

LIGAND FIELD INTERPRETATION OF SOME CASES OF PENTACOORDINATION

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The chemistry of pentacoordinated transition-metal complexes has only recently experienced its most important developments, and is still a rapidly evolving field. One might therefore argue that it is at present too early to attempt a ligand field interpretation, since our experimental knowledge of pentacoordinated complexes is still rather scattered and far from complete, and because the electronic structure of such chromophores depends in a particularly critical manner on their steric structure, which is known exactly in only a limited number of cases. Furthermore, it is not assured, *a priori*, that ligand field theory, which has until now been applied almost exclusively to cubic, quasi-cubic and tetragonal complexes, will also work with pentacoordinated ones. In the author's opinion it is however worthwhile to attempt such an approach, at least in order to ascertain whether it does or does not lead to acceptable results; in the former case, we shall be able to use ligand field theory for classifying molecular functions and molecular energy levels, and we shall possibly get assistance in monitoring further developments of the chemistry of pentacoordination. But also in the negative case, it should be instructive to observe to what point the ligand field model is still acceptable, and where and when it begins to fail. Of course, in the present situation one cannot expect any easy establishment of generally valid interpretative criteria; rather, we shall attempt here a survey of the present interpretative possibilities of the ligand field model for pentacoordinated complexes, including both positive and negative aspects.

As a matter of principle, a model of point charges or of any conventional crystal or ligand field model can be developed for fivefold coordination as well as for cubic symmetry, but in practice there are, with the pentacoordinated complexes, numerous additional difficulties inherent in both the systems to be studied and in the formalism and model to be applied.

To start with, we summarize the experimental material, namely the cases hitherto known of pentacoordination among transition elements, with particular regard to those which lend themselves better to a ligand field interpretation. So we shall disregard here *e.g.* carbonyls and other complexes with noninnocent ligands. It should be recalled that the following will be just a choice of the most significant examples, but by no means a complete list of pentacoordinated complexes; the

reader interested in a more ample information may refer to several recent compilations, *e.g.* to the excellent review by Mutterties and Schunn¹.

It also scarcely needs be mentioned that many older literature reports contain examples of apparent rather than true pentacoordination. Confining ourselves to the most representative cases of authentic pentacoordination, we find some cases known for a long time in the literature (see Fig. 1), such as (i) vanadyl complexes (typical example VOacac₂; however, octahedral coordination is often achieved by addition of a sixth molecule of a base²); (ii) 1:1 adducts of square

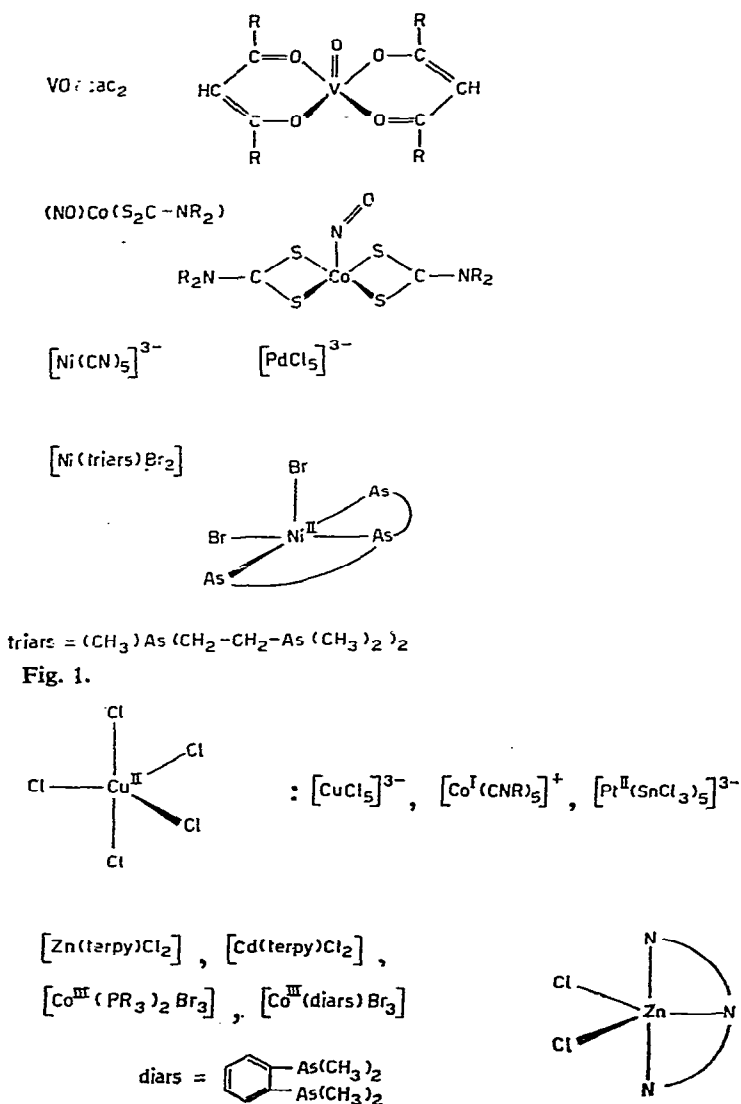


Fig. 2.

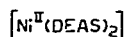
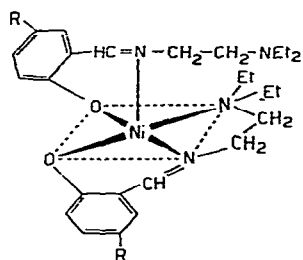
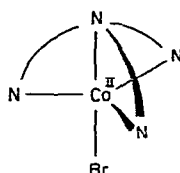
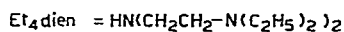
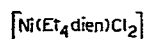
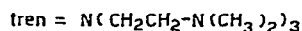
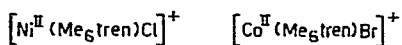
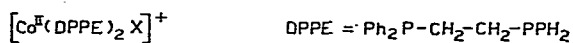
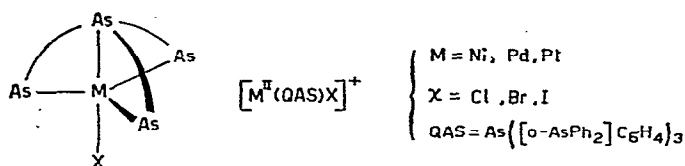


Fig. 3.

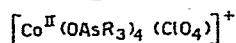
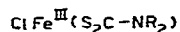
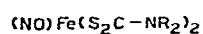
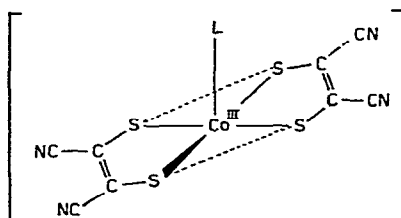
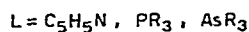
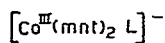
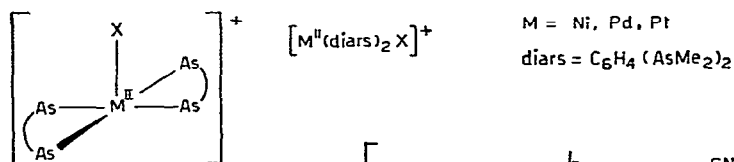


Fig. 4.

planar d^8 systems such as $[\text{PdCl}_5]^{3-}$ ³, $[\text{Ni}(\text{CN})_5]^{3-}$ ⁴, $[\text{Ni triars Br}_2]^{5-}$, etc.; (iii) NO adducts, *e.g.* of Co^{II} diethyldithiocarbamate⁶. Then, in the last few years there has been an enormous increase in the number and type of pentacoordinated species which have been prepared; these include, some ML_5 species and other simple trigonal-bipyramidal structures (Fig. 2), complexes of tetradentate polyarsines, polyphosphines and similar ligands, first introduced by Venanzi⁷, complexes of polydentate polyamines and of quadridentate bis-Schiff bases, as extensively investigated by Sacconi⁸ (Fig. 3), adducts of square planar d^8 complexes, mainly containing soft ligand atoms and/or bi- or tridentate ligands⁹⁻¹¹, and further square pyramidal structures of the Co-NO-dithiocarbamate type, such as $\text{Fe}(\text{NO})\text{dtc}_2$ ¹², $\text{Ru}(\text{NO})\text{dtc}_2$ ¹³ and $\text{FeCl}(\text{dte})_2$ ¹⁴.

Regarding the wide variety of stereochemical arrangements occurring among pentacoordinated complexes, we shall distinguish the following cases:

1) Regular trigonal bipyramids, as for example gaseous PF_5 ¹⁵, $\text{Fe}(\text{CO})_5$ ¹⁶ and $[\text{Co}^{\text{I}}(\text{CNR})_5]^{+}$ ¹⁷, probably only occur among transition metal complexes with the central metal in a normal (*i.e.* not particularly low) oxidation state, *e.g.* $[\text{CuCl}_5]^{3-}$ ¹⁸, $[\text{Pt}(\text{SnCl}_3)_5]^{3-}$ ¹⁹ and $[\text{Ni}(\text{CN})_5]^{3-}$ ²⁰.

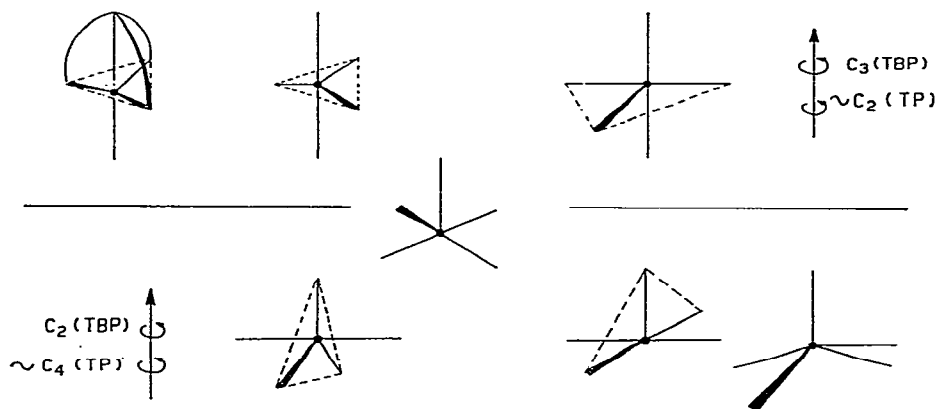


Fig. 5. Relation between pentacoordinated geometries, viewed along different axes.

