

Multiple Bonding and Back-co-ordination in Inorganic Compounds

By L. D. Pettit

DEPARTMENT OF INORGANIC AND STRUCTURAL CHEMISTRY,
THE UNIVERSITY, LEEDS, LS2 9JT

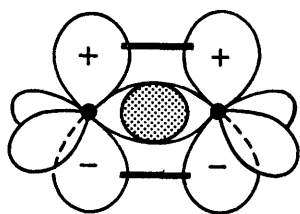
1 Introduction

The formation of multiple bonds is a common phenomenon in chemical compounds, both elementary (*e.g.* N₂, graphite) and containing two or more elements [*e.g.* CO₂, SO₄²⁻, Ni(CO)₄]. Using the molecular orbital approach, multiple bond formation in a diatomic molecule can take place when orbitals of suitable energy and symmetry overlap to give regions of maximum electron density both on the line joining the two nuclei, a σ -bond, and off this line (see I), with more electrons in bonding than in antibonding orbitals. Overlap off the internuclear axis usually results in a single nodal plane containing the nuclei to give a π -bond (III—VI), which has an angular momentum of 1 unit (*i.e.* $\lambda h/2\pi$ with $\lambda = 1$) about the internuclear axis. More rarely overlap can result in two nodal planes at right angles (*e.g.* when two $d_{x^2-y^2}$ or d_{xy} orbitals overlap face to face) giving a δ -bond, with an angular momentum quantum number, $\lambda = 2$. In polyatomic molecules the same terms may be used, σ and π referring to the spatial characteristics of the orbitals, *e.g.* ethylene has a plane of symmetry about which the π -bond can be defined. This description explains most of the properties of multiple bonds (*e.g.* lack of rotation and symmetry) but implies the presence of two distinctly different bonds (σ and π) in the resulting molecule. When molecules without planes or axes of symmetry are considered (*e.g.* tetrahedral molecules) it is impossible to define π -bonds strictly. Rather, individual pairs of atoms have to be considered to the exclusion of the rest of the molecule. This problem is found in MO calculations on tetrahedral molecules (see later).

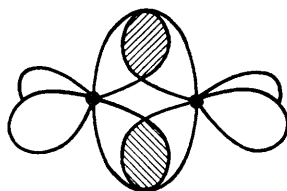
In the valence bond approach, atoms which use only s and p orbitals for bonding are assumed to be essentially tetrahedral. This can be explained as resulting from either sp^3 hybridisation, the minimisation of repulsions between the four spin-paired electrons of the octet¹ or correlation of the two quartets of electrons of opposite spin.² A double bond can then be regarded as two tetrahedra sharing an edge (II) while a triple bond would be two tetrahedra sharing a face. This model could be extended to multiple bonding involving d orbitals in addition to s and p by picturing octahedra or cubes in place of tetrahedra. Such models explain qualitatively most of the properties of multiple bonds with the added advantage that no rigid distinction is drawn between σ and π -bonds. Instead two or more bent

¹ R. J. Gillespie and R. S. Nyholm, *Quart. Rev.*, 1957, **11**, 339.

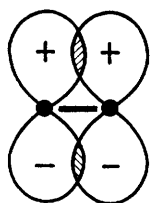
² P. G. Dickens and J. W. Linnett, *Quart. Rev.*, 1957, **11**, 291.



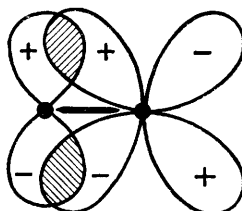
(I)



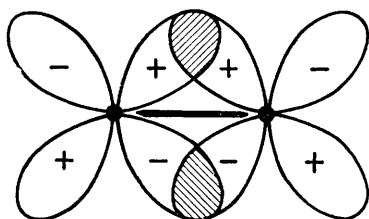
(II)



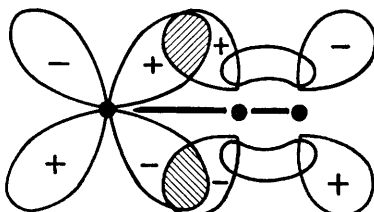
(III)



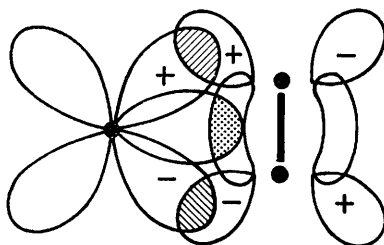
(IV)



(V)



(VI)



(VII)

Diagrammatic representation of:

(I) MO description of a $\pi + \sigma$ bond. (II) VB description of a double bond. (III) $p-p\pi$ overlap. (IV) $d-p\pi$ overlap. (V) $d-d\pi$ overlap. (VI) $d-\pi\pi^*$ overlap. (VII) $d-\pi\mu^*$ overlap.

('banana') bonds are assumed as in (II). They will be analogous to the bent bonds required in cyclopropane, yellow phosphorus (P_4), and possibly some metal-olefin complexes. Mathematically, two bent bonds are equivalent to a $(\sigma + \pi)$ combination, and in a full, quantitative treatment the two formulations represent different interpretations which are essentially correct and meaningful, as has been shown by Pople.³ Various orbitals can overlap to form π -bonds. Those normally considered are p - p overlap (III), d - p overlap (IV), d - d overlap (V), and d - π^* overlap (VI and VII). In addition, the involvement of f orbitals has been considered in some uranium complexes.⁴ Bonds formed by overlaps which are directed towards the centre of a multiple bond (or an aromatic or other conjugated system) and not any particular atom, such as the sp hybrid- π overlap illustrated in (VII), are sometimes called μ -bonds. For the purpose of this Review the d - π^* overlaps shown in (VI) and (VII) will be differentiated as d - π_π^* and d - π_μ^* respectively.

2 Evidence for Multiple Bond Formation

When orbitals containing suitable electrons overlap to form molecular orbitals the energy of the resulting bond is approximately proportional to the overlap integral, S . Since overlap is considerably more effective along the internuclear axis than off it, π -bonds will, in general, be weaker than σ -bonds and will not exist independently. However, the formation of π -bonds will tend to draw the nuclei involved closer together with a consequent increase in σ overlap and hence in overall bond energy. As a general rule among first period elements, double and triple bond formation reduce the covalent radius of an ion by 0.105 Å and 0.17 Å respectively,⁵ although this change may be partly attributed to changes in hybridisation. The increase in bond energy caused by shortening the σ -bond and forming π -bonds will also contain a contribution from a reduction in the mutual repulsions of non-bonding electrons, e.g. those in p_y and p_z orbitals in F_2 . When π -bonding is present (e.g. $N \equiv N$) these electrons are in bonding π -orbitals, with consequent bond shortening and strengthening.

Comparison of bond lengths is a frequently used method of detecting multiple bonding. Bond angles are also of use since they give an indication of the orbitals which can overlap effectively, but in some cases changes in bond angle may be a less reliable guide than changes in bond lengths.^{6a} Bond strengths, measured either as bond energies, force constants, or, far less reliably, as stretching frequencies, are alternatives to measuring bond lengths, and a number of authors have demonstrated the relationship between force constants and bond order. In addition to molecular geometry, the interpretation of u.v. and visible spectra is

³ J. A. Pople, *Quart. Rev.*, 1957, **11**, 273; R. S. Mulliken, *Science*, 1967, **157**, 3784.

⁴ A. Streitwieser and U. Muller-Westerhoff, *J. Amer. Chem. Soc.*, 1968, **90**, 7364.

⁵ L. Pauling, 'The Nature of the Chemical Bond', Cornell, 1960.

⁶ (a) E. A. V. Ebsworth, *Chem. Comm.*, 1966, 530; (b) M. D. Curtis and A. L. Allred, *J. Amer. Chem. Soc.*, 1965, **87**, 2554; A. L. Allred and L. W. Bush, *ibid.*, 1968, **90**, 3352; (c) S. E., Harrison and J. M. Assow, *J. Chem. Phys.*, 1964, **40**, 465; T. R. Reddy and R. Srinivasan, *ibid.*, 1965, **43**, 1404; (d) A. H. Maki and R. R. McGarvey, *ibid.*, 1958, **29**, 31, 35; (e) C. A. Coulson. *Proc. Cambridge Phil. Soc.*, 1942, **38**, 210; R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *J. Chem. Phys.*, 1949, **17**, 1248.

frequently used to give evidence for multiple bonding. If electronic transitions can be reliably assigned, significant population of orbitals potentially able to overlap to form π -bonds can be detected. Such spectra have been of considerable use in understanding a wide variety of molecules such as S_4N_4 , phosphonitrilic halides, ferrocene, and a range of other organometallic compounds. Other properties which have been correlated with multiple bonding include dipole moments, n.m.r. spectra, formation constants of complexes, and magnetic susceptibilities. Arguments based on these methods will be referred to later.

In principle, e.s.r. spectroscopy should be a good technique for detecting delocalised electrons in π -systems but unfortunately very few suitable paramagnetic ions are available for study. The most profitable application of e.s.r. has been in a study of the Si—C and Ge—C bonds ($d-p_\pi$ overlap) where π -bond orders of 0.18 and 0.13 respectively have been reported,^{6b} and the Si—Si bond ($d-d_\pi$).⁴³ Applications to transition-metal complexes are very limited since most such organometallic compounds are diamagnetic, and where paramagnetic species can be prepared, broad spectral lines are found since the electron relaxation times are short and the energy levels close together. The results that are available suggest that there is significant Cu—N and Cu—S π -bonding in the copper phthalocyanine and diethyldithiocarbamate complexes,^{6c} with little π interaction in the acetylacetonate and salicylaldehyde analogues.^{6d}

These methods vary in the information they provide but they can only give an indication of the type of bonding present. When multiple bonding is extensive this is usually satisfactory. However, in the majority of compounds of interest to inorganic chemists [*e.g.* $N(SiH_3)_3$, Cu_2Ac_4 , $Ni(CO)_4$, metal arenes] multiple bond character in the bonds of particular interest is small, making clear-cut distinctions impossible.

Ab initio molecular orbital calculations could, in principle, give more information, but at present they are too complicated for rigorous treatment of all but the simplest molecules. Generally, approximations have to be adopted for the type of functions (usually Gaussian) used to describe the atomic orbitals, which are generally Slater-type with Clementi exponents. The SCF procedure used is also important since calculated energies must be extremely accurate if they are to be meaningful and populations of orbitals of similar energy reliable. More extreme approximations include the selection of only a limited number of valence electrons and assumptions on the orbitals which will be occupied. Extreme care should therefore be taken in interpreting results from theoretical calculations. In cases where dative π -bonding is thought to be present, a very small contribution from the π -bond itself to the total bond energy does not necessarily mean that it is unimportant, since its predominant feature may be the dissipation of charge from the central atom in order to create the conditions for a strong σ -bond with a shorter bond length. Under such conditions the synergic effect of a weak π -bond could be considerable.

In this Review a number of classes of inorganic compounds in which multiple bonding is thought to be present will be considered. These include the elements themselves, tetrahedral oxyions, non-metallic cyclic structures such as the

phosphonitrilic halides, trisilylamine, and related compounds, and, in particular, a wide range of metal complexes with so-called ' π -bonding' ligands and heavy donor atoms. For convenience these transition-metal complexes will be considered separately from non-metallic compounds.

