

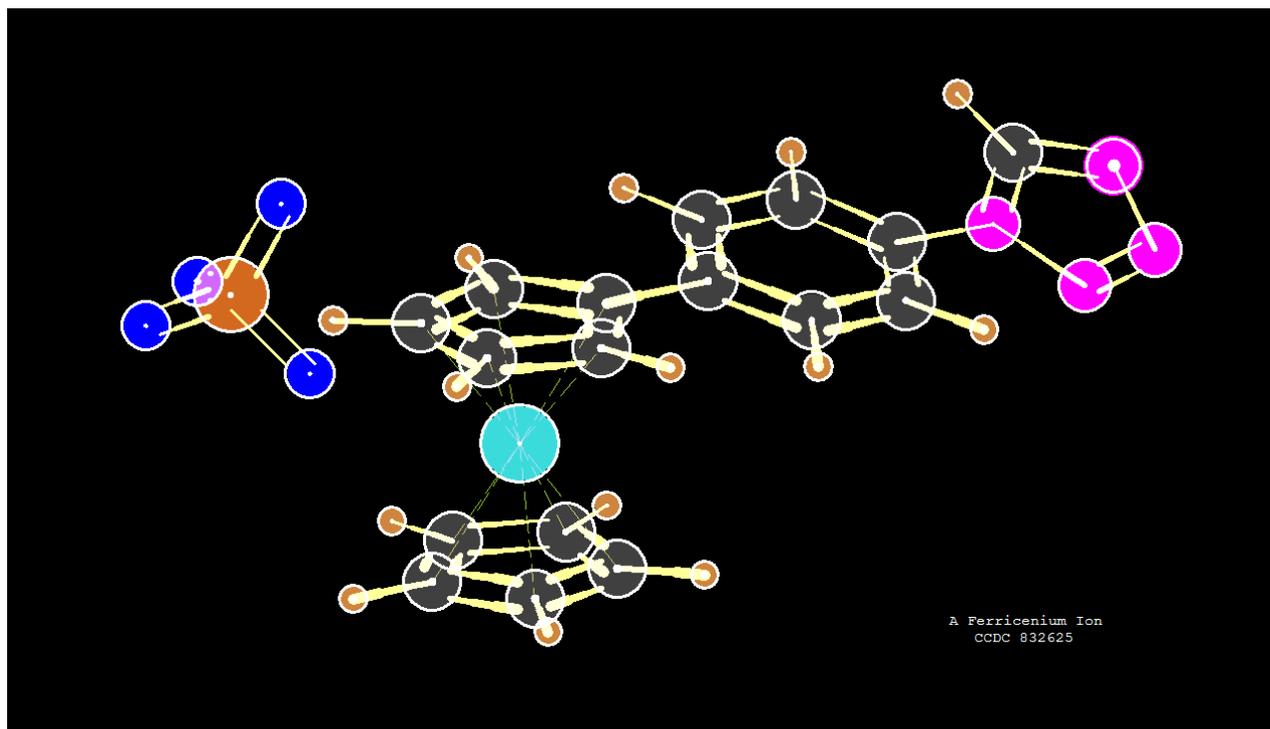
## A Re-examination of The Electronic Structures of the Ferrocenes

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**Abstract** - The X-ray crystallographic data for a large group of ferrocenes have revealed that the central iron atoms are in their Fe(III) state, as is found in their ferricenium ions.

**Key Words** - Ferrocene, Ferricenium ion, structure, x-ray crystallography, oxidation state, charge transfer

### Introduction



The structure of ferrocene has stimulated organic, inorganic and theoretical chemists for decades.[1] Even now, after many of these metallocenes have been made, and their structures confirmed by x-ray crystallography, the unique features of ferrocene still attract considerable attention. Indeed, the details of the bonding in ferrocene cannot be considered to be settled, notwithstanding the efforts of Quantum Chemistry and Molecular Orbital (MO) theoreticians.[2]

While reviewing the x-ray crystallographic structures of organometallic molecules, especially those at the forefront of recently developed catalytic reactions in organic chemistry, many interesting insights into bonding in simple ionic, chelated and organometallic molecules emerged. Among these surprises were intriguing data about the ferrocenes.

In order to be able to understand fully the details of these observations, it was necessary to re-examine the concept of a “bond” in the solid phase. Covalent bonding in organic has been clearly defined by hundreds of years of the chemistry of those molecules, but what of molecules in the solid phase? Do “ionic bond” in the

solid phase have predictable lengths that will enable us to derive meaningful structural information from them?

This work describes only the examination of experimentally obtained (by the diffraction methods) structures in order to avoid the issues that arise from the controversy as to which molecular modeling method is best used to simulate these structures.

