Metal–Metal Interactions in Transition-metal Complexes Containing Infinite Chains of Metal Atoms

By T. W. Thomas† and A. E. Underhill
DEPARTMENT OF CHEMISTRY, UNIVERSITY COLLEGE OF NORTH WALES, BANGOR, CAERNS

1 Introduction

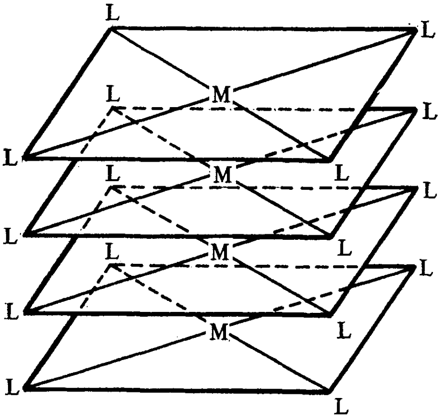
Co-ordination compounds containing direct metal–metal interactions can be divided into two distinct types:

Type A. Complexes containing discrete numbers of directly interacting metal atoms.

Type B. Complexes containing an infinite number of directly interacting metal atoms arranged in linear chains throughout the crystal lattice.

Type A complexes, which include dimeric complexes [*e.g.* copper(II) acetate] and metal cluster compounds (*e.g.* $K_4Mo_6Cl_8$) have been the subject of several extensive reviews.[1] However, no comprehensive review has been published of the Type B complexes, and this present work attempts to classify the known examples of this type of complex and to present an assessment of the factors which affect the formation of such structures, together with a discussion of some of those properties which are unusual.

This review includes only complexes in which direct metal–metal interactions



(1)

---

† Present address: Department of Chemistry, Temple University, Philadelphia 19122, U.S.A.

[1] F. A. Cotton, *Accounts Chem. Res.*, 1969, **2**, 240; F. A. Cotton, *Quart. Rev.*, 1966, **20**, 389; B. R. Penfold in 'Perspectives in Structural Chemistry', Wiley, New York, 1968, Vol. 2, p. 71.

occur, and excludes those structures in which the interaction occurs *via* a bridging atom or group. Thus many mixed-valence complexes, in which non-direct interaction is known to occur,[2] and also many naturally occurring minerals in which the observed interaction[3] may occur *via* bridging oxygen atoms, will not be discussed. Also excluded from this review are compounds such as NbI_4 in which the metal atoms are grouped together in pairs so that the interaction is localized between pairs of adjacent metal atoms and does not extend along the whole metal-atom chain.

A. Occurrence of Type B Complexes.—In general, these complexes have the columnar structure (1) in which planar or nearly planar monomer units are stacked above one another to form metal-atom chains. Most of the Type B complexes are formed from square co-planar monomers, and because such monomeric structures are mainly confined to d^8 metal complexes, this review deals predominantly with complexes of nickel(II), palladium(II), and platinum(II). It is however, more convenient to classify these complexes according to the ligand present rather than the central metal atom, and this classification is adopted in Sections 2—6.

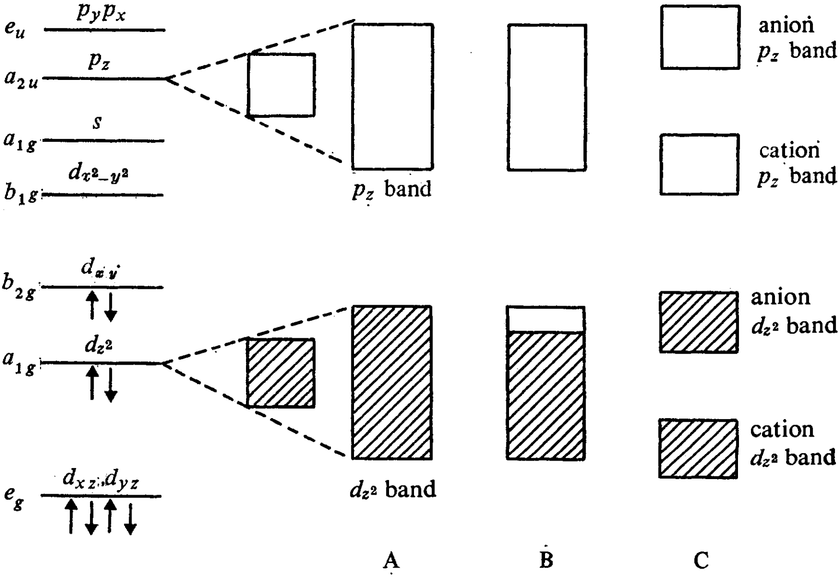


Figure 1 *Diagrammatic representation of the band structure in* d^8 *metal-atom chain compounds. Effect of* (A) *decreasing inter-metallic distance,* (B) *partial oxidation, and* (C) *alternating anion–cation chain. Shaded portion indicates filled band.*

---

[2] M. B. Robin and P. Day, *Adv. Inorg. Chem. Radiochem.*, 1967, **10**, 247; G. C. Allen and N. S. Hush, *Progr. Inorg. Chem.*, 1967, **8**, 357.

[3] D. W. Robbins and R. G. J. Strens, *Chem. Comm.*, 1968, 508.

B. Consideration of the Metal–Metal Interaction within the Chain.—Figure 1 shows the relative energies of the orbitals of a metal atom situated at the centre of a square-coplanar array of ligands (D_{4h} symmetry).[4] In a columnar structure (1), N square-planar molecules may be assumed to be stacked along the z-axis. The interaction between the adjacent molecules in the column may be considered to be one of two types.

(i) *Purely electrostatic interaction.* In this there is no overlap of orbitals of one metal atom with those of its neighbours, and all the changes in spectroscopic properties are considered to be due to intramolecular transitions modified by the presence of the electrostatic crystal field of the neighbouring molecules in the chain. This approach has been discussed in detail recently by Day.[5]

(ii) *Metal–metal orbital overlap.* In this approach, developed by Rundle[6] and Miller,[7] the p_z and d_{z^2} orbitals, or a combination of these orbitals, are considered to overlap with the corresponding orbitals on adjacent metal atoms. If the p_z and d_{z^2} orbitals on adjacent metal atoms do overlap then N delocalized molecular orbitals are formed from the overlapping p_z orbitals and N delocalized molecular orbitals from the d_{z^2} orbitals. Each of these groups of molecular orbitals constitutes a 'band' having energy limits ranging from a value above to a value below that of the unperturbed atomic orbital (see Figure 1). Ingraham[8] has calculated that the spread in energy of the band arising from the overlap of the $3d_{z^2}$ orbitals in bisdimethylglyoximatonickel would vary from $+0{\cdot}509$ to $-0{\cdot}492$ eV compared with the energy of the unperturbed d_{z^2} orbital. Since the width of each band is proportional to the extent of overlap of the individual orbitals and therefore inversely proportional to the interatomic distance, a decrease in interatomic distance produces a wider band, and hence a smaller 'band gap' between the top of the highest filled band and the bottom of the lowest empty band.

The remaining d, s, and p orbitals on adjacent metal atoms are much less likely, for symmetry reasons, to overlap and form bands. These energy levels remain discrete, therefore, and the orbitals remain localized on each metal atom. The presence of another atom in close proximity along the z-axis will, however, perturb these orbitals to various degrees and, therefore, although they do not overlap with neighbouring metal orbitals, electronic transitions which involve these orbitals are sensitive to the presence of metal–metal interactions.

For metal atoms with a d^8 configuration, the d_{z^2} band is full and the p_z band empty. Although full and empty bands, when considered individually, are non-bonding, configuration interactions between them may result in a small net bonding in the ground state.[9] This effect is, however, very small in bisdimethylglyoximatonickel.[8] Oxidation of the central metal atom, however, will result in removal of electrons from the uppermost (antibonding) part of the d_{z^2} band and

---

[4] B. N. Figgis, 'Introduction to Ligand Fields', Interscience, New York, 1966, p. 313.

[5] P. Day, *Inorg. Chim. Acta Rev.*, 1969, **3**, 81.

[6] R. E. Rundle, *J. Phys. Chem.*, 1957, **61**, 45.

[7] J. R. Miller, *J. Chem. Soc.*, 1965, 713.

[8] L. L. Ingraham, *Acta Chem. Scand.*, 1966, **20**, 283.

[9] K. Krogmann, *Angew. Chem. Internat. Edn.*, 1969, **8**, 35.

hence result in a net increase in bonding. A series of compounds of this type, in which the inter-metallic distance is about 0·4 Å shorter than in the corresponding compound with a full d_{z^2} band, has been reported[9] and is discussed in detail in Section 4.

It can be seen from the preceding discussion that the metal orbital overlap approach does not necessarily imply the existence of metal–metal bonds in the ground state, and that both this approach and the purely electrostatic interaction approach deal in a similar way with the modified ligand-field spectrum of crystals of these compounds.