3 p - p_π Bonding

Without a doubt, the most effective overlap to form π -bonds is p - p overlap, since p orbitals are less diffuse than d . However, as the principal quantum number (n) increases, covalent radii increase, and p -orbitals become more diffuse. Increased diffuseness may increase the π overlap but this is generally more than offset by the accompanying increase in covalent radius. The result is that p - p overlap is effective in the first period of the Periodic Table but decreases in the second and is virtually absent in subsequent periods. For instance, the bond lengths in O_2 and S_2 are 1.207 and 1.887 Å respectively. Assuming Slater atomic orbitals and using tables of overlap integrals of Coulson and Mulliken, the p - p_π overlap integrals in O_2 and S_2 are found to be 0.217 and 0.177 respectively.^{6e} The S-S bond length would have to be shortened to 1.76 Å (a decrease of 0.13 Å) for the overlap to equal that calculated for O_2 . The presence of nodes ($n - 2$) in $3p$ orbitals and above should have virtually no influence since they are very close to the nucleus.

π -Orbital overlap can take place both between atoms of the same element and between atoms of different elements. In the elementary state, non-metals containing more than one unpaired electron can polymerise in three ways. They can form (i) diatomic molecules (*e.g.* N_2), (ii) discrete molecules with limited double-bond character (*e.g.* P_4), or (iii) infinite σ -bonded polymers (*e.g.* As). The choice will depend on the free-energy changes for the three alternatives. Formation of diatomic molecules will be favoured by entropy factors while enthalpy changes will, in most cases, favour entirely σ -bonded polymers. Only when π overlap is large and the bond shortening appreciable (*i.e.* in the first period) will the enthalpy changes be sufficient to permit entropy changes to dictate polymerisation to give diatomic molecules: *e.g.* O_2 and N_2 . While the orbitals of carbon are not suitable to form $C\equiv C$, $C=C$ is a distinct spectroscopic species and, compared to diamond, graphite is a high entropy allotrope of carbon with p - p_π bonding. In the second and subsequent periods atomic radii increase, making p - p_π overlap smaller, although the possibility of d - p_π or d - d_π overlap is introduced, and diatomic molecules are not normally formed although a diatomic S_2 molecule, which is similar to oxygen (*e.g.* paramagnetic) but is unstable above $-80^\circ C$,²³ can be prepared. The 'polymerisation' and co-ordination numbers of metallic elements (*e.g.* tin) could also be explained in a similar way using s , p , and d orbitals, but the more straightforward interpretation in terms of ionic character is preferable.

p - p_π Bonding between atoms of the same element can occur in a number of non-elementary compounds, *e.g.* alkenes, and diazo-compounds. An interesting example of the use of bond lengths and angles to detect such multiple bonding is a comparison of the stereochemistries of the Co-O-O-Co chains in

$[(\text{NH}_3)_5\text{Co}\cdot\text{O}_2\cdot\text{Co}(\text{NH}_3)_5](\text{SO}_4)_2$ and $[(\text{NH}_3)_5\text{Co}\cdot\text{O}_2\cdot\text{Co}(\text{NH}_3)_5](\text{SO}_4)_2(\text{HSO}_4)$.^{7,8a} In the former case, the $\text{Co}\cdot\text{O}_2\cdot\text{Co}$ moiety is distinctly non-planar with an O—O bond length of 1.47 Å while in the latter it is virtually planar with a bond length of 1.31 Å. The former resembles H_2O_2 (O—O = 1.49 Å), while the latter resembles the superoxide ion, $\text{O}=\text{O}^-$ (O—O = 1.28 Å) in which oxygens would be sp^2 hybridised. However, not all compounds which have been studied fall unambiguously into one of these two classes. For example, the ligand environment of the cobalt atoms appears to have some influence, and delocalisation of electrons is apparent.^{8b}

Multiple bonding between different elements of the first period is also well established, both in small molecules, *e.g.* CO_2 and HCN , but also in some polymerised species such as $(\text{HCN})_3$ or $(\text{H}_2\text{BN})_3$, which are benzene-like molecules containing conjugated six-membered ring systems, of alternate C and N or B and N atoms. In some cases multiple bonding is not required to ensure that all electrons in bonding orbitals are paired but π -bonding is suspected. The calculated B—F bond length is approximately 1.5 Å while the measured value in BF_3 is 1.30 Å. This shrinkage has been attributed to either π overlap between empty $2p$ orbitals of boron and full $2p$ orbitals of fluorine, or ionic character resulting from the electronegativity differences between B and F. Quantitative calculation of the p - p_π overlap between B and F orbitals should tell whether π -bonding is really important, but the reliability of such calculations depends on the approximations and wave functions used. Approximate calculations for BF_3 and BCl_3 suggest that π -bonding contributes 14% of the total bond energy of planar BF_3 and 12% of planar BCl_3 . If these planar molecules are distorted into trigonal pyramids with tetrahedral angles, changes in π -overlap are comparatively small, estimated contributions to the total bond energy being 9.5% and 7% respectively.⁹ Force constants calculated for the B—F bond also suggest a bond order greater than one.¹⁰ Recent *ab initio* calculations give π overlap populations of 0.204 and 0.147 electrons in the B—F bonds of BH_2F and BF_3 respectively.^{10b} These populations give π -bond energies of 113 and 83 kJ mol^{-1} .

The influence of ionic character on bond lengths has been studied by Schomaker and Stevenson. They produced the empirical relationship:

$$r_{A-B} = r_A + r_B - 0.09(|x_A - x_B|),$$

where r_A and r_B are covalent radii and x_A and x_B electronegativities, to show the effect of electronegativity differences on the additivity of covalent radii.¹¹ For BF_3 this predicts a shortening of 0.18 Å giving reasonably close agreement with the measured length. However, in other cases such as SiF_4 agreement is less satisfactory. Beagley has assumed that electron screenings and repulsions are more important than electronegativity differences and has derived an empirical

⁷ W. P. Schaefer, *Inorg. Chem.*, 1968, **7**, 725.

⁸ (a) W. P. Schaefer and R. E. Marsh, *Acta Cryst.*, 1966, **21**, 735; (b) A. G. Sykes and J. A. Weil, *Progr. Inorg. Chem.*, 1970, **13**, 1.

⁹ D. G. Brown, D. S. Drago, and T. F. Bolles, *J. Amer. Chem. Soc.*, 1968, **90**, 5706.

¹⁰ (a) R. E. Hester, *Co-ordination Chem. Rev.*, 1967, **2**, 319; (b) M. E. Schwartz and L. C. Allen, *J. Amer. Chem. Soc.*, 1970, **92**, 1466.

¹¹ V. Schomaker and D. P. Stevenson, *J. Amer. Chem. Soc.*, 1941, **63**, 37.

relationship between tetrahedral radii and effective nuclear charge.¹² In some cases this appears preferable to the Schomaker–Stevenson equation. In general it seems probable that both multiple bonding and electronegativity differences or electron repulsions can contribute significantly to overall bond shortening.

When second period elements are involved, $p-p_\pi$ bonding is considerably weaker. For instance, while single $p-p_\pi$ bonding appears to be possible between carbon and sulphur (*e.g.* CS₂), there are no examples of C=P bonds although N=P bonds are known in phosphinimines. This is presumably because the phosphorus atom is larger than sulphur, making $p-p_\pi$ overlap less effective. However, if the C—P bond is shortened by allowing a second pair of p -orbitals to overlap, C≡P bonds, although comparatively unstable, can be formed; *e.g.* HCP, in which the C—P bond length is 1.542 Å^{13a} while the C—P single bond length is 1.87 Å. The calculated length for a triple bond, using Pauling's covalent radii, is 1.53 Å. The diatomic molecules NP and P₂ are also known and have only weak π -bonds.

4 $d \leftarrow p_\pi$ Dative Bonding

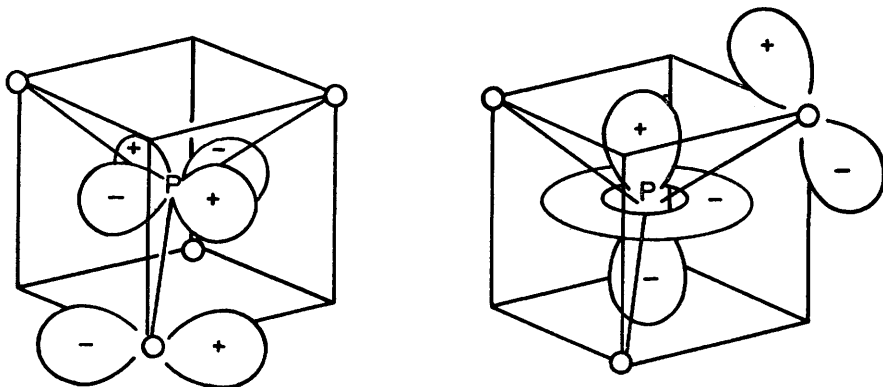
As a result of the large radii of atoms containing d electrons, $d-p_\pi$ overlap would be expected to be small, hence the bonding weak. However, overlap could still influence the stereochemistry and bond lengths of molecules in which it is present. Multiple bonding of this type is much less readily detected than $p-p_\pi$ covalent bonding but the literature on the subject is considerable and expanding rapidly. Only a brief review will therefore be given here. More detailed discussion of the bonding in selected molecules is to be found in a new book by C. F. Bell,^{13b} and the part played by outer d orbitals in bonding, with a survey of experimental evidence for the participation of $3d$ orbitals in π -bonding, has been reviewed by K. A. R. Mitchell.^{13c}

A. Tetrahedral Oxyions.—Cruickshank carried out one of the first detailed studies on the role of $3d$ orbitals in π -bonding with particular emphasis on the tetrahedral oxyions, XO₄^{*n*-}.¹⁴ He demonstrated by structural arguments and approximate molecular orbital calculations that two π -bonding molecular orbitals can be formed with the $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals (e orbitals) of X and appropriate $2p_\pi$ orbitals of oxygen as shown in (VIII). The t_2 orbitals will be of higher energy than the e set and will have overlap integrals more than $\sqrt{3}$ lower. Assuming these π -bonds to be present, Cruickshank showed a linear relationship between bond lengths and π -bond order for a series of oxysulphur compounds, and explained the deviation of bond length in SiF₄ from that predicted by the Schomaker–Stevenson equation¹¹ by F → Si _{π} dative bonding. Assuming the importance of $d \leftarrow p_\pi$ bonding, the non-existence of the FO₄⁻ ion may be explained by the absence of suitable d orbitals on the fluorine able to accept back-co-ordination

¹² B. Beagley, *Chem. Comm.*, 1966, 388.

¹³ (a) J. K. Tyler, *J. Chem. Phys.*, 1964, **40**, 1170; (b) C. F. Bell, 'Syntheses and Physical Studies of Inorganic Compounds', Pergamon, 1970; (c) K. A. R. Mitchell, *Chem. Rev.*, 1969, **69**, 157.

¹⁴ D. W. J. Cruickshank, *J. Chem. Soc.*, 1961, 5486.



(VIII)

$3d_{x^2-y^2}$ and $3d_{z^2}$ π -bonding orbitals in the tetrahedral PO_4^{3-} ion (see ref. 28).

from the oxygen. In the absence of back-co-ordination, the fluorine atom would acquire an unacceptable positive charge.¹⁵

While the stability of tetrahedral oxyacids of Si, P, S, and Cl may be explained by π -bonding, the apparent non-existence of a BrO_4^- ion introduced problems. Early attempts to explain this non-existence assumed that the spherical node in the $4d$ orbitals of bromine would be about 2 Å from the nucleus, so limiting $d \leftarrow p_\pi$ bonding.¹⁶ However, the BrO_4^- ion has, in fact, now been prepared and is found to be a stable species which does not decompose to the bromate below 260 °C.^{17a} Perbromyl fluoride, BrO_3F , has also been prepared.¹⁸ As a result, the apparent non-existence of Br^{VII} species is possibly kinetic in origin rather than thermodynamic.^{17b}

The importance of the nodal surface in $4d$ orbitals depends on its distance from the nucleus. Early calculations assumed simple hydrogen-like orbitals, but these would be too diffuse for effective $d-p_\pi$ overlap. To be of use they must contract considerably from their size in the free atom, but, however, if this contraction does take place the $4d$ nodal surface will also contract toward the nucleus, so reducing its influence on the overlap. Contraction under the influence of the ligand fields of neighbouring atoms, with a concomitant drop in energy, was first treated theoretically by Craig, Magnusson, and Zauli, who calculated a contraction of the mean radius of the $3d$ orbital of sulphur from 3.0 to less than

¹⁵ W. E. Dasent, *J. Chem. Educ.*, 1963, **40**, 130.