### Measuring The Ionic "Bond"

"Molecules" are usually regarded as being ionic if their solutions are largely composed of ions, and so will conduct electricity. This definition is obviously incomplete because it allows for the possibility that these ions might be formed during the solution process, from covalent entities, rather than being present in the pure state of the "molecule". Thus, while the sodium bromide crystal is only be composed of ions, the pure liquid sulfuric acid has no ions, but will become totally ionized when dissolved in water. However, both solutions in water (sodium bromide and sulfuric acid) are regarded as solutions of ionic substances.

Obviously, if there are only ions present in the unit cell of a pure crystalline entity, or liquid, then that material must be regarded as being truly ionic. However, if all the bonds are covalent, and a chemical transformation (solvation) must occur before the ionic nature of the material can be expressed, then the material must be regarded as being covalently bonded.

Ionic organic compounds, for example the common (quaternary) ammonium salts, form an interesting reference group because their simple anions, halides, sulfates, phosphates, etc, are usually independent entities in the unit cells of the crystals of these compounds. The separations of the anions from the centres of the cations are usually controlled by the normal steric, van der Waals and dipolar interactions.

When we examine the unit cell of any inorganic ionic entity, like sodium chloride, that has no other atom/ligand, we expect that the ions will be packed as closely together as is electrostatically feasible, and results in a minimum energy situation. However, we do not intuitively predict the distances of separation of the ions, as we would if these were covalently bonded. Covalent bonds have long been considered to have distinct ranges of lengths, but that concept does not seem applicable to ionic "bonds" or separations.

However, the x-ray crystallographic structures of simple ionic substances revealed that the interionic distances are usually almost identical to the sum of the covalent radii of the elements involved. This observation held for single and multiple bonding.

The metal atom becomes smaller on losing its electrons to become a cation, but the other, electrophilic, atom will increase in size when it accepts these electrons to become an anion. Interestingly, the close packing of these two ions now results in an interionic distance that still is almost identical to that which would have prevailed had covalent bonding had occurred. This simple observation greatly facilitated the development of algorithms for handling, and analyzing, the structures of ionic materials, including clusters and chelates.

As ligands and ions become more structurally complicated, their steric, van der Waals and other dipolar effects will modulate their interatomic/ionic distances. Since the unit cell is a well-defined space, allowing almost no translational movement, we can take the liberty of defining an ionic bond as the interatomic/ionic distance, *only in this context*. Simply measuring distances often is relatively abstract, but measuring bond orders, based on what we would expect if the ionic/atomic separation was indeed covalent, proved to be more informative.

We do not wish to become embroiled in a discussion on the percentage of covalent bonding inherent in each interatomic/ionic separation. Since these measurements are made only in the well-defined geometry of the solid phase, we wish to continue to use bond orders only in this context, the discussion of ionic entities.

These bond orders will later allow us to draw parallels between coordination numbers, bonding type and the total bond order at any given metal atom.

### **Molecular Modeling Considerations**

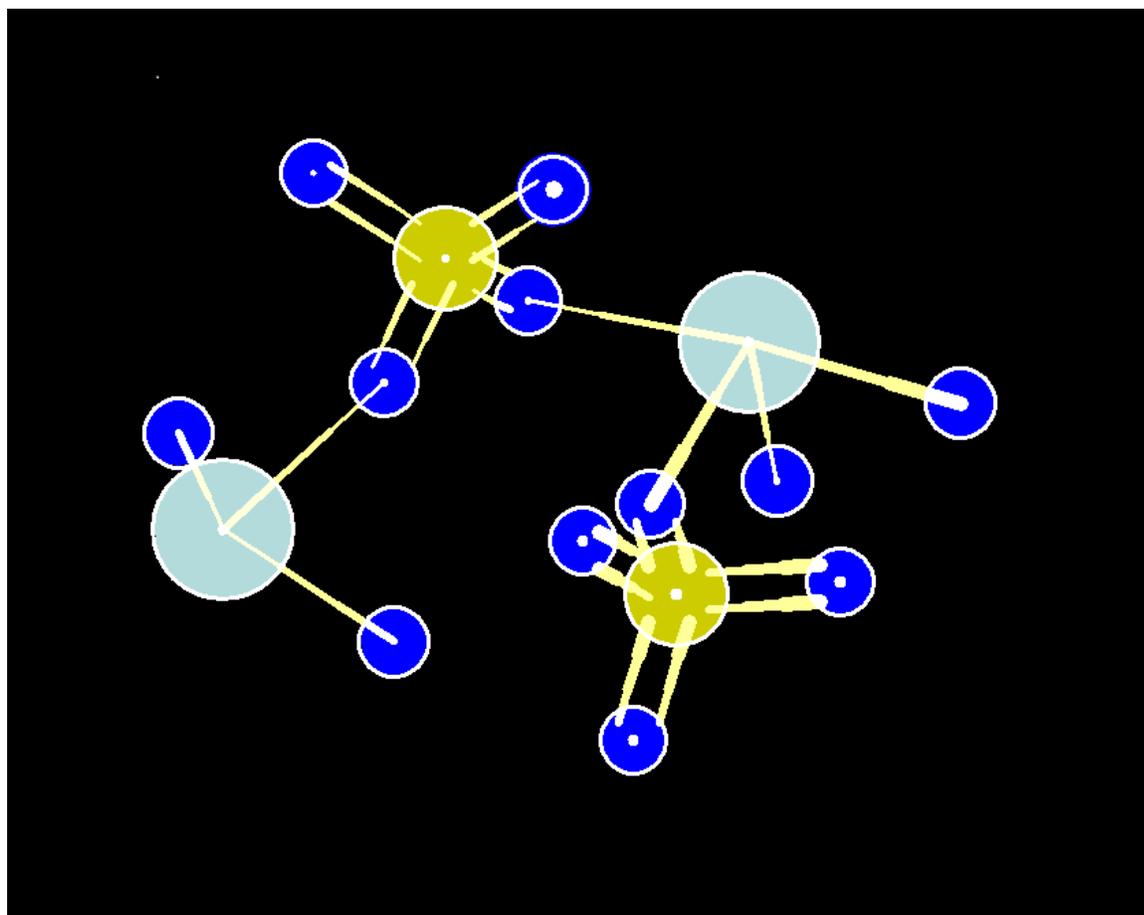
Any molecular modeling programme that will retrieve coordinate data from CIF files will be useful in reproducing this study. It will be very advantageous if the programme can simulate a wide range of molecules by just using the type and coordinates of each atom, since there are often deficiencies/errors in human constructed connectivity tables. The program should be able to determine bond types and bond orders, and to show bond types in the displayed molecular model. The program StruMM3D,<sup>[3]</sup> which fulfills all of the above criteria and has additional useful features, was used to perform this work, and will be referred to herein.