2) Slightly distorted trigonal bipyramids are represented typically by $[\text{M}^{\text{II}}(\text{QAS})\text{X}]^{+}$ ⁷ (QAS = tris-(*o*-diphenylarsinophenyl)arsine); in these cases a model of regular bipyramidal shape may still be a reasonable approximation to the actual structure; actually the bond angles are often close to the regular values, and there is true threefold symmetry, but the central metal atom may be often a little out of the equatorial plane, and the soft ligands (As or P) are usually very different from X both in bond distances and in π -bond ability.

3) Highly distorted trigonal bipyramids, which can be viewed also as highly distorted square pyramids, often occur among Schiff base complexes^{7,21-23}. They are close to the most general case of pentacoordination discussed by Zemmann²⁴ and having only C_{2v} symmetry.

4) "Regular" square pyramidal arrangements should be unstable for several reasons, and have actually never been observed with certainty (for "regular" we mean here a square pyramid with the central metal atom lying in the basal square). Probably the closest cases are the 1:1 adducts of stable square planar d^8 systems, where the apical ligand exerts only a small perturbation upon the practically unchanged planar quadrat unit *e.g.* $[\text{Pt}(\text{diars})_2\text{X}]^{+9}$.

5) Distorted square pyramidal structures with the central metal out of the basal plane and inside the pyramid are on the contrary rather common. Examples include VOacac_2^2 , $\text{Co}(\text{NO})\text{dte}_2^6$, $\text{Ru}(\text{NO})\text{dte}_2^{13}$, $\text{FeCl}(\text{dte})_2^{14}$, $\text{Zn}(\text{salen})_2(\text{H}_2\text{O})^{25}$ ($\text{salen} = \text{N-}\beta\text{-diethylaminoethylsalicylaldimine}$), etc.

In nearly all these square pyramidal examples it should be noted that the apical ligand is of a very different chemical nature from the other four ligands, either because it forms particularly strong π -bonds, or because it is completely foreign to an efficient π -conjugated system established among the basal ligands. There may be of course exceptions to this general trend, one of them being the square pyramidal form of $[\text{Ni}(\text{CN})_5]^{3-20}$.

The problem of the relative stability of the different geometrical forms of pentacoordination has been treated by Zemmann²⁴ for five equal ligands ML_5 on the basis of charge repulsion alone. Zemmann's results show that the trigonal bipyramid is more stable by a small amount than a square pyramid with a bond angle $\widehat{\text{LML}}$ of about 104° ; a "regular" square pyramid should be much less stable.

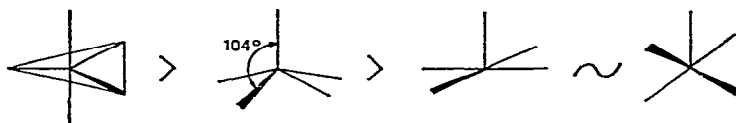


Fig. 6. Order of stability of pentacoordinated structures ML_5 according to Zemmann²⁴.

The consideration of the electrostatic model by Zemmann is only useful in showing that a square pyramidal arrangement is likely to be distorted, and that the differences between the two more probable structures are small, so that the actual structure taken by a complex may be largely influenced, if not completely determined, by minor factors, *e.g.* by loose electrostatic interactions (as in adducts of d^8), or by packing effects in the lattice (as in $[\text{CuCl}_5]^{3-18}$ or in $\text{RuCl}_2 \cdot 3\text{P}(\text{C}_6\text{H}_5)_3^{26}$), or by the conformation of polydentate ligands (QAS⁷, salen^{25} , Schiff bases⁷, polyamines⁷). Further reasons of nonapplicability of Zemmann's treatment lie in the fact that the four basal ligands in square pyramidal complexes are often very different from the apical one, and in the fact that crystal field stabilisation energy (CFSE) may act in the opposite direction and tend to stabilize square pyramids with respect to trigonal bipyramids²⁷; even if the order of magnitude of the CFSE is smaller than that of the electrostatic bond energies considered by Zemmann, the effect may become determining in cases where there is delicate balance in the

formation energies. We can probably still use, with some confidence, Zemann's model to speculate about the extent of the out-of-plane deformation: we expect that it is of the same sign as in Zemann's model (with non-transition elements, the central atom is out of the basal plane *outwards*, e.g. BrF_5) but smaller than predicted by Zemann, especially if the apical ligand is loosely bonded and if there is an extensive network of π -conjugation in the basal square, requiring good planarity. Also if the apical ligand is highly electronegative (e.g. a halogen), the corresponding σ -bonding electron pair is expected to repel only weakly the basal σ -electron pairs. The out-of-plane distortion may possibly be larger when the apical bond is particularly strong and of high bond order (vanadyl complexes, NO adducts etc.). This matter is related to the Gillespie-Nyholm theory which considers the possibility that even in quadratic complexes the central atom might be above the plane of the ligands owing to repulsion of non-bonding electron pairs, but we shall not discuss this point here.

On examining the experimental situation as sketched above, we identify the following difficulties expected in the application of the ligand field model to penta-coordinated complexes.

DIFFICULTIES INHERENT IN THE COMPLEXES

1) A trivial, but often important practical difficulty is the uncertainty as to the real coordination number particularly in solution; apparently 5-coordinated species may easily achieve 6-coordination by addition of one solvent molecule (e.g. VOacac_2^{2-} , complexes of polyamines²⁸).

2) Indirect evidence is often insufficient to establish the true steric structure, unlike the situation with cubic geometry where conductance, infrared or magnetic data are usually highly diagnostic of stereochemistry.

3) X-ray data are still generally lacking.

4) As noted above, the geometry is often irregular; this fact limits the validity of the predictions based on simple regular models, and makes X-ray data more vitally needed.

5) The actual geometry is more frequently imposed by the conformation of the ligands than required freely by the balance of attractive and repulsive interactions between the central metal and the donor atoms alone (QAS, salen, etc.). Any point-charge or similarly simple model can therefore not pretend to predict the stability of the pentacoordinate arrangements, nor infer reliable values of the thermodynamic quantities. By sorting out the enthalpy from the entropy factor in the free energy of formation, rather encouraging results were obtained by Paoletti and Ciampolini²⁹, who achieved the usual monotonous dependence of formation enthalpies on the atomic number, by applying CFSE corrections to measured enthalpies of formation of pentacoordinated complexes; they also explained the

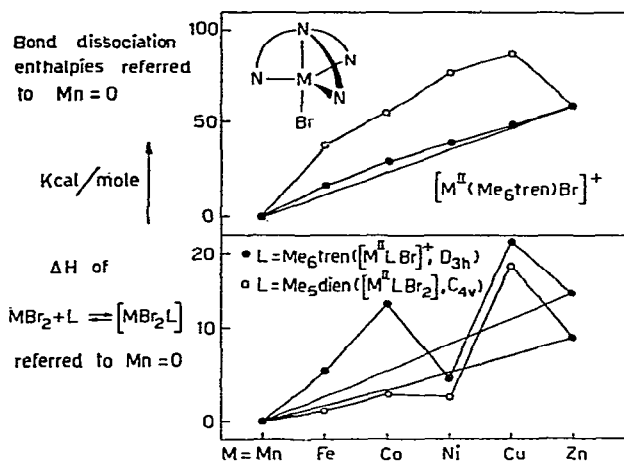


Fig. 7. Thermochemistry of pentacoordinated complexes. (Adapted from P. PAOLETTI AND M. CIAMPOLINI, *Inorg. Chem.*, 6 (1967) 65.)

relative stabilities of different transition metals in both trigonal bipyramidal complexes like $[M(\text{me}_6\text{tren})\text{Br}]^+$ ($\text{me}_6\text{tren} = \text{N}(\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2)_3$) and distorted square pyramidal complexes like $[M(\text{me}_5\text{dien})\text{Br}_2]$ ($\text{me}_5\text{dien} = \text{CH}_3\text{-N}(\text{CH}_2\text{CH}_2\text{-N}(\text{CH}_3)_2)_2$). The results by Paoletti and Ciampolini²⁹ also allow a rationalization of the trends of the heats of conversion of pentacoordinated into octahedral complexes on the ground of the CFSE differences alone: *e.g.* Cu is more stable when pentacoordinated, Ni is more stable when octahedral, Co is relatively more stable in a high-spin configuration when trigonal-bipyramidal rather than square pyramidal, owing to the smaller one-electron promotion energy from the corresponding low-spin configurations. These studies show that it is still possible to exploit the interpretive possibilities of the ligand field model with regard to stability and formation energies, as is more usual and well established for cubic symmetries, even in complexes of other symmetries where predetermined steric constraints are predominant.

DIFFICULTIES INHERENT IN THE MODEL

While the effect of the ligand field on the electronic structure of the partly filled shell in cubic complexes is described by one parameter only (Δ or G_4 or $\langle r^4 \rangle$), five-coordinated structures clearly require at least two parameters (G_2 and G_4 , or $\langle r^2 \rangle$ and $\langle r^4 \rangle$), and we meet here the same difficulties encountered in the interpretation of square planar complexes, where some authors simply claim complete breakdown of the point-charge model³⁰. Even when the actual symmetry of the pseudooctahedral or pseudotetrahedral complexes is very low (*e.g.* MA_5B ,

MA_2BC , etc.), the largest part of the Hamiltonian is still essentially cubic, and the main features of the electronic structure can be confidently related to a parent cubic structure; on the contrary, in truly five-coordinated complexes we cannot rely upon any such parent structure model of higher symmetry, so that even the validity of the qualitative classification of molecular states might be reduced. On the other hand, a first and often reliable preliminary hint as to the relative ordering of levels can be gained through point-charge or similarly simple calculations, so we shall first discuss this type of prediction. Such calculations will be of value also as a test of the practical applicability of the more naive models, and as a more useful indication of where and how the breakdown of the electrostatic model takes place. Rationalization of the experimental facts may be expected to be less accurate than for cubic complexes, we may however anticipate that such predictions might come out more satisfactory with five-coordinated complexes than for the apparently simpler case of planar quadratic complexes. Furthermore the formalism of the calculations of electrostatic type can be still used, but the corresponding results made more valid, if we resort to the "angular overlap" theory³¹, which has proved very promising, at last in the field of trigonal-bipyramidal complexes³².