¹⁶ D. S. Urch, *J. Inorg. Nuclear Chem.*, 1963, **25**, 771.

¹⁷ (a) E. H. Appelman, *Inorg. Chem.*, 1969, **8**, 223. (b) J. R. Brand and S. A. Bunck, *J. Amer. Chem. Soc.*, 1969, **91**, 6500; C. K. Johnson, P. N. Smith, E. H. Appelman, and W. N. Hubbard, *Inorg. Chem.*, 1970, **9**, 119.

¹⁸ E. H. Appelman, *J. Amer. Chem. Soc.*, 1969, **91**, 4561.

1.5 Å,¹⁹ and this value was further reduced to 1.18 Å in SF₆ by using Hartree-Fock orbitals in place of the Slater orbitals used by Craig and Zauli.²⁰ However, as a result of the approximations necessary for the calculations, orbital energies were rather unrealistic. Orbitals in sulphur have been discussed by many workers using semi-empirical MO approaches but the conclusions are indefinite on account of the assumptions required to make calculations practicable.²¹ In particular, Bernardi and Zauli have argued that occupation of the 4s orbitals is always favoured over that of the 3d²² although they consider that in SF₄ and SF₆ the 3d orbitals participate at least as much as 4s to molecular valence states.²³

Recently, Urch has interpreted X-ray fluorescence data for second period oxygens as giving direct evidence for a 3d → 2p transition, *i.e.* direct evidence of dative π-bonding. To reach this conclusion he used a simple MO model neglecting the participation of 4s electrons and assuming that, in the ground state, the 3d level is completely empty.²⁴

Reports of *ab initio* MO calculations for SO₄²⁻, CrO₄²⁻, and MnO₄⁻ have recently been published.²⁴ Although all electrons are now considered, approximations as to the atomic wave-functions still have to be made, and while the calculated total energy may be very close to the true energy, very small errors could cause large errors in the calculated populations of valence orbitals. However, by using Clementi values for the orbital exponents of Slater-type orbitals for all electrons except the 3d (for which they select the most reliable value available to make computation practicable) Hillier and Saunders calculated that the inclusion of 3d orbitals in the bonding of the sulphate ion was important and resulted in a decrease of nearly 1 a.u. in the total molecular energy. They found that the electron population of 3d orbitals was significant (2.58 electrons) but because these ions have T_d symmetry it is impossible to distinguish between π and σ overlap. *Ab initio* calculations on the MnO₄⁻ and CrO₄²⁻ ions indicate small 3d and large 4p populations compared with semi-empirical calculations, with electrons in d orbitals tending to concentrate in the t₂ rather than the e set. A preliminary report of calculations on PF₃ (C_{3v} symmetry) suggests significant 3d ← 2p π-bonding in the P—F bonds.²⁵

B. Cyclic d-p_π Systems.—Compounds containing N—S and N—P bonds are often of unexpected structure, frequently cyclic. Bonding in S₄N₄ is a particular subject of controversy although the molecular geometry is known indisputably

¹⁹ D. P. Craig and E. A. Magnusson, *J. Chem. Soc.*, 1956, 4895; D. P. Craig and C. Zauli, *J. Chem. Phys.*, 1962, 37, 601.

²⁰ B. C. Webster, *J. Chem. Soc. (A)*, 1968, 2909.

²¹ D. W. J. Cruickshank and B. C. Webster, 'Inorganic Sulphur Chemistry', ed. G. Nickless, Elsevier, 1968; D. W. J. Cruickshank, B. C. Webster, and M. A. Spinnler, *Internat. J. Quantum. Chem.*, 1967, 1 s, 225; D. P. Craig and T. Thirunamachandran, *J. Chem. Phys.*, 1965, 43, 4183; 1966, 45, 3355; D. P. Santry and G. A. Segal, *ibid*, 1967, 47, 158; I. H. Hillier, *J. Chem. Soc. (A)* 1969, 878.

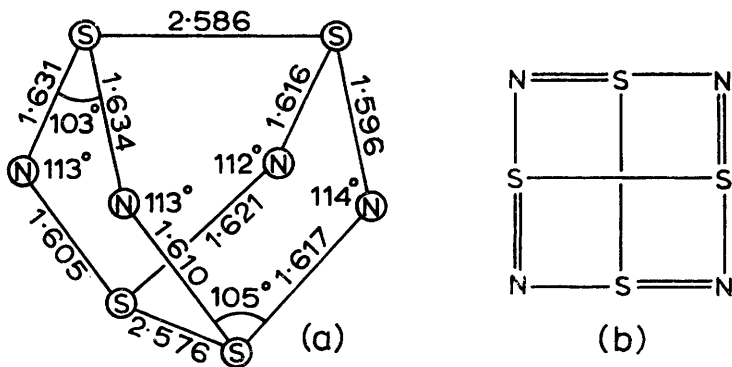
²² F. Bernardi and C. Zauli, *J. Chem. Soc. (A)*, 1968, 2633.

²³ F. Bernardi and C. Zauli, *J. Chem. Soc. (A)*, 1969, 867.

²⁴ I. H. Hillier and V. R. Saunders, *Chem. Comm.*, 1969, 1181, 1275.

²⁵ I. H. Hillier and V. R. Saunders, *Chem. Comm.*, 1970, 316; see also J. Demuyck and A. Veillard, *Chem. Comm.*, 1970, 873.

from X-ray crystallography and is shown in (IX a).²⁶ Braterman has rationalised its visible and u.v. spectra in terms of resonance structures with weak S-S bonding, in which S^{IV} and N^{III} oxidation states predominate. This is idealised in (IXb) and includes sulphur *d*, nitrogen *p*, and S-S bonding orbitals as part of a single resonating system.²⁷



(IX)

The structure of S₄N₄ (see ref. 27).

Cyclic phosphonitrilic halides (PNX₂)_n have been the subject of reviews by Paddock.²⁸ Six- to twelve-membered rings are formed with P-N distances of between 1.51 and 1.60 Å, while the single bond distance is 1.78 Å. The rings in (PNF₂)_n species tend to be planar but other species are non-planar when *n* > 3. The eight-membered ring contains stronger bonds than the six-membered; cyclooctatetraene, in contrast, has a smaller ring-bond energy than benzene, so suggesting an important role for *d* orbitals in the cyclic phosphorus compounds. Phosphonitrilic halides will differ from aromatic carbon compounds in that the bonds will be more polar due to the electronegativity difference between P and N, but in addition phosphorus *d* orbitals can π -bond with nitrogen *p* or *sp*-hybrid orbitals in two ways; in the local NPN plane (π_s or π_r) and at right angles to it (π_a or π).²⁹ In addition, exocyclic π -bonding is also possible. These have been described by Paddock and are illustrated in (X). The effect of increased mixing in of the *d*_{yz} orbital (π_a -bonding) is to reduce the expected differences between the trimeric (*x* = 3) and tetrameric (*x* = 4) species, so partly explaining the increased

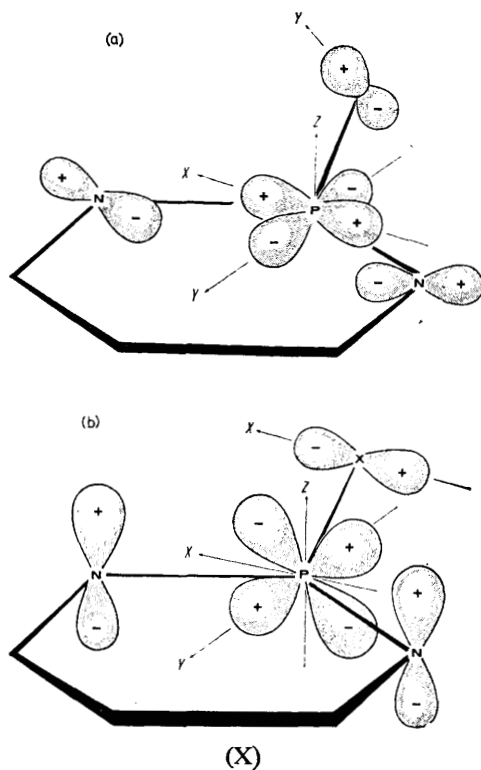
²⁶ B. D. Sharma and J. Donohue, *Acta Cryst.*, 1963, **16**, 891.

²⁷ P. S. Braterman, *J. Chem. Soc.*, 1965, 2297.

²⁸ N. L. Paddock, *Quart. Rev.*, 1964, **18**, 168; Royal Inst. Chem., Lecture series No. 2, 1962.

²⁹ C. R. Branton, C. E. Brion, D. C. Frost, K. A. R. Mitchell, and N. L. Paddock, *J. Chem. Soc. (A)*, 1970, 151.

stability found for the latter species. From a detailed analysis of the ring conformations, bond lengths, and spectra, Paddock concluded that (i) π electron energies in phosphonitrilic chlorides are of the order of 25–42 kJ/bond; (ii) the difference

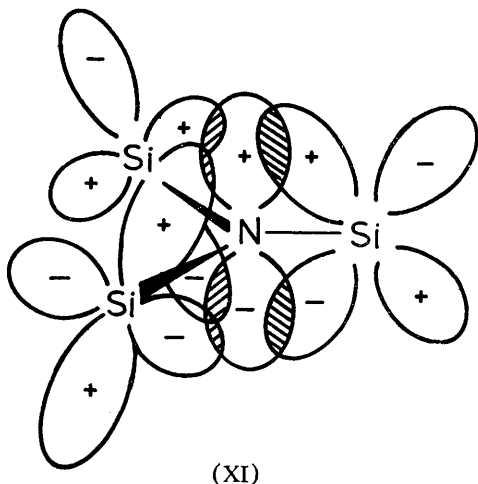


Overlap schemes of the atomic orbitals in $(\text{PNX}_2)_3$, (a) the π_s molecular orbitals, (b) the π_α molecular orbitals (see ref. 29).

in stability between trimeric and tetrameric chlorides is real and distinguishes $p-p_\pi$ systems, and (iii) some electron release to the phosphorus (*i.e.* $\text{N} \rightarrow \text{P}$ back-co-ordination) is apparent. In addition, he correlated the balance of π_α and π_s bonding with the possible ring conformations. In the most recent paper, semi-empirical MO calculations have shown that the most important π interactions involve the $d_{x^2-y^2}(\pi_s)$ and $d_{xz}(\pi_\alpha)$ orbitals. Assuming these π interactions, measured and calculated ionisation potentials are in reasonable agreement.²⁹

C. Trisilylamine and Related Molecules.—Trivalent nitrogen compounds of formula NR_3 are generally pyramidal with a lone pair in the apical position, *i.e.* sp^3 hybridised. While trimethylamine has this structure, trisilylamine, $\text{N}(\text{SiH}_3)_3$,

is planar.³⁰ This was originally explained by assuming that the nitrogen was sp^2 hybridised with the full p_z orbital at right angles to the plane of the molecule overlapping the empty d_{xz} or d_{yz} orbitals of the silicon atoms, since such overlap would be at a maximum when the molecule was planar (XI). A similar argument



The structure of $N(SiH_3)_3$.

could be used to explain the surprisingly large bond angle (144°) of $O(SiH_3)_2$ ³¹ or linear nature of $H_3Si-N-C-S$ ³² whereas the carbon analogues have expected bond angles of rather less than 109° . Further support for double bond character comes from bond lengths; in all the cases quoted the measured lengths are shorter than those calculated from the Schomaker–Stevenson equation as shown in the Table. Perkins has subjected trisilylamine to a semi-empirical MO calculation and concluded that $d \leftarrow p_\pi$ bonding exists with each $Si-N_\pi$ bond having a mean energy which may be as high as 65 kJ mol^{-1} .³³

The essentially simple explanation given above received a setback when $P(SiH_3)_3$ and $As(SiH_3)_3$ were shown conclusively to be pyramidal (see Table),³⁴ as expected for simple σ -bonded compounds. Further, $S(SiH_3)_2$ is bent with an unexceptional bond angle of 97° ³⁵ and bond lengths for all compounds with central elements from the second period do not differ much from those

³⁰ K. Hedberg, *J. Amer. Chem. Soc.*, 1955, **77**, 6491; A. R. Conrad and B. Beagley, unpublished result.

