

retained (Fig. 27.3b). Platinum dichlorides are less well-known. The high temperature modification, α -PtCl₂ is insoluble in water but dissolves in hydrochloric acid forming [PtCl₄]²⁻ ions. It has been reported as both olive-green and black, the latter consisting of edge- and corner-sharing PtCl₄ units⁽⁶⁾ (distinct from α -PdCl₂). The dark-red β -PtCl₂ is isomorphous with β -PdCl₂ and the Pt₆Cl₁₂ unit is retained on dissolution in benzene. Red PdBr₂ and black PdI₂, obtained respectively by the action of Br₂ on Pd and the addition of I⁻ to aqueous solutions of PdCl₂, are both insoluble in water but form [PdX₄]²⁻ ions on addition of HX (X = Br, I). PtBr₂ and α -PtI₂ are obtained by thermal decomposition of the tetrahalides, the latter being accompanied by Pt₃I₈ a mixed-valence (II, IV) iodide made up of octahedral PtI₆ and square planar PtI₄ units.⁽⁷⁾ β -PtI₂ is prepared by hydrothermal synthesis from PtI₄, KI and I₂ at 420°C and is made up of planar PtI₄ and planar Pt₂I₆ units.⁽⁷⁾

Oxohalides in this group are apparently confined to the strongly oxidizing PtOF₃. The compound reported to be PtOF₄ is actually O₂⁺[PtF₆].

27.3.4 Complexes⁽⁸⁾

Apart from the few Pt^{VI} and Pt^V fluoro and oxofluoro compounds mentioned above, there is no chemistry in oxidation states above IV.

Oxidation state IV (d⁶)

All complexes in this oxidation state which have been characterized are octahedral and diamagnetic with the low-spin t_{2g}^6 configuration.

⁶ B. KREBS, C. BRENDL and H. SCHÄFER, *Z. anorg. allg. Chem.* **561**, 119–31 (1988).

⁷ G. THIELE, W. WEIGL and H. WOCHNER, *Z. anorg. allg. Chem.* **539**, 141–53 (1986).

⁸ L. SACCONI, F. MANI and A. BENCINI, Ni, Chap. 50, pp. 1–347; M. J. RUSSELL and C. F. J. BARNARD, Pd, Chap. 51, pp. 1099–130; A. T. HUTTON, Pd(II)–S-donor Complexes, Chap. 51.8, pp. 1131–55; A. T. HUTTON and C. P. MORLEY, Pd(II)–P-donor Complexes, Chap. 51.9, pp. 1157–70; D. M. ROUNDHILL, Pt, Chap. 52, pp. 351–531 in *Comprehensive Coordination Chemistry*, Vol. 5, Pergamon Press, Oxford, 1987.

Fluorination of NiCl₂ + KCl produces red K₂NiF₆ which is strongly oxidizing and will liberate O₂ from water. Dark red complexes of the type [Ni^{IV}(L)](ClO₄)₂ (H₂L is a sixidentate oxime) have been obtained by the action of conc HNO₃ on [Ni^{II}(H₂L)](ClO₄)₂ and are stable indefinitely under vacuum but are reduced in moist air.

Palladium(IV) complexes are rather sparse and much less stable than those of Pt^{IV}. The best known are the hexahalogeno complexes [PdX₆]²⁻ (X = F, Cl, Br) of which [PdCl₆]²⁻, formed when the metal is dissolved in aqua regia, is the most familiar. In all of these the Pd^{IV} is readily reducible to Pd^{II}. In water, [PdF₆]²⁻ hydrolyses immediately to PdO₂·xH₂O while the chloro and bromo complexes give [PdX₄]²⁻ plus X₂. An organometallic chemistry of Pd^{IV} is developing (p. 1167).

By contrast Pt^{IV} complexes rival those of Pt^{II} in number, and are both thermodynamically stable and kinetically inert. Those with halides, pseudo-halides, and N-donor ligands are especially numerous. Of the multitude of conceivable compounds ranging from [PtX₆]²⁻ through [PtX₄L₂] to [PtL₆]⁴⁺, (X = F, Cl, Br, I, CN, SCN, SeCN; L = NH₃, amines) a large number have been prepared and characterized though, curiously, they do not include the [Pt(CN)₆]²⁻ ion. K₂PtCl₆ is commercially the most common compound of platinum and the brownish-red, “chloroplatinic acid”, H₂[PtCl₆](aq), is the usual starting material in Pt^{IV} chemistry. It is prepared by dissolving platinum metal sponge in aqua regia, followed by one or more evaporations with hydrochloric acid. A route to Pt^{II} chemistry also is provided by precipitation of the sparingly soluble K₂PtCl₆ followed by its reduction with hydrazine to K₂PtCl₄. The chloroammines were extensively used by Werner and other early coordination chemists in their studies on the nature of the coordinate bond in general and on the octahedral geometry of Pt^{IV} in particular.

O-donor ligands such as OH⁻ and acac also coordinate to Pt^{IV}, but S- and Se-, and more especially P- and As-donor ligands, tend to reduce it to Pt^{II}.

Oxidation state III (d^7)

Perhaps surprisingly, mononuclear M^{III} compounds are rather better represented by nickel than by either palladium or platinum. K_3NiF_6 has been prepared by fluorinating $KCl + NiCl_2$ at high temperatures and pressures. It is a violet crystalline material which is reduced by water with evolution of oxygen. The observed elongation of the $[NiF_6]^{3-}$ octahedron has been ascribed to the Jahn–Teller effect (p. 1021) to be expected for a $t_{2g}^6 e_g^1$ configuration although the reported magnetic moment of 2.5 BM at room temperature seems rather high for this configuration. Other examples include $[Ni(bipy)_3]^{3+}$, the black trigonal pyramidal $[NiBr_3(PEt_3)_2]$ and a number of compounds with N -donor macrocyclic ligands. Among the very few monomeric trivalent compounds of Pd and Pt, the blue $(NBu_4)[Pt(C_6Cl_5)_4]$ (obtained by oxidizing the Pt^{II} salt) and the red $[Pd(1,4,7-trithiacyclononane)_2](ClO_4)_4 \cdot H_3O \cdot 3H_2O$ (obtained⁽⁹⁾ by cyclovoltammetric oxidation in 70% aqueous $HClO_4$) should be mentioned.

The most abundant examples of this oxidation state, however, are the dinuclear Pt compounds⁽¹⁰⁾ of the type, $[Pt_2(L-L)_4L_2]^{n-}$ with single Pt–Pt bonds and the same tetrabridged structure of Mo^{II} and Cr^{II} (p. 1032). The first of these was $K_2[Pt_2(SO_4)_4(H_2O)_2]$, prepared from $[Pt(NO_2)_2(NH_3)_2]$ and sulfuric acid, but those with phosphate or P -donor, pyrophosphito, $(P_2O_5H_2)^{2-}$, bridges are more numerous. Pt–Pt distances range from 278.2(1) pm, found with pyrophosphito bridges, down to 245.1(1) pm in $Cs_3[Pt_2(\mu-O_2CMe)_2(\mu-O_2CCH_2)_2]$. This yellow complex is obtained by a complex procedure⁽¹¹⁾ from K_2PtCl_4 and $MeCOOAg$ and, besides a pair of O,O -donor acetate bridges, contains a pair of

unique C,O -donor, $-O.CO.CH_2-$, bridges. Stable tetraacetato bridged dimers are not found.

