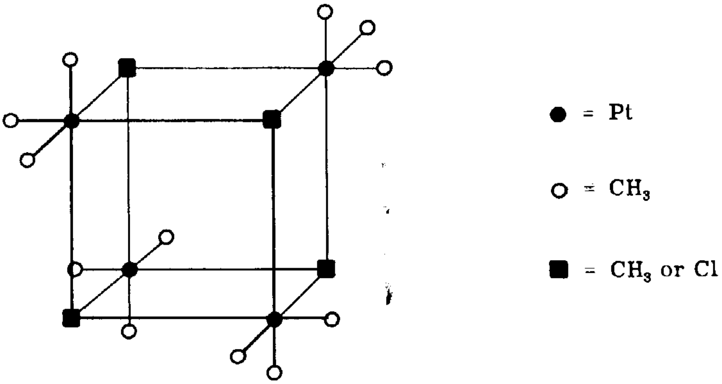


FIG. 21. Structure of $(CH_3)_{16}Pt_4$ and $(CH_3)_{12}Pt_4Cl_4$.

The trimethylplatinum residue forms a series of complexes with β-diketonyl anions, which have the general formula $[(R{\cdot}CO{\cdot}CH{\cdot}CO{\cdot}R')Pt(CH_3)_3]_2$. The two units are held together by bonds between platinum atoms and the central carbon atoms of the diketone groups (*121*); the oxygen atoms of a diketone group are both attached to the other platinum atom in a "normal" way. The structure of the nona-4,6-dione complex (*242*) is shown in Fig. 22. The corresponding complex with ethyl aceto-acetate (*122*) is fully analogous, the bridging being through the central carbon atom, and not through the oxygen of the ester grouping. These compounds offer a new aspect of the coordination chemistry of acetylacetone derivatives, and are in marked contrast to the trimeric bis(acetylacetone)nickel(II), where the metal achieves octahedral coordination through direct sharing of the oxygen atoms (*30*, *31*; see also Section IV,D,*2*,*a*).

In the related compound α-α′-dipyridyl-acetylacetonatotrimethylplatinum, which is monomeric, five of the coordination positions are taken up by the dipyridyl nitrogen atoms and the methyl groups. The sixth position is occupied by the central carbon atom of the acetylacetone, not by one of the oxygen atoms (*242a*). The oxygen atoms then remain uncoordinated, and the rest of the acetylacetone group is considerably distorted from the highly symmetrical form it normally has in complexes. This is the only definite case of a β-diketone anion coordinating only through its central carbon atom. Platinum(IV) seems to form σ-bonds with carbon atoms rather readily.

This bonding to carbon atoms is again found in "cyclopropane platinous chloride," which has recently been shown to contain a four-membered ring of three saturated carbon atoms and a platinum atom *(1a)*. The insolubility in noncoordinating media suggests that it is a polymer held together by chlorine bridges. It is interesting to note that the bonding in this compound is in distinct contrast to that in the π-allyl derivatives described in Section IV,F. The change from π- to σ-bonding of the C_3 residue follows on the addition of a proton to the middle carbon atom.

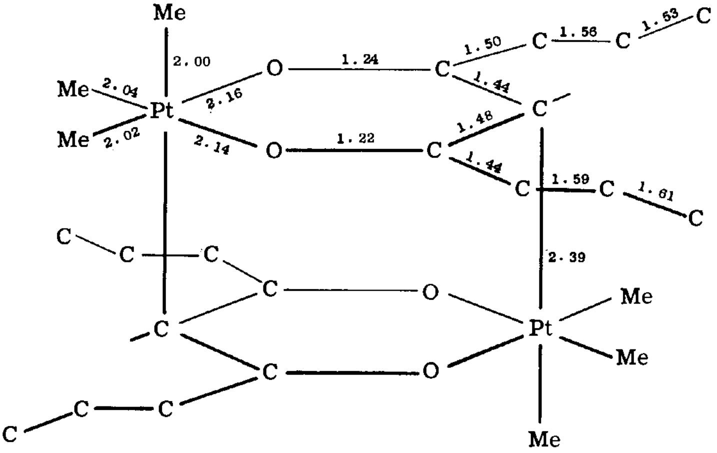


FIG. 22. Structure of $[(C_3H_7 \cdot CO \cdot CH \cdot CO \cdot C_3H_7)Pt(CH_3)_3]_2$.

In the light of the structures described it is clear that platinum(IV) goes to considerable lengths to achieve octahedral coordination. It is therefore extremely surprising that platinum tetrachloride has been reported as tetrahedral *(70)*. This result was obtained from powder photographs, which gave a cubic unit cell of side 10.45 Å, containing eight formula units. The space-group was suggested to be $Pa3(T_h^6)$. The unit cell as described bears a striking resemblance to those of tetramethylplatinum and trimethylplatinum chloride.