C. Investigation and Determination of Metal–Metal Interactions.—(i) *X-Ray crystal structure determination.* The presence of chains of metal atoms running throughout the structure of single crystals of a compound can only be established by a full *X*-ray structure determination. In many of the compounds considered to contain interacting metal atoms, the inter-metallic distance along the chain, although short, is considerably longer than that found in the metal itself and does not indicate, *a priori*, the existence of any interaction. Thus, in all cases, further evidence from other experimental techniques is necessary to establish the presence of an interaction between the adjacent metal atoms.

(ii) *Spectroscopic measurements.* The majority of the experimental evidence for the occurrence of interactions in metal-atom chain compounds is derived from a study of their u.v. and visible spectra. A review[5] has recently appeared which deals in part with the spectroscopic properties of metal chain compounds and, therefore, only a brief account of this subject will be given here. The evidence is of two types.

Difference between the solid-state (polymeric) and solution (monomeric) spectra. Compounds which possess a columnar stacked structure in which the metal atoms are separated by large inter-metallic distances (*e.g.*[10] K_2PtCl_4; Pt–Pt, 4·13 Å) exhibit very similar solution and solid-state spectra.[11] In contrast to this, many of the compounds possessing a much shorter inter-metallic distance (~3·0—3·5 Å) have solid-state spectra which are different from those of the same compounds in solution, often containing a band of considerably lower energy than any of the strong bands observed in solution. This 'solid-state' band has been assigned to the d_{z^2}–p_z transition (often with a contribution from a metal → ligand charge transfer transition) or to a transition from the d_{z^2} band to the p_z band, the energy of which is very dependent on the proximity of the metal atoms in the z direction. In addition to the appearance of the new band there are also changes in the high-energy part of the spectrum. In general, the absorption bands observed in the solution spectra are still recognizable in the solid-state spectra but they undergo significant shifts in frequencies.

Polarization of the low-energy band in the crystal spectra. The absorption bands of planar organic molecules are strongly polarized $\parallel$ to the plane of the

---

[10] R. C. Dickinson, *J. Amer. Chem. Soc.*, 1922, **44**, 2404.
[11] D. S. Martin and C. A. Lenhardt, *Inorg. Chem.*, 1964, **3**, 1368.

molecule. Yamada[12] found that the lowest energy band for certain planar transition-metal complexes was also $\parallel$ polarized but that for some columnar stacked compounds with fairly short inter-metallic distances the lowest energy band was more strongly polarized $\perp$ than $\parallel$ to the plane of the molecule.[13] This dichroism he termed 'unusual' and associated it with the presence of a metal–metal bond perpendicular to the plane of the molecule. Although the resolution of the spectra was poor in this early work, more recent studies[14,15] have confirmed that in many cases the lowest energy absorption band is predominantly $\perp$ polarized. The lowest energy band of bis-*N*-methylsalicylaldiminatonickel, which also has a columnar structure is, however, $\parallel$ polarized indicating that the presence of the columnar structure does not necessarily produce a $\perp$ polarized low-energy band.[16] It has been suggested more recently that the out-of-plane $\perp$ polarization is not abnormal for planar complexes in which the transition is not a pure $\pi \rightarrow \pi^*$ transition of an organic molecule and particularly if it involves transition-metal orbitals.[17] Thus the $\perp$ polarization of the low-energy band cannot be taken as conclusive evidence of a metal–metal interaction.

(iii) *Magnetism and e.s.r. measurements.* As mentioned earlier, the majority of complexes containing chains of metal atoms involve metal ions with a d^8 configuration located in a square-planar environment. The complexes are thus diamagnetic and little information has been gained from these techniques.

(iv) *Electrical conductivity measurements.* Studies have been made of single crystals of some of these complexes and several have been found to be anisotropic semiconductors with greater electron delocalization along the line of the metal–metal chain.

2 Complexes of *vic*-Dioximes and Salicylaldiminates

Some of the best known examples of infinite chains of interacting metal atoms occur in crystals of complexes containing anionic planar organic ligands. The neutral square co-planar monomeric units (ML_2) are stacked above one another to form chains throughout the crystal lattice (see Figure 2). Discussion of the metal–metal interaction in these complexes has been based upon evidence from *X*-ray crystallographic, solubility, spectroscopic, and more recently from electrical conduction studies. It is useful to discuss the evidence from each technique separately as this illustrates the application of these techniques to the investigation of metal–metal chains.

A. Structural Studies.—The general structure shown in Figure 2 has been found

---

[12] S. Yamada, *J. Amer. Chem. Soc.*, 1951, **73**, 1182.

[13] S. Yamada, *J. Amer. Chem. Soc.*, 1951, **73**, 1579.

[14] B. G. Anex and F. K. Krist, *J. Amer. Chem. Soc.*, 1967, **89**, 6114.

[15] P. Day, A. F. Orchard, A. J. Thomson, and R. J. P. Williams, *J. Chem. Phys.*, 1965, **43**, 3763.

[16] J. Ferguson, *J. Chem. Phys.*, 1961, **34**, 611.

[17] G. Basu, G. M. Cook, and R. L. Belford, *Inorg. Chem.*, 1964, **3**, 1361.

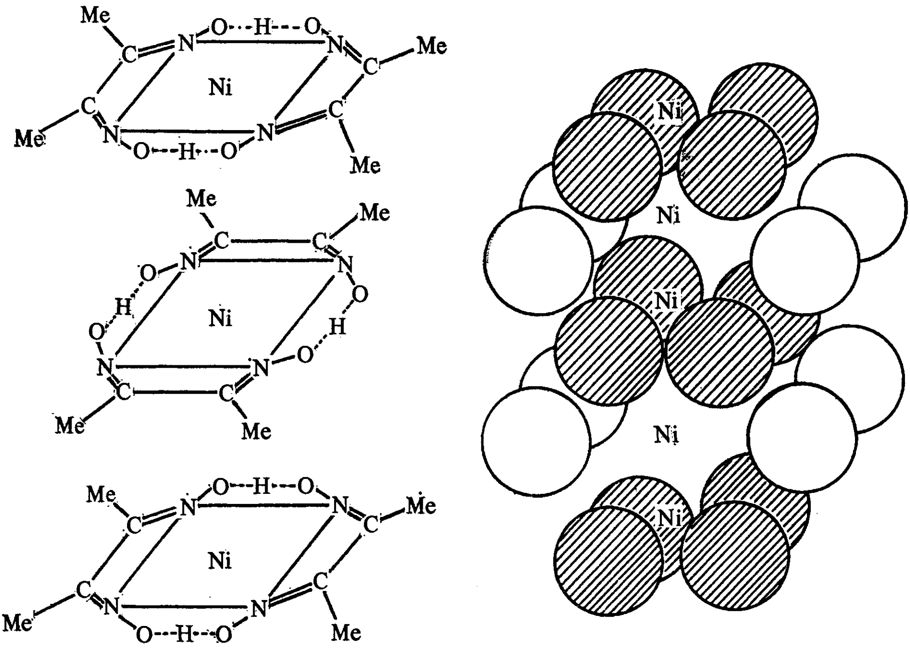


Figure 2 *Structure of bisdimethylglyoximatonickel showing how the methyl groups (represented by circles) on successive molecules interlock.*

for a number of the *vic*-dioximes of nickel(II), palladium(II), and platinum(II).[18–21] In bisdimethylglyoximatonickel [$Ni(dmg)_2$] the monomer units are stacked above one another in the line of the *c*-axis of the orthorhombic crystals with the planes of the individual molecules parallel to the (001) plane.[18] The two ligands within each monomer are linked by short hydrogen bonds (2·40 Å), conferring a rigidity to the planar molecule. Successive molecules are staggered by 90° and because the inter-metallic distance is only 3·245 Å the methyl groups, which form the thickest part of the molecule, interlock in the manner shown in Figure 2. This interlocking of adjacent molecules may add to the stability of the chain structure. The short metal–metal distances determined for $Ni(dmg)_2$ (3·245 Å)[18] and $Pd(dmg)_2$ (3·253 Å)[19] led to the suggestion of metal–metal bonds in these complexes and that the presence of these bonds may further stabilize the columnar structure.

Many complexes of Ni^{II}, Pd^{II}, and Pt^{II} with *vic*-dioxime ligands have been

---

[18] L. E. Godycki and R. E. Rundle, *Acta Cryst.*, 1953, **6**, 487; D. E. Williams, G. Wohlauer, and R. E. Rundle, *J. Amer. Chem. Soc.*, 1959, **81**, 755.

[19] C. Panattoni, E. Frasson, and R. Zannetti, *Gazzetta*, 1959, **12**, 2132.

[20] C. V. Banks and D. W. Barnum, *J. Amer. Chem. Soc.*, 1958, **80**, 4767.