A number of compounds which have in the past been claimed to contain the trivalent metals have later turned out to contain them in more than one oxidation state. One such is H. Wolfram's red salt, $Pt(EtNH_2)_4Cl_3 \cdot 2H_2O$, which has a structure (Fig. 27.4a) consisting of alternate octahedral Pt^{IV} and square-planar Pt^{II} linked by Cl bridges, i.e. $[Pt^{II}(EtNH_2)_4]^{2+} [trans-(\mu-Cl)_2-Pt^{IV}(EtNH_2)_4]^{2-} Cl^- \cdot 4H_2O$. Other examples are

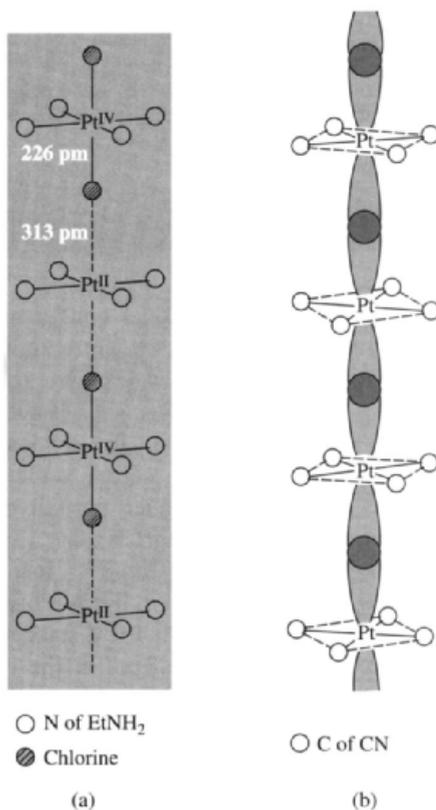


Figure 27.4 Linear chain polymers of Pt. (a) The coordination of platinum in Wolfram's red salt, $Pt(EtNH_2)_4Cl_3 \cdot 2H_2O$, showing alternating Pt^{II} and Pt^{IV} linked by Cl bridges. Four remaining Cl^- ions and 4 H_2O are situated within the lattice. (b) Stacking of square planar units in $[Pt(CN)_4]^{n-}$ showing the possible overlap of d_{z^2} orbitals. (Note the successive 45° rotations, or "staircase staggering", of these units.)

⁹ A. J. BLAKE, A. J. HOLDER, T. I. WHITE and M. SCHRÖDER, *J. Chem. Soc., Chem. Commun.*, 987–8 (1987).

¹⁰ F. A. COTTON and R. A. WALTON, *Multiple Bonds between Atoms*, 2nd Edn., Oxford University Press, Oxford, pp. 508–32 (1993); K. UMAKOSHI and Y. SASAKI, *Adv. Inorg. Chem.* **40**, 187–239 (1994).

¹¹ T. YAMAGUCHI, Y. SASAKI and T. ITO, *J. Am. Chem. Soc.* **112**, 4038–40 (1990).

Development of Ideas on the Stereochemistry of Nickel(II)

The way in which our present understanding of the stereochemical intricacies of Ni^{II} has evolved illustrates rather well the interplay of theory and experiment. On the basis of valence-bond theory, three types of complex of d⁸ ions were anticipated. These were:

- (i) *octahedral*, involving sp³d₂:d_{x²-y²} hybridization and paramagnetism from 2 unpaired electrons;
- (ii) *tetrahedral*, involving sp³ hybridization and, again, paramagnetism from 2 unpaired electrons;
- (iii) *square planar*, involving d_{x²-y²}:sp₂p_z hybridization which implies the confinement of all 8 electrons in four d orbitals, so producing diamagnetism.

Since X-ray determinations of structure were too time-consuming to be widely used in the 1930s and 1940s and, in addition, square-planar geometry was a comparative rarity, any paramagnetic compound, which on the basis of stoichiometry appeared to be 4-coordinate, was presumed to be tetrahedral.

However, with the application in the 1950s of crystal field theory to transition-metal chemistry it was realized that CFSEs were unfavourable to the formation of tetrahedral d⁸ complexes, and previous assignments were re-examined. A typical case was [Ni(acac)₂], which had often been cited as an example of a tetrahedral nickel complex, but which was shown⁽¹²⁾ in 1956 to be trimeric and octahedral. The over-zealous were then inclined to regard tetrahedral d⁸ as non-existent until first L. M. Venanzi⁽¹³⁾ and then N. S. Gill and R. S. Nyholm⁽¹⁴⁾ demonstrated the existence of discrete tetrahedral species which in some cases were also rather easily prepared.

More comprehensive examination of spectroscopic and magnetic properties of d⁸ ions followed which provided an explanation for the different types of Lifschitz salts (p. 1160) and led to studies of systems exhibiting anomalous properties. Rational explanations of these properties were eventually forthcoming.

provided by the one-dimensional conductors of platinum,^(14a) of which the cyano complexes are the best known. Thus K₂[Pt(CN)₄].3H₂O is a very stable colourless solid, but by appropriate partial oxidation it is possible to obtain bronze-coloured, "cation deficient", K_{1.75}Pt(CN)₄.1.5H₂O, and other partially oxidized compounds such as K₂Pt(CN)₄Cl_{0.3}.3H₂O. In these, square-planar [Pt(CN)₄]ⁿ⁻ ions are stacked (Fig. 27.4b) to give a linear chain of Pt atoms in which the Pt-Pt distances of 280–300 pm (compared to 348 pm in the original K₂[Pt(CN)₄].3H₂O and 278 pm in the metal itself) allow strong overlap of the d_{z²} orbitals. This accounts for the metallic conductance of these materials along the crystal axis. Indeed, there is considerable current interest in such "one-dimensional" electrical conductors.

Oxalato complexes [e.g. K_{1.6}Pt(C₂O₄)₂.1.2-H₂O] originally prepared as long ago as 1888

by the German chemist H. G. Söderbaum, are also one-dimensional conductors with analogous structures.

Oxidation state II (d⁸)

This is undoubtedly the most prolific oxidation state for this group of elements. The stereochemistry of Ni^{II} has been a topic of continuing interest (see Panel), and kinetic and mechanistic studies on complexes of Pd^{II} and Pt^{II} have likewise been of major importance. It will be convenient to treat Ni^{II} complexes first and then those of Pd^{II} and Pt^{II} (p. 1161).

Complexes of Ni^{II}. The absence of any other oxidation state of comparable stability for nickel implies that compounds of Ni^{II} are largely immune to normal redox reactions. Ni^{II} forms salts with virtually every anion and has an extensive aqueous chemistry based on the green[†] [Ni(H₂O)₆]²⁺ ion which is always present in the absence of strongly complexing ligands.

¹² G. J. BULLEN, *Nature* **177**, 537–8 (1956).

¹³ L. M. VENANZI, *J. Chem. Soc.* 719–24 (1958).

¹⁴ N. S. GILL and R. S. NYHOLM, *J. Chem. Soc.* 3997–4007 (1959).

^{14a} R. J. H. CLARK, *Chem. Soc. Rev.* **19**, 107–31 (1990).

[†] It was work on the absorption of light by solutions of nickel(II) which led A. Beer in 1852 to formulate the law which bears his name.

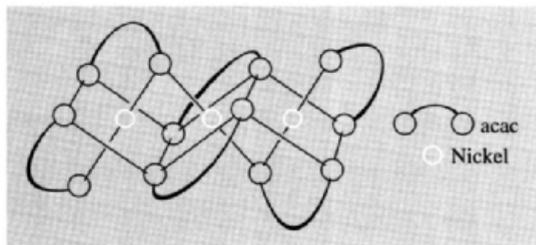


Figure 27.5 Trimeric structure of $[\text{Ni}(\text{acac})_2]_3$.

The coordination number of Ni^{II} rarely exceeds 6 and its principal stereochemistries are octahedral and square planar (4-coordinate) with rather fewer examples of trigonal bipyramidal (5), square pyramidal (5), and tetrahedral (4). Octahedral complexes of Ni^{II} are obtained (often from aqueous solution by replacement of coordinated water) especially with neutral *N*-donor ligands such as NH_3 , en, bipy and phen, but also with NCS^- , NO_2^- and the *O*-donor dimethylsulfoxide, dmsO (Me_2SO).