Examination of the powder photograph shows, however, that the lattice of platinum tetrachloride is certainly primitive, and not body-centered as in trimethylplatinum chloride and tetramethylplatinum. The space-group assignment was made on the grounds of two absent reflections; there are in fact many reflections absent, and the space-group Pn3 is a clear possibility. In this space-group it would be possible to have tetramers, Pt_4Cl_{16}, analogous to those of tetramethylplatinum; they would have to have a slightly different orientation, the molecule in the center of the cubic cell being related to the others by a glide-plane rather than by a direct translation. On these grounds it is concluded that the existence of tetrahedral monomers in the lattice of platinum tetrachloride cannot be unconditionally accepted, and it is suggested that the possibility of at least partially condensed structures should be taken into account. The idea of tetramer-formation is attractive.

VI. Platinum Hexafluoride

This compound is the only one known for these elements in this oxidation state; it is obtained as a highly-colored solid by the high-temperature reaction between fluorine and the metal. The solid is isostructural with the hexafluorides of osmium and iridium, and the Pt-F distance has been estimated at 1 83 Å by extrapolation along the series W-Os-Ir (*255*). The infrared spectrum has been assigned in O_h symmetry (*256*); there are no signs of any distortion, as found for example in osmium hexafluoride.

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REFERENCES

1. Adams, D. M., and Chatt, J., *Chem. & Ind.* (*London*) p. 149 (1960).
1a. Adams, D. M., Chatt, J., Guy, R. G., and Sheppard, N., *Proc. Chem. Soc.* p. 179 (1960).
2. Alderman, P. R. H., Owston, P. G., and Rowe, J. M., *Acta Cryst.* **13,** 149 (1960).
3. Anderson, J. S., *Nature* **130,** 1002 (1932).
4. Asmussen, R. W., and Bostrup, O., *Acta Chem. Scand.* **11,** 745 (1957).
5. Asmussen, R. W., and Bostrup, O., *Acta Chem. Scand.* **11,** 1097 (1957).
6. Asmussen, R. W., and Soling, H., *Z. anorg. u. allgem. Chem.* **283,** 3 (1956).
7. Atoji, M., Richardson, J. W., and Rundle, R. E., *J. Am. Chem. Soc.* **79,** 3017 (1957).
7a. Avram, M., Marica, E., Nenitzescu, C. D., *Chem. Ber.* **92,** 1088 (1959).
7b. Babushkin, A. A., Gribov, L. A., and Gel'man, A. D., *Russian J. Inorg. Chem.* **4,** 695 (1959).
8. Bailey, C. R., and Gordon, R. R., *J. Chem. Phys.* **6,** 225 (1938).
9. Ballhausen, C. J., *Kgl. danske Videnskab. Selskab Mat.-fys. Medd.* **29,** No. 2 (1954).
10. Ballhausen, C. J., *Rec. trav. chim.* **75,** 665 (1956).
11. Ballhausen, C. J., and Liehr, A. D., *J. Am. Chem. Soc.* **81,** 538 (1959).
12. Balz, D., and Plieth, K., *Z. Elektrochem.* **59,** 545 (1955).
13. Banks, C. V., and Barnum, D. W., *J. Am. Chem. Soc.* **80,** 4767 (1958).
14. Bannister, E., Barnes, R. D., Holm, R. H., and Cotton, F. A., *Proc. Chem. Soc.* 158 (1959).
15. Barclay, G. A., and Nyholm, R. S., *Chem. & Ind.* (*London*) p. 378 (1953).