[21] E. Frasson, C. Panattoni, and R. Zannetti, *Acta Cryst.*, 1959, **12**, 1027.

studied but few possess the columnar structure analogous to that of Ni(dmg)$_2$. Table 1 shows the inter-metallic distances in those complexes which possess a columnar structure. It is of note that all the dioxime complexes which have short inter-metallic distances adopt an orthorhombic crystal habit. Surprisingly, the bis-complexes of glyoxime with $\mathrm{Ni^{II}}$, $\mathrm{Pd^{II}}$, and $\mathrm{Pt^{II}}$ do not adopt the

Table 1 *Complexes of* vic-*dioximes and salicylaldimines with short M–M distances*

Complex	*M–M bond length* (Å)	*Solid state colour band* (cm^{-1} × 10^{-3})
Nickel 4-isopropylnioxime	3·19[a]	17·95[a]
Nickel 4-t-amylnioxime	3·2[a]	18·28[a]
Nickel nioxime	3·237[a]	18·12[a] (18·21[d,e])
Nickel 4-methylnioxime	3·24[a]	18·28[a]
Nickel dimethylglyoxime	3·245[f,g]	18·60[b,l] (18·05[a])
β-Nickel ethylmethylglyoxime	3·4[c]	20·49[b]
Nickel furil-α-dioxime	3·448[a]	18·62[a]
Nickel 3-methylnioxime	3·47[a]	19·88[a]
Nickel benzil-α-dioxime	3·547[a]	19·42[a]
Nickel heptoxime	3·596[a]	21·9[b] (21·51[a])
Palladium nioxime	3·250[a]	20·75[a] (21·50[d,e])
Palladium dimethylglyoxime	3·26[f,k]	20·83[a] (22·17[d])
Palladium heptoxime	3·329[a]	23·53[a]
Palladium furil-α-dioxime	3·459[a]	21·74[a]
Palladium benzil-α-dioxime	3·517[a]	22·99[a]
Platinum dimethylglyoxime	3·23[j]	16·28[d]
Nickel *N*-methylsalicylaldiminate (orthorhombic form)	3·29[h]	‡
Copper *N*-methylsalicylaldiminate (orthorhombic form)	3·33[i]	—

‡ Lowest energy band 16 500 cm^{-1} reported polarized in plane of the molecule.[m]

[a] C. V. Banks and D. W. Barnum, *J. Amer. Chem. Soc.*, 1958, **80**, 4767. [b] B. G. Anex and F. K. Krist, *J. Amer. Chem. Soc.*, 1967, **89**, 6114. [c] A. G. Sharpe and D. B. Wakefield, *J. Chem. Soc.*, 1957, 281. [d] J. C. Zahner and H. G. Drickamer, *J. Chem. Phys.*, 1960, **33**, 1625. [e] H. G. Drickamer and J. C. Zahner, *Adv. Chem. Phys.*, 1962, **4**, 161. [f] D. E. Williams, G. Wohlauer, and R. E. Rundle, *J. Amer. Chem. Soc.*, 1959, **81**, 755. [g] E. Frasson and C. Panattoni, *Acta Cryst.*, 1960, **13**, 893. [h] M. R. Fox and E. C. Lingafelter, *Acta Cryst.*, 1967, **22**, 943. [i] E. C. Lingafelter, G. L. Simmons, B. Morosin, C. Scheringer, and C. Freiberg, *Acta Cryst.*, 1961, **14**, 1222. [j] E. Frasson, C. Panattoni, and R. Zannetti, *Acta Cryst.*, 1959, **12**, 1027. [k] C. Panattoni, E. Frasson, and R. Zannetti, *Gazzetta*, 1959, **12**, 2132. [l] Y. Ohashi, I. Hanazaki, and S. Nagakura, *Inorg. Chem.*, 1970, **9**, 2551. [m] J. Ferguson, *J. Chem. Phys.*, 1961, **34**, 611.

$Ni(dmg)_2$ structure,[22] although the molecules are planar and the ligand is similar in structure to dimethylglyoxime. The bismethylethylglyoximatonickel molecule is also planar, but the complex adopts a crystal structure which precludes the possibility of metal–metal interaction.[23] It seems likely that the interlocking of successive planar molecules as described for $Ni(dmg)_2$ is a requisite for a columnar structure with a short metal–metal distance in this type of compound, since this interlocking cannot occur either in the glyoximes, where the bulky methyl groups are replaced by hydrogen atoms, or in complexes with more bulky ligands such as methylethylglyoxime where the larger substituents prevent close packing of successive molecules. The complexes with nioxime ligands have short inter-metallic distances[20] and may also interlock. Molecules of $Cu(dmg)_2$ are not planar[24] and this complex does not have a structure containing metal-atom chains.

A study of some bis-salicylaldiminato and bis-*N*-methylsalicylaldiminato complexes show that whereas Cu^{II} [25] and Ni^{II} [26,27] complexes of bis-*N*-methylsalicylaldiminato can exist in a form isomorphous to $Ni(dmg)_2$, with inter-metallic distances of 3·33 Å and 3·29 Å respectively, the bis-salicylaldiminato complexes cannot.[16,27] It would again appear that the ability of the ligands on successive molecules to interlock may be a prerequisite to the formation of this type of structure, and again the complexes of ligands with more bulky substituents such as bis-*N*-ethyl- and bis-*N*-butyl-salicylaldiminates adopt different structures.[28]

It is significant that complexes of Ni^{II}, Pd^{II}, and Pt^{II} which have the same ligand and possess the $Ni(dmg)_2$-type structure have similar inter-metallic distances. This indicates that the minimum inter-metallic distance in these complexes is probably determined by the packing of the ligand molecules.

B. Solubility Studies.—The extremely low solubility of $Ni(dmg)_2$ and $Pd(dmg)_2$ in many solvents has been known for some time and has led to their use in the gravimetric determination of these metals.[29] It has been suggested that this low solubility is due to the presence of metal–metal bonds in the solid state[30–33] and attempts have been made to relate the solubility of some *vic*-dioximes to the

---

[22] M. Calleri, G. Ferraris, and D. Viterbo, *Acta Cryst.*, 1967, **22**, 468; M. Calleri, G. Ferraris, and D. Viterbo, *Inorg. Chim. Acta*, 1967, **1**, 297; G. Ferraris and D. Viterbo, *Acta Cryst.*, 1969, **B25**, 2066.

[23] E. Frasson and C. Panattoni, *Acta Cryst.*, 1960, **13**, 893.

[24] E. Frasson, R. Bardi, and S. Bezzi, *Acta Cryst.*, 1959, **12**, 201.

[25] E. C. Lingafelter, G. L. Simmons, B. Morosin, C. Scheringer, and C. Freiburg, *Acta Cryst.*, 1961, **14**, 1222.

[26] M. R. Fox and E. C. Lingafelter, *Acta Cryst.*, 1967, **22**, 943.

[27] J. M. Stewart and E. C. Lingafelter, *Acta Cryst.*, 1959, **12**, 842.

[28] E. Frasson, C. Panattoni, and L. Sacconi, *Acta Cryst.*, 1964, **17**, 85, 477.

[29] A. I. Vogel, 'Textbook of Quantitative Inorganic Analysis', Longmans, Green and Co., London, 1961.

[30] A. G. Sharpe and D. B. Wakefield, *J. Chem. Soc.*, 1957, 281.

[31] C. V. Banks and D. W. Barnum, *J. Amer. Chem. Soc.*, 1958, **80**, 3579.

[32] R. E. Rundle and C. V. Banks, *J. Phys. Chem.*, 1963, **67**, 508.

[33] C. V. Banks and S. Anderson, *J. Amer. Chem. Soc.*, 1962, **84**, 1486.

length, and thus the strength, of the proposed metal–metal bond. The work by Banks and Barnum[31] indicated, however, that the solubility of these complexes is also dependent on the nature of the ligands, but if a series of similar ligands is considered, a correlation does exist between solubility and inter-metallic distance. A comparison of the solubilities of Ni(dmg)$_2$ and Ni(emg)$_2$ led to an estimate of 9—11 kcal mol^{-1} for the strength of the Ni–Ni bond in the former compound.[33] This estimate is in good agreement with a value of 10 kcal mol^{-1} calculated by Rundle and Banks[32] from the crystal structures of the two complexes.