The green trimer, $[\text{Ni}(\text{acac})_2]_3$ (Fig 27.5), prepared by dehydrating the monomeric octahedral *trans*-dihydrate, $[\text{Ni}(\text{acac})_2(\text{H}_2\text{O})_2]$ and mentioned in the Panel opposite, has interesting magnetic properties. Down to about 80 K it behaves as a normal paramagnet but below that the magnetic moment per nickel atom rises from about 3.2 BM (as expected for 2 unpaired electrons, i.e. $S = 1$) to 4.1 BM at 4.3 K. This corresponds to the ferromagnetic coupling of all 6 unpaired electrons in the trimer (i.e. $S' = 3$). Replacement of the $-\text{CH}_3$ groups of acetylacetonate by the bulkier $\text{C}(\text{CH}_3)_3$ apparently prevents the formation of

the trimer and leads instead to the red square-planar monomer (Fig. 27.6a).

Of the four-coordinate complexes of Ni^{II} , those with the square planar stereochemistry are the most numerous. They include the yellow $[\text{Ni}(\text{CN})_4]^{2-}$, the red bis(*N*-methylsalicylaldiminato)nickel(II) and the well-known bis(dimethylglyoximate)nickel(II) (Fig. 27.6b and c) obtained as a flocculent red precipitate in gravimetric determinations of nickel. Actually, in the solid state, this last compound consists of planar molecules stacked above each other so that Ni–Ni interactions occur (Ni–Ni 325 pm), and the nickel atoms should therefore be described as octahedrally coordinated. However, in non-coordinating solvents it dissociates into the square-planar monomer, while in bis(ethylmethylglyoximate)nickel(II) a much longer Ni–Ni separation (475 pm) indicates that even in the solid it must be regarded as square planar.

Although less numerous than the square-planar complexes, tetrahedral complexes of nickel(II) also occur. The simplest of these are the blue $[\text{NiX}_4]^{2-}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) ions, precipitated⁽¹⁴⁾ from ethanolic solutions by large cations such as $[\text{NR}_4]^+$, $[\text{PR}_4]^+$ and $[\text{AsR}_4]^+$. Other examples include a number of those of the type $[\text{NiL}_2\text{X}_2]$ ($\text{L} = \text{PR}_3, \text{AsR}_3, \text{OPR}_3, \text{OAsR}_3$) amongst which were the first authenticated examples of tetrahedral nickel(II).⁽¹³⁾

A partial explanation, at least, can be provided for the relative abundances and ease of formation of the above stereochemical varieties of Ni^{II} complexes. It can be seen from Table 26.6 that the CFSEs of the d^8 configuration, unlike those of the d^7 configuration (e.g. Co^{II}), favour an

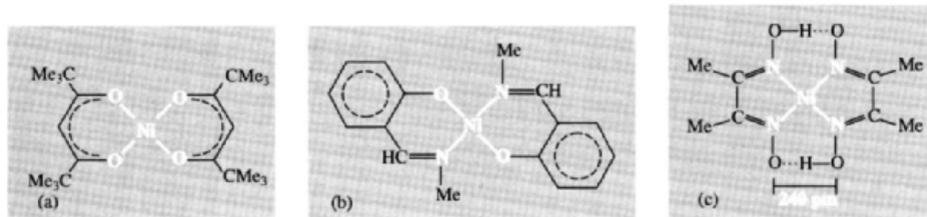


Figure 27.6 Some typical planar complexes of nickel(II): (a) $[\text{Ni}(\text{Me}_6\text{-acac})_2]$, (b) $[\text{Ni}(\text{Me-sal})_2]$ and (c) $[\text{Ni}(\text{dmgH})_2]$. (Note the short O–O distance which is due to strong hydrogen bonding.)

Electronic Spectra and Magnetic Properties of Complexes of Nickel(II)⁽¹⁵⁾

Nickel(II) is the only common d^8 ion and its spectroscopic and magnetic properties have accordingly been extensively studied.

In a cubic field three spin-allowed transitions are expected because of the splitting of the free-ion, ground 3F term and the presence of the 3P term. In an octahedral field the splitting is the same as for the octahedral d^3 ion and the same energy level diagram (p. 1029) can be used to interpret the spectra as was used for octahedral Cr^{III} . Spectra of octahedral Ni^{II} usually do consist of three bands which are accordingly assigned as:

$$\nu_1 = {}^3T_{2g}(F) \leftarrow {}^3A_{2g}(F) = 10Dq; \quad \nu_2 = {}^3T_{1g}(F) \leftarrow {}^3A_{2g}(F); \quad \nu_3 = {}^3T_{1g}(P) \leftarrow {}^3A_{2g}(F)$$

with ν_1 giving the value of Δ , or $10Dq$, directly. Quite often there is also evidence of weak spin-forbidden (i.e. spin triplet \rightarrow singlet) absorptions and, in $[Ni(H_2O)_6]^{2+}$ and $[Ni(dmsO)_6]^{2+}$, for instance, the ν_2 absorption has a strong shoulder on it. This is ascribed to a transition to the spin singlet 1E_g which occurs when the 1E_g and ${}^3T_{1g}(F)$ terms are in close proximity.

For d^8 ions in tetrahedral fields the splitting of the free-ion ground term is the inverse of its splitting in an octahedral field, so that ${}^3T_{1g}(F)$ lies lowest. In this case three relatively intense bands are to be expected, arising from the transitions:

$$\nu_1 = {}^3T_2(F) \leftarrow {}^3T_1(F); \quad \nu_2 = {}^3A_2(F) \leftarrow {}^3T_1(F); \quad \nu_3 = {}^3T_1(P) \leftarrow {}^3T_1(F)$$

Table A gives data for a number of octahedral and tetrahedral complexes.

Table A Electronic spectra of some complexes of nickel(II)

Complex	ν_1/cm^{-1}	ν_2/cm^{-1}	ν_3/cm^{-1}	$10Dq/cm^{-1}$
Octahedral				
$[Ni(dmsO)_6]^{2+}$	7 730	12 970	24 040	7 730
$[Ni(H_2O)_6]^{2+}$	8 500	13 800	25 300	8 500
$[Ni(NH_3)_6]^{2+}$	10 750	17 500	28 200	10 750
$[Ni(en)_3]^{2+}$	11 200	18 350	29 000	11 200
$[Ni(bipy)_3]^{2+}$	12 650	19 200	(a)	12 650
Tetrahedral				
$[NiI_4]^{2-}$		7 040	14 030	3 820
$[NiBr_4]^{2-}$		7 000	13 230, 14 140	3 790
$[NiCl_4]^{2-}$		7 549	14 250, 15 240	4 090
$[NiBr_2(OPPh_3)_2]$		7 250	15 580	3 950

^(a)Obscured by intense charge-transfer absorptions.

The T ground term of the tetrahedral ion is expected to lead to a temperature-dependent orbital contribution to the magnetic moment, whereas the A ground term of the octahedral ion is not, though "mixing" of the excited ${}^3T_{2g}(F)$ term into the ${}^3A_{2g}(F)$ ground term is expected to raise its moment to:

$$\mu_e = \mu_{\text{spin-only}}(1 - 4\lambda/10Dq)$$

where $\lambda = -315 \text{ cm}^{-1}$ and $\mu_{\text{spin-only}} = 2.83 \text{ BM}$. (This is the exact reverse of the situations found for Co^{II} ; p. 1132.) The upshot is that the magnetic moments of tetrahedral compounds are found to lie in the range 3.2–4.1 BM (and are dependent on temperature, and are reduced towards $\mu_{\text{spin-only}}$ by electron delocalization on to the ligands and by distortions from ideal tetrahedral symmetry) whereas those of octahedral compounds lie in the range 2.9–3.3 BM.

The spectra of square-planar d^8 complexes are usually characterized by a fairly strong band in the yellow to blue region (i.e. about $17\,000\text{--}22\,000 \text{ cm}^{-1}$ or $600\text{--}450 \text{ nm}$) which is responsible for the reddish colour, and another band near the ultraviolet. The likelihood of π -bonding and attendant charge transfer makes a simple crystal-field treatment inappropriate, and unambiguous assignments are difficult.

¹⁵A. B. P. LEVER, *Inorganic Electronic Spectroscopy*, (2nd Edn.), pp. 507–611, Elsevier, Amsterdam, 1984.

