

# The Importance of Non-Bonds in Coordination Compounds

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The term “coordination complex” almost invariably brings to mind a transition metal atom to which are bonded six atoms in an octahedron. We now automatically concentrate our thinking on these metal-to-ligand bonds and tend to assume that they are all-important in the behavior of the compound. In fact, the stoichiometry, coordination geometry, and reactivity of many complexes is dictated not by the bonds between the metal and the atoms attached to it, but by the non-bonded repulsions arising from the bulk of parts of the ligands *remote* from the bonding center: the Non-Bonds between the ligands.

## Close Packing

In his classic book, Kitaigorodskii emphasized that molecules have a well-defined volume and shape, and a “hard” contact surface that prevents two nonbonded atoms from approaching closer than the sum of their contact or van der Waals radii (1). He concluded that the molecules pack together in the crystal by a “bump-in-hollow” process, the projections of one molecule fitting into the hollows of adjacent molecules to give material of maximum density with a minimum energy (2). It is important to understand that there is *no* essential physical difference between the nonbonded repulsions between atoms within a molecule and these intermolecular repulsions between molecules in the solid state (3). Thus, for example, two methyl groups within a coordination compound may repel each other, but they will still pack together by the bump-in-hollow meshing with their C–H bonds acting like gears or knuckles. This process considerably reduces the effective van der Waals volume of the group from the typical value of about 2 Å for the radius of a randomly or freely rotating methyl group.

## Steric Approach Control

Dauben described essentially the same concept but from the entirely different point of view of an organic chemist looking at the stereochemistry of the reduction products of a steroid ketone (4). He found that the conformation of the OH group produced by reduction of the C=O group was determined by the pathway of least hindrance of the incoming reducing agent. If the approach route from above was open, then the H atom went onto the keto carbon atom from above and the subsequently formed OH group was *axial* down, the energetically *less* favored conformation. The easier the approach from above, the more likely it was to get the thermodynamically less stable axial hydroxyl group below. When bulky groups were present above, they blocked the top route and the attack came from below, and the OH group was formed on the same side as the bulky groups. Dauben termed this phenomenon “steric approach control”—control by kinetics, where the bulk of the groups *not* bonded to the reacting center control the formation of the products. The implications of Kitaigorodskii’s and Dauben’s ideas are enormously wide-

ranging because they apply not only to organic crystals and molecules but to every coordination compound.

## Rate of Reaction

A beautiful example of this effect of physical blocking of the reaction pathway and thus the reduction in reactivity at the metal center (5) is seen in the series of square planar compounds *trans*-[PtCl(PEt<sub>3</sub>)<sub>2</sub>Ar], where Ar is an ortho-substituted phenyl ring. The rate of nucleophilic substitution of Cl<sup>−</sup> by pyridine systematically decreases as the bulk of the ortho substituent increases:

Ar	$k_{\text{obs}}/\text{s}^{-1}$
Phenyl	$1.2 \times 10^{-4}$
<i>o</i> -Tolyl	$1.7 \times 10^{-5}$
Mesityl	$3.2 \times 10^{-6}$

The cause is easily pictured (Fig. 1). The “top” of the metal atom is screened from the incoming nucleophile by the bulk of the methyl group on the phenyl ring, which is remote, chemically inert, and in no way bonded to the metal atom. The methyl groups simply block the pathway for the incoming ligand.

## Tolman’s Cone Angle for Phosphine Ligands

As a result of his studies of the rates of substitution of nickel carbonyl by various phosphorus ligands L, and of ligand competition equilibria in solutions of NiL<sub>4</sub> and 4L\*, Tolman concluded that in many cases it was not electronic bonding effects that control the reactions, but rather the steric bulk of the phosphine ligands (6). He developed the concept of cone angle for a ligand, defined in terms of an idealized M–PX<sub>3</sub> system, where the M–P distance was 2.28 Å, and the PX<sub>3</sub> ligand was constructed of CPK<sup>R</sup> models. The cone angle  $\theta$  was the apex angle of the ideal cone, which had its apex at the metal atom and just touched the van der Waals surfaces of the peripheral atoms of the ligand, usually hydrogens (Fig. 2) (7). Typical values of  $\theta$ , the cone angle, are PF<sub>3</sub>, 104°; PMe<sub>3</sub>, 118°; PPh<sub>3</sub>, 145°; P(*t*-Bu)<sub>3</sub>, 182°.