C. U.V. and Visible Spectra Studies.—The absorption spectra of Ni(dmg)$_2$ in solution,[20] suspension,[17] polycrystalline films,[17] and single crystals,[14,17,20,34,35] have received much attention during the past 15 years. Discussion of the spectral characteristics of single crystals of Ni(dmg)$_2$ and structurally related *vic*-dioximes have centred on the presence of the lowest energy visible absorption band at about 18 000—20 000 cm^{-1} which is polarized to the plane of the molecule and is not present in the solution spectrum (see Table 1). The band has been assigned to the $3d_{z^2} \rightarrow 4p_z$ transition with some $3d_{z^2} \rightarrow \pi^*b1u$ character,[14,35–37] and its presence interpreted as being due to the presence of metal–metal bonds.[20,34] Day,[5] however, has argued that the band is a result of electrostatic crystal-field interaction between neighbouring intramolecular transition dipoles, and that no metal–metal bond, or band, formation need be invoked to rationalize these phenomena. In a new study of this problem, Ohashi and co-workers[35] conclude that the band is mainly due to the $3d_{z^2} \rightarrow 4p_z$ transition within a nickel atom, but also includes some interatomic $3d_{z^2}$ (atom a) $\rightarrow 4p_z$ (atom b) charge-transfer excitation. A close relationship exists between the energy of this absorption band and the inter-metallic distance for a series of *vic*-dioximes. This relationship has been successfully used to predict the inter-metallic distances in other related *vic*-dioximes. Drickamer and Zahner[37] also found this correlation when they studied the effect of pressure on the visible spectrum of Ni(dmg)$_2$, Pd(dmg)$_2$, and Pt(dmg)$_2$. They found that the energy of the $d_{z^2} \rightarrow p_z$ transition decreased markedly with increasing pressure due to the shortening of the inter-metallic distances.

Molecular orbital calculations performed by Ingraham[8] for Ni(dmg)$_2$ indicate that an overlap of the d_{z^2} orbitals is unlikely in the ground state. In the excited state, however, sufficient overlap of occupied $4p_z$ orbitals may lead to interaction between adjacent nickel atoms.[8,14]

D. Electrical Conduction Studies.—Recent studies of single crystals of Ni(dmg)$_2$[38] have shown that the electrical conductivity along the axis of the metal–metal chain is 10^6 times greater than that of a compressed powder disc of the complex,

---

[34] S. Yamada and R. Tsuchida, *Bull. Chem. Soc. Japan*, 1954, **27**, 156.

[35] Y. Ohashi, I. Hanazaki, and S. Nagakura, *Inorg. Chem.*, 1970, **9**, 2551.

[36] J. R. Miller, *J. Chem. Soc.*, 1961, 4452.

[37] J. C. Zahner and H. G. Drickamer, *J. Chem. Phys.*, 1960, **33**, 1625.

[38] T. W. Thomas and A. E. Underhill, *Chem. Comm.*, 1969, 725.

Table 2 *Tetracyano-complexes*

Complex	M–M *distance* (Å)	*Colour*	*Crystal system*	(z) *polarized absorption band* (cm^{-1} × 10^{-3})	(xy) *polarized absorption band* (cm^{-1} × 10^{-3})	*fluorescence band maximum* (cm^{-1} × 10^{-3})
$Sr[Pt(CN)_4],3H_2O$	3·09^{a}	violet	monoclinic			
$Be[Pt(CN)_4],2H_2O$	3·16^{b}	dark red	orthorhombic			
$Y_2[Pt(CN)_4]_3,21H_2O$	3·16^{c}					16·40^{c}
$Mg[Pt(CN)_4],7H_2O$	3·155^{a,l}	red	tetragonal	18·00; 19·40^{d}	18·00^{e}	
$Li_2[Pt(CN)_4],xH_2O$	3·18^{c}					17·10^{c}
$K_2Sr[Pt(CN)_4]_2,2H_2O$	3·21^{a}	violet red	monoclinic			
$KNa[Pt(CN)_4],3H_2O$	3·24^{c}					17·90^{c}
$(NH_4)_2[Pt(CN)_4],xH_2O$	3·25^{c}					18·90^{c}
$Ba[Pt(CN)_4],4H_2O$	3·32^{a}	yellow green	monoclinic	22·70^{d}	22·00^{e}	19·50^{c}
$K_2Sr[Pt(CN)_4]_2,6H_2O$	3·33^{a}	yellow green	monoclinic			
$Mg[Pt(CN)_4],4{\cdot}5H_2O$	3·36^{a}	yellow	triclinic			
$Ca[Pt(CN)_4],5H_2O$	3·38^{a}	yellow	orthorhombic	23·90^{d}	22·80^{e}	20·20^{c}
$Rb_2[Pt(CN)_4],3H_2O$	3·40^{c}					21·70^{c}
$K_2[Pt(CN)_4],3H_2O$	3·50^{c}				24·00^{f}	22·10^{c}
$Sr[Pt(CN)_4],5H_2O$	3·60^{a}	colourless	monoclinic	28·30^{d}		23·30^{c}
$Na_2[Pt(CN)_4],3H_2O$	3·63^{f}	colourless				
$Ba[Pd(CN)_4],4H_2O$	3·37^{g}	colourless	orthorhombic		30·30^{g}	
$Ca[Pd(CN)_4],5H_2O$	3·42^{h} 3·32^{g}	colourless	orthorhombic		31·70^{g,i}	
$Sr[Pd(CN)_4],5H_2O$	3·63^{g}	colourless	monoclinic		35·70^{g}	
$Mg[Pd(CN)_4],4H_2O$	—	colourless^{b}				
$Ba[Ni(CN)_4],4H_2O$	3·31^{j}					

Table 2 (*continued*)

$Ca[Ni(CN)_4],5H_2O$	3·22[j] 3·38[b]	orange	orthorhombic
$Li_2[Ni(CN)_4],3H_2O$	3·63[j]		
$Sr[Ni(CN)_4],5H_2O$	3·64[j] 3·65[b]	orange	monoclinic
$Na_2[Ni(CN)_4],3H_2O$	3·67[j]		
$K_2[Ni(CN)_4],3H_2O$	3·69[j]		

[a] K. Krogmann and D. Stephan, *Z. anorg. chem.*, 1968, **362**, 290. [b] K. Krogmann, *Angew. Chem. Internat. Edn.*, 1969, **8**, 35. [c] M. L. Moreau-Colin, *Bull. Soc. roy. Sci. Liege*, 1965, **34**, 778. [d] C. Moncuit and H. Poulet, *J. Phys. Rad.*, 1962, **23**, 353. [e] S. Yamada, *Bull. Chem. Soc. Japan*, 1951, **24**, 125. [f] H. Brasseur and A. de Rassenfosse, *Bull. Soc. roy. Sci. Liege*, 1939, **8**, 24. [g] A. Macadre and C. Moncuit, *Compt. rend.*, 1965, **261**, *B*, 2339. [h] F. Fontaine, *Bull. Soc. roy. Sci. Liege*, 1964, **33**, 178. [i] R. LeBras and C. Moncuit, *Compt. rend.*, 1968, **267**, *B*, 1032. [j] M. L. Colin, *Bull. Soc. roy. Sci. Liege*, 1963, **34**, 130. [k] H. Brasseur and A. de Rassenfosse, *Bull. Soc. roy. Sci. Liege*, 1935, **4**, 68. [l] R. M. Bozorth and L. Pauling, *Phys. Rev.*, 1932, **39**, 537.

indicating some degree of electron delocalization along this chain. Crystals of Ni(dmg)$_2$ behave as ohmic semiconductors and the energy of the band-gap closely corresponds to the lowest energy spectral transition present in the single crystal spectrum.[17] The observation of semiconducting behaviour rather than metallic conduction along the metal–metal chains indicates that it is necessary first to promote electrons to an excited state before conduction occurs. This parallels the arguments put forward by Anex and Krist[14] and by Ingraham[8] that overlap of orbitals giving rise to metal–metal bonds is only probable in the excited state.

3 Tetracyano-complexes

X-Ray studies[39] show that in crystals of Mg[Pt(CN)$_4$],7H$_2$O the square-planar [Pt(CN)$_4$]$^{2-}$ are stacked above one another with the Pt atoms forming chains which run through the crystal parallel to the *c*-axis. Successive [Pt(CN)$_4$]$^{2-}$ units are rotated by 45° and the Pt–Pt distance is 3·155 Å. The metal–metal distances in a large number of Pt^{II}, Pd^{II}, and Ni^{II} cyano-complexes possessing a columnar structure of this type have been determined and are given in Table 2.

The inter-metallic distance is strongly influenced by the cation but little affected by the presence of different central transition-metal atoms. This is seen in the two series Ca[M(CN)$_4$],5H$_2$O (M = Ni, Pd, or Pt; Ni–Ni, 3·38; Pd–Pd, 3·42; Pt–Pt, 3·38 Å) and Sr[M(CN)$_4$],5H$_2$O (Ni–Ni, 3·65; Pd–Pd, 3·63; Pt–Pt, 3·60 Å). A detailed study has been made of the platinum series of compounds and a variation in the Pt–Pt distance from 3·09 Å in Sr[Pt(CN)$_4$],3H$_2$O and 3·155 Å in Mg[Pt(CN)$_4$],7H$_2$O to 3·60 Å in Sr[Pt(CN)$_4$],5H$_2$O is observed. This comparison illustrates not only the wide variation in inter-metallic distances found for a given central metal atom, but also the very marked effect of the degree of hydration on the metal–metal distance.