StruMM3D computes the order of a selected bond by comparing the bond's length to the length of the simplest compound containing that bond. So, all C-C single bonds are compared to the length of the ethane bond. Any unsymmetrical, or substituted, alkane will then have, in practice, C-C bond lengths that are longer (smaller bond order) or shorter (larger bond order) than ethane's, and so a bond with order 1.0 is infrequently found in all but the simplest molecules.

Some examples of how the use of StruMM3D facilitated the examination of the structures of some simple inorganic molecules are shown below.

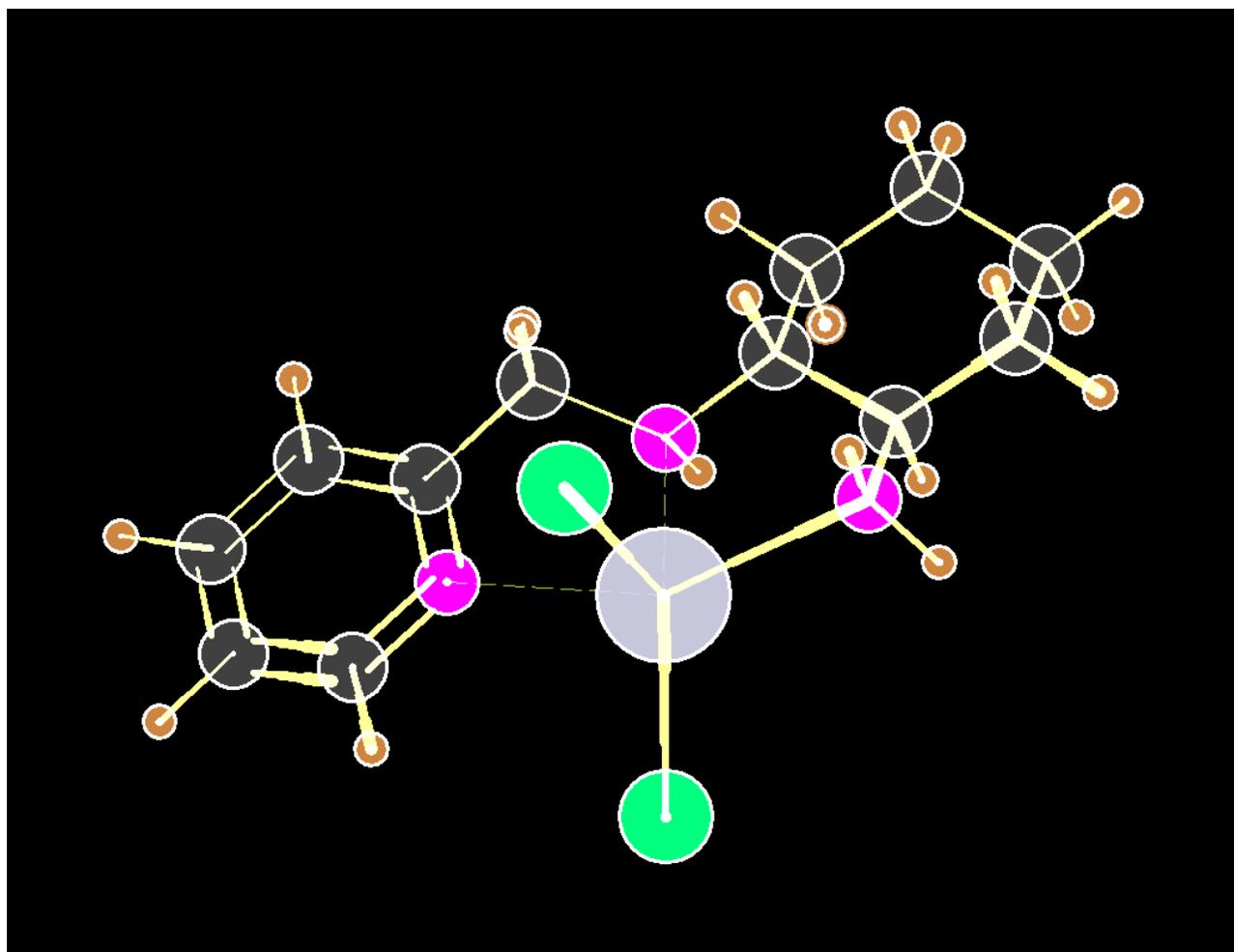
The crystal structure of magnesium sulfate dihydrate[4] is shown in Figure 1. The magnesium atoms are octahedrally coordinated though some ligands are not shown. The average length of the Mg-OSO<sub>3</sub> bond is 206 pm with bond order 0.865. The average length of the Mg-OH<sub>2</sub> bond is 210.6 pm with bond order 0.75. The covalent S=O double bond is about 147 pm with bond order of 1.8. One intuitively expects that since the sulfate oxygen is more negatively charged than the water's, then it should be more closely attracted to the magnesium. The bond lengths and bond orders attest to that. The values of the Mg-OH<sub>2</sub> bond orders are greater than 0.5 and are close to 1, showing that these bonds would be single bonds if they were covalent. The S=O bond length and order are typical of the delocalized sulfate bonds, and their order classify them as delocalized double bonds.

