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A NEW ANISOTROPIC CONDUCTOR BASED ON IRIDIUM COMPLEXES OF TETRACYANOBIIMIDAZOLE

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A NEW ANISOTROPIC CONDUCTOR BASED ON IRIDIUM COMPLEXES OF TETRACYANOBIIMIDAZOLE

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Abstract A new anisotropically conductive system is reported based on the partial oxidation of the anion $[Ir(CO)_2Tcbiim]^-$. Both counter cation and anion are found in the neutral stack. The structure of an Ir(II) precursor is related to the conductive system. ($H_2Tcbiim$ = 4,4',5,5'tetracyano-2,2'-biimidazole.)

In the previous paper[1] we described the solution equilibria and charge transfer spectra of the precursors to the new anisotropically conductive system we have recently discovered. Here we report the composition and properties of the conductive solid and the structure of a metal-metal bonded dimer which is closely related to it. The key starting materials are the salts of general formula $M'[Ir(CO)_2Tcbiim]$ in which the anion is completely planar. These salts have colors in the solid state, which vary with the cation, e.g. when M' = $N(Et)_4^+$, red, $N(Me)_4^+$, green, and $C(NH_2)_3^+$, Na^+, K^+, blue-black, implicating a stack formation; however in dilute solutions of acetonitrile all of these salts are yellow.[2] If bromine is added to solutions of the $M'[Ir(CO)_2Tcbiim]$ salts, the expected oxidative addition occurs and six coordinate Ir(III) products result. If these products are mixed with appropriate quantities of the Ir(I) species intermediate oxidation state compounds do not form.

However if solutions of the Ir(I) salts are electrolyzed in the presence of supporting electrolyte which does not contain coordinating anions such as halides, then a gray, metallic appearing, material forms on the electrode which does not resemble any of the starting materials. The substance has a band edge absorption in the IR and a two probe pellet conductivity of approximately 10^{-3} ohm^{-1} cm^{-1} at 2,000 psi is observed. Although the electrode deposited material gives a powder diffraction pattern, single crystals have not thus far been obtained. In order to characterize the band gap more definitively on the powdered pellet, we measured the dielectric constant as a function of temperature in an impedance bridge operating at 10,000 Hz. The results are shown in Figures 1 and 2. The low temperature limiting values, which change in linear fashion, represent the thermal coefficients of the instrument and are subtracted off by extrapolation. The resulting capacitance values give a log-linear plot vs 1/T. From the slope of this plot the band gap is estimated as 0.21 eV in good agreement with the value obtained from the IR absorption edge. This relatively low value band gap suggests that the intrinsic conductivity of a more highly ordered sample would be substantially higher. Efforts to obtain such samples are continuing, however the composition of the material suggests that it may be difficult.

Analytical data for all elements except oxygen, verify the incorporation of perchlorate, allowing us to formulate the material as follows:

$$[NEt_4]_{1-x}[Ir^{1+z}(CO)_2Tcbiim]\,[ClO_4]_y$$

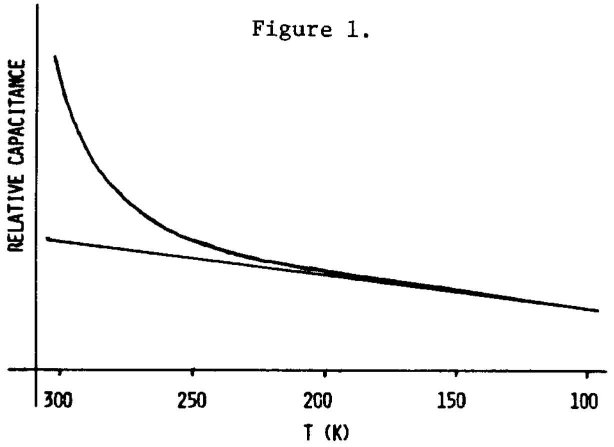


Figure 1.

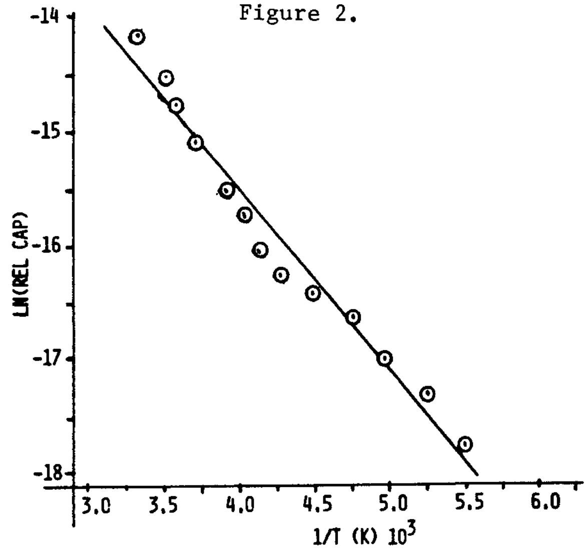


Figure 2.