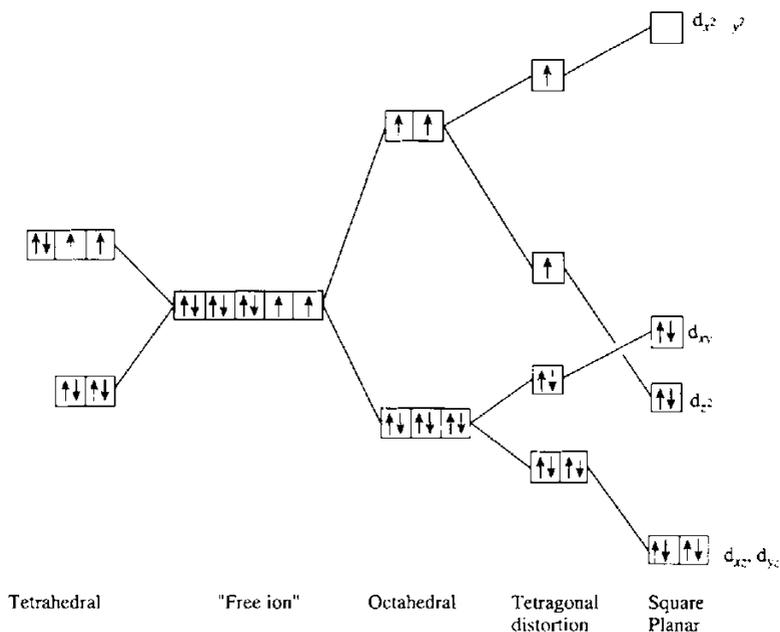


Figure 27.7 The splitting of d orbitals in fields of different symmetries, and the resulting electronic configurations of the Ni^{II} d^8 ion.

octahedral as opposed to a tetrahedral stereochemistry. It is also evident from Fig 27.7 that the square-planar geometry offers the possibility, not available in either the octahedral or tetrahedral cases, of accommodating all 8 d electrons in 4 lower orbitals, thus leaving the uppermost ($d_{x^2-y^2}$) orbital empty. Providing therefore that the ligand field is of sufficiently low symmetry (or is sufficiently strong) to split the d orbitals enough to offset the energy required to pair-up 2 electrons, then the 4-coordinate, square-planar extreme can be energetically preferable not only to the tetrahedral but also to the 6-coordinate octahedral extreme. Thus, with the CN^- ligand which produces an exceptionally strong field, the square-planar $[\text{Ni}(\text{CN})_4]^{2-}$ is formed rather than the tetrahedral isomer or the octahedral $[\text{Ni}(\text{CN})_6]^{4-}$. Also, many compounds of the type $[\text{NiL}_2\text{X}_2]$, in which low-symmetry crystal fields are clearly possible, are planar. However, this selfsame formulation was mentioned above as including examples of tetrahedral complexes: evidently the factors which determine the geometry of a particular complex are finely balanced.

This balance, which apparently involves both steric and electronic factors, is well illustrated by the series of complexes $[\text{Ni}(\text{PR}_3)_2\text{X}_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$). The diamagnetic, planar forms are favoured by $\text{R} = \text{alkyl}$, $\text{X} = \text{I}$, and the paramagnetic tetrahedral forms by $\text{R} = \text{aryl}$, $\text{X} = \text{Cl}$. When mixed alkylarylphosphines are involved, conformational isomerism may occur. For example, $[\text{NiBr}_2(\text{PEtPh}_2)_2]$ has been isolated in both a green, paramagnetic ($\mu_{300} = 3.20 \text{ BM}$), tetrahedral form and a brown, diamagnetic, planar form.

These various stereochemistries are characterized by differing spectroscopic and magnetic properties (see Panel opposite). However, the crude traditional guidelines of colour and magnetism, namely that square planar compounds are red to yellow and diamagnetic whereas tetrahedral ones are green to blue and paramagnetic (due to the $t_{2g}^6 e_g^2$ and $e^4 t_2^4$ configurations respectively), cannot be regarded as rigorously diagnostic. The octahedral $[\text{Ni}(\text{NO}_2)_6]^{4-}$ and square planar $[\text{NiI}_2(\text{quinoline})_2]$ for instance, are respectively paramagnetic and diamagnetic (expected) but are

also brown-red and green (unexpected). Furthermore, the compounds, $[\text{Bu}_2^i\text{P}(\mu\text{-O},\mu\text{-NR})\text{Ni}(\mu\text{-O},\mu\text{-NR})\text{P}(\text{Bu}_2^i)]$ ($\text{R} = \text{Pr}^i$, cyclohexyl) exist as both tetrahedral and square planar isomers of which not only the former but, uniquely, the latter also are paramagnetic.⁽¹⁶⁾ Presumably the separation of $d_{x^2-y^2}$ and d_{xy} orbitals (Fig 27.7) is sufficiently small to allow both to be singly occupied.

Many compounds, of which $[\text{NiBr}_2(\text{PEtPh}_2)_2]$ mentioned above is one, exist in solution as mixtures of isomers giving rise to intermediate values of μ_e (0–3.2 BM). Such behaviour, previously regarded as “anomalous” is due to one of three possible types of equilibria:

1. *Planar–tetrahedral equilibria.* Compounds such as $[\text{NiBr}_2(\text{PEtPh}_2)_2]$ mentioned above as well as a number of *sec*-alkylsalicylaldiminato derivatives (i.e. Me in Fig. 27.6b replaced by a *sec*-alkyl group) dissolve in non-coordinating solvents such as chloroform or toluene to give solutions whose spectra and magnetic properties are temperature-dependent and indicate the presence of an equilibrium mixture of diamagnetic planar and paramagnetic tetrahedral molecules.

2. *Planar–octahedral equilibria.* Dissolution of planar Ni^{II} compounds in coordinating solvents such as water or pyridine frequently leads to the formation of octahedral complexes by the coordination of 2 solvent molecules. This can, on occasions, lead to solutions in which the Ni^{II} has an intermediate value of μ_e indicating the presence of comparable amounts of planar and octahedral molecules varying with temperature and concentration; more commonly the conversion is complete and octahedral solvates can be crystallized out. Well-known examples of this behaviour are provided by the complexes $[\text{Ni}(\text{L-L})_2\text{X}_2]$ ($\text{L-L} =$ substituted ethylenediamine, $\text{X} =$ variety of anions) generally known by the name of their discoverer I. Lifschitz. Some of these Lifschitz salts are yellow, diamagnetic and planar, $[\text{Ni}(\text{L-L})_2]\text{X}_2$, others are blue, paramagnetic, and octahedral, $[\text{Ni}(\text{L-L})_2\text{X}_2]$ or

$[\text{Ni}(\text{L-L})_2(\text{solvent})_2]\text{X}_2$. Which type is produced depends on the nature of L-L, X, and the solvent.

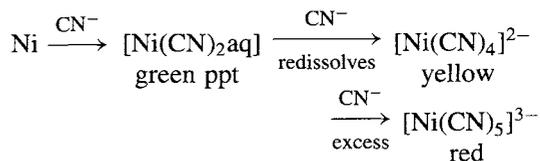
3. *Monomer–oligomer equilibria.* $[\text{Ni}(\text{Me-sal})_2]$, mentioned above as a typical planar complex, is a much studied compound. In pyridine it is converted to the octahedral bispyridine adduct ($\mu_{300} = 3.1$ BM), while in chloroform or benzene the value of μ_e is intermediate but increases with concentration. This is ascribed to an equilibrium between the diamagnetic monomer and a paramagnetic dimer, which must involve a coordination number of the nickel of at least 5; a similar explanation is acceptable also for the paramagnetism of the solid when heated above 180°C. The trimerization of $\text{Ni}(\text{acac})_2$ to attain octahedral coordination has already been referred to but it may also be noted that it is reported to be monomeric and planar in dilute chloroform solutions.