We now pass to a consideration of some specific cases of pentacoordination.

TRIGONAL BIPYRAMIDS

The one-electron splitting scheme is shown in Figure 8. From the technical viewpoint of crystal-field calculations, the same scheme would be produced by an axial $D_{\infty h}$ field; the nondiagonal crystal field matrix element $\langle 2 | V | -1 \rangle$ connects only different γ_i ($e' \neq e''$), so the trigonal potential is not essential in determining the splitting patterns unless the structure of the pentacoordinated arrangement becomes less regular (*e.g.* symmetry C_{3v} as in MA_4B).

Point charge models yield ratios Δ_2/Δ_1 which depend on the ratio G_2/G_4 , but are close to 2. Covalent considerations lead approximately to the same result. The orbital d_{z^2} is strongly σ -antibonding with respect to all 5 ligands, the pair

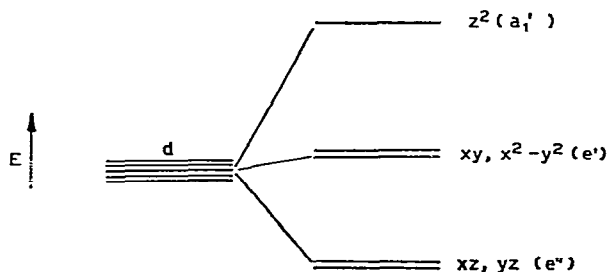


Fig. 8. One-electron splitting scheme for trigonal bipyramidal coordination (D_{3h}).

$$\Delta^2 = E(a_1') - E(e'); \Delta_1 = E(e') - E(e'')$$

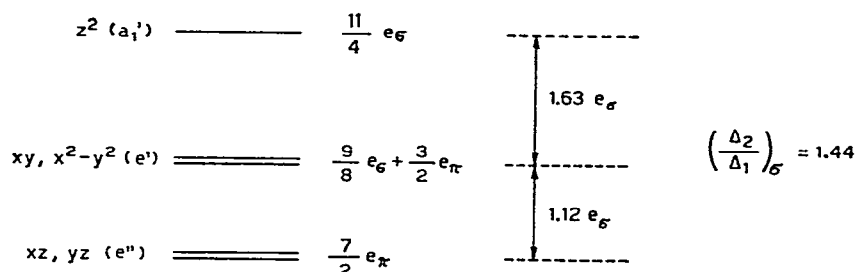


Fig. 9. The angular overlap model for trigonal-bipyramidal coordination.

d_{xy} , d_{xz-yz} is also σ -antibonding, but with less efficient overlap (possibly p_x , p_y are better bond orbitals for the same γ_i), and d_{xz} , d_{yz} are only π -antibonding. The angular overlap coefficients are given in Figure 9.

The relative order of the levels in Figures 8 and 9 is now firmly established experimentally; only the ratio Δ_2/Δ_1 is not quantitatively fixed. The ratio varies and is generally found to be larger than theoretically predicted. The angular overlap model is perhaps more realistic; though it gives a poor Δ_2/Δ_1 ratio on the basis of the σ terms alone (1.44 instead of ≥ 2), it permits much larger Δ_2/Δ_1 values with increasing π -antibonding effects.

An experimental test of the system of energy levels in Figs. 8 and 9 is based on the absorption spectra of systems with one d electron or one d-hole, or one electron (or hole) in a half-filled configuration, i.e. in d^1 , d^9 , high-spin d^4 and high-spin d^6 , and indirectly in low-spin d^6 , d^7 and d^8 which are interpreted in the strong-field limiting scheme. Figure 10 shows a case of trigonal bipyramidal Fe^{II}

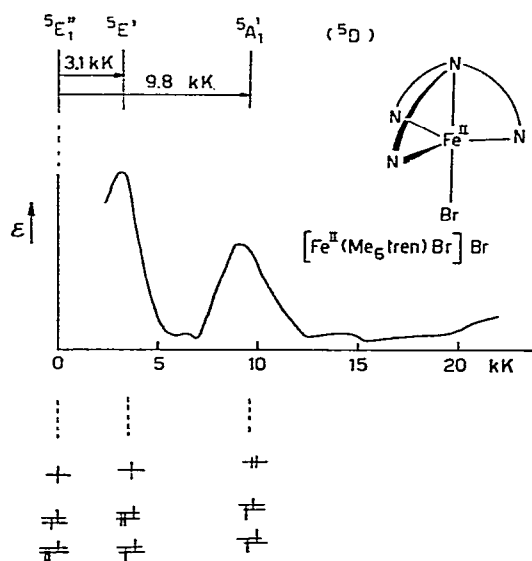


Fig. 10. From M. CIAMPOLINI AND N. NARDI, *Inorg. Chem.*, 5 (1966) 1150.

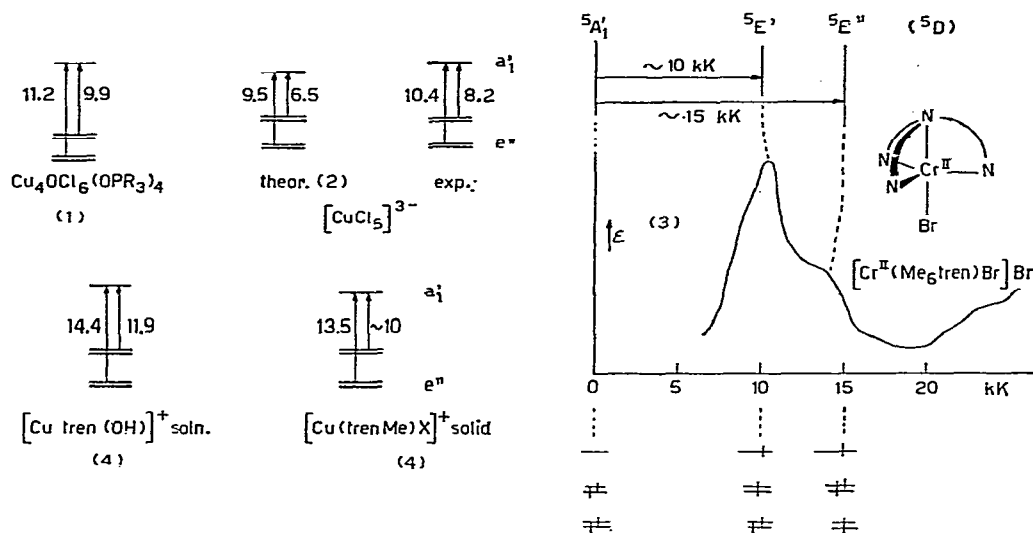


Fig. 11. (1) J. A. BERTRAND, *Inorg. Chem.*, 6 (1967) 495. (2) W. E. HATFIELD AND T. S. PIPER, *Inorg. Chem.*, 3 (1964) 841. (3) M. CIAMPOLINI, *Chem. Comm.*, (1966) 47. (4) M. CIAMPOLINI AND N. NARDI, *Inorg. Chem.*, 5 (1966) 41.

(high-spin d^6 , one electron outside a half-filled configuration)³³, and Figure 11 contains a schematic description of some cases of trigonal bipyramidal coordination having one electron short of the half-filled configuration (d^4 : high-spin Cr^{II} in $[\text{Cr}(\text{me}_6\text{tren})\text{Br}]\text{Br}$ ³⁴ or of the filled configuration (d^9 in Cu^{II}), the most thoroughly investigated example being $[\text{CuCl}_5]^{3-}$ ^{18,35,36-39}. In all these cases there is generally good agreement with theory, as in any weak-field case when the ligand perturbation is small; Δ_2/Δ_1 is often, however, much larger than would be theoretically predicted by simple point-charge models.

Next we consider low-spin d^8 complexes (Figure 12); such complexes usually contain a tetradentate ligand L with soft donor atoms (S, P or As) besides an apical halide ligand $[\text{MLX}]^+$; typical examples of such polydentate ligands, whose conformation is essential in determining the occurrence of coordination number 5, include QAS = $\text{As}(\text{o}-(\text{C}_6\text{H}_5)_2\text{As}-\text{C}_6\text{H}_4)_3$ ⁷, TSP = $\text{P}(\text{o}-(\text{CH}_3\text{S}-\text{C}_6\text{H}_4)_3)$ ⁴⁰, TAP = $\text{P}(\text{CH}_2\text{CH}_2\text{As}(\text{CH}_3)_2)_3$ ⁴¹, and TPN = $\text{N}(\text{CH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2)_3$ ⁴² (the presence of one nitrogen is possible, but a majority of soft atoms among the donors is required in order to stabilize low-spin behaviour). In this class of compounds, the Ni^{II} complexes have a very typical visible spectrum with an intense band in the region 14–18 kK, followed by a less intense band at higher frequency (see Fig. 12); such a spectrum can be interpreted in the one-electron scheme of Fig. 8 or 9, even if we neglect, to a first approximation, interelectronic repulsion (see Fig. 12). The progressive splitting of the lower-frequency band on passing from Ni^{II} to Pd^{II} and to Pt^{II} can be easily related to a symmetry descent ($\rightarrow C_{2v}$) caused by the larger size of the central metal. That the one-electron scheme is valid, is