Evidence for metal–metal interactions in these compounds, apart from the actual inter-metallic distances is again obtained from extensive studies of the u.v. and visible spectra of these compounds.

A. Platinum(II) Cyanides.—Yamada first studied[40] the polarized crystal spectra of Ca[Pt(CN)$_4$],5H$_2$O, Mg[Pt(CN)$_4$],7H$_2$O, and Ba[Pt(CN)$_4$],4H$_2$O. He observed a very strong broad $\perp$ polarized band and a much sharper $\parallel$ polarized band both at lower frequencies than any of the absorption bands observed for these compounds in solution. The polarized spectra for several other [Pt(CN)$_4$]$^{2-}$ complexes have now been determined (see Table 3) and an approximately linear correlation between the Pt–Pt distance and the position of the $\parallel$ polarized band has been noted.[41] A similar relationship is found for the $\perp$ polarized band using the data of Moncuit and Poulet[42] and for the band maximum observed in the

---

[39] R. M. Bozorth and L. Pauling, *Phys. Rev.*, 1932, **39**, 537.

[40] S. Yamada, *Bull. Chem. Soc. Japan*, 1951, **24**, 125.

[41] S. Yamada, 'Essays in Co-ordination Chemistry', ed. W. Schneider, G. Anderegg, and R. Gutt, *Experentia*, Supplementum IX, 1964.

[42] C. Moncuit and H. Poulet, *J. Phys. Rad.*, 1962, **23**, 353.

Table 3 *Partially oxidized chain compounds*

Complex	*Oxidation number of platinum*	Pt–Pt *distance* (Å)
$K_2[Pt(CN)_4]Cl_{0\cdot32},2\cdot6H_2O$	+2·32	2·880[a]
$K_2[Pt(CN)_4]Br_{0\cdot30},2\cdot3H_2O$	+2·30	2·887[a]
$Mg[Pt(CN)_4]Cl_{0\cdot28},7H_2O$	+2·28	2·985[b]
$K_{1\cdot74}[Pt(CN)_4],1\cdot8H_2O$	+2·26	2·96[c]
$H_{1\cdot60}[Pt(C_2O_4)_2],2H_2O$	+2·40	2·80[d]
$Li_{1\cdot64}[Pt(C_2O_4)_2],6H_2O$	+2·36	2·81[d]
$K_{1\cdot62}[Pt(C_2O_4)_2],xH_2O$	+2·38	2·81[d]
$K_{1\cdot64}[Pt(C_2O_4)_2],xH_2O$	+2·36	2·82[d]
$(NH_4)_{1\cdot64}[Pt(C_2O_4)_2],H_2O$	+2·36	2·82[d]
$H_{1\cdot60}[Pt(C_2O_4)_2],3H_2O$	+2·40	2·82[d]
$K_{1\cdot64}[Pt(C_2O_4)_2],xH_2O$	+2·36	2·83[d]
$Ca_{0\cdot84}[Pt(C_2O_4)_2],4H_2O$	+2·32	2·83[d]
$Mg_{0\cdot82}[Pt(C_2O_4)_2],xH_2O$	+2·36	2·84[d]
$Mg_{0\cdot82}[Pt(C_2O_4)_2],xH_2O$	+2·36	2·84[d]
$K_{1\cdot62}[Pt(C_2O_4)_2],2H_2O$	+2·38	2·85[d]
$Mg_{0\cdot82}[Pt(C_2O_4)_2],5\cdot3H_2O$	+2·36	2·85[e]
$Sr_{0\cdot84}[Pt(C_2O_4)_2],4H_2O$	+2·32	2·85[d]
$Ba_{0\cdot84}[Pt(C_2O_4)_2],4H_2O$	+2·32	2·85[d]
$Na_{1\cdot67}[Pt(C_2O_4)_2],4H_2O$	+2·33	2·88[d]
$Ir(CO)_{2\cdot93}Cl_{1\cdot07}$	+1·07	2·845[f]

[a] K. Krogmann and H. D. Hausen, *Z. anorg. Chem.*, 1968, **358**, 67. [b] K. Krogmann and G. Ringwald, *Z. Naturforsch.*, 1968, **23b**, 1112. [c] K. Krogmann and H. D. Hausen, *Z. Naturforsch.*, 1968, **23b**, 1111. [d] K. Krogmann, *Angew. Chem. Internat. Edn.*, 1969, **8**, 35. [e] K. Krogmann, *Z. anorg. Chem.*, 1968, **358**, 97. [f] K. Krogmann, W. Binder, and H. D. Hausen, *Angew. Chem. Internat. Edn.*, 1968, **7**, 812.

fluorescence spectra as determined by Moreau-Colin[43] (see Figure 3). The ⊥ polarized band has been assigned[42] to the $5d_{z^2} \rightarrow 6p_z$ transition and it has been suggested[44] that the || polarized band occurring at approximately the same frequency also arises from this transition due to a vibronic coupling mechanism.

There is some disagreement concerning the colourless compound $Sr[Pt(CN)_4],5H_2O$ in which the Pt–Pt distance is 3·60 Å.[45] Yamada reported[41] no additional bands present in the solid-state spectrum compared with the solution spectrum and therefore suggested that there could be no inter-metallic interaction. Moncuit and Poulet,[42] however, recorded a spectrum for the solid which is very similar in shape to those they obtained for the barium, magnesium, and calcium salts. The band system, however, occurs entirely in the u.v. and not partially in the visible region as observed for other salts and, in addition, the bands occur at much lower frequencies than those observed for $[Pt(CN)_4]^{2-}$ in

[43] M. L. Moreau-Colin, *Bull. Soc. Roy. Sci. Liège*, 1965, **34**, 778.

[44] C. Moncuit, *J. Phys. Rad.*, 1964, **25**, 833.

[45] K. Krogmann and D. Stephan, *Z. anorg. Chem.*, 1968, **362**, 290.

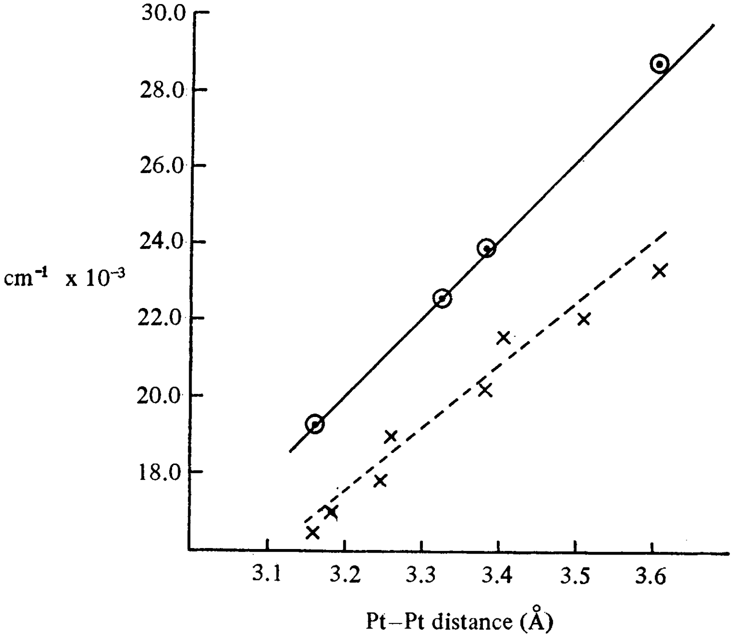


Figure 3 *Variation of band position with Pt–Pt distance for a series of platinocyanides.* ⊙, *z-polarized band;* ×, *fluorescence band maximum.*

solution. It can be seen from Figure 3 that both the ⊥ polarized band maximum[42] and the fluorescence band maximum[43] fall on the same curves as those of the other complexes and this absorption therefore probably arises from a similar transition to that present in the other complexes.

The observation of an intense colour associated with compounds having a Pt–Pt distance of less than 3·25 Å is explained by the occurrence of the strong absorption bands in the visible region but, as discussed above, the absence of an intense colour does not necessarily indicate the absence of a metal–metal interaction. These results also indicate that a weak interaction occurs even at a Pt–Pt distance of 3·60 Å.

B. Palladium(II) Cyanides.—The $[Pd(CN)_4]^{2-}$ ion exhibits no absorption bands in solution below 40 000 cm^{-1} but above this frequency there is an intense and complex band system in the 41—50 000 cm^{-1} region.[46] The polarized crystal spectra of the calcium, barium, and strontium salts have been studied[46] and all three possess bands in the solid-state spectra below 40 000 cm^{-1}. The spectra have similar polarization properties to those observed for the platinocyanides but the band maxima occur at higher frequencies for the same inter-metallic

[46] A. Macadre and C. Moncuit, *Compt. rend.*, 1965, **261**, *B*, 2339.

distance (see Table 2). The variation in the position of the || polarized band maximum with inter-metallic distance is similar to that found for the platinum complexes.