Figure 1. MgSO<sub>4</sub>·2H<sub>2</sub>O



Another revealing example is the crystal structure of mercury(II) chloride chelated by the ligand trans-1-amino-2-(2-pyridylmethylamino)cyclohexane.[5] The three nitrogen atoms are bonded to the mercury(II) ion, but two of these bonds have orders less than 0.5 and are shown as green dashed lines. The bond lengths and orders are Hg-NH<sub>2</sub>R - 232 pm (0.71), Hg-NHRR' - 245.8 pm (0.411) and Hg-N(pyridine) - 246 pm (0.411). These bond lengths and orders are in the sequence of the basicities of the nitrogen atoms, and their nucleophilic abilities.

Figure 2. HgCl<sub>2</sub> and Tridentate Ligand, (RK2329.CIF)



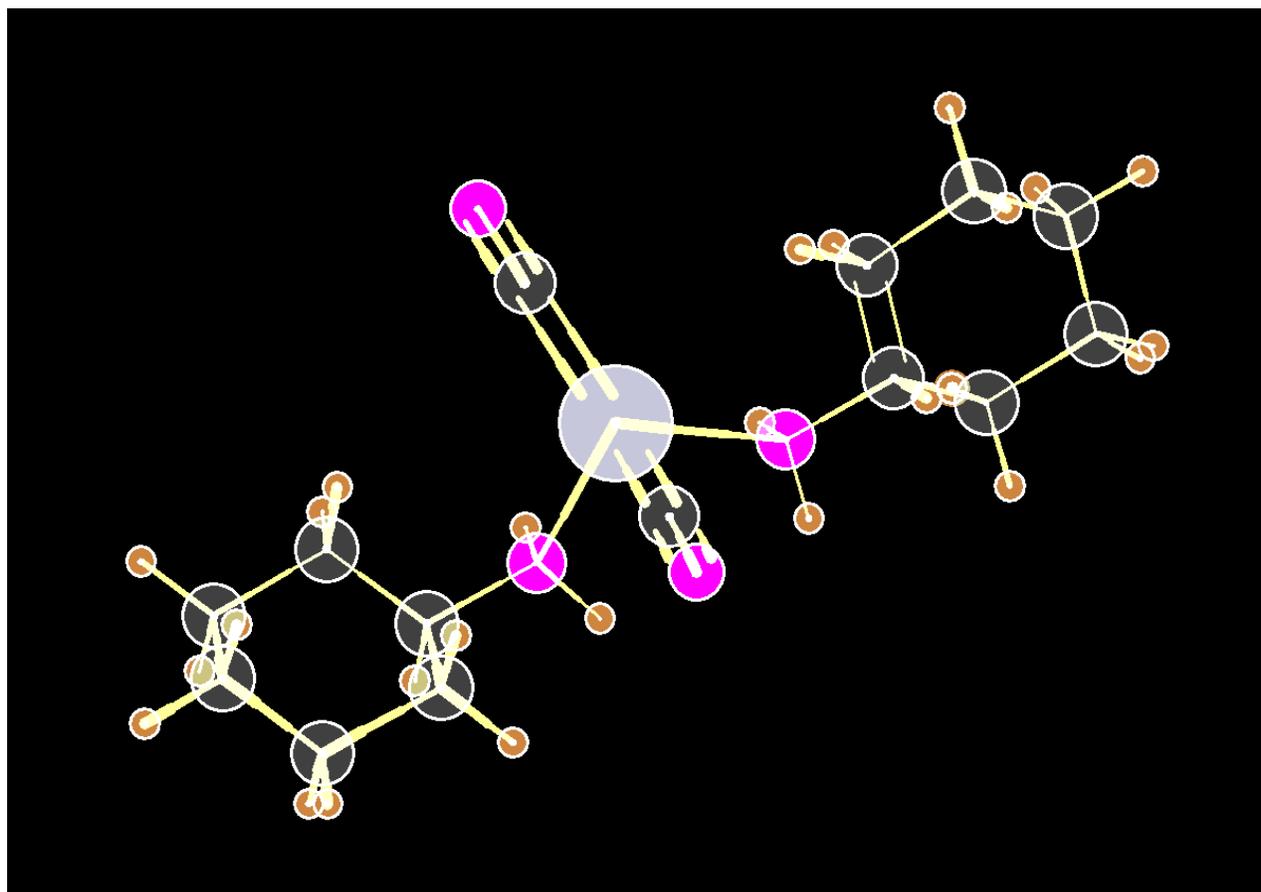
The Hg-Cl bonds are 254.1 and 244.3 pm long with bond orders of 0.92 and 1.16 respectively.