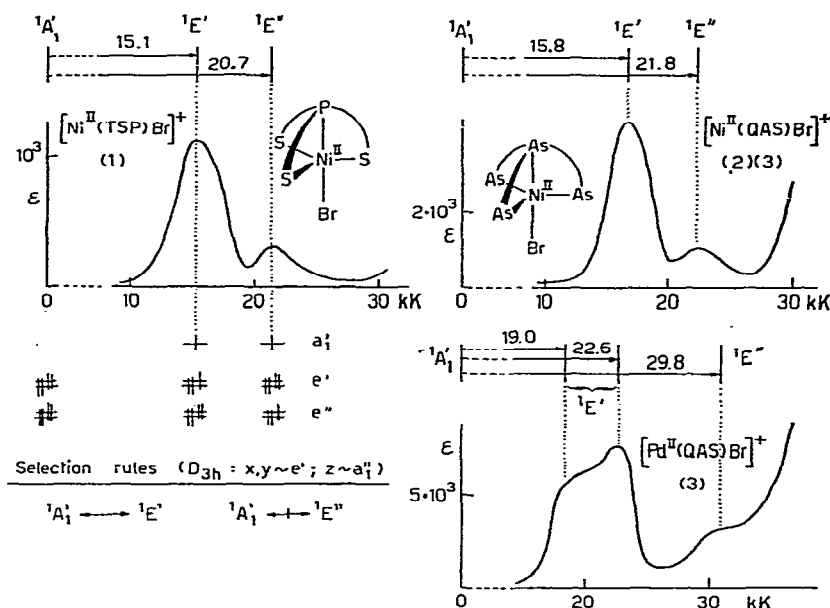


Fig. 12. (1) G. DYER AND D. W. MEEK, *Inorg. Chem.*, 4 (1965) 1938. (2) G. DYER AND L. M. VENANZI, *J. Chem. Soc.*, (1965) 2771. (3) L. M. VENANZI *et al.*, *J. Chem. Soc.*, A, (1967) 540.

shown by the validity of selection rules based upon it; the low-energy transition $(e'')^4 (e')^4 \rightarrow (e'')^4 (e')^3 (a'_1)^1$, *i.e.* ${}^1\text{A}'_1 \rightarrow {}^1\text{E}'$, is dipole-allowed in D_{3h} , and therefore intense; the high energy transition $(e'')^4 (e')^4 \rightarrow (e'')^3 (e')^4 (a')^1$, *i.e.* ${}^1\text{A}'_1 \rightarrow {}^1\text{E}''$ is forbidden, hence the band is less intense. The general one-electron scheme of Fig. 8 still proves useful with d^6 and d^7 low-spin systems such as $[\text{Fe}^{\text{II}}(\text{QAS})\text{X}]^+$ and $[\text{Co}^{\text{II}}(\text{QAS})\text{X}]^+$, whose spectra are far more complicated than those of d^8 , but can nevertheless be assigned in a straightforward manner⁷ (see Fig. 13); in

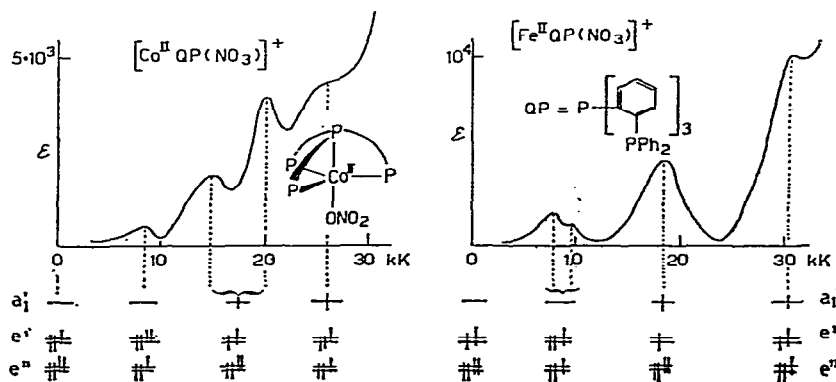


Fig. 13. From M. J. NORGETT, J. H. M. THORNLEY AND L. M. VENANZI, *J. Chem. Soc.*, A, (1967) 540.

passing we note that this energy level sequence can easily explain why Fe^{II} compounds have the unusual spin moment of $S = 1$ (cubic symmetries allow only $S = 0$ or $S = 2$), as is evident from the groundstate occupancy of levels depicted schematically in Figure 13.

In some other many-electron configurations, the one-electron scheme alone is insufficient to allow a complete rationalization of the observed electronic spectra. So *e.g.* for high-spin d^7 and d^8 complexes having trigonal-bipyramidal structure, inclusion of interelectronic repulsion appears to be necessary, and is more appropriately accomplished in the weak-field scheme. Ciampolini⁴³ performed such calculations, and obtained good agreement with the experimental spectral data for some complexes of Ni^{II} and Co^{II} with tetraamines or with Schiff bases (see Fig. 14

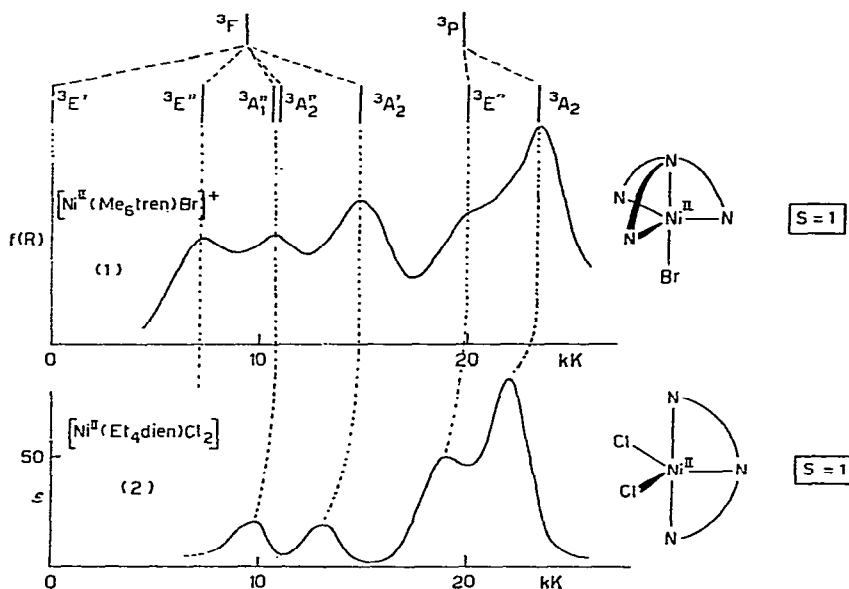


Fig. 14. (1) From M. CIAMPOLINI AND N. NARDI, *Inorg. Chem.*, 6 (1967) 445.

(2) From Z. DORI AND M. B. GRAY, *J. Am. Chem. Soc.*, 88 (1966) 1394.

$\text{Me}_6\text{tren} = \text{N}\{-\text{CH}_2-\text{CH}_2-\text{N}(\text{CH}_3)_2\}_3$ $\text{Et}_4\text{dien} = \text{HN}\{-\text{CH}_2-\text{CH}_2-\text{N}(\text{C}_2\text{H}_5)_2\}_2$.

and 15). The ligands involved contain only O or N as the donor atoms, *i.e.* only hard-type donors; the spectra measured by Dori and Gray⁴⁴ on similar complexes containing a tri- instead of a tetraamine, can be satisfactorily assigned using Ciampolini's treatment (Fig. 14).

As a general comment on the ligand-field interpretation of the electronic structure of complexes whose coordination type is classified as trigonal-bipyramidal, it should be borne in mind that their actual geometry is never regularly trigonal bipyramidal, while the theoretical models employed are exactly D_{3h} . One cannot attach therefore too much significance to details, nor expect too close

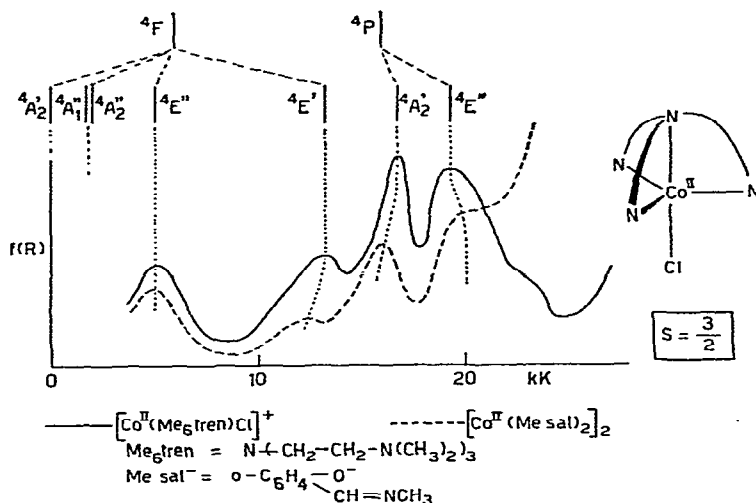


Fig. 15. Adapted from M. CIAMPOLINI AND N. NARDI, *Inorg. Chem.*, 5 (1966) 41 and 6 (1967) 445.

quantitative agreement between theory and experiment. Even if the true geometry would be known, insertion of lower-symmetric potential components makes the agreement worse rather than better, probably because of inherent inadequacy in the choice of the ligand field parameters of the non-cubic effects G_2 and G_4 . Ciampolini³³ performed some ligand-field calculations on models of trigonal bipyramids including some types of distortions; however, shifting the central metal out of the equatorial plane, or weakening one of the apical ligands results in lower

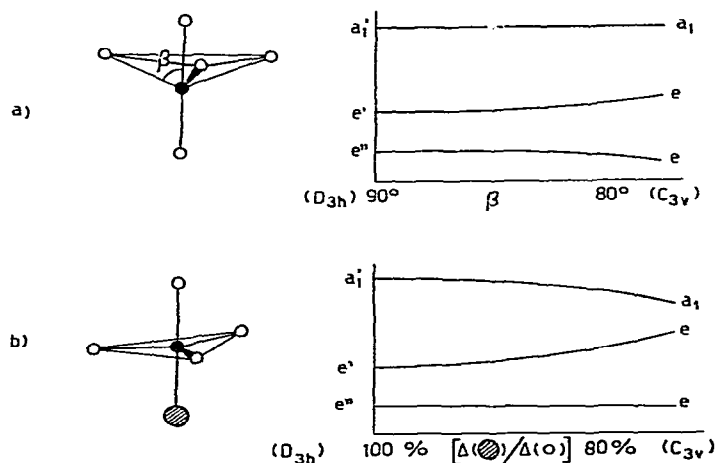


Fig. 16. Predicted effects of distortions on the trigonal-bipyramidal energy levels. From M. CIAMPOLINI AND N. NARDI, *Inorg. Chem.*, 5 (1966) 1150.