Apart from the probably 5-coordinate Ni^{II} in the above oligomers, a number of well-characterized 5-coordinate complexes are known. These are either trigonal bipyramidal or square pyramidal, though the two forms are energetically similar and the stereochemistry is often imposed by the ligands. Thus the trigonal bipyramidal complexes, which are the more common, often involve tripod ligands (p. 907), while the quadri-dentate chain ligand,



(tetars) produces square pyramidal complexes of the type $[\text{Ni}(\text{tetars})\text{X}]^+$. These 5-coordinate complexes can be of either high-spin or low-spin type. The former is found in $[\text{NiBr}\{\text{N}(\text{C}_2\text{H}_4\text{NMe}_2)_3\}]^+$ but with *P*- or *As*-donor ligands low-spin configurations are found.

The $\text{Ni}^{\text{II}}/\text{CN}^-$ system illustrates nicely the ease of conversion of the two stereochemistries. Although, as already pointed out, there is no evidence of a hexacyano complex, a square pyramidal pentacyano complex is known:



¹⁶ T. FRÖMMEI, W. PETERS, H. WUNDERLICH and W. KUCHERN, *Angew. Chem. Int. Edn. Engl.* **31**, 612–13 (1992); *ibid.* **32**, 907–9 (1993).

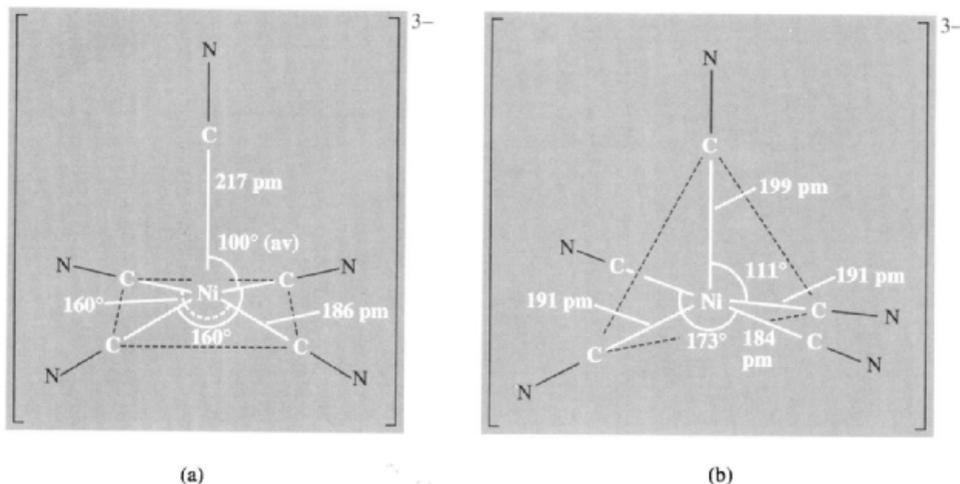


Figure 27.8 The structure of the distorted (a) square-pyramidal and (b) trigonal bipyramidal $[\text{Ni}(\text{CN})_5]^{3-}$ ions in $[\text{Cr}(\text{en})_3][\text{Ni}(\text{CN})_5] \cdot 1\frac{1}{2}\text{H}_2\text{O}$.

The fascinating crystalline compound $[\text{Cr}(\text{en})_3][\text{Ni}(\text{CN})_5] \cdot 1\frac{1}{2}\text{H}_2\text{O}$ contains both square pyramidal and trigonal bipyramidal anions though each is distorted from true C_{4v} or D_{3h} symmetry as shown in Fig. 27.8.

Another interesting cyanide derivative of nickel(II)^(16a) which may conveniently be mentioned here is the *clathrate* compound, $[\text{Ni}(\text{CN})_2(\text{NH}_3)] \cdot x\text{C}_6\text{H}_6$ ($x \leq 1$). If CN⁻ is added to the blue-violet solution obtained by mixing aqueous solutions of Ni^{II} and NH_3 , and this is then shaken with benzene, a pale-violet precipitate is obtained. This precipitate is soluble in conc NH_3 . The benzene and ammonia can be removed by heating it above 150°C but not by washing or by application of reduced pressure. The benzene molecule is, in fact, trapped inside a cage formed by the lattice in which the nickel ions are coordinated to 4 cyanides situated in a square plane, and half are additionally coordinated to 2 ammonias (Fig. 27.9). The observed magnetic moment per Ni atom of 2.2 BM is entirely consistent with this since this average moment arises solely from the octahedrally coordinated Ni atoms, the square-planar Ni being diamagnetic.

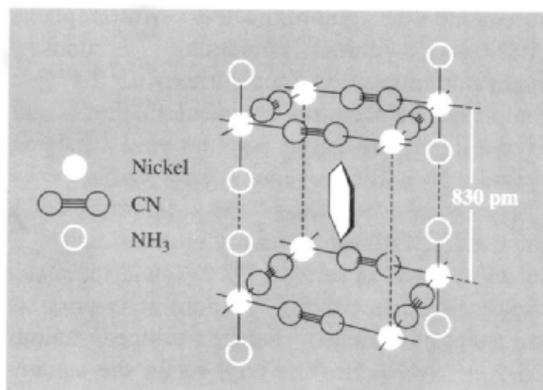


Figure 27.9 A "cage" in the structure of $[\text{Ni}(\text{CN})_2(\text{NH}_3)] \cdot x(\text{C}_6\text{H}_6)$, showing a trapped benzene molecule.

Complexes of Pd^{II} and Pt^{II}. The effect of complexation on the splitting of d orbitals is much greater in the case of second- and third-row transition elements, and the associated effects already noted for Ni^{II} are even more marked for Pd^{II} and Pt^{II} , as a result, their complexes are, with rare exceptions, diamagnetic and the vast majority are planar also. Not many complexes are formed with *O*-donor ligands but, of the few that are, $[\text{M}(\text{H}_2\text{O})_4]^{2+}$ ions, and the polymeric anhydrous acetates $[\text{Pd}(\text{O}_2\text{CMe})_2]_3$ and $[\text{Pt}(\text{O}_2\text{CMe})_2]_4$ (Fig. 27.10), are the most

^{16a} K. R. DUNBAR and R. A. HEINTZ *Prog. Inorg. Chem.* **45**, 283-391 (1997).

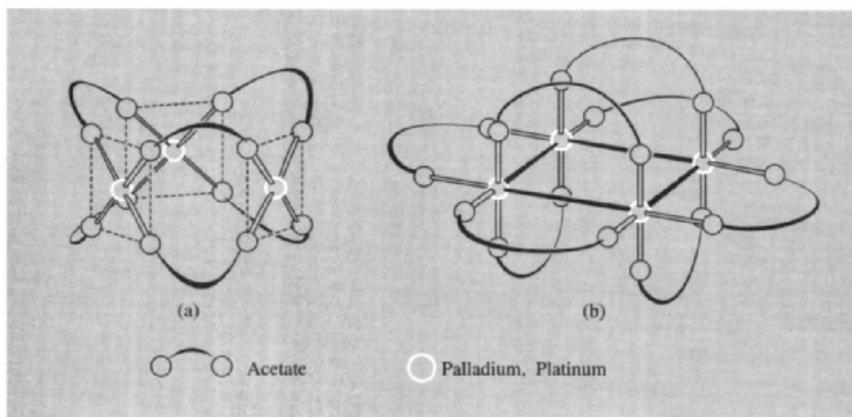


Figure 27.10 Anhydrous acetates of Pd^{II} and Pt^{II}: (a) trimeric $[\text{Pd}(\text{O}_2\text{CMe})_2]_3$ involving square-planar coordinated Pd but no metal-metal bonding (average Pd-Pd = 315 pm), and (b) tetrameric $[\text{Pt}(\text{O}_2\text{CMe})_2]_4$ involving octahedrally coordinated Pt and metal-metal bonds (average Pt-Pt = 249.5 pm). The four bridging ligands in the Pt₄ plane are much more labile than the others.

important.^(17,18) Approximately square planar $[\text{M}(\text{NO}_3)_4]^{2-}$ anions containing the unusual unidentate nitrate ion are also known.⁽¹⁹⁾ Fluoro complexes are even less prevalent, the preference of these cations being for the other halides, cyanide, *N*- and heavy atom-donor ligands.