The last example,[6] shown in Figure 3, illustrates an intriguing feature of mercury chemistry.

The mercury-nitrogen bonds are about 240 pm long with bond orders of 0.523. The mercury-cyanide bonds are 209.8 and 208.9 pm long with bond orders of 1.50 and 1.53 respectively. The C-Hg-C bond angle is 145.97 degrees, and so the molecule is a highly distorted tetrahedron, at best. The back bonding between the mercury atom and each of the cyanide carbons is apparent, but quite weak since the  $\pi$ -bond length lower limit has a bond order of 1.5. The cyanide ligands are therefore firmly held by the mercury and the cyclohexylamines much less so.

StruMM3D automatically generates its own connectivity list, and automatically detects all bonds (including hydrogen bonds of all types), just from the atom types and their coordinate data. Thus, flawed preconceived ideas as to bonding patterns, that could taint a human generated connectivity list, are normally excluded. In this way, StruMM3D not only reproduces the x-ray crystallographic structure being examined, *in silico*, but also reveals subtle details of the bonding within the structure. This draws the user's attention to interesting structural features, and greatly facilitates the analysis to be performed.

Figure 3. DicyclohexylaminoDicyanoMercury(II), (WM2295.CIF)



## The Total Bond Order at an Atom

StruMM3D automatically measures the Total Bond Order (TBO) at any atom/ion in the molecule being examined *in silico*, and displays these when needed. It simply measures the Bond Order of each of the bonds hosted by the target atom and sums these.

There is a useful, empirically derived,[7] relationship between the Residual Charge (RC) on an atom/ion, its oxidation state (OxS) and the total bond order at that atom/ion. The oxidation state must be the integral value, and the TBO will be a real number, the sum of the orders of all the bonds hosted by the atom. For covalently bonded molecules, the relationship is -

$$RC = K \cdot (OxS - TBO)^k$$

K and k are constants. The sign of K must be adjusted for the donor/acceptor status of the target atom. Symbolically, if the values of K and k are +/-1 and 1 respectively, then one gets an idea of the magnitude of the residual charge on the atom/ion. Obviously, in a neutral molecule or salt, if we ignore complicating factors like electronegativity and back bonding, the oxidation number at any atom is matched by the integral value of the total bond order at that atom, and RC is zero.

For example, the TBO at any benzene carbon is about 4.3 since each ring carbon has bonds to one hydrogen and carbons via delocalized  $\pi$ -bonds whose orders are about 1.66. The oxidation number of a benzene ring carbon ought to be 4 (its valence state). Thus, the benzene ring carbon ought to have an elevated electron density and be nucleophilic.

By the same analysis, in the transition state during the ionization of iodomethane, where the C-I bond is breaking and has a bond order less than 0.5, the oxidation number of the carbon is still 4, the TBO will be less than 4, and so the carbon must carry a decreased electron density.

The x-ray crystallographic structure of mercury(II) cyanide,[6] above, shows back bonding between the metal and the cyanide groups, the oxidation state of the mercury is +2 and the TBO was 3.03. Hence, if we ignore the contributions of the other ligands, the back bonding bestows a significant charge on the mercury atom/ion.