Δ_2 and higher Δ_1 , hence a smaller (Δ_2/Δ_1) ratio. This is no improvement, since the regular trigonal bipyramidal models already yield too low a (Δ_2/Δ_1) ratio. Therefore, the ligand field model cannot be embellished by insertion of lower-symmetry effects, which are so widely exploited in cubic complexes; nevertheless, this situation shows even more clearly the validity of the central concept and of the basic splitting scheme of Figs. 8 and 9. It is astonishing, that so many spectral features can be interpreted on the ground of the one-electron scheme alone. This situation leads to characteristic absorption patterns which sometimes may be used as diagnostic of structure (*e.g.* low-spin d^8 , see Fig. 12, and high-spin d^8 , see Fig. 14); however in some other cases the difference in spectral pattern from cubic symmetry (by chance perhaps) is less evident (*e.g.* high-spin Fe^{II} and Cu^{II} , figures 10 and 11), and cannot therefore be used for the diagnosis of structure. The ligand-field interpretation of trigonal bipyramidal structures also calls to our attention the interconnected roles of π -bonding and the nephelauxetic effect. We notice that high-spin behaviour can be associated with ligands of high field strength (*e.g.* N), provided there is little or no π -bonding (back-donation), or only a small nephelauxetic effect. On the other hand, low-spin behaviour can also occur with weak ligands provided there is extensive π -bonding and nephelauxetic delocalization. It is therefore very clear that high-spin or low-spin behaviour is not only a matter of ligand field strength, but rather a balance of ligand field strength with the magnitude of the interelectronic repulsion integrals; the latter factor is perhaps even more important to us, since it is directly related to a chemical fact, namely the extent of π -backbonding. This state of affairs is known of course in octahedral complexes, but it finds more striking evidence among trigonal-bipyramidal (and also square-planar) complexes.

SQUARE PYRAMIDS

Before going into details of the ligand-field interpretation of the system of energy levels, it will be useful to review briefly the conditions for occurrence of square pyramidal coordination.

In a pentacoordinated complex we expect, as a general tendency, the trigonal bipyramidal structure to be favored with respect to the square pyramidal structure whenever:

- (i) the five ligands are equivalent or nearly so;
- (ii) the ligands are mono- or oligodentate with no particular steric constraints (or, alternatively, with steric constraints favorable to a trigonal-bipyramidal arrangement);
- (iii) the coordination forces are mainly electrostatic or σ -covalent;
- (iv) non-innocent ligands are bonded to a central atom in a particularly low oxidation state.

On the other hand, a square pyramidal structure can possibly be stabilized if one or more of the following three requirements are met:

- (i) peculiar conformation of the ligands, demanding square pyramidal arrangement;
- (ii) looseness, or weaker character of the fifth bond to be formed by 1:1 addition to a square planar moiety;
- (iii) loss of π -bond order if the 1:1 addition to a square planar moiety acquires a configuration other than square pyramidal.

The first point is trivial, and is exemplified by Sacconi's $\text{Ni}(\text{salen})_2$ ⁴⁵. Referring to the second point, we note that pentacoordination often results from the addition of a fifth (apical) ligand to a quadratic system, the fifth ligand being more loosely bonded (often only electrostatically). In fact, 5-coordinate complexes of this type may frequently be prepared from d^8 complexes of charge 2+, e.g. $[\text{Pd}^{\text{II}}(\text{diars})_2]^{2+}$ ⁹⁻¹¹, where the charge on the metal is made more positive by π -backdonation. The formation of a 5-coordinate complex can be regarded in these cases as only a small perturbation upon the square planar coordination, and the factors responsible for stability of the square planar environment are grossly maintained.

With regard to the third point (π -effects), we notice that square planar complexes represent perhaps the best condition for efficient π -backbonding in the d-shell; of the five d-orbitals, (x^2-y^2) is only σ^* , (z^2) is neither σ nor π (or only weakly σ^*), while three orbitals (xy , xz , yz) are available for π -bonding over a total of eight possible π -bonds with no possibility of being replaced by s or p orbitals, since the latter belong to different irreducible representations: this situation might be called "full π -function". Ligands can accept $\pi(d)$ electrons in their vacant π^* orbitals both *perpendicular* to the coordination plane (conjugated ligand π^* with d_{xz} and d_{yz} orbitals, if z is the C_4 axis), and *in* the coordination plane (ligand d_{xy}).

In a "regular" square pyramid, the π situation is equally good (d_{z^2} becomes more fully σ^* , but d_{xy} , d_{xz} and d_{yz} remain fully π for both in-plane and out-of-plane bond). However, a distorted pyramid (central atom out of plane) is in a worse situation because (i) the empty $d_{x^2-y^2}$ orbital becomes partly π , so the π -function is not fully exploited since (at least for d^n with $n \leq 8$) this orbital is empty. (ii) d_{xz} and d_{yz} become partly σ^* , so the number of filled orbitals available for π -bonding becomes smaller than 3. Consideration of π -bonding tends therefore to stabilize a "regular" square pyramid, while an electrostatic model (Zemann)²⁴ favours the distorted pyramid, with $\widehat{\text{XMY}} \simeq 104^\circ$.

The situation is different if the central metal has an effectively low oxidation number, such as in $\text{Fe}(\text{CO})_5$ or $[\text{Co}^{\text{I}}(\text{CNR})_5]^+$, since then the $4p_x$, $4p_y$ orbitals are practically as low in energy as $3d_{xy}$ and $3d_{x^2-y^2}$, with the consequence that σ bonds are then predominantly p orbital in character and the d_{xy} and $d_{y^2-z^2}$ orbitals remain more available for π -bonding. Our argument (ii) applies actually only to cases where M has a decisively positive effective charge, so that $E(4p) \gg E(3d)$ and $\sigma^ \sim 3d$.

Compared with a square pyramid, the total possibility of π bond formation in a trigonal bipyramid as expressed by the angular overlap parameters e_{π} is unchanged ($= 10 e_{\pi}$), but is in practice far less effective because:

(i) only d_{xz} and d_{yz} are purely π functions in a trigonal bipyramid (and even less so, if the trigonal bipyramid is distorted with the central atom out of the equatorial plane, as is often the case), while d_{xy} and $d_{x^2-y^2}$ are in part σ and in part π , so one should expect their contribution to the π electron population in the partly filled shell to be small:

(ii) in the case of ligands with d orbital π -acceptor character, both the d_{xz} and d_{xy} orbitals of the *apical* ligand atoms are able to accept π electrons from M (x is the bond direction M-L, y is *in* the chelating plane, if any, but perpendicular to L-M), while the equatorial ligands of the trigonal bipyramids can still accept π electrons from the d_{xz} or d_{yz} orbitals of the metal into their d_{xy} orbital but their d_{xz} orbital could only accept from the d_{xy} and $d_{x^2-y^2}$ orbitals of the metal which are already strongly engaged in σ^* -antibonding; this reduces the extent of π -backdonation and thus weakens one of the main reasons for transformation of 4- into 5-coordination*.

The latter effect is particularly important with chelating ligands having a system of organic-type π -orbitals, which are therefore only perpendicular to the chelation plane; in such an event, the equatorial ligands *cannot* π bond with the central metal, except through the almost ineffective metal d_{xy} and $d_{x^2-y^2}$ orbitals; this situation will practically destroy π -back-donation in half of the chelate donors. In this case, and more generally for any chelating ligands, no two-end conjugation can occur in the system of π^* orbitals perpendicular to the chelation plane (in-plane π -conjugation with M is possible, but it does not occur *within* the ligand), thereby lowering the efficiency of chelation. Finally, interligand conjugation (which is important in *mnt* and similar complexes^{46,47} is only made possible by coplanarity of the ligands; it is therefore preserved in regular square pyramids, is less efficient in distorted (out-of-plane) square pyramids, and is completely destroyed in trigonal bipyramids. Figure 17 summarizes the π -bonding situation in penta-coordinated chelates of the $M(AA)_2B$ type in both geometrical arrangements.

As a result of the above discussion of the factors which may stabilize square pyramidal coordination, we should also expect (particularly as a consequence of points (ii) and (iii), p. 151) the favored square pyramidal arrangement to be "regular" rather than to have an out-of-plane distortion of the central atom; this is in contrast with the predictions of more naive models which consider only electrostatic packing forces²⁴ or CFSE's in a point charge model²⁷.

Once a square pyramidal coordination, has been established, the electronic

* The relative ordering of the d_{xz} , d_{xy} and d_{yz} , d_{xz} , d_{yz} orbitals in strongly tetragonal complexes is still subject to considerable controversy⁴⁸⁻⁵¹ and might, in some cases, be different from the ordering presented in Figure 18. The system of energy levels shown in Fig. 18 is thought to be the most appropriate one to the cases which will be discussed in the present chapter.