16. Bartlett, N., and Maitland, R., *Acta Cryst.* **11,** 747 (1958).
17. Basolo, F., and Matoush, W. R., *J. Am. Chem. Soc.* **75,** 5663 (1953).
18. Baur, W. H., *Acta Cryst.* **11,** 488 (1958).
19. Bellucci, I., and Corelli, R., *Atti reale accad. Lincei. Rend. classe sci. fis. mat. e nat.* **22II,** 485 (1913).
20. Bellucci, I., and Corelli, R., *Z. anorg. Chem.* **86,** 88 (1914).
21. Berndt, A., and Schomaker, V., *Chem. & Chem. Eng., Calif. Inst. Technol., Research Rept. No.* **52,** (1956–1957).
22. Bjerrum, J., and Jørgensen, C. K., *Rec. trav. chim.* **75,** 658 (1956).
23. Blackie, M. S., and Gold, V., *J. Chem. Soc.* p. 4033 (1959).
23a. Blinc, R., and Hadži, D., *J. Chem. Soc.* p. 4536 (1958).
24. Bor, G., and Markó, L., *Spectrochim. Acta* **11,** 747 (1959).
25. Boston, C. R., and Smith, G. P., *J. Phys. Chem.* **62,** 409 (1958).
26. Bostrup, O., and Jørgensen, C. K., *Acta Chem. Scand.* **11,** 1223 (1957).
27. Brockway, L. O., and Cross, P. C., *J. Chem. Phys.* **3,** 828 (1935).
28. Buffagni, S., and Dunn, T. M., *Nature* **188,** 937 (1960).
29. Bukovska, M., and Porai-Kojic, M. A., *Kristallografiya* **5,** 137 (1960).
30. Bullen, G. J., *Nature* **177,** 537 (1956).
31. Bullen, G. J., Mason, R., and Pauling, P., *Nature* **189,** 291 (1961).
32. Burbage, J. J., and Fernelius, W. C., *J. Am. Chem. Soc.* **65,** 1484 (1943).
33. Cable, J. W., Nyholm, R. S., and Sheline, R. K., *J. Am. Chem. Soc.* **76,** 3373 (1954).
34. Cable, J. W., and Sheline, R. K., *Chem. Revs.* **56,** 1 (1956).
35. Callomon, H. J., McKean, D. C., and Thompson, H. W., *Proc. Roy. Soc.* **A208,** 341 (1951).
36. Callomon, H. J., and Thompson, H. W., *Proc. Roy. Soc.* **A222,** 431 (1954).
37. Calvin, M., and Melchior, N. C., *J. Am. Chem. Soc.* **70,** 3270 (1948).
37a. Chatt, J., and Duncanson, L. A., *J. Chem. Soc.* p. 2939 (1953).
38. Chien, J. C. W., and Dehm, H. C., *Chem. & Ind. (London)*, p. 745 (1961).
38a. Chopoorian, J. A., Lewis, J., and Nyholm, R. S., *Nature* **190,** 528 (1961).
39. Clark, H. C., and Odell, A. L., *J. Chem. Soc.* p. 3431 (1955).
40. Cotton, F. A., and Bannister, E., *J. Chem. Soc.* p. 1873 (1960).
41. Cotton, F. A., Faut, O. D., and Goodgame, D. M. L., *J. Am. Chem. Soc.* **83,** 344 (1961).
42. Cotton, F. A., and Francis, R., *J. Am. Chem. Soc.* **82,** 2986 (1960).
43. Cotton, F. A., Francis, R., and Horrocks, W. D., *J. Phys. Chem.* **64,** 1534 (1960).
44. Cotton, F. A., and Goodgame, D. M. L., *J. Am. Chem. Soc.* **82,** 5774 (1960).
45. Cotton, F. A., Stammreich, H., and Wilkinson, G., *J. Inorg. & Nuclear Chem.* **9,** 3 (1959).
46. Cotton, F. A., and Zingales, F., *J. Am. Chem. Soc.* **83,** 351 (1961).
47. Cowan, R. D., *J. Chem. Phys.* **18,** 1101 (1950).
48. Cox, A. P., Thomas, L. F., and Sheridan, J., *Nature* **181,** 1157 (1958).
49. Cox, A. P., Thomas, L. F., and Sheridan, J., *Spectrochim. Acta* **15,** 542 (1959).
50. Cox, E. G., Pinkard, F. W., Wardlaw, W., and Preston, G. H., *J. Chem. Soc.* p. 2527 (1932).
51. Cox, E. G., Pinkard, F. W., Wardlaw, W., and Webster, K. C., *J. Chem. Soc.* p. 459 (1935).
52. Crawford, B. L., and Cross, P. C., *J. Chem. Phys.* **6,** 525 (1938).
53. Crawford, B. L., and Horwitz, W., *J. Chem. Phys.* **16,** 147 (1948).
54. Criegee, R., and Schröder, G., *Angew. Chem.* **71,** 70 (1959).