C. Nickel(II) Cyanides.—Nickel complexes of the type M[Ni(CN)$_4$] are coloured owing to the presence of ligand-field absorption bands in the visible region. A series of these complexes has been shown[47] to exhibit intense absorption bands at about 20 000 cm^{-1} in the solid state, but as the position of these bands is not affected by the nature of the cation, the degree of hydration, or the inter-metallic distance, it appears that these bands are not due to inter-metallic interactions.

4 Partially Oxidized Chain Compounds

It has been suggested in Section 1 that for columnar stacked compounds in which the metal atoms have a d^8 configuration, the d_{z^2} band of molecular orbitals is fully occupied. The upper part of this band has an antibonding effect on the complex because it is higher in energy than the unperturbed d_{z^2} atomic orbital of the monomer unit which comprises the chain. Krogmann[9,48] suggested that the bonding within the metal-atom chain could be strengthened if electrons were removed from the upper part of this band by partial oxidation of the metal ions. This oxidation can be achieved in a columnar stacked Pt^{II} compound if the ratio of negatively to positively charged ions is increased either by the addition of anions (*e.g.* $K_2[Pt(CN)_4] \rightarrow K_2[Pt(CN)_4]Cl_{0.32}$[49]) or by the removal of cations {*e.g.* $Mg[Pt(C_2O_4)_2],5{\cdot}3H_2O \rightarrow Mg_{0.82}[Pt(C_2O_4)_2],5{\cdot}3H_2O$[50]}. Several of the compounds which have been examined in this manner are related to the tetracyano-complexes discussed in Section 3.

In the partially oxidized compound $K_2[Pt(CN)_4]Cl_{0.32},2{\cdot}6H_2O$ the $[Pt(CN)_4]^{2-}$ ions are stacked one above the other[49] as in $Mg[Pt(CN)_4],7H_2O$.[39] The Cl$^-$ ion is in the centre of the unit cell surrounded by a tetrahedral arrangement of K$^+$ ions. However, only 64% of the unit cells contain Cl$^-$ ions, and this corresponds to 0·32 Cl$^-$ per Pt atom, and results in an oxidation number of 2·32 for the platinum. The effect of the removal of electrons from the antibonding part of the d_{z^2} band is to decrease the Pt–Pt inter-metallic distance from 3·155 Å in $Mg[Pt(CN)_4],7H_2O$[39] to 2·88 Å in $K_2[Pt(CN)_4]Cl_{0.32},2{\cdot}6H_2O$.[49] It is significant that the platinum atoms are all crystallographically identical, and that the structure does not contain Pt^{II} and Pt^{IV} complexes. It appears impossible to increase the oxidation number of the platinum above 2·32 and this may be due to the detailed structure of the d_{z^2} band.[9]

A range of compounds containing partially oxidized chains due to vacancies in cation sites has been reported (see Table 3).[9] The structure of $Mg_{0.82}[Pt(C_2O_4)_2],5{\cdot}3H_2O$ has been shown[50] to contain the $[Pt(C_2O_4)_2]^{2-}$ ions

---

[47] M. L. Colin, *Bull. Classe Sci. Acad. Roy. Belg.*, 1963-64, **49**, 973.

[48] K. Krogmann, P. Dodel, and H. D. Hausen, *Proc. VIII Internat. Conf. Coord. Chem.*, ed. V. Gutmann, p. 157.

[49] K. Krogmann and H. D. Hausen, *Z. anorg. Chem.*, 1968, **358**, 67.

[50] K. Krogmann, *Z. anorg. chem.*, 1968, **358**, 97.

stacked one above the other to give a Pt–Pt chain with an inter-metallic distance of 2·85 Å. Only 40% of the Mg^{2+} sites are occupied and this results in an oxidation number of 2·36 for the platinum atoms. Certain of the non-bonding distances between C and O atoms in adjacent $[Pt(C_2O_4)_2]^{2-}$ groups in the chain are shorter than is normally observed, and this too has been interpreted[9] as indicating strong Pt–Pt bonds.

If oxidation of these chain compounds does result in a partially occupied d_{z^2} band then this should produce profound differences in the physical properties of these compounds compared with the unoxidized chain compounds. Partially occupied bands are responsible for metallic conduction in metals and some metal oxides, whereas systems possessing only completely filled or completely empty bands exhibit semiconducting properties. Metallic conduction is characterized by a high value for the specific conduction and a slight fall in conductivity with increasing temperature. The value of 10^{-3} ohm^{-1} cm^{-1} in the chain direction observed[49] for $K_2[Pt(CN)_4]$ $Cl_{0.32},2{\cdot}6H_2O$ is larger than the value reported for Magnus's Green Salt[51] and much larger than that reported for bisdimethylglyoximatonickel,[38] but no work on the variation of σ with temperature has been reported.* The observed conductivity is low for metallic conduction in general, but it has been suggested[9] that lattice imperfections may hinder the movement of electrons in one-dimensional conductors to a greater extent than in two- or three-dimensional conductors.

Preliminary data[52] on the strongly dichroic partially oxidized Ir^I compound, $Ir(CO)_{2.93}Cl_{1.07}$, indicate that its structure contains chains of metal atoms with an Ir–Ir distance of 2·85 Å. The inter-metallic distance is similar to those found in the partially oxidized Pt^{II} compounds and is much less than that present in unoxidized Ir^I metal chain compounds [*e.g.* $Ir(CO)_2$acac, 3·20 Å,[53] see later]. In the $Ir(CO)_{2.93}Cl_{1.07}$ monomer units the positive charge arising from partial oxidation of the iridium atoms is compensated by a statistical replacement of some of the CO groups with Cl^-. The degree of partial oxidation of Ir^I (+0·07) is much smaller than that found in Pt^{II} (+0·3).

5 Anion–Cation Alternating Chains

Magnus's Green Salt (MGS) $[Pt(NH_3)_4]$ $[PtCl_4]$ crystallizes as small tetragonal needles containing planar $[Pt(NH_3)_4]^{2+}$ cations and $[PtCl_4]^{2-}$ anions stacked

---

* The electrical conduction properties of these compounds are now receiving a great deal of attention. The value of σ in the chain direction in $K_2Pt(CN)_4Br_{0.30},2{\cdot}3H_2O$ has now been variously reported as 10^{-4} ohm^{-1} cm^{-1} (P. S. Gomm and A. E. Underhill, *Chem. Comm.*, 1971, 511), 4 ohm^{-1} cm^{-1} (M. J. Minot and J. H. Perlstein, *Phys. Rev. Letters*, 1971, **26**, 371), and 10^2 ohm^{-1} cm^{-1} (A. S. Berenblyum, L. I. Buravov, M. D. Khidekel, I. F. Shchegolev, and E. B. Yakimov, *Zh.E.T.F. Pis. Red.*, 1971, **13**, 619; D. Kuse and H. R. Zeller, *Phys. Rev. Letters*, 1971, **27**, 1060). Berenblyum *et al.* also showed the conductivity to increase with increasing temperature.

[51] J. P. Collman, *Chem. Eng. News*, 1967, **45**, No. 52, 50.

[52] K. Krogmann, W. Binder, and H. D. Hausen, *Angew. Chem. Internat. Edn.*, 1968, **7**, 812.

[53] N. A. Bailey, E. Coates, G. B. Robertson, F. Bonati, and R. Ugo, *Chem. Comm.*, 1967, 1041.