Methods of estimating the cone angle of asymmetric ligands of the class PXYZ have been proposed (8–10). The effective bulk of the ligand, as measured from crystal structures, is often considerably smaller than its cone angle as deduced from the rigid CPK<sup>R</sup> model. This is a result of the bump-in-hollow gearwheel effect as well as of compression of the M–P–R angles. Nevertheless, the principle is correct, and the concept is of great value, as is made clear in the review by McAuliffe (11). The importance of cone angle in metal-catalyzed reactions in organic synthesis has also been elegantly described (12). In the years since Tolman’s original pioneering publication, much effort has been expended on attempts to quantify the combined electronic and steric effects of phosphorus(III) ligands. The most comprehensive and successful synthesis to date has been the QALE model of Giering and co-workers

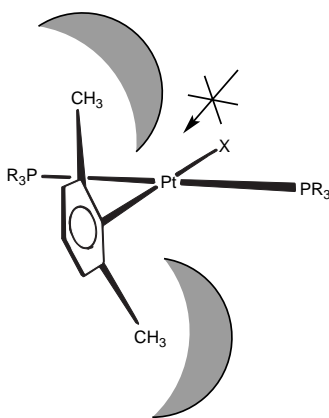


Figure 1. A schematic diagram of the compound  $\text{trans-[PtCl(PEt}_3)_2\text{Ar]}$  (Ar = mesityl) showing how the bulk of the two methyl groups blocks access to the platinum atom.

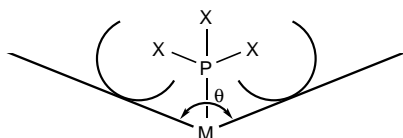


Figure 2. The cone angle  $\theta$  as defined for a typical phosphine ligand  $\text{PX}_3$ .

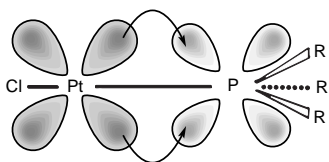


Figure 3. The back-bonding in the  $\text{trans-Cl-Pt-P}$  moiety.

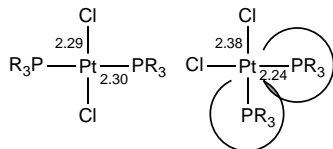


Figure 4. The cis and trans isomers of  $[\text{PtCl}_2(\text{PR}_3)_2]$  showing Pt-P and Pt-Cl bond lengths and how the van der Waals envelopes of the cis phosphines interfere. R = propyl.

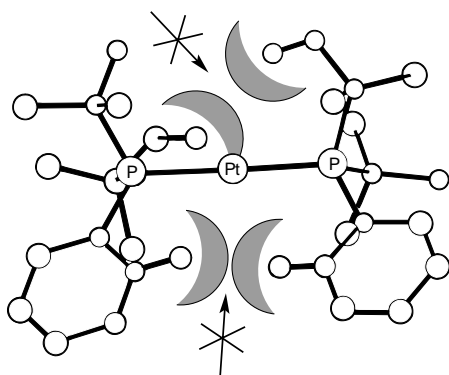


Figure 5. The molecule  $[\text{Pt}\{\text{PPh}(\text{t-Bu})_2\}_2]$ , showing how the van der Waals surfaces of some hydrogen atoms block access to the platinum atom.

(13), which of necessity is a far more complex function than the simple physical bulk that is being considered here.

### *cis- or trans-[PtCl<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>]?*

Fifty years ago Chatt and Wilkins studied the *cis-trans* equilibria for the square planar platinum complexes  $[\text{PtCl}_2(\text{PR}_3)_2]$  (14). It was evident that bond energies favored the *cis* isomer. This is caused by the  $\pi$  back-bonding from the metal d-orbital being concentrated on only one phosphorus atom, and this strengthening of the Pt-P bond will be favored by the *trans* arrangement Cl-Pt-PR<sub>3</sub> (Fig. 3). The isomer that has the greater Pt-P double-bond character will have the larger overall bond strength. Thus the *cis* square planar isomer will be favored if bonding effects *alone* were in control. (In the *trans* case two phosphorus atoms would of necessity be competing for the favors of the same d-orbital on the P atom).