This same analysis, which seems to hold for covalently bonded and ionic molecules, will be useful in our discussion of the ferrocenes and the ferricenium ions, below.

## Coordination Number

From the discussion above, it ought to be clear that the number of ligands to a metal ion ought not to be taken as the number of fully formed bonds between the metal and the ligands. Bonds that have bond orders well below 0.5 are very weak transition state bonds, involve very little sharing of electron density, and cannot be seen to be equivalent to fully formed two electron bonds..

## The Ferrocenes and Ferricenium Ions

If we examine the x-ray structures of the ferrocenes and ferricenium ions, one finds, remarkably, that they have identical geometries, and their cyclopentadienide anions are identical in geometry to that of a metal-free cyclopentadienide ring, as in tris(1,2-dimethoxyethane-O,O')sodium pentaphenylcyclopentadienide.[8]

There is no puckering of the rings, or departure from planarity of any atoms of the cyclopentadienide rings, in the ferrocenes and ferricenium ions, just as in the isolated cyclopentadienide ion. The cyclopentadienide anions in the ferrocenes and the ferricenium ions are therefore just as aromatic as the metal free anion.

Indeed, the electrophilic aromatic substitution chemistry of the cyclopentadienide rings of the ferrocenes is facile and well known, even in undergraduate experiments. If the central iron ions in the ferrocenes and ferricenium ions were indeed formally covalently bonded to the carbons of their cyclopentadienide rings, then a loss of aromaticity ought to have occurred, as well as detectable distortions in these rings.

Thus, the cyclopentadienide units of the ferrocenes and ferricenium ions show no evidence of being covalently bonded to the iron core atom/ion and must be held in position, as in a true salt, by electrostatic forces only.

What is most remarkable about the ferrocenes and ferricenium ions is that their Fe-C bonds are all the same lengths, approximately 206 pm within the limits of experimental error, and, further, the “thickness” of the complex (from one cyclopentadienide ring plane to the other) is the same, about 330 pm. If, indeed, the oxidation states of the iron ions in the ferrocenes were +2, and those in the ferricenium ions were +3, then the ferrocene Fe-C bond lengths ought to be different from those of the ferricenium ions, and thus too the width of the complexes.

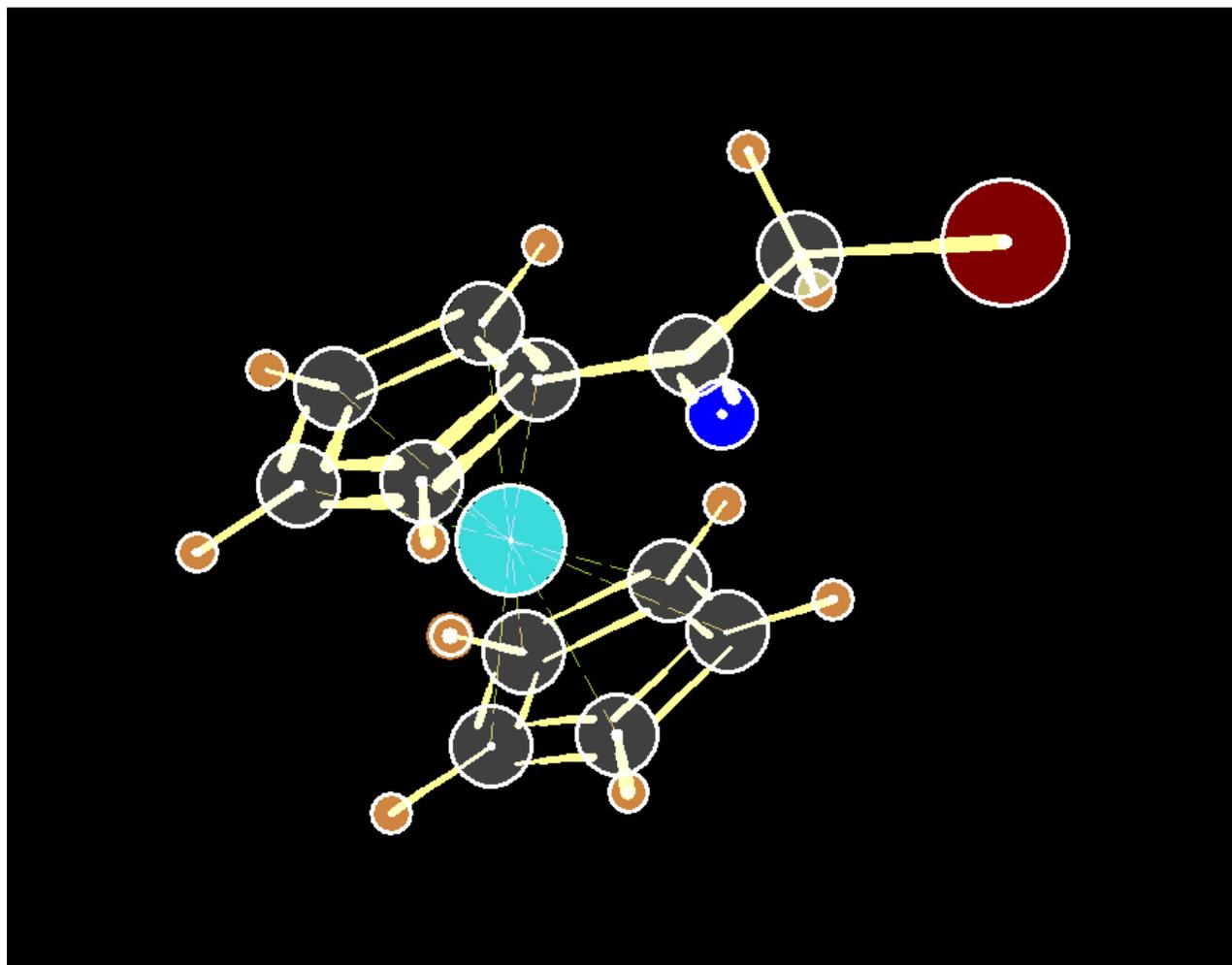
This data suggests that somehow, in both the ferrocenes and the ferricenium ions, the oxidation state of the central iron ion must be identical, and be +3. Fortunately, molecular modeling can help us to confirm this hypothesis.