³¹ A. Almennigen, O. Bastiansen, V. Ewing, K. Hedberg, and M. Traettenberg, *Acta. Chem. Scand.*, 1963, **17**, 2455.

³² D. R. Jenkins, R. Kewley, and T. M. Sugden, *Trans. Faraday Soc.*, 1962, **58**, 1284.

³³ P. G. Perkins, *Chem. Comm.*, 1967, 268.

³⁴ B. Beagley, A. G. Robiette, and G. M. Sheldrick, *J. Chem. Soc. (A)*, 1968, 3002, 3006.

³⁵ A. Almennigen, K. Hedberg, and R. Seip, *Acta Chem. Scand.*, 1963, **17**, 2264.

predicted assuming no double bond character. The fact that a molecule such as $\text{P}(\text{SiH}_3)_3$ is not planar does not necessarily rule out substantial $d-p_\pi$ overlap, but when the angle becomes smaller than tetrahedral, π overlap will decrease rapidly. Therefore the values of bond angles coupled with reasonable bond lengths do suggest that $d \leftarrow p_\pi$ bonding is not significant in phosphines, arsines, or sulphides. Bond shortening in the nitrides, oxides, and similar compounds is, however, significant. This can be interpreted in two ways. Either (i) $3d \leftarrow 2p_\pi$ bonding is more effective than $3d \leftarrow 3p_\pi$ (or $3dp$ -hybrid) as a result of differences in the size of $2p$ and $3p$ orbitals, or (ii) other effects such as ionic character are important. The latter interpretation is supported by the linear structures of Li_2O ³⁶ and RbOH . In neither of these cases would π -bonding be anticipated, and the linear structure may be explained by ionic repulsions overcoming lone-pair repulsions. In silylamine it could be that, as a result of the polar nature of the Si—N bonds, the silicon atoms have large δ^+ charges which will repel one another strongly, so encouraging a planar configuration. By a similar argument, $(\text{SiH}_3)_2\text{O}$ would approach linearity but, since the residual charges in phosphines and sulphides will be smaller, the electrostatic repulsions will also be smaller. However, when the molecules are forced into planar or linear configurations there must be increased $d-p$ overlap giving weak π -bonding which would stabilise these structures and shorten the bonds. In addition, bond shortening of approximately 0.03 Å is also to be expected from changes in hybridisation necessitated by the changes in structure. The differences in stereochemistry between $\text{N}(\text{SiH}_3)_3$ and $\text{P}(\text{SiH}_3)_3$ and similar molecules can therefore be thought of as due to different degrees of ionic character coupled with more effective π -overlap between $3d-2p$ orbitals than between $3d-3p$. Silicon hydrides and their derivatives have recently been reviewed by Aylett.³⁷

Since very precise structure determinations, coupled with more reliable theoretical calculations, are now being carried out the problem of $d \leftarrow p_\pi$ bonding in non-metals is likely to be resolved in the near future.

5 $d-d_\pi$ and $d-d_\delta$ Overlap

The $\text{Re}_2\text{Cl}_8^{2-}$ ion has the structure (XII). The Re—Re bond length is very short (2.24 Å), the chlorine atoms are eclipsed, and it is diamagnetic.³⁸ The technetium analogue is similar with an even shorter bond length of 2.13 Å.³⁹ The M—M distances in the bulk metals are 2.75 and 2.72 Å respectively. The structure and properties have been explained by formation of an M—M bond of bond order 4; a $d-d_\sigma$ bond formed by overlap of d_{z^2} orbitals, two $d-d_\pi$ bonds from the d_{xz} and d_{yz} orbitals, and a $d-d_\delta$ bond by face-to-face overlap of the d_{xy} orbitals. Cotton has applied a simple MO treatment to the $\text{Re}_2\text{X}_8^{2-}$ ion assuming overlap of this type and found the treatment realistic and internally consistent with ionic

³⁶ D. White, K. S. Seshadri, D. F. Dever, D. E. Mann, and M. J. Linevsky, *J. Chem. Phys.*, 1963, 39, 2463.

³⁷ B. J. Aylett, *Adv. Inorg. Chem. Radiochem.*, 1968, 11, 249.

³⁸ F. A. Cotton and C. B. Harris, *Inorg. Chem.*, 1965, 4, 330.

³⁹ F. A. Cotton and W. K. Bratton, *J. Amer. Chem. Soc.*, 1965 87, 921.

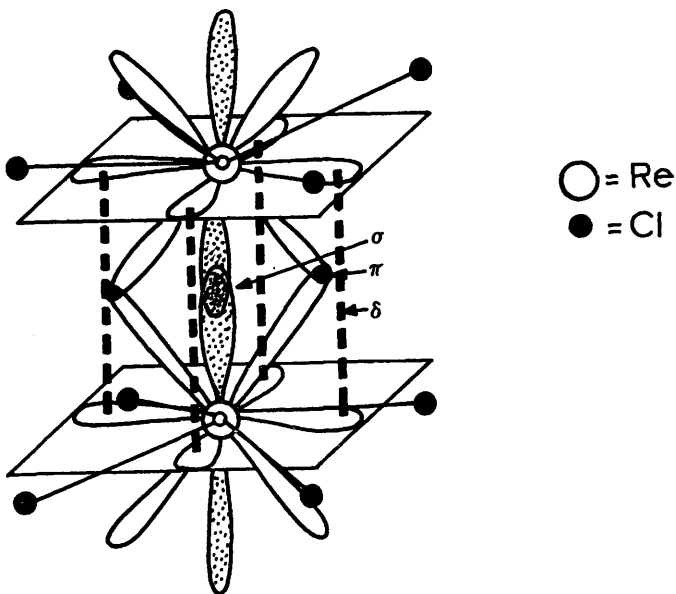
Multiple Bonding and Back-co-ordination in Inorganic Compounds

Table Geometries of some simple molecules (e.s.d.'s in parentheses)

<i>Molecules</i>	<i>Central bond angle (degrees)</i>	<i>Bond length (Å)</i>	<i>Reference</i>
Li ₂ O	linear	1.59	36
(CH ₃) ₂ O	111.7(3)	1.410(3)	<i>a</i>
(SiH ₃) ₂ O	144.1(9)	1.634(2)	31
(GeH ₃) ₂ O	126.5(3)	1.766(4)	<i>b</i>
(CH ₃) ₂ S	98.9(2)	1.802(2)	<i>c</i>
(SiH ₃) ₂ S	97.4(7)	2.136(2)	35
(GeH ₃) ₂ S	98.9(1)	2.209(4)	<i>b</i>
(CH ₃) ₂ Se	96.2	1.977(12)	<i>d</i>
(SiH ₃) ₂ Se	96.6(7)	2.274(4)	<i>e</i>
CH ₃ .O.SiH ₃	120.6	1.640(Si—O)	<i>f</i>
C ₆ H ₅ .O.SiH ₃	121	1.648(Si—O)	<i>f</i>
(CH ₃) ₃ N	110.6(6)	1.454(2)	<i>g</i>
(SiH ₃) ₃ N	119.6(5)	1.736(2)	30
(GeH ₃) ₃ N	planar	1.836(5)	<i>h</i>
(CH ₃) ₃ P	98.6(3)	1.847(3)	<i>i</i>
(SiH ₃) ₃ P	96.5	2.247	34
(GeH ₃) ₃ P	95.4(1)	2.380(3)	<i>j</i>
(CH ₃) ₃ As	96(5)	1.98(2)	<i>k</i>
(SiH ₃) ₃ As	93.8	2.352	34
(SiH ₃) ₃ Sb	88.6(2)	2.557(4)	<i>j</i>
CH ₃ .NCS	142	1.47(N—CH ₃)	<i>l</i>
SiH ₃ .NCS	linear	1.714(Si—N)	32
HN(SiH ₃) ₂	planar	1.725(3)(Si—N)	<i>m</i>
HN[Si(CH ₃) ₃] ₂	planar	1.735 (Si—N)	<i>m</i>
BF ₂ N(SiH ₃) ₂	planar	1.737(4) (Si—N)	<i>n</i>
CH ₃ N(SiH ₃) ₂	planar	1.725(3) (Si—N)	<i>n</i>
(CH ₃) ₂ NSiH ₃	111.1 (CNC)	1.715	<i>o</i>
	120.0 (SiNC)		

^aU. Blukis, P. H. Kasai, and R. J. Myers, *J. Chem. Phys.* 1963, **38**, 2753; ^bC. Glidewell, D. W. H. Rankin, A. G. Robiette, G. M. Sheldrick, B. Beagley, and S. Craddock, *J. Chem. Soc. (A)*, 1970, 315; ^cL. Pierce and M. Hayashi, *J. Chem. Phys.*, 1961, **35**, 479; ^dE. Goldish, K. Hedberg, R. E. March, and V. Schomaker, *J. Amer. Chem. Soc.*, 1955, **77**, 2948; ^eA. Almenningen, L. Fernholt, and H. M. Seip, *Acta Chem. Scand.*, 1968, **22**, 51; ^fC. Glidewell, D. W. H. Rankin, A. G. Robiette, G. M. Sheldrick, B. Beagley, and J. M. Freeman, *J. Mol. Structure*, 1970, **5**, 417; ^gB. Beagley and T. G. Hewitt, *Trans. Faraday Soc.*, 1968, **64**, 256; ^hC. Glidewell, D. W. H. Rankin, and A. G. Robiette, *J. Chem. Soc. (A)*, 1970, 2935; ⁱL. S. Bartell and L. O. Brockway, *J. Chem. Phys.*, 1960, **32**, 512; ^jD. W. H. Rankin, A. G. Robiette, G. M. Sheldrick, B. Beagley, and T. G. Hewitt, *J. Inorg. Nuclear Chem.*, 1969, **31**, 2351; ^kH. D. Springall and L. O. Brockway, *J. Amer. Chem. Soc.*, 1938, **60**, 996; ^lC. I. Beard and B. P. Dailey, *J. Amer. Chem. Soc.*, 1949, **71**, 929; ^mA. G. Robiette, G. M. Sheldrick, W. S. Sheldrick, B. Beagley, D. W. J. Cruickshank, J. J. Monaghan, B. J. Aylett, and I. A. Ellis, *Chem. Comm.*, 1968, 909; ⁿC. Glidewell, D. W. H. Rankin, A. G. Robiette, and G. M. Sheldrick, *J. Mol. Structure*, 1969, **4**, 215; 1970, **5**, 423; ^oC. Glidewell, D. W. H. Rankin, A. G. Robiette, and G. M. Sheldrick, *J. Mol. Structure*, 1970, **6**, 231.

geometry, magnetic properties, and spectra.⁴⁰ While the δ -bond would be weak compared to the σ and π -bonds, it is strong enough to prevent rotation around the M—M bond and to hold the chlorine atoms in the energetically unstable



(XII)

δ -Bonding in the $\text{Re}_2\text{Cl}_8^{2-}$ ion.