Table 4 *Magnus's Green Salt and Related Complexes*

Compound		*Absorption spectra* (cm^{-1} × 10^{-3}) $^1A_{1g}\to{}^1B_{1g}$	$^1A_{1g}\to{}^1E_g$	$^1A_{1g}\to{}^1A_{2g}$	$^1A_{1g}\to{}^3B_{1g}$	$^1A_{1g}\to{}^3E_g$	$^1A_{1g}\to{}^3A_{2g}$	$^1A_{1g}\to{}^1A_{2u}$	*Colour*	M–M *distance* (Å)
K_2PtCl_4	S[a]	(37·9)	30·2(64)	25·5(59)	—	21·0(15)	17·7(2·6)		Pink	4·13[c]
	xy[b]	(36·5)	28·5(57)	26·0(45)		20·4(17·5)	17·3(5)			
	z[b]	(36·5)	29·3(70)			20·2(20)	—			
	R[b]	(36·5)	29·0	27·0		20·4	17·5			
$[Pt(NH_3)_4][PtCl_4]$	xy[b]	(30)	24·9(170)			16·5(20)			Green	3·25[d]
	z[b]		24·9(305)		(23·0)(190)	16·5(150)		7·5(1·75)		
	R[b]	30	25·2		(23·0)	16·5		6·8		
$[Pt(MeNH_2)_4][PtCl_4]$	R[b]	(30)	25·4			17·3		7·0	Green	3·25[e]
$[Pt(EtNH_2)_4][PtCl_4]$	R[b]	(33·5)	27·0			19·0			Pink	‡
$[Pt(en)_2][PtCl_4]$	R[e]		25·1			18·9			Purple	3·40[e]
$[Pd(en)_2][PtCl_4]$	R[e]		27·1			19·3			Pink	3·40[e]
$[Pd(NH_3)_4][PtCl_4]$	R[b]	(34)	25·5			18·3			Pink	3·25[e]
$[Pt(NH_3)_4][PtCl_4]$	R[b]	(32·5)	26·5			19·2			Pink	~5[d]
K_2PtBr_4	R[b]	(32·5)	26·3	24·5		18·8	16·5		Red	
$[Pt(NH_3)_4][PtBr_4]$	R[b]		23·4			15·7		6·5	Green	3·31[e]
$[Pt(MeNH_2)_4][PtBr_4]$	R[b]		23·2			16·3		6·8		3·31[e]
$[Pt(EtNH_2)_4][PtBr_4]$	R[b]		23·7			16·6				
$[Pd(NH_3)_4][PtBr_4]$	R[b]		24·4			17·5				
K_2PdCl_4	xy[b]	(29·5)(67)	22·6(128)	(20·0)(67)		18·0(19)				4·10[f]
	z[b]		23·0(80)			17·0(7)				
	R[b]	(31·5)	21·5			18·0				
$[Pt(NH_3)_4][PdCl_4]$	R[b]	(29)	20·2			(17·0)			Pink	3·23[g]
$[Pd(NH_3)_4][PdCl_4]$	R[b]	(29·5)	20·0			(16·5)			Pink	3·25[g]
$[Pd(NH_3)_4][PdBr_4]$									Red	3·33[g]
$[Pt(NH_3)_4][Pt(SCN)_4]$	R[b]		(25·0)			19·6			Red	3·35[g]
$[Pd(NH_3)_4][Pt(SCN)_4]$	R[b]		(26·0)			20·0				

S, solution spectrum; R, reflectance spectrum; xyz, polarized light single crystal spectrum.
‡ does not possess a tetragonal structure[e,b]

[a] J. Chatt, G. A. Gamlen, and L. E. Orgel, *J. Chem. Soc.*, 1958, 486. [b] P. Day, A. F. Orchard, A. J. Thomson, and R. J. P. Williams, *J. Chem. Phys.*, 1965, **42**, 1973; 1965, **43**, 3763. [c] R. G. Dickinson, *J. Amer. Chem. Soc.*, 1922, **44**, 2404. [d] M. Atoji, R. W. Richardson, and R. E. Rundle, *J. Amer. Chem. Soc.*, 1957, **79**, 3017. [e] J. R. Miller, *J Chem. Soc.*, 1965, 713. [f] W. Theilacker, *Z. anorg. Chem.*, 1937, **234**, 161. [g] J. R. Miller, *J. Chem. Soc.*, 1961, 4452.

alternately above one another in the direction of the *c* (needle)-axis.[54] In MGS alternate ions are staggered by 28° allowing a close approach of the platinum atoms (Pt–Pt, 3·25 Å) along the chain. A range of Pt and Pd complexes exists with structures analogous to MGS[7,55,56] and many of these have short intermetallic distances in the direction of the metal–metal chain[7] (see Table 4). A great deal of discussion has centred on the colours of the salts with short intermetallic distances since the green colour of MGS cannot arise from the superimposition of the colours of the anion (red) and the cation (colourless). Many early workers[13] associated the green colour with metal–metal interactions. A pink modification of MGS also exists in which the closest metal–metal contact distance is about 5 Å.[54] The spectrum of this modification is similar to that of K_2PtCl_4[11] which possesses a columnar structure of $[PtCl_4]^{2-}$ ions with an intermetallic distance within the chains of 4·13 Å.[10] Therefore there can be little or no metal–metal interaction.[56]

The spectrum of MGS contains three main bands (see Table 4) in the region 15—30 000 cm^{-1} which are related to the three bands observed in this region in the spectrum of K_2PtCl_4.[11] The cation, $[Pt(NA_3)_4]^{2+}$, possesses no absorption bands below 40 000 cm^{-1}. In crystals of MGS, however, there is also a band at 6 000 cm^{-1} which is not present in compounds containing either the isolated cation or anion. This low-energy band occurs only in the spectra of complexes in which platinum is present in both the anion and the cation, and then only in those complexes which have the shorter metal–metal distances (see Table 4). The presence of this additional band is not, however, the cause of the green coloration, which is due to a red-shift in the positions of the higher energy bands and which will be discussed later.

The occurrence of the band at ~6000 cm^{-1} which is polarized in the direction of the *c*-axis in MGS[15] led to the postulation that this absorption band is due to an intermolecular transition from anion to cation. Miller suggested[7] that, because the columnar structure in MGS consists of alternate cations and anions, the $5d_{z^2}(a_{1g})$ orbitals may interact to give two bands of molecular orbitals and, likewise, the empty $6p_z(a_{2u})$ orbitals may give two further bands. The formation of these bands would be essentially non-bonding. These bands of molecular orbitals would extend throughout the crystals in the direction of the *c*-axis, with the lower two bands being occupied and the upper two bands unoccupied in the ground state. The transition ${}^1A_{1g} \rightarrow {}^1A_{2u}$ $(5d_{z^2} \rightarrow 6p_z)$ from the top of the occupied band to the bottom of the unoccupied band (see Figure 1) is then dipole-allowed, and an absorption corresponding to such a transition would be polarized in the z direction, which is the *c*-axis of the crystal. Such a transition corresponds to partial electron transfer from anion $5d_{z^2}$ to cation $6p_z$ orbitals and would be expected to give rise to the greater intensity of the band which is observed for

---

[54] M. Atoji, J. W. Richardson, and R. E. Rundle, *J. Amer. Chem. Soc.*, 1957, **79**, 3017.

[55] S. Yamada and R. Tsuchida, *Bull. Chem. Soc. Japan*, 1958, **31**, 813.

[56] P. Day, A. F. Orchard, A. J. Thomson, and R. J. P. Williams, *J. Chem. Phys.*, 1965, **42**, 1973.

shorter inter-metallic distances. Recently it has been suggested[5,57] that the 6000 cm^{-1} band is a N–H overtone of the cation. However, the close relationship between the energy of this transition and the band gap for conduction in the direction of the metal-atom chain,[51] and the observation of a photoconduction threshold at 4650 cm^{-1} in MGS[51] indicate an intermolecular origin for the transition. It may be that the absence of this low energy band in the salts containing palladium is due to less overlap of the relevant d and p orbitals. Since the spectra of the MGS analogues in the region 15—30 000 cm^{-1} are essentially similar to that of the $[PtCl_4]^{2-}$ ion,[56] the shifts in the positions of the three main bands represent the perturbation of the anion molecular orbitals by the proximity of the cation neighbours. The assignment of the absorption bands in the $[PtCl_4]^{2-}$ ion and the MGS type of compounds[7,11,56] are given in Table 4.

There is a marked red-shift in the $^1A_{1g} \rightarrow {}^1E_g$ and $^1A_{1g} \rightarrow {}^1B_{1g}$ transitions compared with K_2PtCl_4 and these correspond to transitions from the anion d_{xz}, d_{yz}, and d_{z^2} to the anion $d_{x^2-y^2}$ orbitals respectively. Since the $d_{x^2-y^2}$ orbitals lie in the plane of the anions they are unlikely to be perturbed by the neighbouring cations, so that the band shifts are probably indicative of the perturbation of the anion d_{xz}, d_{yz}, and d_{z^2} orbitals by the cation d_{z^2} orbital. This interaction can be produced either by electrostatic repulsion between pairs of electrons in neighbouring atoms or, possibly, by overlap of the d_{z^2} orbitals. In as much as this shift is due to perturbation by neighbouring cations, the early ideas that the green coloration of MGS is due to metal–metal interactions were thus essentially correct. The absence of a green colour, however, cannot be taken as being indicative of the absence of metal–metal interaction, but any such interaction would be weak in these circumstances. In the bromo- and iodo-analogues of MGS only a small shift in the positions of the $^1A_{1g} \rightarrow {}^1E_g$ and $^1A_{1g} \rightarrow {}^1B_{1g}$ transitions is necessary to give the complex a green colour; thus many of these complexes appear green[58] although the inter-metallic distance indicates that only weak interactions can occur. The polarizations of the u.v. bands in MGS have been determined[59] using the specular reflection technique and have been discussed by Day.[5]

Promotion of electrons from the highest filled band to the lowest unoccupied band should facilitate electrical conduction in the direction of the c-axis of crystals of MGS, but not in the direction perpendicular to this axis. MGS behaves as an anisotropic semiconductor with a ratio of the conductivity along the c-axis to that perpendicular to this axis of about 100 : 1.[51,60,61] Photoconduction along the c-axis has also been observed[51] with a threshold of about 4500 cm^{-1}, which corresponds to the onset of absorption of the low-energy band and suggests a correlation between the band gap for conduction and this band. Similar conduction studies[62] on crystals of $[Cu(NH_3)_4][PtCl_4]$, which also has

[57] Y. Kondo and C. K. Jørgensen, personal communication.