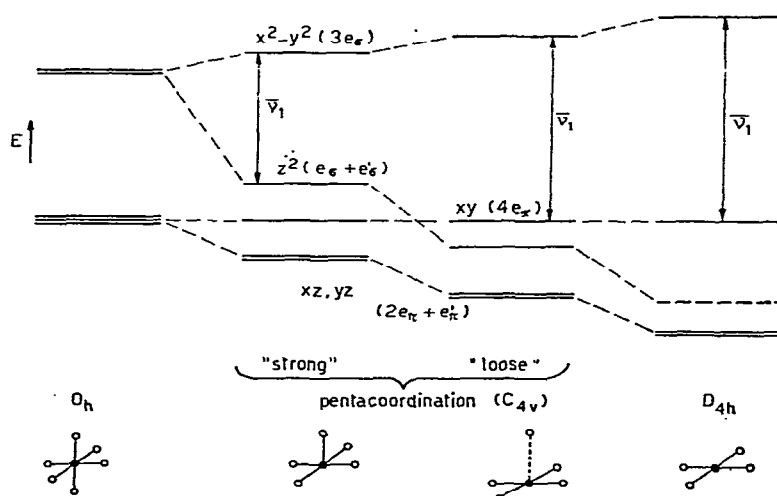
π -bonding in pentacoordinated geometries $M(AA)_2B$

π -efficiency of metal orbitals	xz, yz and xy : full π function	xz, yz and xy : full π function	xz, yz : full π function xy, x^2-y^2 : partly σ , partly π
acceptance of $d_\pi(M)$ electrons into $\pi_L^*(L)$ orbitals (ligand π^* orbitals \perp to chelating plane)	full acceptance ($8e_\pi$) for all 4 ligands (4 electrons from xz, yz (M) into 4 $\pi_L^*(L)$)	full acceptance ($8e_\pi$) for all 4 chelating ligands (4 electrons from xz, yz (M) into 4 $\pi_L^*(L)$)	apical ligands : full acceptance ($4e_\pi$) from xz, yz (M). Equatorial ligands : reduced acceptance ($\alpha_\pi^2 \cdot 4e_\pi$) from the partly σ^* xy, x^2-y^2 (M) orbitals.
Possibility of interligand π -conjugation	yes	yes	no

Fig. 17. π -Bonding in pentacoordinated geometries $M(AA)_2B$.

structure and spectra of the corresponding chromophores can be interpreted on the basis of one general system of one-electron energy levels, as shown in Figure 18 together with the related octahedral and square planar energy levels. The d-orbital splitting scheme of Fig. 18 can be rationalized as follows:

- $d_{x^2-y^2}$ is strongly σ^* (exactly as in octahedral or square planar complexes);
- d_{z^2} is also σ^* (far more so than in D_{4h} square planar, but less than in O_h ,

Fig. 18. d-Orbitals in square pyramidal complexes. (The prime on e_λ refers to the apical ligand.)

since it still has one free lobe, and is therefore less antibonding or, in the language of the electrostatic theory, less repelled than $d_{x^2-y^2}$;

d_{xy} is strongly π^* as in square planar systems, and d_{xz} , d_{yz} are somewhat more strongly π^* than in D_{4h} , but less so than in O_h .

On adding a fifth ligand to a square planar complex, the energy of the d_z^2 orbital is greatly influenced, whilst the energies of the d_{xz} and d_{yz} orbitals are also affected but to a lesser extent.

COMPLEXES DERIVED FROM SQUARE PLANAR SYSTEMS BY LOOSE ADDITION OF A FIFTH LIGAND IN THE APICAL POSITION

Starting from the square planar d^8 energy level system and assuming the perturbation is small enough to preserve diamagnetism, a *very* small axial perturbation will shift d_z^2 upwards, but if d_{xy} remains the highest filled level, the first transition ($xy \rightarrow x^2-y^2$) would remain unchanged (the energy difference $(E(x^2-y^2) - E(xy))$ is the crystal-field matrix element $\langle 2 | \hat{V} | -2 \rangle \Sigma_L \approx \sin 4\phi_L$, and is therefore independent of pentacoordination) if only the first spin-allowed ligand-field transition ν_1 is observed.

Pentacoordination begins to be observed spectroscopically when $E(xy)$ becomes $< E(z^2)$; increasing strength of the axial distortion now causes a *red* shift of ν_1 (now $z^2 \rightarrow x^2-y^2$), possibly accompanied by enhanced intensity owing to the removal of the center of symmetry. The angular overlap model accounts for the effect of the axial ligand through increasing values of e'_σ and e'_π , as shown in

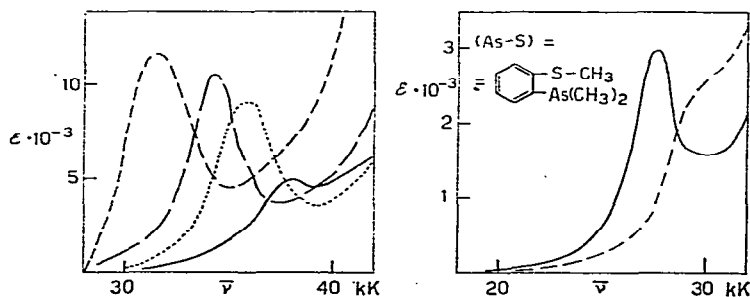


Fig. 19. Spectra of quadratic complexes and of related 1 : 1 adducts.

Left (from G. DOLCETTI, A. PELOSO AND L. SINDELLARI, *Gazz. Chim. Ital.*, 96 (1966) 1648):

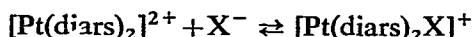
- [Pt diars₂]²⁺
- [Pt diars₂ Cl]⁺
- [Pt diars₂ Br]⁺
- [Pt diars₂ I]⁺

Right (from B. CHISWELL AND S. E. LIVINGSTONE, *J. Chem. Soc.*, (1960) 1071):

- [Pt(As-S)₂I]⁺
- [Pt(As-S)I₂]⁺

Fig. 18. For a quantitative account of the observed spectral patterns, the effect of interelectronic repulsion has also to be considered, although this is not likely to qualitatively change the sequence of levels given in Fig. 18; the corrections to the excited states with respect to the groundstate $(xz, yz)^4(xy)^2(z^2)^2$ are $-C$ for the first excited square planar state ${}^1A_{2g}(xz, yz)^4(z^2)^2(xy)^1(x^2-y^2)^1$, and $-4B-C$ for the first excited square pyramidal state ${}^1B_1(xz, yz)^4(xy)^2(z^2)^1(x^2-y^2)^1$.

Several d^8 complexes with a doubly positively charged ion in a square planar environment and with soft π -acceptor ligand, add one X^- ion^{9-11,52} eg. ^{9,52}



the behaviour of which is illustrated in Fig. 19.

In some instances, the incoming X^- ligand causes substitution of the soft ligand; then the net charge is reduced, and we revert to true tetracoordination $[ML_4]^{2+} + 2X^- \rightleftharpoons ML_2X_2 + 2L$. This behaviour is expected whenever the axial perturbation becomes large, and therefore severely distorts the square pyramid, which then becomes unstable with respect to the trigonal bipyramid, and this in turn becomes unstable towards the square planar structure. We have the spectra of the sequence *e.g.* $[PdL_4]^{2+}$, $[PdL_4X]^+$ and PdL_2X_2 , with increasing red shifts of $\bar{\nu}_1$ due respectively to the above discussed red shift on pentacoordination plus lower interelectronic repulsion in the first excited state of the square pyramid, and to the lower field strength of X ($=$ halide) compared to L (usually S , P or As as the donor atoms) (see Fig. 19). A recent example of this behaviour has been investigated in the author's laboratory with reference to complexes of Pd^{II} and of Pt^{II} with thioureas and selenoureas^{53,54}. Complexes such as PdL_4Cl_2 ($L = N, N'$ -disubstituted thio or selenourea) usually dissolve in organic solvents as a mixture of species (see Fig. 20); in the presence of excess X^- they behave as square planar $[PdL_2X_2]$ ($\log \epsilon \bar{\nu}_1 \sim 2.5$), in the presence of excess L as pentacoordinated $[PdL_4X]^+$ (diamagnetic) having the first $d-d$ band ($\bar{\nu}_1 \sim 25$ kK, $\log \epsilon \sim 3.5$) at lower frequencies than expected for the hypothetical square planar $[PdL_4]^{2+}$ (~ 27 kK; the value can be inferred from the average environment rule from $[PdCl_4]^{2-}$ ($\nu_1 = 21.1$ kK) and $[PdCl_2L_2]$ ($\bar{\nu}_1 \sim 24$ kK)). Actually, we think that $[PdL_4]^{2+}$ never occurs free. It prefers to coordinate solvent molecules or even ClO_4^- ions forming five-coordinate species, as is shown by conductimetric evidence (both PdL_4Cl_2 and $PdL_4(ClO_4)_2$ behave in noncoordinating solvents as 1:1 electrolytes suggesting dissociation into $[PdL_4A]^+ + A^-$; $A = Cl$ or ClO_4), by chemical evidence (direct substitution with perchlorate can replace only one chlorine in PdL_4Cl_2 yielding $[PdL_4Cl]^+[ClO_4]^-$), and lastly by spectrochemical evidence. Solutions of $PdL_4(ClO_4)_2$ in coordinating solvents S behave as 1:2 electrolytes, having dissociated both perchlorate ions, yet their spectrum is much more closely allied to the spectra of the pentacoordinated $[PdL_4X]^+$ species than to those of the related square planar species, suggesting formation of a pentacoordinated $[PdL_4S]^{2+}$ chromophore (Figure 21). The sequence of $\bar{\nu}_1$ frequencies $[M^{II}L_4]^{2+}(\text{hyp.}) >$

$[M^{II}L_4X]^+ > [M^{II}L_2X_2]$, illustrated in Figs. 20 and 21, follows the general trend discussed above. Selenoureas give values of both $\bar{\nu}_1$ and the charge-transfer frequencies which are slightly lower than those occurring with thiourea ligands (Figure 22). For all these species (Figs. 20 to 22), the spectra can be regarded as a small modification of the spectral patterns of the square planar chromophores. The stronger the fifth (apical) bond, the lower is $\bar{\nu}_1$, and we can even attempt a classification of the "strength" of apical ligands; among those investigated, coordinated