eclipsed conformation. Cotton estimated the energy of the δ -bond to be (within a factor of two) 370 kJ mol^{-1} . If bond order for a number of complexes containing Re—Re bonds is plotted against bond length, a smooth curve is obtained, assuming a bond order of 4 for $\text{Re}_2\text{X}_8^{2-}$. The structure of $\text{Li}_4\text{Cr}_2(\text{CH}_3)_8 \cdot (\text{C}_4\text{H}_8\text{O})_4$ is similar to that of $\text{Re}_2\text{X}_8^{2-}$. The Cr—Cr bond length is only 1.980 \AA and the methyl groups are in eclipsed positions, 3.26 \AA apart. The molecule is stabilised by co-ordination of the methyls to lithium.⁴¹

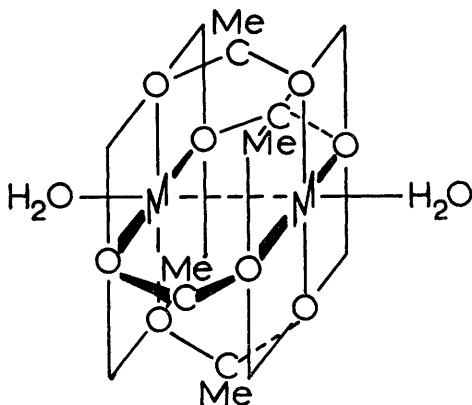
Metal-metal δ -bonds formed by overlap of $d_{x^2-y^2}$ orbitals are also suspected in the dimeric acetates, M_2Ac_4 where $\text{M} = \text{Cu}, \text{Cr}, \text{Mo},$ or Rh .⁴² Evidence for spin pairing in the M—M bond (XIII) is mainly magnetic; it is virtually complete in the Cr, Mo, and Rh species but only partial in the copper complex. Spin pairing, however, is no evidence of a strong bond since an interaction energy as low as

⁴⁰ F. A. Cotton, *Inorg. Chem.*, 1965, 4, 337.

⁴¹ J. Krause, G. Marx, and G. Schodl, *J. Organometallic Chem.*, 1970, 21, 159.

⁴² B. N. Figgis and R. L. Martin, *J. Chem. Soc.*, 1956, 3837; R. L. Martin, 'New Pathways in Inorganic Chemistry', ed. Ebsworth, Maddock, and Sharpe, Cambridge U.P., 1968, p. 175.

about 10 kJ is sufficient to induce it. Similar structures are assumed for many metal alkanoates.



(XIII)

The structure of dimeric acetates, $M_2Ac_4, 2H_2O$.

It is possible that cyclic structures such as S_8 or $(SiMe_2)_x$, $(PPh)_x$, and $(AsPh)_x$ where x can be 4, 5, or 6, may be stabilised by $d-d_\pi$ overlap forming a delocalised system similar to the phosphonitrilic halides. Evidence for this delocalisation comes from e.s.r. studies of the anion $[Si(CH_3)_2]_6^-$.⁴³

6 Back-co-ordination in Metal Complexes

Back-co-ordination is a concept used widely when considering metal complexes, in particular those formed between class (b)⁴⁴ or 'soft'⁴⁵ ligands and 'soft' acceptors. The concept has provided a pictorial representation of the structures, stabilities, and reactions of a wide range of organometallic compounds which a few years ago would have been thought non-existent, although it must be admitted that some unlikely compounds have been known for a long time, e.g. Zeise's salt ($PtCl_3 \cdot C_2H_4^-$). Back-co-ordination has therefore been of considerable assistance in the teaching and exploitation of a whole new field of inorganic chemistry. However, in practice, the true extent of back-co-ordination and its thermodynamic importance may have been over-rated, and explanations in terms of covalent character and polarisation, which superficially can be equally readily envisaged, may have been overlooked.⁴⁶

⁴³ G. R. Husk and R. West, *J. Amer. Chem. Soc.*, 1965, **87**, 3993.

⁴⁴ S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev.*, 1958, **12**, 265.

⁴⁵ R. G. Pearson, *Science*, 1966, **151**, 172.

⁴⁶ R. J. P. Williams and J. D. Hale, *Structure and Bonding*, 1966, **1**, 249.

Experimental evidence for back-co-ordination is generally contentious since a variety of interpretations are usually available. As with covalent π -bonding, back-co-ordination should be accompanied by an increase in bond force constants and a decrease in interatomic distance. However, interatomic distances cannot be measured precisely by X-ray diffraction methods because of the high atomic numbers of the metal ions, and metal-ligand bands in the i.r. are often broad and difficult to assign reliably. Experimental evidence which has been interpreted in terms of back-co-ordination will be outlined in the next section.

Explanations of the stability of silver-olefin and platinum-olefin complexes in terms of $d-\pi_{\mu}^*$ overlap were made by Dewar⁴⁷ and Chatt and Duncanson,⁴⁸ and the stability of complexes of class (b) acceptors with heavy donor atoms has been attributed to $d \rightarrow d_{\pi}$ bonding by Chatt and co-workers.⁴⁴ In each case back-co-ordination from filled metal $d(t_2)$ orbitals to empty ligand π^* or $d(t_2)$ orbitals was assumed [see (V—VII)]. When the ligand is CO or CN⁻ it will have to be colinear with the metal ion (VI) while olefin ligands will have to be at right angles (VII) if overlap is to be maximised. It would therefore be anticipated that the larger the metal ion, the more stable would be the pi-olefin complex (where pi- is used as a conventional symbol rather than defining a particular type of bond). It must be remembered that all of these classes of compounds require stable σ co-ordinate bonds, using either ligand pairs or electrons in olefin bonding orbitals; the π -bond acts only as a mechanism for transferring charge back to the ligands which, in normal circumstances, would be thought of as only a weak donor. Co-ordination is not limited to individual olefinic bonds; pi-complexes with C=S bonds are known⁴⁹ and there is a vast field of chemistry in which co-ordination with delocalised aromatic systems is clearly present, e.g. sandwich molecules such as ferrocene. Here again, bonding to the metal can be described as σ -donor and π -acceptor overlap using various combinations of delocalised ligand orbitals.^{50,51} Back-co-ordination in these various classes of compounds is best classified according to the types of overlap suspected, whether $d \rightarrow d_{\pi}$ (V), $d \rightarrow \pi_{\pi}^*$ (VI), or $d \rightarrow \pi_{\mu}^*$ (VII).

7 Detection of Back-co-ordination

Four major lines of argument have been used. They are:

- (a) The *trans* effect.
- (b) N.m.r. coupling constants.
- (c) The i.r. spectra of complexes, particularly the stretching frequencies, ν_{C-O} , of carbonyl complexes.
- (d) Thermodynamic properties, particularly the quantitative expression of inductive effects by means of Taft or Hammett functions.

These arguments are certainly not independent. Basically they depend on either

⁴⁷ M. J. S. Dewar, *Bull. Soc. chim. France*, 1951, **18**, C71.

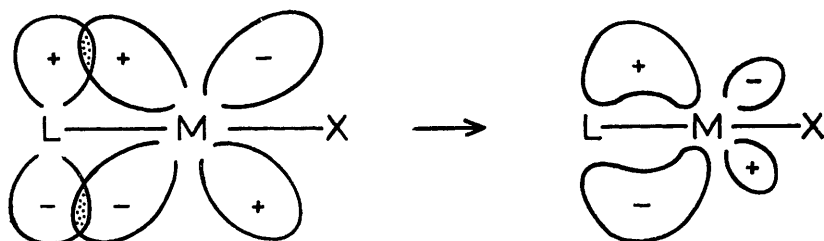
⁴⁸ J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 1953, 2939.

⁴⁹ M. Baird, G. Hartwell, R. Mason, A. I. M. Rae, and G. Wilkinson, *Chem. Comm.*, 1967, 92.

⁵⁰ D. A. Brown, *Transition Metal Chem.*, 1966, **3**, 1.

⁵¹ M. Baird, *Progr. Inorg. Chem.*, 1968, **9**, 1.

(a) the influence of a ligand, L, which is able to accept electrons from a $d(t_2)$ orbital of a metal on the lobes of that orbital *trans* to L (see XIV), or (b) the assumption that inductive effects are transmitted along σ -bonds and that their



(XIV)

The *trans* influence of a ligand able to π -bond with M.

influence on π back-bonds is not related linearly to their influence on σ -bonds. In addition to the specific approaches enumerated above, methods of detecting covalent multiple bonding will also be applicable. In particular Churchill and Mason have reviewed the bond lengths and geometries of organometallics⁵² and several workers have used dipole moments to argue both for and against back-bonding.⁵³

8 $d \rightarrow d$ Back-co-ordination

This type of multiple bonding can only take place with heavy donor atoms (*i.e.* second period and above) having suitable d orbitals. As with all other forms of back-co-ordination from d orbitals it will be strongest with metals with well-filled d orbitals (preferably of a high principal quantum number) and a low charge. Evidence supporting back-co-ordination is provided by (i) the high stability of these complexes compared to their analogues with donor atoms from the first period, (ii) the ability of heavy donor atoms to stabilise low oxidation states, (iii) the effect of electronegative substituents on the donor giving an apparent increase in π acceptor properties for a series such as PR_3 , PCl_3 , PF_3 , (iv) the high *trans*-effect of ligands such as SiR_3^- or SnCl_3^- , and (v) the ^{195}Pt -P n.m.r. spin coupling constants or ^{19}F n.m.r. shielding parameters.

While back-co-ordination provides an attractive explanation for many of these phenomena, definite evidence is surprisingly weak and alternative explanations are generally possible. Metals with nearly full d orbitals are typically soft and

⁵² M. R. Churchill and R. Mason, *Adv. Organometallic Chem.*, 1967, 5, 93.

⁵³ J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1960, 1378; M. Bigorgne and C. Messier, *J. Organometallic Chem.*, 1964, 2, 79.

polarising; similarly, heavy donor atoms are also soft and readily polarised, giving the M—L bond a high degree of covalent character. Williams and Hale, while avoiding the use of vague terms such as 'soft' have interpreted the class (a)–(b) character of a wide range of ligands in terms of factors influencing covalent character, without introducing any form of back-co-ordination.⁴⁶ In addition, Ahrland has summarised a large body of data in the generalisation that soft–soft interactions are basically covalent in nature, stabilised by favourable enthalpy changes, while hard–hard interactions are basically ionic and therefore entropy stabilised.⁵⁴ Soft–hard interactions would therefore tend to be discouraged, explaining why heavy donor atoms have little affinity for weakly polarising acceptors with electron configurations of an inert gas, such as alkali-metal or alkaline-earth metal ions. The problems of covalent character and back-co-ordination have been resolved by Jorgensen by thinking of charge transfer into continuum orbitals of the ligand.⁵⁵ Very soft ligands such as PR_3 or SR_2 have continua starting at lower energies than the hard analogues, NR_3 or OR_2 , and charge transfer into the continuum can be thought of as polarisation. This explanation is conceptually very difficult to grasp.