55. Curtiss, D. H., Lyle, F. K. C., and Lingafelter, E. C., *Acta Cryst.* **5,** 388 (1952).
56. Dehm, H. C., and Chien, J. C. W., *J. Am. Chem. Soc.* **82,** 4429 (1960).
57. Dempsey, J. N., and Baenziger, N. C., *J. Am. Chem. Soc.* **77,** 4984 (1955).
58. Dodge, R. P., and Schomaker, V., *Nature* **186,** 798 (1960).
59. von Dohlen, W. C., and Carpenter, G. B., *Acta Cryst.* **8,** 646 (1955).
60. Dubeck, M., and Filbey, A. H., *J. Am. Chem. Soc.* **83,** 1257 (1961).
61. Duncan, A. B. F., and Murray, J. W., *J. Chem. Phys.* **2,** 636 (1934).
62. Dunitz, J. D., Mez, H. C., Mills, O. S., Pauling, P., and Shearer, H. M. M., *Acta Cryst.* **13,** 1041 (1960).
63. Dunitz, J. D., and Orgel, L. E., *J. Chem. Phys.* **23,** 954 (1955).
64. Dunn, T. M., *in* "Modern Coordination Chemistry," p. 229 (J. Lewis and R. G. Wilkins, eds.), Interscience, New York, 1960.
65. Eastes, J. W., and Burgess, W. M., *J. Am. Chem. Soc.* **64,** 1187 (1942).
66. El-Sayed, M. A., and Sheline, R. K., *J. Am. Chem. Soc.* **78,** 702 (1956).
67. El-Sayed, M. A., and Sheline, R. K., *J. Am. Chem. Soc.* **80,** 2047 (1958).
68. Emeléus, H. J., and Anderson, J. S., "Modern Aspects of Inorganic Chemistry." Routledge, London, 1952.
69. Fackler, J. P., and Cotton, F. A., *J. Am. Chem. Soc.* **82,** 5005 (1960).
70. Falqui, M. T., *Ann. chim. (Rome)* **48,** 1160 (1958).
71. Falqui, M. T., and Rollier, M. A., *Ann. chim. (Rome)* **48,** 1154 (1958).
72. Ferguson, J., *J. Chem. Phys.* **34,** 611 (1961).
73. Ferguson, J., *Spectrochim. Acta* **17,** 316 (1961).
74. Figgis, B. N., *Nature* **182,** 1568 (1958).
75. Figgis, B. N., and Lewis, J., *in* "Modern Coordination Chemistry," p. 400 (J. Lewis and R. G. Wilkins, eds.). Interscience, New York, 1960.
76. Fischer, E. O., and Bürger, G., *Z. Naturforsch.* **16b,** 77 (1961).
77. Fischer, E. O., and Bürger, G., *Chem. Ber.* in press (1961).
78. Fischer, E. O., and Jira, R., *Z. Naturforsch.* **8b,** 217 (1953).
79. Fischer, E. O., and Palm, C., *Chem. Ber.* **91,** 1725 (1958).
80. Fischer, E. O., and Öfele, K., *Chem. Ber.* **90,** 2532 (1957).
81. Fischer, E. O., and Werner, H., *Chem. Ber.* **92,** 1423 (1959).
82. Fischer, E. O., and Werner, H., *Chem. Ber.* **93,** 2075 (1960).
83. Fischer, E. O., and Werner, H., *Tetrahedron Letters* p. 17 (1961).
84. Francis, R., and Cotton, F. A., *J. Chem. Soc.* p. 2078 (1961).
85. Frasson, E., Bardi, R., and Bezzi, S., *Acta Cryst.* **12,** 201 (1959).
86. Frasson, E., and Panattoni, C., *Acta Cryst.* **13,** 893 (1960).
87. Frasson, E., and Panattoni, C., *Acta Cryst.* **13,** 1028 (1960).
88. Frasson, E., Panattoni, C., and Sacconi, L., *J. Phys. Chem.* **63,** 1908 (1959).
89. Freedman, H. H., *J. Am. Chem. Soc.* **83,** 2194 (1961).
90. French, H. S., Magee, M. Z., and Sheffield, E., *J. Am. Chem. Soc.* **64,** 1924 (1942).
91. Friedel, R. A., Wender, I., Shufler, S. L., and Sternberg, H. W., *J. Am. Chem. Soc.* **77,** 3951 (1955).
92. Fritz, H. P., *Chem. Ber.* **94,** 1217 (1961).
93. Fritz, H. P., *Naturwissenschaften* in press (1961).
94. Fritz, H. P., McOmie, J. F. W., and Sheppard, N., *Tetrahedron Letters* p. 35 (1960).
95. Fritz, H. P., and Schneider, R., *Chem. Ber.* **93,** 1171 (1960).
96. Fritz, H. P., and Schrauzer, G. N., *Chem. Ber.* **94,** 650 (1961).
97. Furlani, C., *Gazz. chim. ital.* **88,** 279 (1958).
98. Furlani, C., and Morpurgo, G., *Z. phys. Chem. (Frankfurt)* [N. S.] **28,** 93 (1961).
99. Giacometti, G., *J. Chem. Phys.* **23,** 2068 (1955).

100. Giacometti, G., Scatturin, V., and Turco, A., *Gazz. chim. ital.* **88,** 434 (1958).

101. Gill, N. S., and Nyholm, R. S., *J. Chem. Soc.* p. 3997 (1959).

102. Gill, N. S., Nyholm, R. S., and Pauling, P., *Nature* **182,** 168 (1958).

103. Gilliam, O. R., Johnson, C. M., and Gordy, W., *Phys. Rev.* **78,** 140 (1950).

104. Glaser, H., and Pfeiffer, P., *J. prakt. Chem.* **153,** 300 (1939).

105. Godycki, L. E., and Rundle, R. E., *Acta Cryst.* **6,** 487 (1953).

106. Goodgame, D. M. L., and Cotton, F. A., *J. Am. Chem. Soc.* **82,** 5774 (1960).

107. Gordy, W., Ring, H., and Burg, A. B., *Phys. Rev.* **78,** 512 (1950).

108. Graddon, D. P., and Watton, E. C., *Nature* **190,** 906 (1961).

109. Griffith, J. S., and Orgel, L. E., *Quart. Revs.* (*London*) **11,** 381 (1957).

110. Griffith, W. P., Cotton, F. A., and Wilkinson, G., *J. Inorg. & Nuclear Chem.* **10,** 23 (1959).

111. Griffith, W. P., Lewis, J., and Wilkinson, G., *J. Chem. Soc.* p. 1775 (1959).

112. Griffith, W. P., Lewis, J., and Wilkinson, G., *J. Chem. Soc.* p. 775 (1961).

113. Griffith, W. P., Lewis, J., and Wilkinson, G., *J. Chem. Soc.* p. 2259 (1961).

114. Griffith, W. P., and Wilkinson, G., *J. Inorg. & Nuclear Chem.* **7,** 295 (1958).

115. Gruen, D. M., and McBeth, R. L., *J. Phys. Chem.* **63,** 393 (1959).

116. Halverson, F., and Williams, V. Z., *J. Chem. Phys.* **15,** 552 (1947).

117. Harris, C. M., Lenzer, S. L., and Martin, R. L., *Australian J. Chem.* **11,** 331 (1958).

118. Harris, C. M., Livingstone, S. E., and Reece, I. H., *Australian J. Chem.* **10,** 282 (1957).

118a. Harris, C. M., Livingstone, S. E., and Reece, I. H., *J. Chem. Soc.* p. 1505 (1959).