When the coordinate data of the ferrocenes were imported into the molecular modeler, and the central iron atom was assumed to be Fe(II), the TBOs measured at these iron atoms were about 6.5. On the other hand, the TBOs for the iron atom in the ferricenium ions, which must be Fe(III), were about 2.8.

Normally the TBO at an atom, or ion, is approximately equal to the oxidation number of the atom or ion, so minimizing the Residual Charge value, unless unusual stereoelectronic events, like back bonding, are occurring. Therefore, these RC values signaled that there was a problem with the molecular modeling assumptions regarding the core iron ion in the ferrocenes.

We know that the ferricenium ion has the central Fe(III) ion. However, as mentioned above, the Fe-C bond lengths, and the thickness of the ferrocene and ferricenium complexes were identical. Thus, the assumption that the ferrocene structure possessed the central Fe(II) ion can no longer be justified. That assumption ignores the difference in the sizes of the Fe(II) and Fe(III) ions.

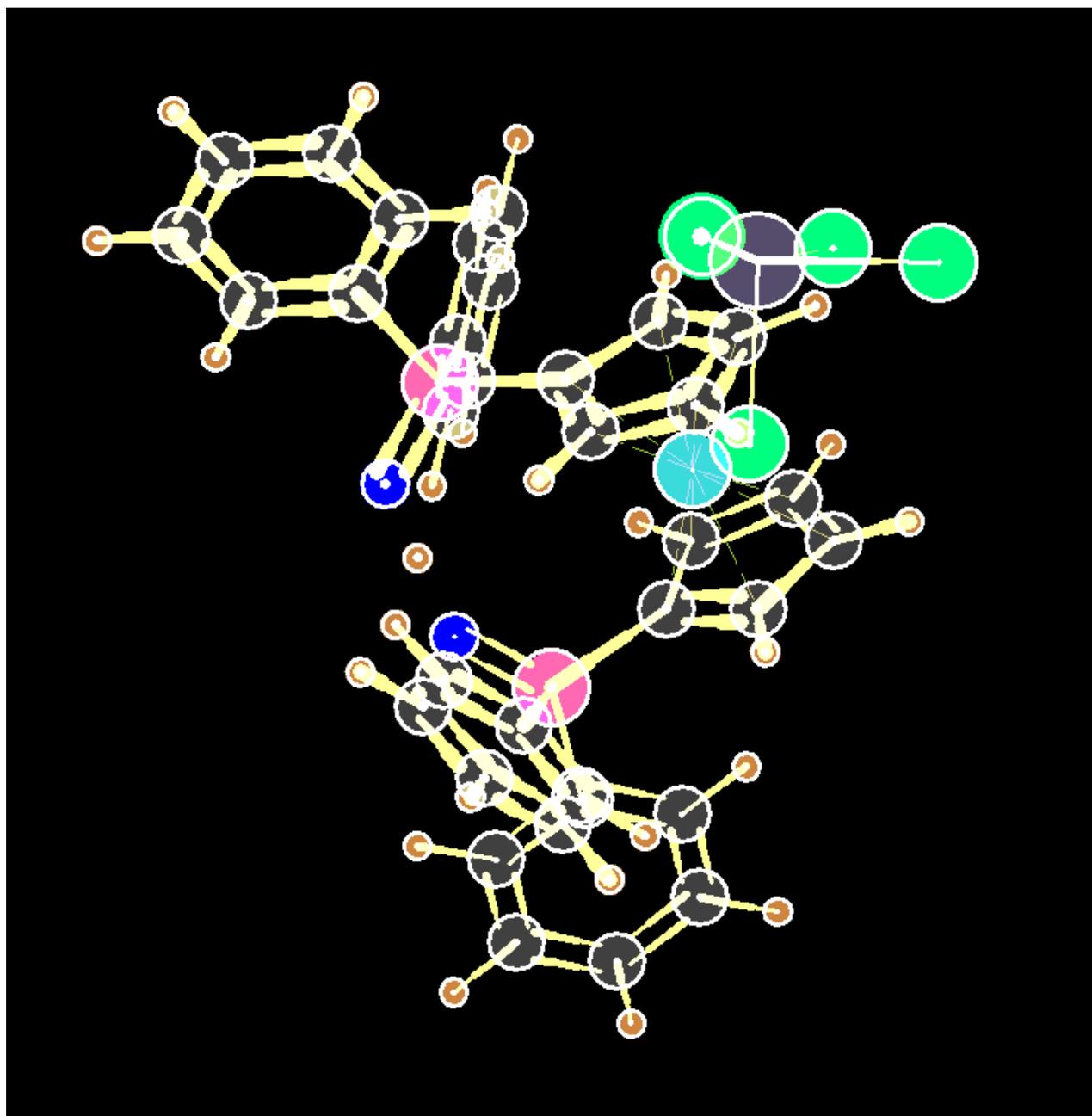
Figure 4. (2-Bromoacetyl)ferrocene, (HG5144.CIF) [9]