The effect is also clearly seen in the facial and meridional isomers of  $[\text{IrCl}_3(\text{PMe}_2\text{Ph})_3]$  (15). In the *fac* isomer the mean bond lengths are Ir-Cl, 2.46 Å; Ir-P, 2.29 Å. In the *mer* isomer, the mean length for the *trans* pair of Ir-P bonds is 2.37 Å, whereas the *trans* pair of Ir-Cl bonds are 2.36 Å long. On the other hand, the lengths of the unique bonds of the *trans* Cl-Ir-P moiety are Ir-Cl, 2.43 Å; Ir-P, 2.28 Å (values very close to those found in the facial isomer). The Ir-P bond is considerably shorter and stronger in the *trans* Cl-Ir-P arrangement, indicating that M-P bond strengths favor the facial isomer for octahedral  $[\text{MX}_3(\text{PR}_3)_3]$  as well as the *cis* isomer for square planar  $[\text{MX}_2(\text{PR}_3)_2]$ .

However, if the alkyl groups on the phosphines are large, the inter-ligand van der Waals repulsions between the bulky PR<sub>3</sub> groups will cause the square planar compound to isomerize to yield the *trans* isomer, which does not suffer from inter-ligand compression strain (Fig. 4). The larger the cone angle of the phosphine ligand, the more the *trans* isomer is favored. A good example is  $[\text{PtCl}_2\{\text{P}(i\text{-Pr})_3\}_2]$ , which can be prepared as the pure *cis* isomer, but on equilibration in benzene for half an hour, it yields an equilibrium mixture that contains 97% of the *trans* isomer (5). Non-bonds are clearly beating bonds.

### Phosphine Complexes of Zero-Valent Platinum and Palladium

The compounds  $[\text{Pt}(\text{PPh}_3)_4]$  and  $[\text{Ni}(\text{PMe}_3)_4]$  are easily made (16). However, in solution  $[\text{Pt}(\text{PPh}_3)_4]$  dissociates, forming the three-coordinate trigonal planar complex  $[\text{Pt}(\text{PPh}_3)_3]$  with P-Pt-P angles of 120°. The crystal structure of  $[\text{Pt}(\text{PPh}_3)_4]$  shows quite certainly that the metal atom is four-coordinate with P-Pt-P angles close to 109°; that is, it is tetrahedral (17). It seems that the spatial requirement of triphenylphosphine can be both 120° and 109°, both of which are considerably smaller than Tolman's value of 145° for the cone angle. In fact, there is no contradiction, because in this tetrakis case the phenyl rings are locked together like gears. There are also severe compression strains within the ligand: enlarged Pt-P-C and compressed C-P-C angles. Relief of these strains accompanies the dissociation of the complex in solution. By the same token, the inter-ligand repulsions in the compound  $[\text{Pt}\{\text{P}(\text{cyclohexyl})_3\}_3]$  are surprisingly small, a result of the "intermeshing" of the cyclohexyl groups which reduces the effective bulk of the ligand far below Tolman's

estimate of about  $170^\circ$  for its cone angle (18). If the phosphine ligand is large enough, only two ligands can be fitted onto the platinum atom, and the P–Pt–P backbone is linear. The compound  $[\text{Pt}\{\text{PPh}(t\text{-Bu})_2\}_2]$  is an example (Fig. 5) (19).

### Addition of $\text{O}_2$ to $[\text{Platinum(0)}(\text{phosphine})_2]$

It is possible to prepare a variety of these linear bis-phosphine complexes of platinum(0) and palladium(0) (19). Some of these compounds are sensitive to oxygen, forming compounds of the class  $[\text{Pt}(\text{PR}_3)_2\text{O}_2]$ ; others are quite inert to oxygen (11). The explanation is given by simple consideration of the cone angles of the phosphine ligands involved. Where the ligand has a sufficiently large cone angle (e.g.,  $\text{PPh}(t\text{-Bu})_2$ ,  $\theta = 170^\circ$ ), the compound is inert. The platinum atom is shielded from the outside world by the bulky organic moieties, rendering it inert to attack because there is no pathway for the oxygen molecule to approach the metal atom; nor is there space in the coordination sphere about the metal atom to accommodate the  $\text{O}_2$  should it come within bonding distance. When the cone angle is smaller, the compound is easily formed; for example,  $[\text{Pt}(\text{PPh}_3)_2]$  immediately reacts with oxygen to yield  $[\text{Pt}(\text{PPh}_3)_2\text{O}_2]$  (20). The compound  $[\text{Pt}\{\text{PPh}(t\text{-Bu})_2\}_2\text{O}_2]$  can be made by an indirect route (21) and the crystal structure shows beautifully how the anisotropy of the ligand allows the compound to exist (Fig. 6). The phenyl rings of the phosphine ligands lie face to face, just touching, in a typical Kitaigorodskii close-packing mode, reducing the effective size of the ligands to give a P–Pt–P angle of  $113^\circ$ , well below its cone angle. It is impossible to fit the two phosphine ligands onto the metal in any other orientation.