[58] S. Yamada, *Bull. Chem. Soc. Japan*, 1962, **35**, 1427.

[59] B. G. Anex, M. E. Ross, and M. W. Hedgcock, *J. Chem. Phys.*, 1967, **46**, 1090.

[60] P. S. Gomm, T. W. Thomas, and A. E. Underhill, *J. Chem. Soc.* (*A*), 1971, 2154.

[61] C. N. R. Rao and S. N. Bhat, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 531.

[62] H. P. Fritz and H. J. Keller, *Z. Naturforsch.*, 1965, **20b**, 1145.

the MGS structure, have shown them to be anisotropic conductors with the highest conduction again in the direction of the metal–metal chains.

6 Miscellaneous Compounds containing Metal-atom Chains

A. $Rh(CO)_2(acac)$, $Ir(CO)_2(acac)$, and Related Complexes.—Recently the preparations[63] and crystal structures[53] of a series of bisdicarbonyl-β-diketonates of Rh^I and Ir^I have been reported and these complexes shown to possess columnar structures with close metal–metal contact distances. Electrical conduction in single crystals of $Rh(CO)_2(acac)$ and $Ir(CO)_2(acac)$ has been studied[64] and the conductivity in the direction of the metal–metal chain is 500 times that perpendicular to the chain, indicating electron delocalization along the chain. The conductivity in crystals of the Ir^I complex is 10^6 times greater than that observed in the Rh^I complex, probably owing to the shorter metal–metal distance (Ir–Ir, 3·20 Å; Rh–Rh, 3·26 Å) and the greater overlap of the larger orbitals in the Ir^I atoms.

B. Dioxalato-complexes.—Dioxalatoplatinates can often exist in two coloured forms both containing square-planar $[Pt(C_2O_4)_2]^{2-}$ ions. In the yellow forms there are no Pt–Pt interactions,[65] but in the red phases, however, metal–metal interactions do occur and Krogmann has shown that the red modification of $Ca[Pt(C_2O_4)_2],4H_2O$ possesses a Pt–Pt chain with an inter-metallic distance of only 3·18 Å.[66]

C. $Au^I(dmg)_2\,Au^{III}Cl_2$.—The structure of this mixed valence compound contains square-planar $[Au(dmg)_2]^-$ and linear $[AuCl_2]^+$ ions stacked alternately along the *c*-axis of the crystal with an inter-metallic distance of 3·26 Å.[67] The dichroism[68] and absorption spectrum of this complex indicate that any interaction must be weak, and the low electrical conduction ($\sigma < 10^{-12}$ ohm^{-1} cm^{-1}) along the *c*-axis of the crystal[69] supports this conclusion.

D. Platinum Blue and Related Complexes.—Crystals of Platinum Blue [empirical composition $Pt(MeCO{\cdot}NH)_2H_2O$] are reported to exhibit red–blue dichroism similar to that found in bis(dimethylglyoximato)platinum, and it has been suggested that the compound contains polymeric Pt–Pt bonds.[70] An *X*-ray diffraction study of the dichroic blue crystals formed by the addition of sulphuric acid

---

[63] F. Bonati and G. Wilkinson, *J. Chem. Soc.*, 1964, 3156; F. Bonati and R. Ugo, *Chimica e Industria*, 1964, **46**, 1486.

[64] C. G. Pitt, L. K. Monteith, L. F. Ballard, J. P. Collman, J. C. Morrow, W. R. Roper, and D. Ulkü, *J. Amer. Chem. Soc.*, 1966, **88**, 4286.

[65] R. Mattes and K. Krogmann, *Z. anorg. Chem.*, 1964, **332**, 247.

[66] K. Krogmann, *Z. Naturforsch.*, 1968, **23b**, 1012.

[67] R. E. Rundle, *J. Amer. Chem. Soc.*, 1954, **76**, 3101.

[68] R. Tsuchida and S. Yamada, *Ann. Report Fac. Sci. Osaka Univ. Japan*, 1956, **4**, 79.

[69] P. S. Gomm, T. W. Thomas, and A. E. Underhill, unpublished results.

[70] R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 1964, 2835.

to *cis*-dichlorodiammineplatinum(II) indicates the presence of Pt atom chains in this compound with a Pt–Pt distance of only 3·06 Å.[70]

7 Conclusions

The formation of a columnar structure containing chains of interacting metal atoms is very dependent upon the monomeric units which constitute the columns. As this review shows, complexes containing chains of metal atoms almost invariably contain metal atoms with a d^8 configuration since this configuration favours the formation of square-planar monomers. Whereas Pt^{II} forms planar complexes with nearly all ligands, Ni^{II} only forms planar complexes with ligands situated at the strong-field end of the spectrochemical series. Under strong-field conditions, electrons in the d_{z^2} orbital are stabilized to a greater extent in a square-planar environment than in octahedral or tetragonal environments and this stabilization is further increased by the presence of positively charged ligands along the z-axis, and in these metal chain compounds the metal ions of the adjacent monomers act as 'positively charged ligands'. The stabilization produced by the ligand field is opposed by the coulombic repulsion between the ligands of one monomer unit with those of the units above and below. In K_2PtCl_4, where 10Dq is small and the repulsion between the chloride ligands is large, a long inter-metallic distance (4·13 Å) is found.[10] In the platinocyanides 10Dq is much larger and the ligands are smaller, so that shorter inter-metallic distances (3·1—3·6 Å) are observed.[43,45] Oxalate ligands are also small and their charge more dispersed, thus lessening the coulombic repulsion still further and allowing inter-metallic distances of 3·18 Å.[66]

In the past, the short inter-metallic distances in Type B complexes and the observed changes in the energy levels of the monomers on formation of the columnar structure, have been interpreted as indicating the presence of metal–metal bonds,[6,7] although more recently they have been discussed[5] on the basis of purely electrostatic interactions. As discussed earlier (Section 1) the interaction may lead to the formation of delocalized band systems in Type B complexes containing d^8 metal ions which are either non-bonding or only very weakly bonding. An examination of several series of d^8 metal chain compounds indicates that the inter-metallic distances are the same for the first, second, and third row transition metals. Thus in the bisdimethylglyoximes (Ni–Ni, 3·23; Pd–Pd, 3·25; Pt–Pt, 3·23 Å) the inter-metallic distance appears to be primarily determined by repulsions between ligands, and in the series $Ba[M(CN)_4],4H_2O$ (M = Ni, Pd, or Pt; Ni–Ni, 3·31; Pd–Pd, 3·37; Pt–Pt, 3·32 Å) by the size of the other ions present in the lattice. This is probably a reflection of the weakness of the bonding between the metal atoms in the chains, since partial oxidation of the cyano- and oxalato-Pt^{II} complexes, which is expected to result in stronger metal–metal bonds, produces a greatly reduced Pt–Pt distance.[49,50]

Although the inter-metallic distances are not significantly affected by the central transition metal in the *vic*-dioxime, tetracyano, or MGS series of Ni^{II}, Pd^{II}, and Pt^{II} complexes (see Tables 1, 2, and 4) the extent of the interactions, as deduced from the spectra of these complexes, does decrease in the order

Pt > Pd > Ni. This decrease is probably due to the spatial distribution of the *d*- and *p*-orbitals which decreases in the order $5d > 4d > 3d$ and $5p > 4p > 3p$. Further evidence of this effect is obtained from studies of the semiconduction properties of $Rh(CO)_2(acac)$ and $Ir(CO)_2(acac)$,[64] and of $[Pt(NH_3)_4][PtCl_4]$, $[Pd(NH_3)_4][PtCl_4]$, and $[Pt(NH_3)_4][PdCl_4]$,[60] in which a much lower conductivity and hence decreased interaction is observed in those complexes which contain the second-row transition-metal atom, Rh or Pd.

It has been suggested[1] that the strength of metal–metal bonding decreases across the transition series and increases from the first to the third transition series. However, for a d^n configuration where $n < 5$ the formation of metal–metal bonds leads preferentially to the formation of dimers and metal cluster compounds. The work on partially oxidized chain systems indicates that metal ions with a d^7 configuration and low oxidation state should be capable of forming strongly-bonded metal–metal chains, but no examples have yet been observed.

The complexes described in this review possess a unique one-dimensional array of metal atoms. If future work can lead to compounds in which the extent of electron delocalization along the metal atom is increased then the anisotropy of these compounds might be expected to find important application in the field of semiconductor technology.