Ferrocene with the larger Fe(II) ion in the complex should have longer Fe-C bonds, and with longer Fe-C bonds, the molecule should be wider. However, this molecular geometry would not be consistent with the experimental x-ray crystallographic coordinate data.

Molecular modeling enables us to examine this ferrocene issue by changing the value (in the molecular modeling program used) of the covalent radius of the iron ion from that of Fe(II) to Fe(III), and measuring the TBO of the iron ion. In this exercise no changes would be made to the coordinate data from the crystallographic studies, so avoiding any controversy.

Figure 5. A ferricenium hexachloroantimonate salt, (LN1132.CIF) [10]



Indeed, when the covalent radius of the iron atom in the ferrocenes was assumed to be that of Fe(II), the TBO of the iron in these ferrocenes was about 6.5. However, when the covalent radius of the iron atom was that of Fe(III), the TBO of the iron was only about 2.8, similar to the oxidation number and identical to that seen in the ferricenium ions.

From the empirical relationship shown above,  $RC = K \cdot (OxS - TBO)^k$ , the Residual Charge on the central iron ions in the ferrocenes with an Fe(II) nucleus would have been  $RC = K \cdot (2 - 6.5)^k$ , i.e.  $RC = 4.5$ . With a central Fe(III) ion, the Residual Charge value on that ion would be  $RC = K \cdot (3 - 2.8)^k$ , i.e.  $RC = 0.2$ , identical to that of the iron in the ferricenium ions. The large RC value, of 4.5, would suggest extensive

electron density exchange, or covalent bonding, between the iron of the ferrocenes and their cyclopentadienide rings. These extensive electron density exchanges would have had a detrimental effect on the geometry and aromaticity of each cyclopentadienide ring.

So, when the molecular modeling program was instructed to use the Fe(III) covalent radius for the ferrocenes and the Ferricenium ions, the most stable molecular situations were predicted. Thus, the iron ion in the ferrocenes and the ferricenium ions must, indeed, be in their Fe(III) state.

It is now obvious that in ferrocene, one of the  $3d^6$  electrons must have been transferred to the LUMO  $\pi^*$ -orbitals of the cyclopentadienide rings, leaving the central atom in its very stable  $3d^5$  state. Since the transferred single electron's density is spread over both the cyclopentadienide rings, the impact on the aromaticities of these rings should be marginal. In fact, their slightly augmented electron densities should enhance their reactivities in electrophilic aromatic substitution reactions.

The ferrocenes thus join the examples of molecules that have achieved greater stability by an intramolecular charge transfer process.[11] Electron transfers from ferrocenes and to ferricenium ions do not directly involve the iron ion, but instead are from and to the cyclopentadienide rings, respectively.

### **The Ruthenocenes and Osmocenes**

There aren't as many available x-ray structural determinations of ruthenocenes and osmocenes as there are of ferrocenes. However, the data available certainly do suggest that ruthenocenes and osmocenes also have the Ru(III) and Os(III) ions as their nuclear entities, and have undergone intramolecular electron transfer processes.

### **Conclusion**

The structures of the metallocenes should be re-examined for evidence of intramolecular electron transfer, since that feature will alter our understanding of their redox chemistry. Molecular modeling will play an important role in those studies. It might also be prudent to re-examine the QM model of bonding in the ferrocenes.

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