The complexes $[\text{MX}_4]^{2-}$ (M = Pd, Pt; X = Cl, Br, I, SCN, CN) are all easily obtained and may be crystallized as salts of $[\text{NH}_4]^+$ and the alkali metals. By using $[\text{NR}_4]^+$ cations it is possible to isolate binuclear halogen-bridged anions $[\text{M}_2\text{X}_6]^{2-}$ (X = Br, I) which retain the square-planar coordination of M. Aqueous solutions of yellowish-brown $[\text{PdCl}_4]^{2-}$ and red $[\text{PtCl}_4]^{2-}$ are common starting materials for the preparation of other Pd^{II} and Pt^{II} complexes by successive substitution of the chloride ligands. In both $[\text{M}(\text{SCN})_4]^{2-}$ complexes the ligands bond through their π -acceptor (*S*) ends, though in the presence of stronger π -acceptor ligands such as PR_3 and AsR_3 they tend to bond through their *N* ends.[†] Not surprisingly, therefore, several

instances of linkage isomerism (p. 920) have been established in compounds of the type *trans*- $[\text{M}(\text{PR}_3)_2(\text{SCN})_2]$.

Complexes with ammonia and amines, especially those of the types $[\text{ML}_4]^{2+}$ and $[\text{ML}_2\text{X}_2]$, are numerous for Pd^{II} and even more so for Pt^{II}. Many of them were amongst the first complexes of these metals to be prepared and interest in them has continued since. For example, the colourless $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2 \cdot \text{H}_2\text{O}$ can be obtained by adding NH_3 to an aqueous solution of PtCl_2 and, in 1828, was the first of the platinum amines to be discovered (by G. Magnus). Other salts of the $[\text{Pt}(\text{NH}_3)_4]^{2+}$ ion are easily derived, the best known being Magnus's green salt $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$. That a green salt should result from the union of a colourless cation and a red anion was unexpected and is a consequence of the crystal structure, which consists of the square-planar anions and cations stacked

¹⁷ D. P. BANCROFT, F. A. COTTON, L. R. FALVELLO and W. SCHWOTZER, *Polyhedron* **7**, 615-21 (1988).

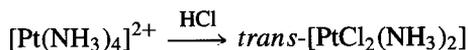
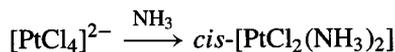
¹⁸ T. YAMAGUCHI, T. UENO and T. ITO, *Inorg. Chem.* **32**, 4996-7 (1993).

¹⁹ L. I. ELDING, B. NORÉN and Å. OSKARSSON, *Inorg. Chim. Acta* **114**, 71-4 (1986).

[†] Steric, as well as electronic, effects are probably involved. When the ligand is *N*-bonded, $\text{M} \leftarrow \text{N} \equiv \text{C} - \text{S}$ is linear and so sterically undemanding. However, when the ligand is *S*-bonded, $\text{M} - \text{S} - \text{C}$ is nonlinear, the bonding and nonbonding electron pairs around the sulfur being more or less tetrahedrally disposed. On purely steric grounds, therefore, the latter type of bonding is expected to be less favoured than the former when bulky ligands such as PR_3 and AsR_3 are present.

alternately to produce a linear chain of Pt atoms only 325 pm apart. Interaction between these metal atoms shifts the d-d absorption of the $[\text{PtCl}_4]^{2-}$ ion from the green region (whence the normal red colour) towards the red, so producing the green colour.

Magnus's salt is an electrolyte and non-ionized polymerization isomers (p. 921) of the stoichiometry $\text{PtCl}_2(\text{NH}_3)_2$ are also known which can be prepared as monomeric *cis* and *trans* isomers:



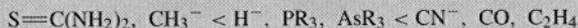
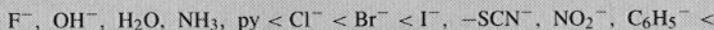
Their existence led Werner to infer a square-planar geometry for Pt^{II} .

Many substitution reactions are possible with these amines and were studied extensively in the 1920s by the Russian, I. I. Chernyaev (also transliterated from the Cyrillic as Tscherniaev, etc.). He noticed that when there are alternative positions at which an incoming ligand might effect a substitution; the position chosen depends not so much on the substituting or substituted ligand as on the nature of the ligand *trans* to that position. This became known as the “*trans*-effect” and has had a considerable influence on the synthetic coordination chemistry of Pt^{II} (see Panel).

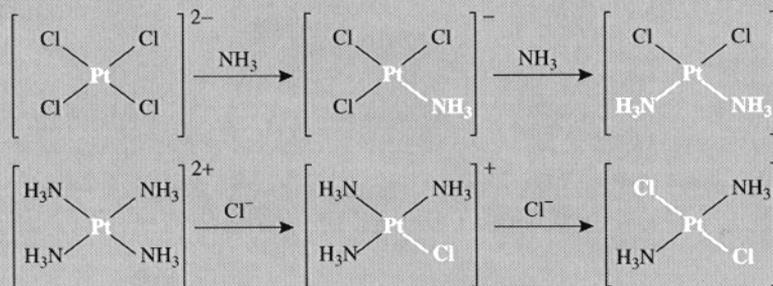
A resurgence of interest in these seemingly simple complexes of platinum started in 1969 when B. Rosenberg and co-workers discovered the anti-tumour activity of *cis*- $[\text{PtCl}_2(\text{NH}_3)_2]$

The Trans Effect⁽²⁰⁾

Because their rates of substitution are convenient for study, most work has been done with platinum complexes, and for these it is found that ligands can be arranged in a fairly consistent order indicating their relative abilities to labilize ligands *trans* to themselves:



The reason why the particular substitution reactions of $[\text{PtCl}_4]^{2-}$ and $[\text{Pt}(\text{NH}_3)_4]^{2+}$, mentioned above, produce respectively *cis* and *trans* isomers is now evident. It is because, in both cases, in the second of the stepwise substitutions there is a choice of positions for the substitution and in each case it is a ligand *trans* to a Cl^- which is replaced in preference to a ligand *trans* to an NH_3 :



Similar considerations have been invaluable in devising synthetic routes to numerous other isomeric complexes of Pt^{II} but, as can be seen in Fig. A, other considerations such as the relative stabilities of the different Pt-ligand bonds are also involved.

Panel continues

²⁰A. K. BABKOV, *Polyhedron* 7, 1203-6 (1988).

Explanations for the *trans*-effect abound and it seems that either π or σ effects, or both, are involved. The ligands exerting the strongest *trans*-effects are just those (e.g. C_2H_4 , CO, PR_3 , etc.) whose bonding to a metal is thought to have most π -acceptor character and which therefore remove most π -electron density from the metal. This reduces the electron density most at the coordination site directly opposite, i.e. *trans*, and it is there that nucleophilic attack is most likely. This interpretation is not directly concerned with stabilizing a particular ligand but rather with encouraging the attachment of a further ligand. It has consequently been applied most successfully to explaining kinetic phenomena such as reaction rates and the proportions of different isomers formed in a reaction (which depend on the rates of reaction), due to the stabilization of 5-coordinate reaction intermediates.

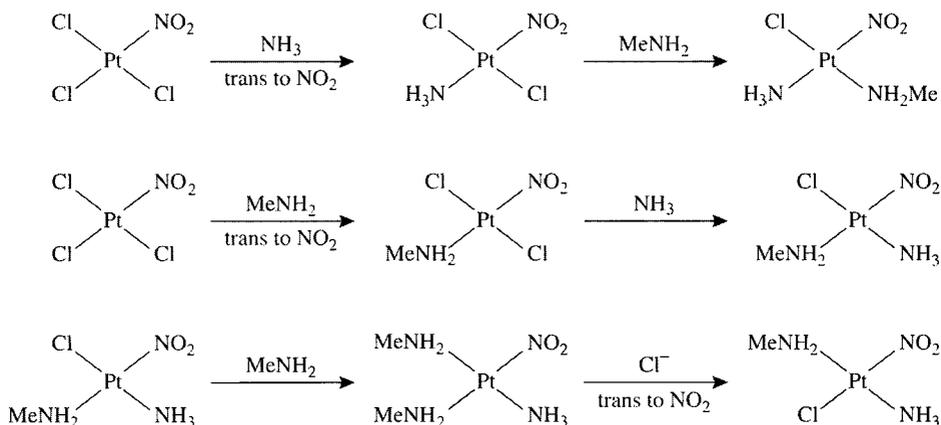


Figure A Preparation of the three isomers of $[PtCl(NH_3)(NH_2Me)(NO_2)]$. Where indicated these steps can be explained by the greater *trans*-effect of the NO_2^- ligand. Elsewhere the weakness of the Pt–Cl as compared to the Pt–N bond must be invoked.