Let z equal the degree of partial oxidation DPO, then charge compensation could be by cation deficiency i.e. y = 0 and x = z. However y is fixed by the chlorine content. The iridium content fixes the carbon and nitrogen content of the stacking anion and the remainder must be associated with cation. The result of this calculation suggests that another condition approximately holds, namely that x = y. This condition would hold if only one site were available for non-stacking ions and if a requirement for a precipitation were that the non-stacking sites be filled. It is noteworthy that NR_4^+ and ClO_4^- are approximately the same size when R = Et, Me. Thus our best fit from the analytical data gives x = 0.17, y = 0.17, z = 0.33. Since z is also the DPO, it can be checked against the the number of Faradays passed through the cell assuming 100% current efficiency. This value is in agreement giving a value z = 0.33 This type of charge compensation is a novel contrast to the tetracyanoplatinate systems where cation deficiency or anion deficiency both occur but not together. (We follow the common usage in the literature on tetracyanoplatinates and call y the anion deficiency although it would seem more reasonable in our system to call it the anion surplus.) In our preceeding paper we described the formation in solution of a mixed valence ion $[Ir(CO)_2Tcbiim]_6^{4-}$, abbreviated $[Ir(1.33)]_6^{4-}$, as the precursor to the semiconductive solid. In the presence of supporting electrolyte the composition given above can be written as forming from this ion by:

$$[Ir(1.33)]_6^{4-} + 5NEt_4^+ + ClO_4^- \longrightarrow [NEt_4]_5[Ir(1.33)]_6[ClO_4]$$

It is interesting that this material, which incorporates supporting electrolyte anion, is much less soluble than the anion-free semiconductor described earlier. The role of anion in stabilizing the solid is unclear and it may not be ordered on the site which it presumably shares with the cation. Although direct structural information is not available on this point, we do have structural data about the likely stack motif from a closely related Ir(II) dimer.

If the electrolysis is carried out in the absence of supporting electrolyte, the solution darkens but no semiconductor forms on the electrode. If continued to the point of oxidation of one electron per iridium, a pale green solid precipitates. This solid has the composition $Ir_2(CO)_4(Tcbiim)_2 \cdot (CH_3CN)_2$ and was shown <u>vide supra</u> to be the direct precursor to the semiconductor by an equilibrium involving the Ir(I) salt. If triethylphosphite is added to a suspension of this dimer in acetonitrile, a solution forms, from which crystals can be grown. The crystal structure of $Ir_2(CO)_2(CH_3CN)_2[P(OEt)_3]_2(Tcbiim)_2$ will be reported in detail elsewhere.[3] Here we focus on those aspects which can elucidate the stacking in the semiconductor. A labelled structure is shown in Figure 3 and a view down the metal-metal axis in Figure 4. In the process of oxidation, one carbonyl group from each iridium is replaced by one acetonitrile. This change does not occur in the semiconductor, but is in accord with the necessity for better donors as the oxidation state rises. Except for this change the stacking unit is identical in the two cases. At this time, this is a unique example of Ir(II) dimerization in the absence of bridging ligands.

Figure 3.

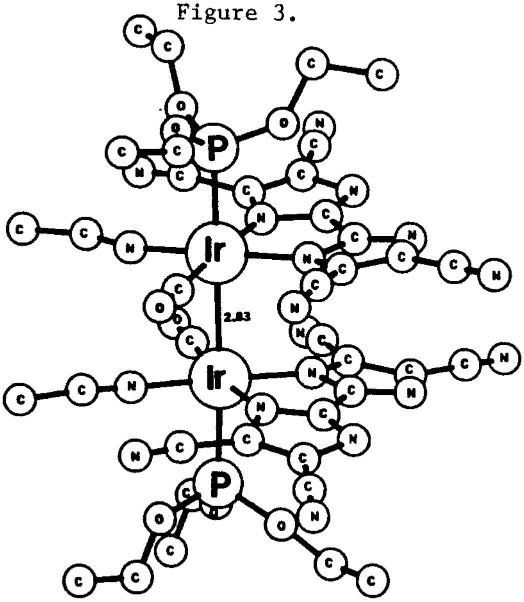
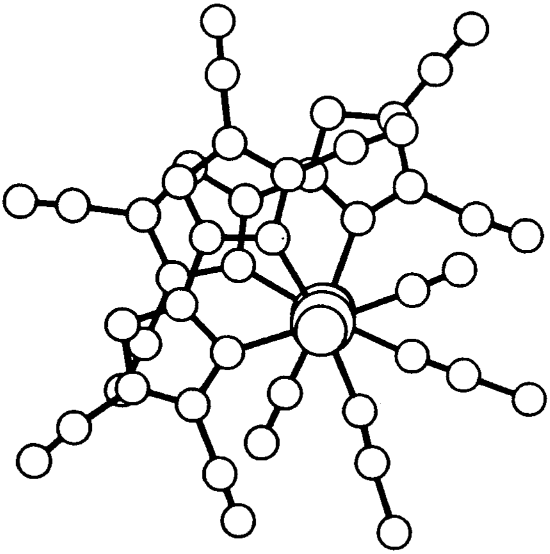


Figure 4.



The metal-metal distance has fallen from 3.183 Å in the unoxidized association dimer to 2.826 Å in the Ir(II) dimer, corresponding to a full single bond. The bond axis is nearly linear and the $Tcbiim^{2-}$ units are rotated by 45° about this axis, compared to 180° orientation about an inversion center in the association dimer. Whether this orientation results from favorable HOMO-LUMO interactions of the sort described by Miller[4] in the platinum oxalate systems is under further investigation by our group. There is some evidence of strain imposed by the metal-metal bond because the Tcbiim best planes bend away from each other with a dihedral angle of 9.6°. This strain will be less in the semiconductor structure where the metal-metal bond is likely longer but it could be accommodated in any case by the adoption of a helical structure for the stack. A number of interesting questions remain unanswered. Does periodicity of the counter ions match the periodicity of the stack? Can the long range order be altered by variation of the counter ions? These and related questions are under further investigation.

The utility of the tetracyanobiimidazole ligand for participation in stacking structures has been demonstrated. The delocalized charge structure which it offers is apparently compatible with layered conductors. This is one of the few cases of deliberate ligand design which has been successful in this field. On the other hand nature can always provide surprises. Although we are able to synthesize the isoelectronic Pt(II) analog to our Ir(I) monomer, $[Pt(CN)_2Tcbiim]^{2-}$, it has not proven possible to prepare analogs to the tetracyanoplatinate conductors.[5]

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