A. *trans* Effect.—Discussions of the *trans* effect probably illustrate the conflicting evidence for back-co-ordination most strongly since some ligands, alkyl and the hydrido-group in particular, are incapable of forming π -bonds yet they have extremely large *trans* effects, so that any explanation in terms of π -bonding can only be a partial one. The *trans* effect can apply to both *trans* bond weakening (lengthening) and *trans* bond labilising. While the former refers to the energy required for bond breaking and the latter refers to the energy difference between the reactants and the activated complex, similar arguments appear to apply to both. The π -bonding explanation considers the effect of a ligand able to π -bond with the metal on the metal $d(t_2)$ orbitals and is well summarised by Basolo and Pearson.⁵⁶ Alternative explanations in terms of σ -bonding only have been given by Venanzi,⁵⁷ (based on Syrkin's arguments) and by Gray and Langford.⁵⁸ In the latter case, the *trans* effect was correlated with the magnitude of the M–L and M–N σ overlap integrals where the ligands L and X are *trans* to one another. The argument was that, if the σ -donor orbital on L has a greater overlap with the metal p_σ orbital than does the σ orbital of X, then the M—L bond will be strengthened at the expense of the M—X bond. These overlap calculations have now been extended by McWeeny, Mason, and Towl to give a *trans*-effect order basically the same as that deduced from a study of bond lengths in Pt^{II} complexes.⁵⁹ Additional support for the claim that the *trans* effect is inductive (σ) in origin rather than mesomeric (π) comes from a comparison of the *trans* effects of SiPh_3^- and SiPh_2Me^- . The latter has a larger effect, while SiMe_3^- appears to have

⁵⁴ S. Ahrland, *Structure and Bonding*, 1966, 1, 207; 1968, 5, 118.

⁵⁵ C. K. Jorgensen, *Structure and Bonding*, 1967, 3, 106.

⁵⁶ F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions', Wiley, 1967.

⁵⁷ L. M. Venanzi, *Chem. in Britain*, 1968, 4, 162.

⁵⁸ M. B. Gray and C. Langford, 'Ligand Substitution Processes', Benjamin, 1966

⁵⁹ R. McWeeny, R. Mason, and A. D. C. Towl, *Discuss. Faraday Soc.*, 1969, No 47, p. 20.

such a large effect that complexes cannot be formed.⁶⁰ Were back bonding important the opposite would be expected. It therefore appears that either σ -donor or π -acceptor properties may be important, the predominant property depending on the particular ligand. Criteria for choice will be discussed later.

B. N.m.r. Spectra.—Evidence from n.m.r. spectroscopy is contradictory. The measurement of Pt-P coupling constants in planar Pt^{II} complexes originally led to the conclusion that Pt-P π -bonding was important,⁶¹ but more detailed study of the factors contributing to the constants led to the conclusion that it is not necessary to invoke π -bonding to explain the differences in physical and chemical properties between *cis*- and *trans*-isomeric Pt^{II} and Pt^{IV} complexes.⁵⁷ This conclusion is based on the argument that the magnitude of (Pt-P) coupling constants is predominantly due to the Fermi contact term, indicating that changes in coupling constants reflect directly changes in the *s*-electron wave-function since only these have finite values at the nucleus, where nuclear energies can be influenced. As a result of their symmetry, *s* orbitals can take part in σ -bonding only. Coupling constants are therefore a direct measure of changes in the M \leftarrow L _{σ} bond and will be largely influenced by inductive effects. If extensive M \rightarrow L _{π} back-co-ordination is present the M \leftarrow L _{σ} bond may be strengthened by a synergic effect, and back-co-ordination *via* the bond *trans* to L restricted. To a first approximation, *cis* bonds should be unaffected. This synergic influence, however, would be a secondary effect and should be influenced markedly by the oxidation state of the metal. Since coupling constants for ¹⁹⁵Pt^{II} and ¹⁹⁵Pt^{IV} are close to the expected ratio of 3:2 it may be argued that this synergic mechanism is unimportant, making the Pt-P bond predominantly σ in nature. If π -bonding is unimportant in Pt^{II} complexes, it would be expected to be of even less importance with other metals. Hydrogen shifts in the complexes π -C₅H₅(CO)₃FeSnR₃ have also been interpreted in terms of inductive (σ) effects of the substituents, R.⁶² In contrast to this, *J*(P-W) values in the complexes PR₃W(CO)₅ have been interpreted as indicating a σ bond strengthened synergically by π interaction.⁶³ A correlation was found between *J*(W-P) values and the carbonyl stretching frequencies and it was suggested that *J*(W-P) is a better measure of π -acceptor ability than ν_{C-O} although there does not appear to be a convincing reason for this conclusion.

The use of coupling constants to detect π -bonding is not entirely satisfactory since, as explained earlier, they are only measures of changes in *s*-electron wave-functions. No matter how significant changes in π -bonding are, n.m.r. spectroscopy will not detect them directly but only by their influence on the *s* or *sp*-hybrid orbitals. An alternative use of n.m.r. data has been made by Parshall, who has argued that ¹⁹F shielding parameters in *m*-F·C₆H₄·PtR₂X complexes will depend on the σ donor properties of X while the parameters for the *para* com-

⁶⁰ J. Chatt, C. Eaborn, and S. Ibekwe, *Chem. Comm.*, 1966, 700.

⁶¹ A. Pidcock, R. E. Richards, and L. M. Venanzi, *Proc. Chem. Soc.*, 1962, 184.

⁶² R. Ugo, S. Cenini, and F. Bonati, *Inorg. Chim. Acta*, 1967, 1, 451.

⁶³ S. O. Grim, P. R. McAllister, and R. M. Singer, *Chem. Comm.*, 1969, 38.

pounds will depend on the π -acceptor nature of X, since the metal $5d_{xy}$ orbital overlaps not only with the p_{π} orbital of the carbon atom bound to Pt but also with X.⁶⁴ The results confirm that the methyl group is not π -bonding, while the aryl group is. In addition, he explains the large *trans* effect of SnCl_3^- in terms of strong π -acceptor properties.

C. Infrared Spectra.—Spectral evidence is equally ambiguous. The argument most frequently used assumes detectable $d \rightarrow \pi_{\pi}^*$ back-co-ordination in the M—CO bonds, giving resonance hybrids such as $\text{M}-\text{C}\equiv\text{O} \leftrightarrow \text{M}=\text{C}=\text{O}$. Any multiple bond character between the metal and a ligand *trans* to the CO will limit the ability of the metal $d(t_2)$ orbitals to donate to the CO, so weakening the M—CO bond, stabilising the $\text{M}-\text{C}\equiv\text{O}$ hybrid, and causing a concomitant increase in the C—O force constant: which in turn will tend to increase the frequency $\nu_{\text{C-O}}$. Because of the geometry of $d(t_2)$ orbitals, this frequency should be influenced by the extent of back-co-ordination in the M—L bond *trans* to the CO rather than *cis*, where different d orbitals would be involved.

Values for $\nu_{\text{C-O}}$ in complexes such as $\text{L}_3\text{M}(\text{CO})_3$, where L covers a range of heavy donor atoms, suggest extensive $\text{M} \rightarrow \text{L}$ back-co-ordination, but $\nu_{\text{C-O}}$ is not a direct measure of force constants, k , and changes in the group L other than changes in π -bonding could influence both $\nu_{\text{C-O}}$ and $k_{\text{C-O}}$. Bigorgne has correlated the $\nu_{\text{C-O}}$ values for series of complexes $\text{Ni}(\text{CO})_{4-n}(\text{PR}_3)_n$ with the Taft functions of the substituents R.⁶⁵ He found a linear relationship and concluded that either $\text{M} \rightarrow \text{L}_{\pi}$ bonding was negligible or was constant and independent of the substituent. Similar linear relationships between $\nu_{\text{C-O}}$ and Taft functions have been found for complexes of the type $(\text{CO})_5\text{Mn}\cdot\text{MR}_3$, where M = C, Si, Ge, or Pb.⁶² Angelici and Malone have also explained $\nu_{\text{C-O}}$ values in a series of complexes $\text{LW}(\text{CO})_5$ (L = amine, pyridine, and phosphine) without introducing π -bonding.⁶⁶ In this case, force constants were calculated and related to the basicities ($\text{p}K$ values) of the ligands. Since Taft functions are obtained from $\text{p}K$ values, the argument is similar to that of Bigorgne, and Ugo and co-workers.

Not all recent interpretations of carbonyl force constants have discounted π -bonding, however. Cotton and Kraihanzel have argued for extensive π -bonding between phosphines and $\text{M}(\text{CO})_5$, where M = Cr, Mo, and W.^{67,68} Graham has analysed the *trans* and *cis* force constants in the complexes $\text{LMn}(\text{CO})_5$ and $\text{LMo}(\text{CO})_5$.⁶⁹ He suggests that, for changes in inductive effect as L is changed, the k_{CO} values for all CO groups will change by the same amount, while differences in π -bonding between two ligands will affect the *trans* force constant twice as much as the *cis*. On this basis he constructed relative σ -donor and π -acceptor characters for a range of ligands and concluded that most heavy donor atoms were

⁶⁴ G. W. Parshall, *J. Amer. Chem. Soc.*, 1966, **88**, 704.

⁶⁵ M. Bigorgne, *J. Inorg. Nuclear Chem.*, 1964, **26**, 107.

⁶⁶ R. J. Angelici and M. D. Malone, *Inorg. Chem.*, 1967, **6**, 1731.

⁶⁷ F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, 1962, **84**, 4432.

⁶⁸ F. A. Cotton, *Inorg. Chem.*, 1964, **3**, 702.

⁶⁹ W. A. Graham, *Inorg. Chem.*, 1968, **7**, 315.

both strong π -acceptors and σ -donors; possibly as a result of synergic effects. Graham's conclusions appear to be contrary to those of Angelici and Malone and the difference must result from the different ways in which they treated their data. If strong π -bonds can markedly strengthen σ -bonds by a synergic effect, it could be that methods which detect σ -bonding only, such as the use of Taft functions, fail to identify the cause of the changes in σ -bond strength. The underlying cause may be changes in back π -bonding, but in this case it is difficult to understand why linear relationships are found. Stewart and Treichel have compared Graham's conclusions with those of Angelici and Malone and argue that, in the complexes $\text{PR}_3\text{W}(\text{CO})_6$, while P-W bonding is important it is not possible to explain both *cis* and *trans* $\nu_{\text{C-O}}$ values in terms of σ -bonding *alone*.⁷⁰ The only suitable interpretation is σ - and π -bonds reinforcing one another to give an observed effect which happens to vary approximately linearly with changes in inductive effect. Stretching frequencies other than $\nu_{\text{C-O}}$ have been used as indicators for back-co-ordination. For instance $\nu_{\text{C}\equiv\text{C}}$ in complexes of $\text{Ph}_2\text{P}\cdot\text{C}\equiv\text{C}\cdot\text{PPh}_2$ have been used as a measure of π -bonding in the P-M bonds, but no allowance was made for changes in the electronegativity of the metal.⁷¹

D. Thermodynamic Properties.—A linear free-energy relationship between the stability constant of a metal complex, K_{ML} , and that of the proton complex, K_{HL} , as the ligand L is varied, was first demonstrated by Irving and Rossotti.⁷² For similar ligands the gradient of a graph of $\log K_{\text{ML}}$ vs $\log K_{\text{HL}}$ would be expected to be unity if bonding were similar in both sets of species, and Williams and co-workers first suggested that deviations from unity may be due to π -bonding in the metal complexes.⁷³ Electron-repelling groups ($+I$) bonded to a donor atom should increase its σ donor and decrease its π -acceptor properties; such inductive effects may be expressed quantitatively by the Taft functions of the substituents or, in aromatic systems, by suitable Hammett functions. Following this argument, Da Silva and Calado produced a well-reasoned and quantitative estimation of the extent of π -bonding by correlating changes in $\log K_{\text{ML}}$ and $\log K_{\text{HL}}$, as substituents on the ligand are varied, with the Hammett functions of the substituents.⁷⁴ The basic assumption of their argument was that the proton is incapable of π -bonding, so that, if changes in substituents affect the stability of a metal complex more than that of the proton complex, back-co-ordination must be present in the former since this would oppose the normal inductive effects of substituents as expressed by their Hammett functions. However, silver is a very soft acceptor but in all cases electron-repelling ($+I$) substituents on the ligands $\text{R}\cdot\text{C}_6\text{H}_4\cdot\text{As}(\text{CH}_2\text{CO}_2\text{H})_2$, $\text{R}\cdot\text{C}_6\text{H}_4\cdot\text{XCH}_2\text{CO}_2\text{H}$ (where $\text{X} = \text{S}$ and Se), $\text{R}\cdot\text{SCH}_2\text{CO}_2\text{H}$, and $\text{R}\cdot\text{SC}_6\text{H}_4\text{CO}_2\text{H}$ increase the stability of the silver complexes relative to those of the unsubstituted ligands, $\log K$ values varying linearly with

⁷⁰ R. P. Stewart and P. M. Treichel, *Inorg. Chem.*, 1968, 7, 1942.