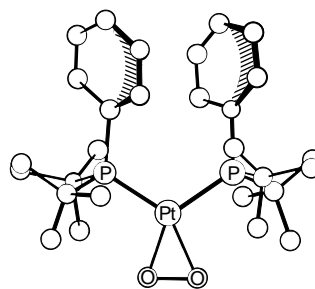


Figure 6. The molecule  $[\text{Pt}\{\text{PPh}(t\text{-Bu})_2\}_2\text{O}_2]$ . The two phenyl rings lie face to face, just touching.

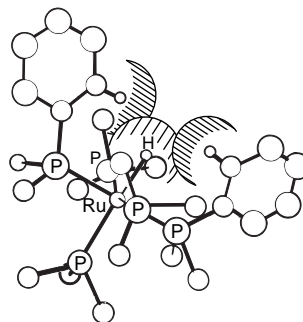


Figure 7. Cation  $[\text{RuH}(\text{PMe}_2\text{Ph})_5]^+$ , showing how the van der Waals surfaces of the hydrogen atoms on the two phenyl rings protect the H atom that is bonded to the ruthenium.

### Reactive $[\text{RuH}(\text{PMe}_2\text{Ph})_5]^+$

In 1974 a number of cationic hydride complexes of the type  $[\text{RuHL}_5]^+$ ,  $\text{L} = \text{P}(\text{OR})_3$ , were prepared and found to be remarkably inert in solution. Subsequently, the compound  $[\text{RuH}(\text{PMe}_2\text{Ph})_5]^+$ , with a far bulkier phosphine ligand, was prepared and found to be highly reactive in solution and a precursor to a large range of new Ru(II) complexes formed by the substitution of one or more of the five phosphine ligands (22). The crystal structure of the  $\text{PF}_6^-$  salt clearly showed the severe compression strains of the  $\text{PMe}_2\text{Ph}$  ligands, (Ru–P–C angles opened and C–P–C angles closed) and the “interlocking” of the methyl and phenyl groups of adjacent ligands to effectively reduce the cone angle. The H atom on the ruthenium atom is shielded by the van der Waals bulk of the phenyl and methyl groups of four of the  $\text{PMe}_2\text{Ph}$  ligands (Fig. 7). What should have been a labile H atom is rendered inert by non-bonds.

### “Umbrella” Effect in the Purple Isomer of $[\text{Ru}(\text{S}_2\text{CH})(\text{PMe}_2\text{Ph})_4]^+$

Reaction of  $[\text{RuH}(\text{PMe}_2\text{Ph})_5]\text{PF}_6$  with  $\text{CS}_2$  yields an octahedral orange dithioformato complex  $[\text{Ru}(\text{S}_2\text{CH})(\text{PMe}_2\text{Ph})_4]^+$  (23), which rearranges in boiling methanol to a purple isomer (Fig. 8) (24). This isomer has three  $\text{PMe}_2\text{Ph}$  ligands arranged facially on the ruthenium atom, while the P atom of the fourth is bonded to the carbon of the  $\text{CS}_2$  group. The effective cone angles of the  $\text{PMe}_2\text{Ph}$  groups are larger in the purple isomer