118b. Harris, C. M., and Nyholm, R. S., *J. Chem. Soc.* p. 4375 (1956).

119. Harris, C. M., Nyholm, R. S., and Phillips, D. J., *J. Chem. Soc.* p. 4379 (1960).

119a. Harris, C. M., Nyholm, R. S., and Stephenson, N. C., *Nature* **177,** 1127 (1956).

119b. Harris, C. M., and Stephenson, N. C., *Chem. & Ind.* (*London*) p. 426 (1957).

120. Hartmann, H., and Fischer-Wasels, H., *Z. physik. Chem.* (*Frankfurt*) [N. S.] **4,** 297 (1955).

121. Hazell, A. C., Swallow, A. G., and Truter, M. R., *Chem. & Ind.* (*London*) p. 564 (1959).

122. Hazell, A. C., and Truter, M. R., *Proc. Roy. Soc.* **A254,** 218 (1960).

123. Heck, R. F., Chien, J. C. W., and Breslow, D. S., *Chem. & Ind.* (*London*) p. 986 (1961).

124. Hein, F., and Müller, H., *Z. anorg. u. allgem. Chem.* **283,** 172 (1956).

125. Herzberg, G., and Herzberg, L., *J. Opt. Soc. Am.* **43,** 1037 (1953).

125a. Holden, J. R., and Baenziger, N. C., *J. Am. Chem. Soc.* **77,** 4987 (1955).

126. Holm, R. H., and McKinney, T. M., *J. Am. Chem. Soc.* **82,** 5506 (1960).

127. Horrocks, W. D., and Cotton, F. A., *Spectrochim. Acta* **17,** 134 (1961).

128. Hübel, W., quoted in reference 93.

129. Issleib, K., and Mitscherling, B., *Z. anorg. u. allgem. Chem.* **304,** 73 (1960).

130. Jaffé, H. H., *J. Chem. Phys.* **21,** 156 (1953).

131. Jahn, H. A., and Teller, E., *Proc. Roy. Soc.* **A161,** 220 (1937).

132. Jensen, K. A., *Z. anorg. u. allgem. Chem.* **229,** 272 (1936).

133. Job, A., and Samuel, A., *Compt. rend. acad. sci.* **177,** 188 (1923).

134. Jones, D., Parshall, G. W., Pratt, L., and Wilkinson, G., *Tetrahedron Letters* p. 48 (1961).

135. Jones, L. H., *J. Chem. Phys.* **23,** 2448 (1955).

136. Jones, L. H., *J. Chem. Phys.* **28,** 1215 (1958).

136a. Jørgensen, C. K., *Acta Chem. Scand.* **9,** 1362 (1955).