On the other hand, a ligand which is a strong σ -donor is expected to produce an axial polarization of the metal, its lone-pair inducing a positive charge on the near side of the metal and a concomitant negative charge on the far side. This will weaken the attachment to the metal of the *trans* ligand. This interpretation has been most successfully used to explain thermodynamic, “ground state” properties such as the bond lengths and vibrational frequencies of the *trans* ligands and their nmr coupling constants with the metal.

In order to distinguish between kinetic and thermodynamic phenomena it is convenient to refer to the former as the “*trans*-effect” and the latter as the “*trans*-influence” or “static *trans*-effect”, though this nomenclature is by no means universally accepted. However, it appears that to account satisfactorily for the kinetic “*trans*-effect”, both π (kinetic) and σ (thermodynamic) effects must be invoked to greater or lesser extents. Thus, for ligands which are low in the *trans* series (e.g. halides), the order can be explained on the basis of a σ effect whereas for ligands which are high in the series the order is best interpreted on the basis of a π effect. Even so, the relatively high position of H^- , which can have no π -acceptor properties, seems to be a result of a σ mechanism or some other interaction.

(“cisplatin”). Binding of cisplatin to DNA appeared to be the central feature of the action and, since the *trans*-isomer is inactive, it was evident that chelation (or at least coordination to donor atoms in close proximity) is an essential part of the activity. Extensive studies, involving in particular proton nmr, suggested that Pt loses the Cl^- ligands and binds to N-7

atoms of a pair of guanine bases on adjacent strands of DNA.⁽²¹⁾ Recent X-ray work⁽²²⁾ on a 12-base-pair fragment of double stranded DNA

²¹ J. L. van der VEER and J. REEDIJK, *Chem. in Brit.* **20** 775–80 (1988).

²² P. M. TAKAHARA, A. C. ROSENZWEIG, C. A. FREDERICK and S. J. LIPPARD, *Nature* **377**, 649–52 (1995).

confirms that the binding of Pt distorts the local DNA structure therefore inhibiting the cell division inherent in the proliferation of cancer cells.

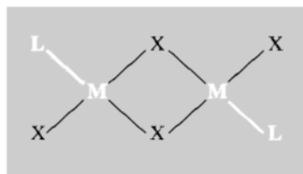
In order to avoid serious side effects of cisplatin (kidney- and neuro-toxicity) alternative Pt compounds have been developed. The most important of these is "carboplatin" in which the *cis*-chlorides are replaced by the *O*-chelate, cyclobutanedicarboxylate but all of them have ligands with NH groups which facilitate the hydrogen bonding thought to stabilize the distortions of the DNA structure.

Treatment of aqueous solutions of *cis*-[PtCl₂(NH₃)₂] with a variety of pyrimidines yields blue, oligomeric (Pt₄) compounds of the type known since the early 20th century as "platinum blues." They are mostly, mixed valence, paramagnetic compounds and although some have been characterized⁽²³⁾ others are less well-defined and include green and violet materials.

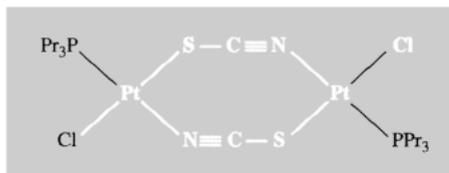
Stable complexes of Pd^{II} and Pt^{II} are formed with a variety of *S*-donor ligands which includes the inorganic sulfite (SO₃⁻) and thiosulfate (S₂O₃²⁻ apparently coordinating through 1 S and 1 O) but those with organo-sulfur ligands such as 1,2-dithiolenes are of more interest. The anions [M(mnt)₂]²⁻ (mnt = S₂C₂(CN)₂, M = Ni, Pd, Pt) have a facile redox chemistry yielding products with unusual electrical properties. Most salts of the square planar [M(mnt)₂]⁻ crystallize in stacks, in which the anions associate in pairs, and are semiconductors but the nonstoichiometric (H₃O)_{0.33}Li_{0.8}[Pt(mnt)₂]1.67H₂O is a linear conductor and Cs_{0.82}[Pd(mnt)₂]0.5H₂O shows metallic conductance when subject to high pressure.⁽²⁴⁾

The essentially class-b character of Pd^{II} and Pt^{II} is further indicated by the ready formation of complexes with phosphines and arsines. [M(PR₃)₂X₂] and the arsine analogues are

particularly well known. Zero dipole moments indicate that the palladium complexes are invariably *trans*, whereas those of platinum may be either *cis* or *trans* the latter being much the more soluble and having lower mps. When these bisphosphines and bisarsines are boiled in alcohol, or alternatively when they are fused with MX₂, the dimeric complexes [MLX₂]₂ are frequently obtained. Again, zero dipole moments (in some cases confirmed by X-ray analysis) indicate that these are all of the symmetrical *trans* form (a).



(a)



(b)

By involving SCN⁻ a novel 8-membered ring system has been produced (b).

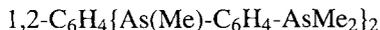
Nuclear magnetic resonance has proved to be a particularly useful tool in studying phosphines of platinum. The nuclear spins of ³¹P and ¹⁹⁵Pt (both equal to 1/2) couple, and the strength of this coupling (as measured by the "coupling constant" *J*) is affected much more by ligands *trans* to the phosphine than by those which are *cis*. This has helped in determinations of structure and also in studies of the "*trans* influence". Platinum(II) also forms a number of quite stable monohydrido (H⁻) phosphines which have proved similarly interesting, the ¹H-¹⁹⁵Pt coupling constants being likewise sensitive to the *trans* ligand.

It has already been pointed out that the overwhelming majority of complexes of Pd^{II} and Pt^{II} are square planar. However, 5-coordinate intermediates are almost certainly involved in many of the substitution reactions of these 4-coordinate complexes, and 5-coordinate trigonal

²³ see for instance, T. V. O'HALLORAN, P. K. MASCHARAK, I. D. WILLIAMS, M. M. ROBERTS and S. J. LIPPARD, *Inorg. Chem.* **26** 1261-70 (1987).

²⁴ M. B. HURSTHOUSE, R. L. SHORT, P. I. CLEMENSON and A. E. UNDERHILL, *J. Chem. Soc., Dalton Trans.*, 1101-4 (1989).

bipyramidal complexes with "tripod" ligands (p. 907) are well established. These ligands include the tetraarsine, $\text{As}(\text{C}_6\text{H}_4\text{-2-AsPh}_2)_3$ (qas, p. 1150), its phosphine analogue and also $\text{N}(\text{CH}_2\text{CH}_2\text{NMe}_2)_3$ i.e. (Me_6tren). The somewhat less-rigid tetraarsine,



(tpas), however forms a red, square-pyramidal complex $[\text{Pd}(\text{tpas})\text{Cl}]\text{ClO}_4$ with palladium.