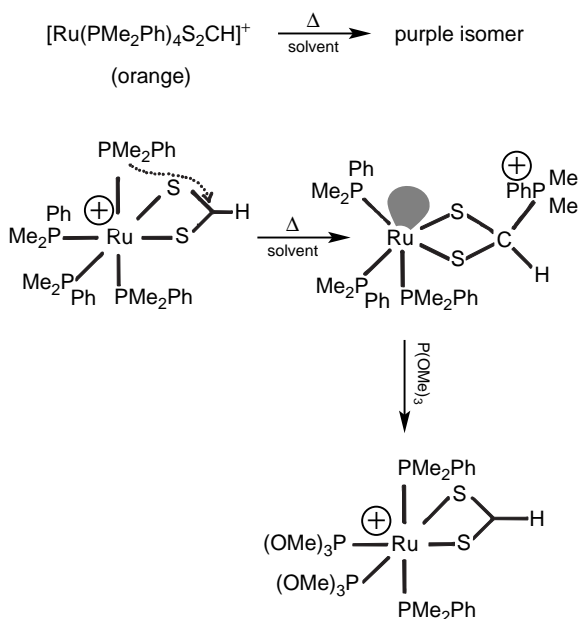


Figure 8. A schematic pathway showing how reaction of the “purple” isomer with phosphite ligands of small cone angle will cause reversal of the reaction and thus yield the “orange” isomer.

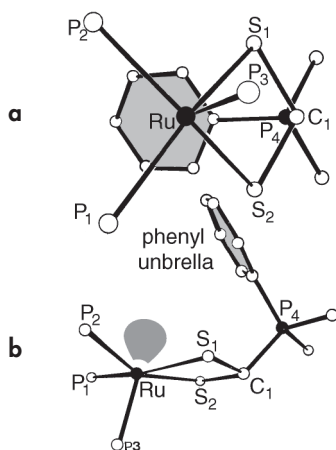


Figure 9. (a) Top view and (b) side view of the "purple" isomer of  $[\text{Ru}(\text{S}_2\text{CH})(\text{PMe}_2\text{Ph})_4]^+$ , showing how the phenyl ring bonded to P4 protects the back of the ruthenium atom.

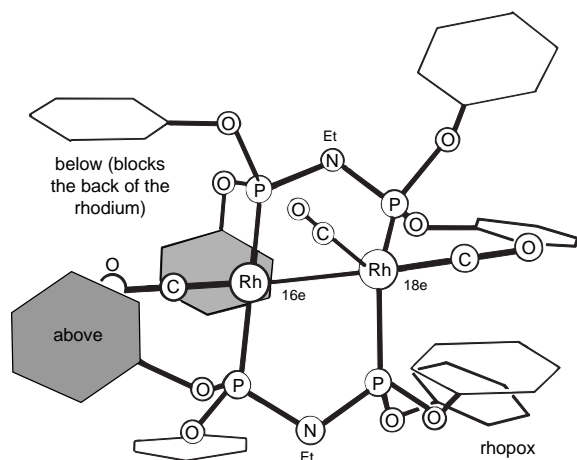


Figure 10. The structure of  $[\text{Rh}_2(\text{CO})_3\{(\text{PhO})_2\text{PN}(\text{Et})\text{P}(\text{OPh})_2\}_2]$ , showing how the square planar Rh atom is protected by the phenyl ring, which blocks the approach of any potentially reactive species such as a CO molecule.

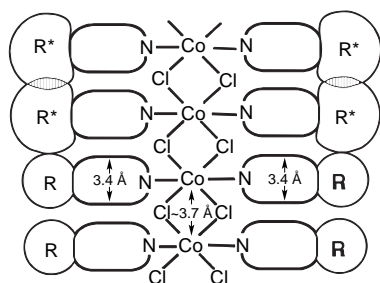


Figure 11. A schematic diagram of the crystal structure of a typical violet  $[\text{CoCl}_2(4\text{-Rpy})_2]$  compound. When the van der Waals diameter of the group  $\text{R}^*$  is about 4 Å, they will have to interpenetrate if the molecules pack in this chainlike mode. This is impossible, and so the molecule is tetrahedral and monomeric.

with a coordination number of 5 than in the orange isomer with a coordination number of 6, indicating that relief of nonbonded repulsions accompanied the transfer of the unique  $\text{PMe}_2\text{Ph}$  group from the Ru to the C atom. This rearrangement is reversible if the purple isomer is heated with  $\text{P}(\text{OR})_3$  ligands of smaller cone angle, giving an orange dithioformate compound with the two smaller ligands as the equatorial cis pair, trans to the two S atoms of the  $\text{S}_2\text{CH}$  moiety. Reducing the steric compressions in the equatorial plane thus allows the Ru-P bonds to become favored.