137. Jørgensen, C. K., *Rept. 10th Solvay Council Meeting, Brussels* p. 355 (1955).
137a. Jørgensen, C. K., *Acta Chem. Scand.* **10,** 887 (1956).
138. Jørgensen, C. K., *Mol. Phys.* **1,** 410 (1958).
139. Keller, H., personal communication (1961).
139a. Knox, K., *Acta Cryst.* **14,** 583 (1961).
140. Ladell, J., Post, B., and Fankuchen, I., *Acta Cryst.* **5,** 795 (1952).
141. Lewis, J., Irving, R. J., and Wilkinson, G., *J. Inorg. & Nuclear Chem.* **7,** 32 (1958).
142. Liehr, A. D., quoted in reference 98.
143. Liehr, A. D., and Ballhausen, C. J., *Acta Chem. Scand.* **11,** 207 (1957).
144. Lifschitz, I., and Bos, J. G., *Rec. trav. chim.* **59,** 407 (1940).
145. Lifschitz, I., Bos, J. G., and Dijkema, K. M., *Z. anorg. u. allgem. Chem.* **242,** 97 (1939).
146. Lifschitz, I., and Dijkema, K. M., *Rec. trav. chim.* **60,** 582 (1941).
147. Lingafelter, E. C., *Nature* **182,** 1730 (1958).
148. Lingafelter, E. C., Breazeale, J. D., Stewart, J. M., *Acta Cryst.* **10,** 785 (1957).
149. Lingafelter, E. C., Morosin, B., and Simmons, G. L., *Acta Cryst.* **13,** 1025 (1960).
149a. Lippincott, E. R., and Nelson, R. D., *J. Am. Chem. Soc.* **77,** 4990 (1955).
150. Longuet-Higgins, H. C., and Orgel, L. E., *J. Chem. Soc.* 1969 (1956).
151. Lyle, F. K. C., Morosin, B., and Lingafelter, E. C., *Acta Cryst.* **12,** 938 (1959).
152. McClellan, W. R., Hoehn, H. H., Cripps, H. N., Muetterties, E. L., and Howk, B. W., *J. Am. Chem. Soc.* **83,** 1601 (1961).
153. McCullough, R. L., Jones, L. H., and Crosby, G. A., *Spectrochim. Acta* **16,** 929 (1960).
154. McCullough, R. L., Jones, L. H., and Penneman, R. A., *J. Inorg. & Nuclear Chem.* **13,** 286 (1960).
155. McDowell, R. S., Horrocks, W. D., and Yates, J. T., *J. Chem. Phys.* **34,** 530 (1961).
156. Mackle, H., and Sutton, L. E., *Trans. Faraday Soc.* **47,** 937 (1951).
157. Mair, G. A., Powell, H. M., and Henn, D. E., *Proc. Chem. Soc.* p. 415 (1960).
158. Mair, G. A., Powell, H. M., and Venanzi, L. M., *Proc. Chem. Soc.* p. 170 (1961).
159. Maki, G., *J. Chem. Phys.* **28,** 651 (1958).
160. Maki, G., *J. Chem. Phys.* **29,** 162 (1958).
161. Maki, G., *J. Chem. Phys.* **29,** 1129 (1958).
162. Malatesta, L., *Prog. in Inorg. Chem.* **1,** 283 (1959).
163. Malatesta, L., and Angoletta, M., *J. Chem. Soc.* p. 1186 (1957).
164. Malatesta, L., and Cariello, C., *J. Chem. Soc.* p. 2323 (1958); *J. Inorg. & Nuclear Chem.* **8,** 561 (1958).
165. Malatesta, L., Santarella, G., Vallarino, L., and Zingales, F., *Angew. Chem.* **72,** 34 (1960).
166. Matsen, F. A., *J. Am. Chem. Soc.* **81,** 2023 (1959).
166a. Matsuda, H., Osaki, K., and Nitta, I., *Bull. Chem. Soc. Japan* **31,** 611 (1958).
167. Meek, D. W., Straub, D. K., and Drago, R. S., *J. Am. Chem. Soc.* **82,** 6013 (1960).
168. Mellor, D. P., and Craig, D. P., *J. Proc. Roy. Soc. N.S. Wales* **74,** 475 (1941).
169. Merritt, L. L., Guare, C., and Lessor, A. E., *Acta Cryst.* **9,** 253 (1956).
170. Meuthen, B., and von Stackelberg, M., *Z. anorg. u. allgem. Chem.* **305,** 279 (1960).
171. Miller, J. R., *Proc. Chem. Soc.* p. 318 (1960).
172. Miller, J. R., *J. Chem. Soc.*, p. 4452 (1961).
173. Miller, J. R., and Fritz, H. P., unpublished data (1961).
174. Miller, J. R., and Sharpe, A. G., *J. Chem. Soc.* p. 2594 (1961).
175. Miller, J. R., and Waddington, T. C., unpublished data (1960).

176. Mills, O. S., *Acta Cryst.* **11,** 620 (1958).

177. Mills, O. S., Hock, A. A., and Robinson, G., *Congr. Intern. Union Pure and Appl. Chem., Munich,* No. **A143** (1959).