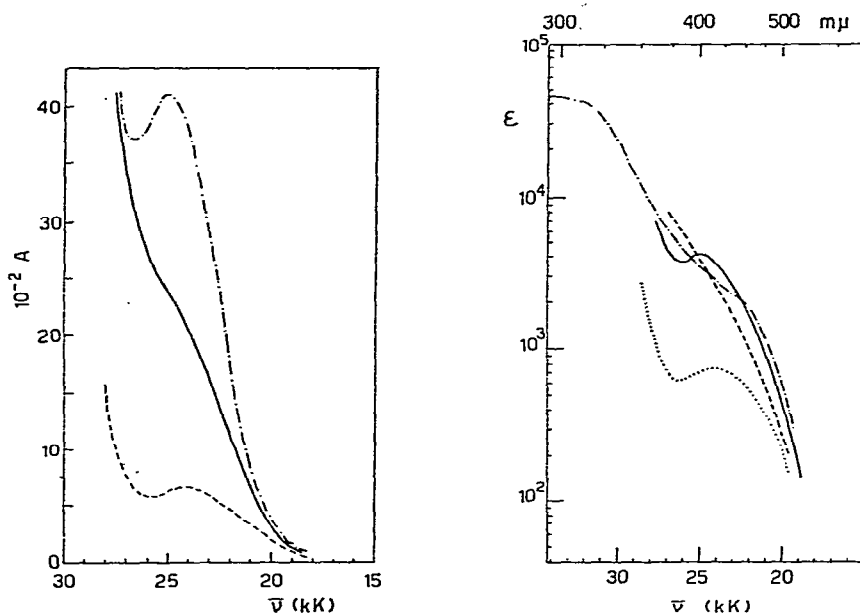


Fig. 20. Absorption spectra of PdL_4Cl_2 in acetone ($L = N,N'$ -diphenylthiourea):

— alone (mixture of species)
 - - - + excess L (predominant species $[PdL_4Cl]^+$)
 . . . + excess Cl^- (predominant species $[PdL_2Cl_2]$).

Fig. 21. Molar absorption spectra of pentacoordinated palladium (II)-thioureas species:

— PdL_4ClClO_4 in acetone (chromophore: $[PdL_4Cl]^+$)
 - - - $PdL_4(ClO_4)_2$ in acetone (chromophore: $[PdL_4(solv)]^{2+}$)
 . . . $PdL_4(ClO_4)_2$ in CH_2Cl_2 (chromophore: $[PdL_4(ClO_4)]^+$)
 For comparison: $PdL_4Cl_2 + Cl^-$ in acetone (chromophore: $[PdL_2Cl_2]$),
 ($L = N,N'$ -diphenylthiourea).

perchlorate would seem the strongest, followed by molecules of polar solvents such as acetone, alcohol or acetonitrile, and in turn by the halides in the usual spectrochemical order $Cl > Br > I$ ⁵⁴. The strong tendency to 5-coordination in thiourea complexes is evidence for π -backdonation and is good support for the explanation of the stability and regularity of square pyramids based upon π -bonding. Although the ligands are monodentate, some conjugation must take place

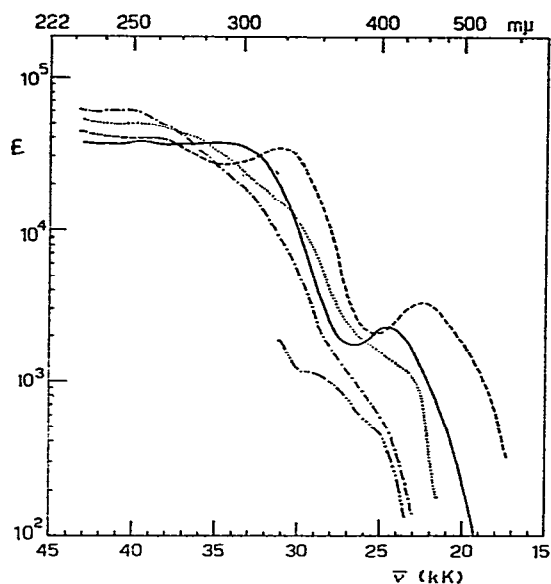


Fig. 22. Molar absorption spectra of $[M^{II}L_4Cl]^+$ species in ethanol:

- $[PdL_4Cl]^+$ ($L = N\text{-phenyl, } N'\text{-benzhydrylthiourea}$)
- $[PdL'_4Cl]^+$ ($L' = N\text{-phenyl, } N'\text{-benzhydrylselenourea}$)
- · - · - $[PtL_4Cl]^+$ ($L = N\text{-phenyl, } N'\text{-benzhydrylthiourea}$)
- $[PtL''_4Cl]^+$ ($L'' = N,N'\text{-diethylthiourea}$)
- $[PtL'_4Cl]^+$ ($L' = N\text{-phenyl, } N'\text{-benzhydrylselenourea}$).

between different ligand molecules in order to stabilize the square pyramidal form with respect to the trigonal bipyramidal one.

STRONG SQUARE PYRAMIDAL PENTACOORDINATION

By "strong" square pyramidal coordination we mean those cases where all five ligands form bonds whose strengths are of the same order of magnitude, or where pentacoordination results in significant changes in the physicochemical properties (*e.g.* in magnetic behaviour) with respect to possible related species of different symmetries.

$FeCl_2dc_2$ is a case of a molecule with square pyramidal geometry¹⁴, forced by a compromise between the necessity of planarity for optimum π -bonding and the best σ -overlap, having the unusual spin moment $S = \frac{3}{2}$. The ordering of the levels is undoubtedly as in Fig. 23 (supported by e.s.r. data), but the measured spectrum is too uncertain to allow certain identification of the bands; Fig. 23 shows one possible interpretation.

$Ni^{II}(\text{dietsalen})_2$ is an example of a molecule where square pyramidal geo-

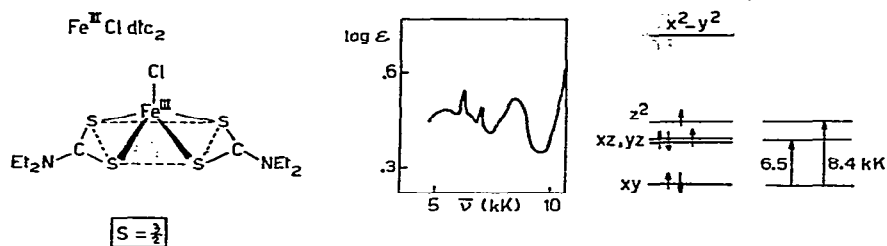


Fig. 23. FROM B. F. HOSKINS, R. L. MARTIN AND A. H. WHITE, *Nature*, 211 (1966) 627 and R. L. MARTIN AND A. H. WHITE, *Inorg. Chem.*, 6 (1967) 712.

metry is forced by a peculiar conformation of the ligand. This is a high-spin complex, and the one-electron strong-field scheme alone is no longer a good approximation. Ciampolini and Nardi⁴³ performed a weak-field calculation and obtained good agreement for the lower energy bands, showing that the model can be adequate. We notice however that the predictions for a trigonal bipyramid would not be greatly different, so that the spectrum can be scarcely diagnostic of stereochemistry, although its dissimilarity from cubic complexes makes it diagnostic of pentacoordination.

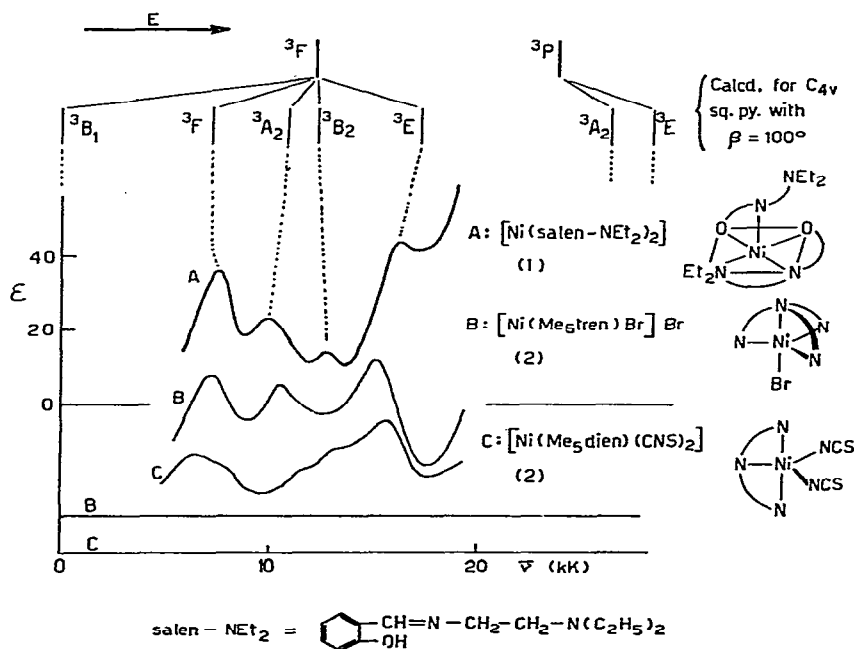


Fig. 24. (1) L. SACCONI, P. NANNELLI, N. NARDI AND U. CAMPIGLI, *Inorg. Chem.*, 4 (1965) 943. (2) M. CIAMPOLINI AND N. NARDI, *Inorg. Chem.*, 6 (1967) 445.

In this regard, we have an even more striking example⁵⁵. Square planar Ni^{II} complexes with sulphur-containing ligands (*e.g.* $\text{Ni}^{\text{II}}\text{dtp}_2$, $\text{dtp}^- = (\text{C}_2\text{H}_5\text{O})_2\text{PSS}^-$) readily form paramagnetic octahedral 1:2 adducts with several nitrogen bases, but in some instances also form 1:1 adducts, *e.g.* with secondary amines⁵⁶, pyridine⁵⁷, quinoline⁵⁷, etc. which are monomeric and therefore pentacoordinated. We investigated the 1:1 adduct of Ni dtp_2 with *n*-butylamine (which is an intermediate before formation of the octahedral 1:2 adduct); we are inclined to believe that it has a square pyramidal structure in view of the importance of π -bonding effects in Ni dtp_2 , and because it would be most unusual to have a high-spin Ni-trigonal bipyramid with sulphur ligands*, but we shall discuss its spectrum with regard to all possible structures, to analyze the usefulness of the spectrum for structure diagnosis.