This example shows how delicate is the balance between bonds and non-bonds; how fine the line is between the electronic covalent bonding forces and the repulsions due to the bulk of inert groups. More interesting, however, is the inertness of the 5-coordinate Ru atom in the purple isomer. The reason is simple: the vacant coordination site on the Ru atom is protected by a phenyl ring "umbrella", which completely blocks access to the Ru atom. The Ru...C distances exceed the sum of their van der Waals radii, but the gap is nevertheless small enough to exclude approach of either solvent or reactant molecules (Fig. 9).

## 16 Electrons or 18 Electrons?

Reduction of  $[\{\text{RhCl}(\text{CO})(\text{PhO})_2\text{PN}(\text{Et})\text{P}(\text{OPh})_2\}_2]$  with Zn/Hg in methanol under CO gas yields the unexpected: *not* the symmetrical structure with four CO and two 18-electron rhodium atoms but  $[\text{Rh}_2(\text{CO})_3\{(\text{PhO})_2\text{PN}(\text{Et})\text{P}(\text{OPh})_2\}_2]$ , a compound with only three CO groups, all terminal (25). The crystal structure shows that one Rh atom is 5-coordinate and obeys the EAN rule, while the other is square planar with a 16-electron configuration (Fig. 10). The back of this Rh atom is completely shielded by a phenyl ring that blocks all access, preventing possible reaction with a CO molecule in solution to give the hypothetical 18-electron product. The 16-electron configuration is thus protected by a distant phenyl ring "umbrella", remote from the rhodium atom, which blocks the approach of the potential electron-pair donor.

## Complexes of $\text{CoCl}_2$ with 4-Substituted Pyridines—Tetrahedral or Tetragonal?

Ethanol solutions of compounds  $[\text{CoCl}_2(4\text{-Rpy})_2]$  are deep blue. For some substituents, R, violet-pink crystals are formed on evaporation; for other substituents the crystals are deep blue, suggesting that only in these cases is the species in the crystal identical with that in solution (26). Violet crystals are formed where R is H, CN, vinyl, or phenyl. Determination of the crystal structures gives an explanation (27, 28). In the crystals of the violet compounds (Fig. 11), the molecules are stacked to give a polymeric ladder of  $-\text{CoCl}_2\text{CoCl}_2-$  atoms. Each Co atom is bonded to four Cl atoms in a square plane, and to the N atoms of two pyridine rings, with the pyridine rings perpendicular to this plane, giving the cobalt a coordination number of 6 with a tetragonal geometry. The Co...Co repeat distance is about 3.7 Å, which can accommodate the pyridine ring, whose thickness is about 3.4 Å. This polymeric stacking will occur for any of the  $[\text{CoCl}_2(4\text{-Rpy})_2]$  complexes on condition that the van der Waals diameter of the group R is 3.7 Å or less. If R is larger, then it becomes impossible to stack the groups R while maintaining the infinite  $\text{CoCl}_2$  chain ladder.



Whatever bonding advantages this chain of  $\text{CoCl}_2$  atoms may have in the tetragonally coordinated violet structures, it is insufficient to overcome the nonbonded repulsions between the R groups once their diameter exceeds the critical value of about 3.7 Å. As a result, the compound simply crystallizes as individual blue tetrahedral molecules, with the cobalt atom having the coordination number of four—which is what occurs for  $[\text{CoCl}_2(4\text{Me-py})_2]$  (27). Interestingly, these latter compounds are isostructural with the zinc analogues in which the zinc atom is always tetrahedrally coordinated both in solution and in the crystal, independent of the bulk of the group R.

### Acetylacetonate Derivatives of Nickel(II), $[\text{Ni}(\text{Acac})_2]_n$

Nickel(II) is found in low-spin square planar compounds such as  $[\text{Ni}(\text{DMG})_2]$ , as low-spin/high-spin tetragonal Lifschitz complexes of the general formula  $[\text{Ni}(\text{en})_2\text{X}_2]$ , and as high-spin octahedral compounds like  $[\text{Ni}(\text{en})_3]^{2+}$  and  $[\text{Ni}(\text{OH}_2)_6]^{2+}$ . These differences in bonding and stereochemistry are due to the differences in the character of the atoms bonded to the nickel. However, the bonding and stereochemistry of  $d^8$  nickel(II) is also susceptible to the bulk of groups remote from the metal atom even when the atoms bonded to the nickel atom are the same. The anhydrous acetylacetonate is trimeric, green, and paramagnetic  $[\text{Ni}_3(\text{Acac})_6]$ , and each nickel atom is bonded to six oxygen atoms (Fig. 12) (29). Of course, the mode of packing of the individual trimeric molecules of  $[\text{Ni}_3(\text{Acac})_6]$  within the crystal is exactly as predicted by Kitaigorodskii: bump-in-hollow.