178. Mills, O. S., and Robinson, G., *Proc. Chem. Soc.* p. 156 (1959).

179. Moffitt, W., *J. Am. Chem. Soc.* **76,** 3386 (1954).

180. Moffitt, W., and Ballhausen, C. J., *Ann. Rev. Phys. Chem.* **7,** 107 (1956).

181. Murata, H., and Kawai, K., *J. Chem. Phys.* **26,** 1355 (1957).

182. Nakamoto, K., *J. Am. Chem. Soc.* **74,** 1739 (1952).

183. Nast, R., *Intern. Conf. Coordination Chem., London, 1959, Chem. Soc. Special Publ., No.* **13,** 103.

184. Nast, R., and Böhme, H., *Z. Naturforsch.* **13b,** 625 (1958).

185. Nast, R., Hieber, W., and Proeschel, E., *Z. anorg. u. allgem. Chem.* **256,** 145 (1948).

186. Nast, R., and von Krakkay, T., *Z. anorg. u. allgem. Chem.* **272,** 233 (1953).

187. Nast, R., and von Krakkay, T., *Z. Naturforsch.* **9b,** 798 (1954).

188. Nast, R., and Pfab, W., *Naturwissenschaften* **39,** 300 (1952).

189. Nast, R., and Pfab, W., *Z. Naturforsch.* **12b,** 122 (1957).

190. Nast, R., and Roos, H., *Z. anorg. u. allgem. Chem.* **272,** 242 (1953).

191. Nast, R., and Vester, K., *Z. anorg. u. allgem. Chem.* **279,** 146 (1955).

192. Nyholm, R. S., *Chem. Revs.* **53,** 263 (1953).

193. Nyholm, R. S., *Rept. 10th Solvay Council Meeting, Brussels* p. 225 (1955).

194. Nyholm, R. S., and Short, L. N., *J. Chem. Soc.* p. 2670 (1953).

195. Orgel, L. E., *J. Chem. Phys.* **23,** 1004 (1955).

196. Orgel, L. E., *Rept. 10th Solvay Council Meeting, Brussels* p. 289 (1955).

197. Orgel, L. E., "Introduction to Transition Metal Chemistry." Methuen, London, 1960.

198. Pachler, K., and von Stackelberg, M., *Z. anorg. u. allgem. Chem.* **305,** 286 (1960).

199. Palm, C., Doctorate Thesis, Technische Hochschule, Munich, 1959.

200. Panattoni, C., Frasson, E., and Zanetti, R., *Acta Cryst.* **12,** 1027 (1959).

201. Panattoni, C., Frasson, E., and Zanetti, R., *Gazz. chim. ital.* **89,** 2132 (1959).

202. Pauling, L., "The Nature of the Chemical Bond," 2nd ed. Cornell Univ. Press, Ithaca, New York, 1948.

203. Pauling, L., "The Nature of the Chemical Bond," 3rd ed. Cornell Univ. Press, Ithaca, New York, 1960.

204. Pauson, P. L., *Quart. Revs. (London)* **9,** 391 (1955).

205. Pfab, W., and Fischer, E. O., *Z. anorg. u. allgem. Chem.* **274,** 316 (1953).

206. Pfab, W., and Nast, R., *Z. Krist.* **111,** 259 (1959).

207. Piper, T. S., Cotton, F. A., and Wilkinson, G., *J. Inorg. & Nuclear Chem.* **1,** 165 (1955).

208. Pistorius, C. W. F. T., *Spectrochim. Acta* **15,** 717 (1959).

209. Porai-Kojic, M. A., Antzishkina, A. S., Dickareva, L. M., and Jukhov, E. K., *Acta Cryst.* **10,** 784 (1957).

209a. Powell, D. B., and Sheppard, N., *Spectrochim. Acta* **13,** 69 (1958).

210. Quin, L. D., *J. Am. Chem. Soc.* **79,** 3681 (1957).

211. Rayner, J. H., *Acta Cryst.* **13,** 1028 (1960).

212. Rayner, J. H., and Powell, H. M., *J. Chem. Soc.* p. 319 (1952).

213. Rayner, J. H., and Powell, H. M., *J. Chem. Soc.* p. 3412 (1958).

213a. Reeves, L. W., *Can. J. Chem.* **38,** 736 (1960).