Oxidation state I (d^9)

Although nickel(I) is thought to be involved in some nickel-containing enzymes, this oxidation state is best represented by yellow to red, tetrahedral phosphines such as $[\text{Ni}(\text{PPh}_3)_3\text{X}]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) which are paramagnetic, as expected for a d^9 configuration, and relatively stable. $[\text{Ni}(\text{PMe}_3)_4][\text{BPh}_4]$ has also been structurally characterized. A more recent⁽²⁵⁾ example is $\text{K}_3[\text{NiO}_2]$. This dark red, air- and water-sensitive compound, like the Fe^{I} (p. 1082 footnote) and Co^{I} (p. 1134) analogues, is prepared by heating K_6CdO_4 in a closed Ni cylinder at 500°C for 49 days when it reacts with the cylinder walls:

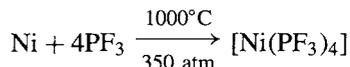


These anions are remarkable not only for the low coordination number but also for the low oxidation state of the metals in combination with oxygen which is more commonly to be found stabilizing *high* oxidation states.

Oxidation state 0 (d^{10})

Besides $[\text{Ni}(\text{CO})_4]$ and organometallic compounds discussed in the next section, nickel is found in the formally zero oxidation state with ligands such as CN^- and phosphines. Reduction of $\text{K}_2[\text{Ni}^{\text{II}}(\text{CN})_4]$ with potassium in liquid ammonia precipitates yellow $\text{K}_4[\text{Ni}^0(\text{CN})_4]$, which is sensitive to aerial oxidation. Being

isoelectronic with $[\text{Ni}(\text{CO})_4]$ it is presumed to be tetrahedral. Similarity with the carbonyl is still more marked in the case of the gaseous and tetrahedral $[\text{Ni}(\text{PF}_3)_4]$, which also can be prepared directly from the metal and ligand:



The pale yellow $[\text{Ni}(\text{PET}_3)_4]$ is also tetrahedral but with some distortion.⁽²⁶⁾ In sharp contrast to nickel, palladium forms no simple carbonyl, $\text{Pt}(\text{CO})_4$ is prepared only by matrix isolation at very low temperatures and reports of $\text{K}_4[\text{M}(\text{CN})_4]$ ($\text{M} = \text{Pd}, \text{Pt}$) may well refer to hydrido complexes; in any event they are very unstable. The chemistry of these two metals in the zero oxidation state is in fact essentially that of their phosphine and arsine complexes and was initiated by L. Malatesta and his school in the 1950s. Compounds of the type $[\text{M}(\text{PR}_3)_4]$, of which $[\text{Pt}(\text{PPh}_3)_4]$ has been most thoroughly studied, are in general yellow, air-stable solids or liquids obtained by reducing M^{II} complexes in H_2O or $\text{H}_2\text{O}/\text{EtOH}$ solutions with hydrazine or sodium borohydride. They are tetrahedral molecules whose most important property is their readiness to dissociate in solution to form 3-coordinate, planar $[\text{M}(\text{PR}_3)_3]$ and, in traces, probably also $[\text{M}(\text{PR}_3)_2]$ species. The latter are intermediates in an extensive range of addition reactions (many of which may properly be regarded as *oxidative* additions) giving such products as $[\text{Pt}^{\text{II}}(\text{PPh}_3)_2\text{L}_2]$, ($\text{L} = \text{O}, \text{CN}, \text{N}_3$) and $[\text{Pt}^{\text{II}}(\text{PPh}_3)_2\text{LL}']$, ($\text{L}, \text{L}' = \text{H}, \text{Cl}; \text{R}, \text{I}$) as well as $[\text{Pt}^0(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$ and $[\text{Pt}^0(\text{CO})_2(\text{PPh}_3)_2]$.

The mechanism by which this low oxidation state is stabilized for this triad has been the subject of some debate. That it is not straightforward is clear from the fact that, in contrast to nickel, palladium and platinum require the presence of phosphines for the formation of stable carbonyls. For most transition metals the π -acceptor properties of the ligand are thought to be of considerable importance and there is

²⁵ A. MÖLLER, M. A. HITCHMAN, E. KRAUSZ and R. HOPPE, *Inorg. Chem.* **34**, 2684–91 (1995).

²⁶ M. HURSTHOUSE, K. J. IZOD, M. MOTEVALLI and P. THORNTON, *Polyhedron* **13**, 151–3 (1994).

no reason to doubt that this is true for Ni⁰. For Pd⁰ and Pt⁰, however, it appears that σ -bonding ability is also important, and the smaller importance of π backbonding which this implies is in accord with the higher ionization energies of Pd and Pt [804 and 865 kJ mol⁻¹ respectively] compared with that for Ni [737 kJ mol⁻¹].

27.3.5 The biochemistry of nickel⁽²⁷⁾

Until the discovery in 1975 of nickel in jack bean urease (which, 50 years previously, had been the first enzyme to be isolated in crystalline form and was thought to be metal-free) no biological role for nickel was known. Ureases occur in a wide variety of bacteria and plants, catalyzing the hydrolysis of urea,



Results from an array of methods, including X-ray absorption, EXAFS, esr and magnetic circular dichroism, suggest that in all ureases the active sites are a pair of Ni^{II} atoms. In at least one urease,^(27a) these are 350 pm apart and are bridged by a carboxylate group. One nickel is attached to 2 N atoms with a fourth site probably used for binding to urea. The second nickel has a trigonal bipyramidal coordination sphere.

Three other Ni-containing enzymes found in bacteria have now been identified:

Hydrogenases, most of which also contain Fe and catalyse the reaction, $2\text{H}_2 + \text{O}_2 \longrightarrow 2\text{H}_2\text{O}$. The Ni has a coordination sphere of 5 or 6 mixed S-, N-, O-donors and is believed to undergo redox cycling between III, II and I oxidation states.

CO Dehydrogenase, also incorporating Fe and catalysing the oxidation of CO to CO₂. The attachment of CO to a nickel centre coordinated to perhaps four S-donors is postulated.

²⁷ A. F. KOLODZIEJ, *Prog. Inorg. Chem.* **41**, 493–597 (1994); J. R. LANCASTER (ed.), *The Bioinorganic Chemistry of Nickel*, VCH, Weinheim, 1988, 337 pp.; H. SIGEL (ed.), *Metal Ions in Biological Systems*, Vol. 23, *Nickel and its Role in Biology*, Dekker, New York, 1988, 488 pp.

^{27a} S. J. LIPPARD, *Science*, **268**, 996–7 (1995); E. JABRI, M. B. CARR, R. P. HAUSINGER and P. A. KARPLUS, *ibid.* pp. 998–1004.

Methyl-coenzyme M reductase participates in the conversion of CO₂ to CH₄ and contains 6-coordinate nickel(II) in a highly hydrogenated and highly flexible porphyrin system. This flexibility is believed to allow sufficient distortion of the octahedral ligand field to produce low-spin Ni^{II} (Fig. 27.7) which facilitates the formation of a Ni^I–CH₃ intermediate.

27.3.6 Organometallic compounds^(4,28)

All three of these metals have played major roles in the development of organometallic chemistry. The first compound containing an unsaturated hydrocarbon attached to a metal (and, indeed, the first organometallic compound if one excludes the cyanides) was [Pt(C₂H₄)Cl₂]₂, discovered by the Danish chemist W. C. Zeise as long ago as 1827 and followed 4 years later by the salt which bears his name, K[Pt(C₂H₄)Cl₃].H₂O. [Ni(CO)₄] was the first metal carbonyl to be prepared when L. Mond and his co-workers discovered it in 1888. The platinum methyls, prepared in 1907 by W. J. Pope, were amongst the first-known transition metal alkyls, and the discovery by W. Reppe in 1940 that Ni^{II} complexes catalyse the cyclic oligomerization of acetylenes produced a surge of interest which was reinforced by the discovery in 1960 of the π -allylic complexes of which those of Pd^{II} are by far the most numerous.

σ -Bonded compounds

These are of two main types: compounds of M^{IV}, which for platinum have been known since the beginning of this century and commonly involve the stable {PtMe₃} group; and compounds of the divalent metals, which were first studied by J. Chatt and co-workers in the late 1950's and are commonly of the type [MR₂L₂] (L = phosphine). In the Pt^{IV} compounds the metal is always octahedrally coordinated and this is frequently achieved in interesting ways. Thus the trimethyl halides, conveniently obtained

²⁸ G. WILKE, *Angew. Chem. Int. Edn. Engl.* **27**, 185–206 (1988).