If the methyl groups of the Acac ligands are replaced by tertiary butyl groups, the anhydrous compound is now red, diamagnetic, monomeric, and square planar  $[\text{Ni}(t\text{-BuAcac})_2]$  (Fig. 13) (30). It is the bulk of the tertiary butyl groups that prevents the formation of the complicated arrangement of ligands required for the hypothetical “trimeric” structure in which the nickel atom would have the octahedral geometry (Fig. 14).

### Neocuproin: 2,9-Dimethyl-1,10-phenanthroline and Copper

A final example of how bulk can make a ligand specific, not only to the metal but also to its oxidation state, is the case of neocuproin and copper(I). Copper(II) forms a square planar complex with regular phenanthroline. However, the 2,9-dimethyl molecule cannot coordinate with  $\text{Cu}^{2+}$  to give a square planar complex  $[\text{CuL}_2]^{2+}$  because of the collisions between the methyl groups on the two ligands. Reduction of  $d^9 \text{Cu}^{2+}$  to  $d^{10} \text{Cu}^+$  immediately and quantitatively yields a colored product  $[\text{CuL}_2]^+$  with neocuproin in which the four Cu–N bonds are arranged in a tetrahedron with the two ligands lying in mutually perpendicular planes (Fig. 15). In this arrangement the methyl groups no longer collide and the complex is stable (31)—so much so that it can be used for the quantitative colorimetric determination of copper in solution.

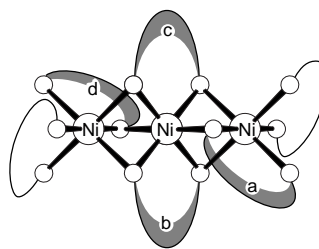


Figure 12. The trimeric complex  $[\text{Ni}_3(\text{Acac})_6]$ . The planar Acac groups are represented by the curved lines and shading.

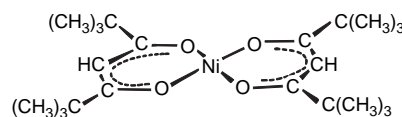


Figure 13. The square planar molecule  $[\text{Ni}(t\text{-BuAcac})_2]$ .

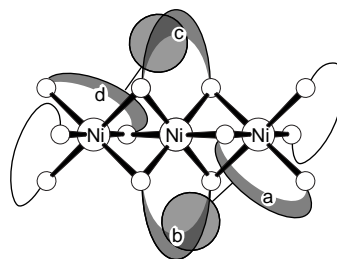


Figure 14. The hypothetical trimeric isomer of  $[\text{Ni}(t\text{-BuAcac})_2]$  cannot form because it would cause collision of the tertiary butyl group on ring a with ring b and the tertiary butyl group on ring d with ring c.

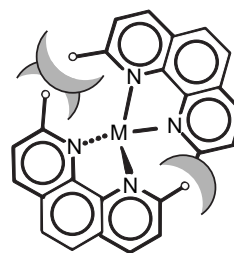


Figure 15. The complex  $[\text{Cu}(\text{neo-cuproin})_2]^+$ , showing the tetrahedral coordination about the  $\text{Cu}(\text{I})$  ion and the manner in which the methyl groups are accommodated.

## Conclusion

These examples are not “recent” but were chosen because from them one can learn many valuable lessons, all of which are encompassed by one simple concept: in a coordination compound it is the bulk of the groups *not* directly bonded to the metal atom that can dictate the stereochemistry, that will control the reactivity, that can cause decomposition to relieve compression, that can speed up reactions, and that can cause inertness by blocking the pathway of a potential reactant. Thus, the nonbonded repulsions between those parts of ligands remote from the metal center have a critical influence on the behavior of the metal atom and can control the structure and reactivity at the metal center of that coordination compound. This is the importance of Non-Bonds.

## Acknowledgment

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