214. Robertson, J. M., "Organic Crystals and Molecules." Cornell Univ. Press, Ithaca, New York, 1953.

215. Romeijn, F. C., *Chem. Abs.* **48,** 1764 (1954).

216. Ruch, E., *Rec. trav. chim.* **75,** 638 (1956).
216a. Ruddlesdon, S. N., and Popper, P., *Acta Cryst.* **10,** 538 (1957).
217. Rundle, R. E., *J. Phys. Chem.* **61,** 45 (1957).
218. Rundle, R. E., and Holman, E. J., *J. Am. Chem. Soc.* **71,** 3264 (1949).
219. Rundle, R. E., and Parasol, M., *J. Chem. Phys.* **20,** 1487 (1952).
220. Rundle, R. E., and Sturdivant, J. H., *J. Am. Chem. Soc.* **69,** 1561 (1947).
221. Sacconi, L., *Accad. nazl. Lincei. chim. inorg. IV Corso est. chim.* p. 367 (1961).
221a. Sacconi, L., Ciampolini, M., Maggio, F., and Del Re, G., *J. Am. Chem. Soc.* **82,** 815 (1960).
222. Sacconi, L., Cini, R., Ciampolini, M., and Maggio, F., *J. Am. Chem. Soc.* **82,** 3487 (1960).
223. Sacconi, L., Cini, R., and Maggio, F., *J. Am. Chem. Soc.* **79,** 3933 (1957).
224. Sacconi, L., Paoletti, P., and Cini, R., *J. Am. Chem. Soc.* **80,** 3583 (1958).
225. Sacconi, L., Paoletti, P., and Del Re, G., *J. Am. Chem. Soc.* **79,** 4062 (1957).
226. Samuel, R., and Jan-Khan, M., *Z. Physik* **84,** 87 (1933).
227. Schläfer, H. L., and Schaffernicht, W., *Angew Chem.* **72,** 618 (1960).
228. Schmitz-DuMont, O., Gössling, H., and Brokopf, H., *Z. anorg. u. allgem. Chem.* **300,** 157 (1959).
229 Schrauzer, G. N., *J. Am. Chem. Soc.* **81,** 5310 (1959).
230. Schrauzer, G. N., *Chem. Ber.* **94,** 642 (1961).
231. Selbin, J., Bull, W. E., and Holmes, L. H., *J. Inorg. & Nuclear Chem.* **16,** 219 (1961).
231a. Sharpe, A. G., and Wakefield, D. B., *J. Chem. Soc.* p. 496 (1957).
232. Shaw, B. L., *Proc. Chem. Soc.* p. 247 (1960).
232a. Shaw, B. L., and Sheppard, N., *Chem. & Ind.* (*London*) p. 517 (1961).
233. Simonsen, S. H., and Pfluger, C. E., *Acta Cryst.* **10,** 471 (1957).
234. Simonsen, S. H., and Pfluger, C. E., *Acta Cryst.* **10,** 536 (1957).
235. Sly, W. G., *J. Am. Chem. Soc.* **81,** 18 (1959).
236. Smidt, J., and Hafner, W., *Angew. Chem.* **71,** 284 (1959).
237. Stammreich, H., Kawai, K., Tavares, Y., Krumholz, P., Behmoiras, J., and Bril, S., *J. Chem. Phys.* **32,** 1482 (1960).
238. Stewart, J. M., and Lingafelter, E. C., *Acta Cryst.* **12,** 842 (1959).
239. Stout, J. W., and Reed, A., *J. Am. Chem. Soc.* **76,** 5279 (1954).
240. Strandberg, M. W. P., Wentink, T., and Hill, A. G., *Phys. Rev.* **75,** 827 (1949).
241. Sundheim, B. R., and Harrington, G., *J. Chem. Phys.* **31,** 700 (1959).
242. Swallow, A. G., and Truter, M. R., *Proc. Roy. Soc.* **A254,** 205 (1960).
242a. Swallow, A. G., and Truter, M. R., *Proc. Chem. Soc.* p. 166 (1961).
243. Sweeney, D. M., Nakagawa, I., Mizushima, S., and Quagliano, J. V., *J. Am. Chem. Soc.* **78,** 889 (1956).
244. Szegö, L., and Ostinelli, P., *Gazz. chim. ital.* **60,** 946 (1930).
245. Thompson, H. W., and Linnett, J. W., *J. Chem. Soc.* p. 1291 (1937).
246. Thompson, H. W., and Linnett, J. W., *J. Chem. Soc.* p. 1384 (1937).
247. Tilney-Bassett, J. F., *J. Chem. Soc.* p. 576 (1961).
248. Tilney-Bassett, J. F., and Mills, O. S., *J. Am. Chem. Soc.* **81,** 4757 (1959).
249. Truter, M. R., and Cox, E. G., *J. Chem. Soc.* p. 948 (1956).
250. Tyson, G. N., and Adams, S. C., *J. Am. Chem. Soc.* **62,** 1228 (1940).
251. Venanzi, L. M., *J. Chem. Soc.* p. 719 (1958); *J. Inorg. & Nuclear Chem.* **8,** 137 (1958).
252. Wallwork, S. C., *Proc. Chem. Soc.* p. 311 (1959).

253. Watt, G. W., McCarley, R. E., and Dawes, J. W., *J. Am. Chem. Soc.* **79,** 5163 (1957).

254. Watt, G. W., Walling, M. T., and Mayfield, P. I., *J. Am. Chem. Soc.* **75,** 6175 (1953).

255. Weinstock, B., Claasen, H. H., and Malm, J. G., *J. Am. Chem. Soc.* **79,** 5832 (1957).

256. Weinstock, B., Claasen, H. H., and Malm, J. G., *J. Chem. Phys.* **32,** 181 (1960).

257. Wells, A. F., "Structural Inorganic Chemistry." Oxford Univ. Press, London and New York, 1945.

258. Wells, A. F., *J. Chem. Soc.* p. 55 (1949).

259. Wilkinson, G., Pauson, P. L., and Cotton, F. A., *J. Am. Chem. Soc.* **76,** 1970 (1954).

260. Williams, D. E., Wohlauer, G., and Rundle, R. E., *J. Am. Chem. Soc.* **81,** 755 (1959).

261. Willis, T. B., and Mellor, D. P., *J. Am. Chem. Soc.* **69,** 1237 (1947).

262. Woodward, L. A., and Hall, J. R., *Nature* **181,** 831 (1958).

263. Woodward, L. A., and Hall, J. R., *Spectrochim. Acta* **16,** 654 (1960).

263a. Wunderlich, J. A., and Mellor, D. P., *Acta Cryst.* **7,** 130 (1954).

263b. Wunderlich, J. A., and Mellor, D. P., *Acta Cryst.* **8,** 57 (1955).

264. Yamada, S., *J. Am. Chem. Soc.* **73,** 1579 (1951).

265. Yamada, S., and Tsuchida, R., *J. Am. Chem. Soc.* **75,** 6351 (1953).

266. Yamada, S., and Tsuchida, R., *Bull. Chem. Soc. Japan* **31,** 813 (1958).

267. Yamazaki, M., *J. Chem. Phys.* **24,** 1260 (1956).

268. Zahner, J. C., and Drickamer, H. G., *J. Chem. Phys.* **33,** 1625 (1960).

269. Zeise, W. C., *Ann. Physik* **9,** 632 (1827).

270. Zeise, W. C., *Ann. Physik* **21,** 497 (1831).