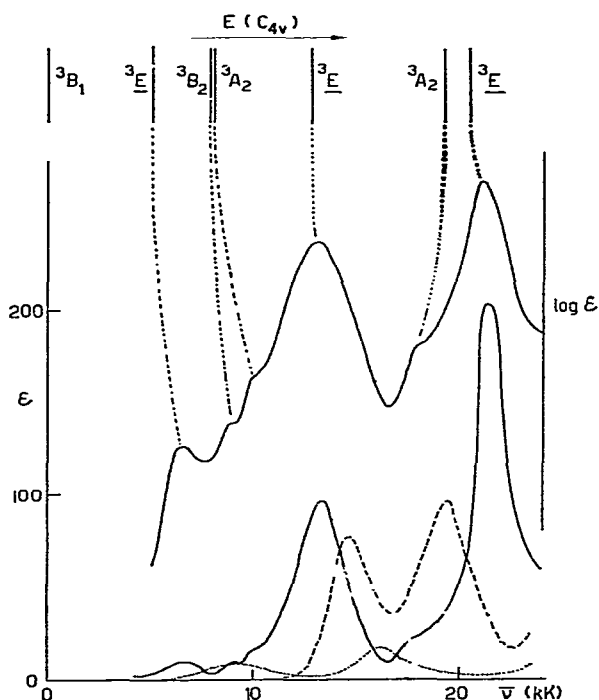


Fig. 25. Absorption spectra of:

- $[\text{Ni dtp}_2 \cdot \text{am}]$
- $[\text{Ni dtp}_2 \cdot \text{am}_2]$
- $[\text{Ni dtp}_2]$
- (am = Et_2NH or BuNH_2).

* The only reported example⁵⁸ of high-spin trigonal-bipyramidal Ni^{II} is $\text{Ni}(\text{DPES})\text{Cl}_2$ with DPES = bis-(2- β -pyridylethyl)-sulphide, having however only one sulphur donor among four harder donors (chromophore $[\text{Ni}^{\text{II}}\text{SN}_2\text{Cl}_2]$).

As for all other 1:1 adducts of this sort, the spectrum of the 1:1 adduct of Ni dtp_2 with BuNH_2 has two very intense bands at about 13 and 21 kK, which had been reported some time ago⁵⁶. On closer inspection however, several other less intense bands are observed (see Figure 25). The 1:1 adducts are paramagnetic with 2 unpaired electrons. Since we know the spectrum and therefore the ligand-field parameters of the octahedral 1:2 adducts (having the same spin and hence probably the same metal-ligand distances), this is a favorable occasion to attempt an *a priori* calculation of the pentacoordinated system of energy levels. Since this is a high-spin case, the inclusion of interelectronic repulsion is appropriate; we used the strong-field scheme, but Figure 26 also shows the weak-field parentage.

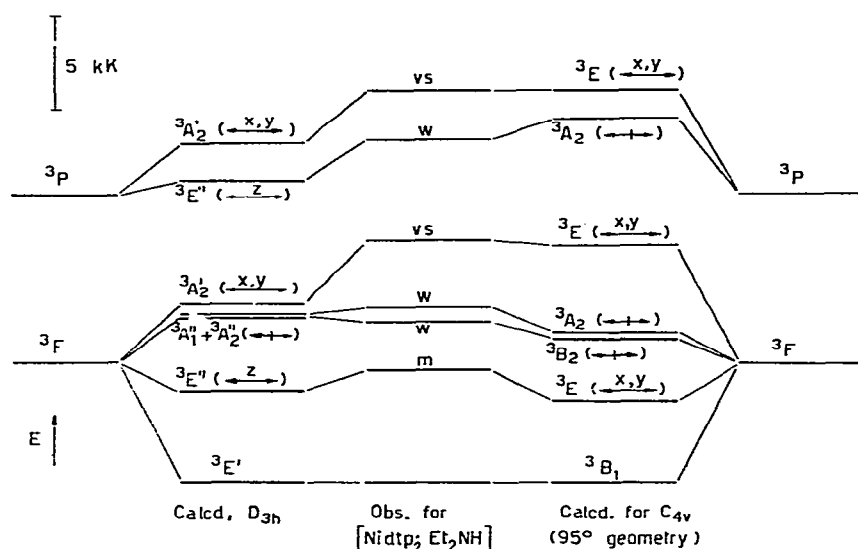


Fig. 26. Experimental and predicted d-d spectrum of a pentacoordinated 1:1 adduct of Ni dtp_2 . Ligand-field parameters are chosen 5% higher than the values fitting the observed spectrum of the octahedral 1:2 adduct $[\text{Ni dtp}_2 \cdot \text{am}_2]$ (vs, m and w denote band intensities).

It turns out that the agreement is not satisfactory, for a trigonal bipyramidal arrangement, rather, it is better for a regular square pyramidal structure with the same parameters derived from the octahedral 1:2 adduct, or for a slightly distorted square pyramid with slightly higher ligand field strength (which seems reasonable), but not so much better as would be needed to make the spectrum undisputably diagnostic of stereochemistry. This is perhaps a general situation; after all, in a weak field scheme, which is appropriate for high-spin Ni^{II} species, there will always be two terms (except in cubic symmetry) at approximately 20–26 kK derived from the ^3P term, while the ^3F -sublevels will always have their highest component at ~ 12 –16 kK, and there will always be a number of ^3F -terms (depending on the actual low-symmetry components) below that. In this situation we should resort, for

the diagnosis of structure, to other data. For lack of data from X-ray studies (1:1 adducts cannot to be isolated as solids, but merely exist in solution), from e.s.r. (probably because of large zero field splitting), and from p.m.r. (signals are smeared out in the paramagnetic adduct), we resorted to some speculations about the band intensities in the electronic spectrum. In a trigonal bipyramid (D_{3h}) both transitions to the split products of 3P are allowed, and only transitions to two intermediate terms of 3F would be forbidden (they would however become allowed in C_{3v}). In the square pyramidal group, C_{4v} , there is a much sharper distinction between dipole-allowed ($\rightarrow ^3E$) and dipole-forbidden transitions (see figure 26). Furthermore, an out-of-plane deformation of the square pyramid does not change the symmetry group. Therefore the selection rules maintain full validity (only rhombic distortions of C_{2v} symmetry can lift their validity). The two most intense bands observed at 13 and 21 kK can be assigned to 3E levels of the square pyramid, while the second component of 3P at 19 kK is distinctly less intense, as is demanded by the selection rules of square pyramidal C_{4v} symmetry.

So we have some evidence from the intensities in favour of the square pyramidal structure of the 1:1 adduct formed between $Nidtp_2$ and bases such as n-butylamine. However, we must realize that such evidence is a rather weak one, and that the decision is no more clear cut in many other similar cases. To make the situation even less clear, we realize that pure, regular trigonal bipyramids or square pyramids practically never occur; what we call "trigonal bipyramids" or "square pyramids" are often nothing else than idealized geometries, and we have plenty of reasons to suspect that in actual cases there are serious distortions. For example it would be difficult, not to say impossible, to exclude a C_{2v} structure of the general type discussed by Zemann²⁴ for our 1:1 $Nidtp_2$:BuNH₂ adduct, which would then have a structure intermediate between the pure trigonal bipyramid and the pure square pyramid. This is a general point, and we want to stress it; as Fig. 5 and 27 shows, the trigonal bipyramid and the square pyramid when viewed

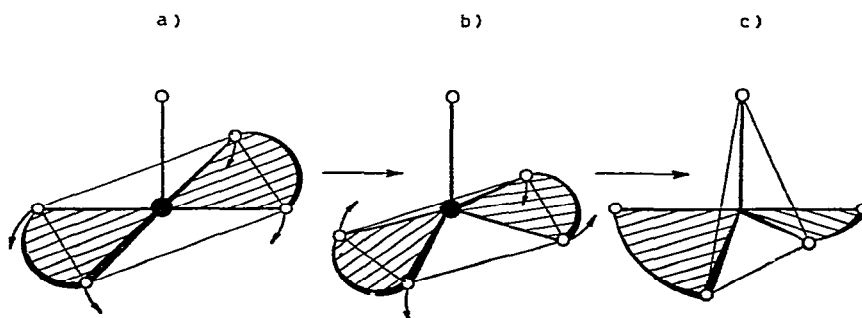


Fig. 27. Interconversion of pentacoordinated geometries possible for the 1 : 1 adducts $[Ni dtp_2 \cdot am]$.

- (a) regular square pyramid
- (b) square pyramid with out-of-plane deformation
- (c) trigonal bipyramid

along the same axis are not so different as is commonly believed¹. Furthermore a continuous variation between these two limiting geometries is possible, and can actually occur by a normal vibration of either structure. We can but stress therefore, when dealing with pentacoordinated transition-metal complexes, that it is necessary to realize that no pentacoordinated geometry is absolutely stable, nor exists in pure, regular form, except in special cases where it is strongly demanded and rigidly stabilized by the steric structure of polydentate ligands or by lattice packing requirements (or possibly) by easy availability of $(n+1)p$ orbitals for sharp establishment of rare gas E.A.N., as is the case with carbonyls, isonitrile complexes, and in general complexes where the central element is in a low oxidation state). In most practical cases we must recognize an inherent instability of any simple 5-coordinated geometry; the energy difference between trigonal bipyramids, square pyramids and related structures is always small, and often switching among these geometries can be accomplished in the course of genuine molecular vibrations. No too rigid model should therefore be employed when attempting an interpretation of these nonrigid structures.

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