⁷¹ A. J. Carty and E. Efraty, *Chem. Comm.*, 1968, 1559.

⁷² H. M. Irving and H. Rossotti, *Acta Chem. Scand.*, 1956, 10, 72.

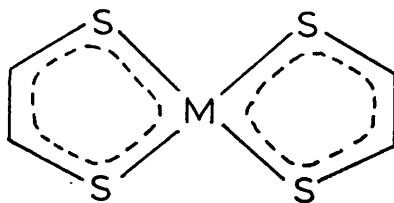
⁷³ J. G. Jones, J. B. Poole, J. C. Tomkinson, and R. J. P. Williams, *J. Chem. Soc.*, 1958, 2001.

⁷⁴ J. Da Silva and J. G. Calado, *J. Inorg. Nuclear Chem.*, 1964, 86, 4594.

the inductive effects of the substituents, R.⁷⁵ The corresponding proton complexes are too weak to detect quantitatively, so that Da Silva and Calado's reasoning cannot be applied. The fact that all of the free-energy relationships appear to be linear indicates that either inductive (σ) effects only are operative or, if π -bonding is present, it also varies linearly with inductive effects. Hence the ability of substituents to influence proton complexes more than metal complexes may well be a result of very different degrees of covalent character and polarisation in two very different types of complex. Further applications of linear free-energy relationships will be discussed in the section on $d \rightarrow \pi^*$ back-co-ordination.

If back-co-ordination involves the transfer of electrons from metal d orbitals, ionisation potentials of these electrons should be of quantitative importance.⁷⁶ In the zerovalent metals Ni, Pd, and Pt this would make nickel (5.8 eV) a better π -donor than Pd or Pt (8.3 eV approximately). However, the electron is promoted rather than ionised, so that the promotion energy $d^{10} \rightarrow d^9s$ should be more meaningful. The values Ni = 1.72, Pd = 4.23, and Pt = 3.28 eV again oppose the normal assumption that Pt is a better π -donor than Ni, showing that softness depends more on polarisability, well-filled d orbitals, and the density of adjacent energy states than on ionisation and simple $M \rightarrow L$ electron transfer.

Some sulphur ligands which may possibly form strong π -bonds with metal ions are the 1,2-dithiolenes, the chemistry of which has recently been reviewed by McCleverty.⁷⁷ The bonding in these complexes is complicated and is best represented by the delocalised form shown in (XV) where it is difficult to assign



(XV)

an oxidation state to the metal or a bond order to the M—S bond. Magnetic and spectral properties of many of the complexes lead to the conclusion that the sulphur atoms have an intermediate 'thioketo-thiol' character with M—S bond orders markedly greater than one. The spectra and electronic structures of sulphur-containing ligands, both 'innocent' and 'suspect' (*e.g.* conjugated ligands such as dithiolenes) have recently been reviewed by Jorgensen.⁷⁸

⁷⁵ L. D. Pettit, C. Sherrington, and R. J. Whewell, *J. Chem. Soc. (A)*, 1968, 2204; L. D. Pettit and C. Sherrington, *ibid*, 1968, 3078; L. D. Pettit and A. Royston, *ibid*, 1969, 1570.

⁷⁶ R. Ugo, *Co-ordination Chem. Rev.*, 1968, 3, 319.

⁷⁷ J. A. McCleverty, *Progr. Inorg. Chem.*, 1968, 10, 49.

⁷⁸ C. K. Jorgensen, *Inorg. Chim. Acta, Rev.*, 1968, 2, 65.

9 $d \rightarrow \pi^*$ Back-co-ordination

The stability of complexes formed between class (b) metals and the isoelectronic ions, CO, CN⁻, and NO⁺ is generally attributed to $d \rightarrow \pi^*$ bonding (VI). Although the CN⁻ ion is basic and able to act as a σ -donor, CO and NO⁺ are neutral and acidic respectively. Since they form stable complexes there must be some factors which enhance their donor properties, and the synergic effect of back-co-ordination is an attractive explanation.

Evidence for extensive back-co-ordination in cyanide complexes is very limited. The *trans* effect in Co^{III} complexes derived from Vitamin B₁₂ has been explained entirely in terms of σ -bonding using both thermodynamic evidence and changes in CN⁻ stretching frequencies as ligands *trans* to the CN group are exchanged.⁷⁹ Spectral evidence suggests that M—CN bonds are very weak, with low force constants; accumulation of negative charge on the metal atom being avoided by polarisation of the M—C σ -bond towards the carbon.¹⁰ The C—N force constants on the other hand are consistently high, giving further evidence for σ -only bonding. The spectra of both cyanide and carbonyl complexes have recently been reviewed by Hester¹⁰ and James and Nolan.⁸⁰

There is considerable evidence for π -bonding in carbonyl complexes. Many of the arguments for $d \rightarrow d_{\pi}$ bonding discussed in the previous section assume the presence of extensive $d \rightarrow \pi^*$ overlap, and the spectra of metal carbonyls have been interpreted as giving positive confirmation although the assignment of CO stretching and bending modes is often ambiguous.⁸⁰ Early approximate MO calculations by Cotton and Kraihanzel⁶⁸ have been followed by more rigorous semi-empirical MO calculations. Caulton and Fenske considered the ions M(CO)₆, where M = V⁻, Cr, and Mn⁺, and concluded that the (C—O) _{σ} framework is approximately constant in each compound, changes in C—O charge density being in the π orbitals only,⁸¹ and Kettle has shown that the CO force constant strongly reflects changes in π -bond strength while being relatively insensitive to σ -bond changes.⁸² From orbital population analyses, Beach and Gray found marked $d \rightarrow \pi^*$ back-co-ordination in the anion V(CO)₆⁻ but, as expected, it is almost negligible in the cation Mn(CO)₆⁺.⁸³ More recent calculations on the spectra of M(CO)₆, where M = V⁻, Cr, W, and Re⁺, confirm these conclusions.⁸⁴ A study of orbital overlaps in the ions V(CN)₅NO, Mn(CO)₅NO, V(CO)₆, and Mn(CO)₆ placed ligands in the expected π -acceptor order NO⁺ > CO > CN⁻,³³ and from a study of Cr(CO)₆, Fe(CO)₅, and Ni(CO)₄, zero-valent metal ions have been placed in the π -donor order Cr ~ Fe > Ni.⁸⁵

The consensus of opinion as a result of these theoretical calculations is that

⁷⁹ R. A. Firth, H. A. O. Hill, J. M. Pratt, R. G. Thorp, and R. J. P. Williams, *J. Chem. Soc. (A)*, 1968, 2428.

⁸⁰ D. W. James and M. J. Nolan, *Progr. Inorg. Chem.*, 1968, **9**, 195.

⁸¹ K. G. Caulton and R. F. Fenske, *Inorg. Chem.*, 1968, **7**, 1273.

⁸² S. F. A. Kettle, *Spectrochim. Acta*, 1966, **22**, 1388.

⁸³ N. A. Beach and H. B. Gray, *J. Amer. Chem. Soc.*, 1968, **90**, 5713.

⁸⁴ E. W. Abel, R. A. N. McLean, S. P. Tyfield, P. S. Braterman, A. P. Walker, and P. J. Hendra, *J. Mol. Spectroscopy*, 1969, **30**, 29.

⁸⁵ A. F. Schreiner and T. C. Brown, *J. Amer. Chem. Soc.*, 1968, **90**, 3366.

$d \rightarrow p_{\pi}$ bonding in the $M \rightarrow CO$ bond is considerable, often producing as much charge transfer as the $M \leftarrow CO_{\sigma}$ bond. This has been demonstrated very recently for the complexes $Mo/Cr/W(CO)_6$, where the π -bonding order is somewhat unexpected, being $Mo < Cr < W$.⁸⁶ While virtually full d orbitals provide plenty of electrons for back-co-ordination, d^5-d^7 configurations are not bound so tightly, and hence energetically, should back-co-ordinate more readily. This could explain the high stability of mid-transition-period carbonyls. It is interesting to note that, while carbon monoxide appears to bond most strongly with transition elements with d^5-d^8 configurations, phosphines and other heavy donor atoms prefer d^8-d^{10} configurations. Slight deviations from linearity in the $M-C-O$ bond have been explained by Kettle without eliminating π -bonding.⁸⁷

The $M-CO$ bond length, where M is a heavy atom, is difficult to determine with high precision, but there appears to be a good correlation between apparent bond order and bond length in the complexes $RMo(CO)_3$ as R is changed.⁸⁸ A possible handicap to total acceptance of extensive $d \rightarrow \pi_{\pi}^*$ bonding in the $M-CO$ bond is its weakness. Force constants vary between 1.5 and 3.5 mdyne \AA^{-1} and even the highest value is well below that normally considered reasonable for a simple σ -bond with no π contribution whatsoever.⁸⁹

Linear free-energy relationships based on Da Silva and Calado's treatment and described in Section 8D have usually been applied to first-period donor atoms. Systems considered include Fe^{3+} -substituted phenols,⁸⁹ and Co^{2+} -substituted pyridines.⁹⁰ The latter system is particularly interesting since trends in the series have been explained by σ -bonding only, considering repulsion between non-bonding ligand pairs and metal d -orbitals or non-bonding pairs on other ligands.⁹¹ The very small change in the i.r. spectrum of pyridine on co-ordination has been cited as evidence for an absence of π -bonding. This explanation has been questioned by other workers and since evidence in support of $M \rightarrow Ph$ back co-ordination is considerable and broad-based, $M \rightarrow Py$ back-bonding is highly reasonable.

10 $d \rightarrow \pi_{\mu}^*$ Back-co-ordination

Co-ordination of the type illustrated in (VII) is even more difficult to explain than other types discussed. Ligands can contain either individual double-bonds or extended conjugated systems. Taking ethylene as an example of the former, co-ordination can take place in two ways: the ethylene can take one co-ordination position, as in Zeise's salt, $[PtCl_3C_2H_4]^-$ (*i.e.* planar Pt^{IV}), or act as a possible bidentate ligand as in $Pt(PPh_3)_2C_2H_4$ (*i.e.* planar Pt^0). As in other classes of potential back-co-ordination, i.r. spectra have been variously interpreted as

⁸⁶ D. R. Lloyd and E. W. Schlag, *Inorg. Chem.*, 1969, 8, 2544.

⁸⁷ S. F. A. Kettle, *Inorg. Chem.*, 1965, 4, 1661.

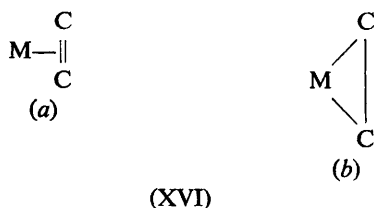
⁸⁸ F. A. Cotton and R. M. Wing, *Inorg. Chem.*, 1965, 4, 314.

⁸⁹ Z. L. Ernst and F. G. Herring, *Trans. Faraday Soc.*, 1965, 61, 454.

⁹⁰ J. O. Cabral, H. C. A. King, S. M. Nelson, T. M. Shepherd, and E. Koros, *J. Chem. Soc. (A)*, 1966, 1348; M. S. Sun and D. G. Brewer *Canad. J. Chem.*, 1967, 45, 2729.

⁹¹ D. P. Graddon and E. C. Watton, *Austral. J. Chem.*, 1965, 18, 507.

supporting both σ -bond formation only⁹² and $\sigma + \pi$ -bonding. For instance, i.r. and mass spectra of the complexes $\text{pi-L}\cdot\text{Fe}(\text{CO})_4$, where pi-L is a pi-bonded olefin, have been studied and a ratio of donor-acceptor strength for the olefins derived⁹³; thermochemical properties of some silver-olefin complexes have been interpreted as showing that π -acceptor properties are more important than σ -donor properties.⁹⁴ On co-ordination, the C=C bond length is increased, $\nu_{\text{C}=\text{C}}$ decreased by 80–150 cm^{-1} , and the barrier to rotation about the C=C bond is lowered. All of these factors suggest a decrease in C-C bond order, possibly due to σ -bonding to form a three-membered ring of the type shown in (XVIb).



Semi-empirical MO calculations on Zeise's salt followed by orbital population analyses suggest a population of the ethylene π^* orbital of 0.36e: this would be empty in the ground state and the charge could result from donation from metal 5d orbitals. Population of the ligand π -bonding orbitals is reduced by 0.33e, suggesting that σ -donation to the metal is almost exactly compensated by π -acceptance leaving the ethylene neutral.⁹⁵ This picture is compatible with a strong synergic effect although, as expected, the absolute precision of such semi-empirical calculations is poor.

The geometry of pi-co-ordinated double bonds has been shown to be almost identical to that of the excited state of the free ligand. Hence co-ordinated CS_2 is no longer linear⁴⁹ and ethylene in Zeise's salt is no longer planar.⁹⁶ It has been argued that the excited state components of the wave-function of a metal complex increase with increasing charge transfer from metal to ligand and *vice versa*.⁵⁹ Hence the geometries of co-ordinated 'pi-bonded' molecules support the view that both σ -acceptor and π -donor properties are important. When the ligand is a very strong 'pi-acid' such as tetracyanoethylene (TCNE), the C=C bond length increases to a normal C—C bond length (from 1.31 to 1.54 Å) on co-ordination in $\text{Pt}(\text{PPh}_3)_2\text{TCNE}$.⁹⁷ In such an extreme case the ligand can be readily regarded as a bidentate σ -bonded donor similar to (XVIb). Mathematically an MO description in terms of a pure π -bond and the VB description in terms of two σ -bonds are the

⁹² S. Cenini, R. Ugo, F. Bonati, and G. La Monica, *Inorg. Nuclear Chem. Letters*, 1967, 3, 191.

⁹³ E. K. von Gustorf, M. C. Henry, and D. J. McAdoo, *Annalen*, 1967 707, 190.

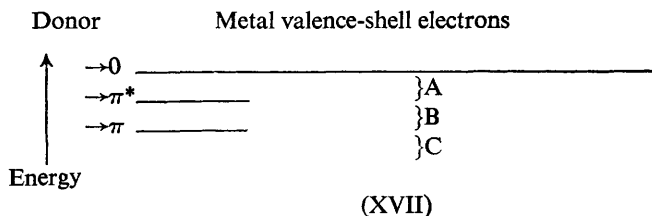
⁹⁴ R. G. Denning, F. R. Hartley, and L. M. Venanzi, *J. Chem. Soc. (A)*, 1967, 324.

⁹⁵ J. W. Moore, *Acta Chem. Scand.*, 1966, 20, 1154.

⁹⁶ W. C. Hamilton, Proc. VIIIth Internat. Congress. Cryst., Stony Brook 1969, paper XIV-46.

⁹⁷ C. Panattoni, G. Bombieri, U. Belluco, and W. H. Baddley, *J. Amer. Chem. Soc.*, 1968, 90, 799; J. A. McGinney and J. A. Ibers, *Chem. Comm.*, 1968, 235.

same, but chemically the C—Pt—C bond angle of only 42° is not compatible with the high thermal stability of the complex. Since TCNE is one of the strongest pi-acids known, the complex can be visualised as containing a $d \rightarrow \pi^*$ bond with virtually no σ -bond. This implies almost complete $M \rightarrow L$ charge transfer making the C—C bond a single bond. Allenes, *e.g.* $R_2C=C=CR_2$, appear to co-ordinate to a particular metal ion through one double bond only⁹⁸ and are in many ways similar to olefins. Acetylenes may also be treated like olefins, but in the σ -bonded structure (XVIb) the ring will be of a cyclopropene type. Both π and σ structures find experimental and theoretical support, but recently a comprehensive explanation, covering both extremes, has been presented.⁹⁹ This explanation is based on the pioneering work of Chatt⁴⁸ and others and can be extended to cover olefin complexes and co-ordination to delocalised π -electron systems. In addition to the basic assumptions of MO theory that orbitals of suitable symmetry and overlap must be available for bonding to take place, the explanation emphasises the assumption that the orbitals involved must be of similar energy. In (XVII) metals with valence-shell electrons in the energy range A will form strongest bonds with the ligand π^* orbitals. This will be favoured by metals in low oxidation states and with electron-donating ligands already bonded. Electron-withdrawing groups on the ligand will also be favourable, making $Pt^0(TCNE)$ complexes a good example.⁹⁶ In the extreme case this will then correspond to (XVIb). Metals possessing electrons having energies in the region B will show both donor and acceptor



properties, and in region C will be predominantly acceptors (hard). There is widespread support for the view that energy levels overlapping to permit back-co-ordination must be energetically close if effective bonding is to take place, *e.g.* the increase in back-donation in $V(CO)_6^-$ compared to $Cr(CO)_6$ has been attributed to the fact that d orbitals in $V(CO)_6^-$ are closer in energy to the π^* orbitals rather than to differences in overlap.⁸⁴ Since valence electrons in Pt^0 will be nearer range A in energy than will those in Pt^{II} , ethylene in $[Pt(PPh_3)_2C_2H_4]$ will have more 'bidentate' character than in $[PtCl_2C_2H_4]^-$. Hence, in the former complex, the ethylene will tend to co-ordinate in the plane of the molecule whilst in the latter it will tend to align itself at right angles to this plane to optimise overlap with orbitals directed along the z -axis. More detailed semi-empirical

⁹⁸ J. A. Osborn, *Chem. Comm.*, 1968, 1231.

⁹⁹ E. O. Greaves, C. J. L. Lock, and P. M. Maitlis, *Canad. J. Chem.*, 1968, 46, 3879.

MO calculations show that the Dewar–Chatt–Duncanson model for olefin complexes can be extended to include acetylene complexes.¹⁰⁰

The allyl group, $-\text{CH}_2\cdot\text{CH}=\text{CH}_2$, can act as either a sigma-ligand, a symmetrical pi-ligand as in bis(π -methallyl)nickel,¹⁰¹ or as an unsymmetrical ligand as in $[\text{PdCl}(\text{methallyl})\text{PPh}_3]$.¹⁰² Approximate MO calculations on bis(π -allyl) palladium show that ligand π orbitals contribute most to the bonding, which is strongest between the metal and terminal carbon atoms.¹⁰³ The Pd has a resultant negative charge of $-0.3e$ with relatively low $4d_{xy}$ and high $5s$, $5p_x$, and $5p_y$ populations. *Ab initio* MO calculations on the nickel analogue suggest that $3d$ metal orbitals are of lower energy than some ligand orbitals and that the main bonding is between the ligand and metal $4s$ and $4p$ orbitals, not the $3d$.¹⁰⁴ These calculations suggest that $\text{M} \leftarrow \text{L}$ bonding is probably more important than $\text{M} \rightarrow \text{L}$ back-bonding, although the latter cannot be ignored.

Butadiene can act as a bidentate ligand and cyclic, conjugated olefins can act as either bidentate or multidentate symmetrical ligands. The geometries of such species have been reviewed by Churchill and Mason⁵² and their electronic spectra by Brown and Baird.^{50,51} Taking ferrocene as an example, $\text{M} \leftarrow \text{L}$ bonding can result from overlap of filled delocalised ligand orbitals of suitable symmetry with empty metal d_{xz} or d_{yz} orbitals while $\text{M} \rightarrow \text{L}$ bonding is possible between filled metal d_z^2 , $d_x^2-y^2$, or d_{xy} orbitals and empty delocalised antibonding orbitals on the ligand. The tendency has been to regard the $\text{M} \rightarrow \text{L}$ bonding as more important, hence the name pi-complexes. Approximate MO calculations do not give a specific answer, disagreeing on the relative importances of the ligand σ and π frameworks,^{103,105} but the name pi-complexes may be misleading since $\text{M} \leftarrow \text{L}$ bonding is clearly very important. This lack of agreement between different approximation methods and the differences between measured and calculated energies demonstrate a limited understanding of the bonding in these more complicated systems.

11 Conclusion

Molecules in which back-co-ordination is suspected cannot be classified simply into those with back-bonding and those without. Such a simple VB approximation is unacceptable in all but the more extreme cases. The explanation of back-bonding in terms of the basic assumptions that, for effective bonding, the orbitals involved must (i) have suitable symmetry, (ii) have large overlaps, and (iii) be of comparable energy provides an easy, pictorial explanation. When these requirements are fulfilled charge transfer through π -bonding orbitals appears to take place, evidence being provided by both MO calculations and trends in properties which are influenced by back-co-ordination.

¹⁰⁰ J. H. Nelson, K. S. Wheelock, L. C. Cusachs, and H. B. Jonassen, *J. Amer. Chem. Soc.* 1969, **91**, 7005.

¹⁰¹ R. Uttech and H. Dietrich, *Z. Krist.*, 1965, **122**, 60.

¹⁰² R. Mason and D. R. Russell, *Chem. Comm.*, 1966, 26.

¹⁰³ I. H. Hillier and R. M. Canadine, *Discuss. Faraday Soc.*, 1969, No. 47, pp. 27, 62.

¹⁰⁴ A. Veillard, *Chem. Comm.*, 1969, 1022, 1427.

¹⁰⁵ A. T. Armstrong, D. G. Carroll, and S. P. McGlynn, *J. Chem. Phys.*, 1967, **47**, 1104.

In most cases, however, charge transfer is limited and seldom appears to exceed $0.2e$, but comparatively limited charge transfer would be expected to have an appreciable effect on bond length, molecular geometry, and chemical properties. If π overlap between orbitals of suitable symmetry and energy does take place, bond formation must result, tending to increase the overlap in the bonding orbital. This will cause a much larger increase in σ overlap along the internuclear axis, so giving a reason for a large synergic effect, producing a very stable σ -bond as a result of only weak π interaction. Correlations between bond type and quantities directly dependent on σ -bonding or s electron density, such as n.m.r. coupling constant or quantitative expressions for inductive effects, are of use but must be treated with care. However extensive the back-co-ordination, this will be detected as a secondary effect only and the exact nature of synergic influences on the σ -bonds is uncertain. Such correlations may therefore act as indicators but must not be taken as quantitative expressions of π -bond strength. Correlations between the properties of ligands *cis* and *trans* to the ligands under study appear to give more reliable scales of donor-acceptor properties.

Precise *ab initio* MO calculation will give far more complete answers in the near future to problems in some specific small molecules but larger, transition-metal complexes will probably be beyond the scope of such refined techniques for a long time. It is by no means certain that detailed answers to the bonding in a few small molecules can be extrapolated to provide general classifications. Measurements of bond length and molecular geometry to a higher precision may be of more general use. Electron diffraction is, at the moment, providing precise data on compounds of non-metals, and the use of new techniques in X-ray crystallography will make more precise M—L bond lengths available in the near future. Interpretation of this data should provide more helpful guidelines to the quantitative prediction of donor-acceptor properties.

I should like to thank Drs. W. S. McDonald and B. L. Shaw for helpful discussion and comment.