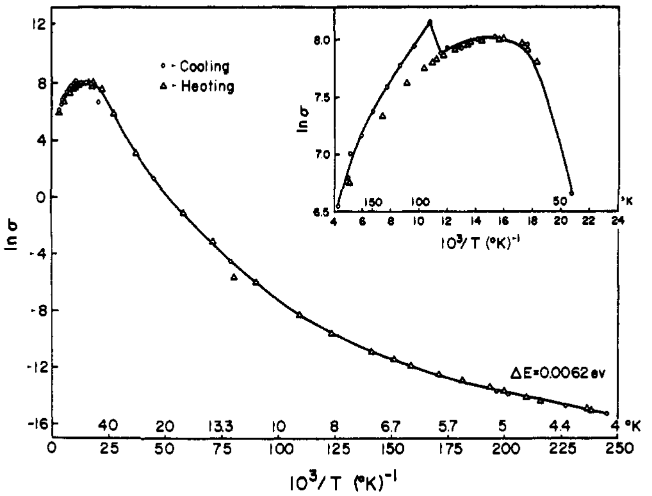

Figure 1. Natural logarithm of σ in ohm^{-1} cm^{-1} *vs.* $10^3/T$ for sample no. JPF-5. ΔE is calculated from $\sigma = \sigma_0 e^{-\Delta E/2kT}$. Insert shows high-temperature region expanded showing hysteresis between cooling and heating curves at the transition; cooling curve determined first.

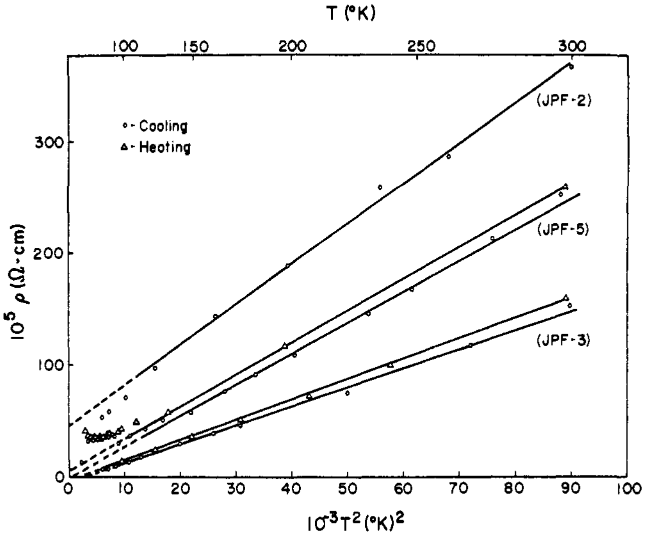

Figure 2. Resistivity, ρ, *vs.* T^2 above the insulator-metal transition temperature for three samples. The slopes are different for different samples.

of TCNQ was used in the synthesis, only the 1 : 1 complex could be obtained.

Single-crystal conductivity measurements along the long axis were made using a four probe method to eliminate contact resistance and thermal emf's as previously described.[1]

Figure 1 shows the temperature dependence of the electrical conductivity (σ) from 4 to 300°K. The insert shows the high-temperature region expanded. The room temperature values are 192, 275, 397, and 652 ohm^{-1} cm^{-1} for four samples, significantly higher than found for any other TCNQ salt [*e.g.*, σ = 100 ohm^{-1} cm^{-1} for quinolinium (TCNQ)$_2$].[8] Qualitatively the data show a semiconductor to metal transition at 66°K, the lowest ever observed for TCNQ salts, with a hysteresis between the heating and cooling curves due to possible structural changes. The transition temperature is independent of sample so that the presence of random concentrations of donor or acceptor impurity levels is not responsible for the observed behavior. The high mobility inferred by the unusually large value of σ at the transition (2980–14,700 ohm^{-1} cm^{-1} depending on sample) makes electrons transfer *via* hopping among localized states an unlikely mechanism.

A positive temperature coefficient of the magnetic susceptibility from 2 to 359°K[18] and a conductivity of 1 ohm^{-1} cm^{-1} perpendicular to the long axis of a crystal were also observed. The activation energy for conduction, ΔE, below 8°K calculated from the relation $\sigma = \sigma_0 e^{-\Delta E/2kT}$ is 0.0062 eV $\equiv$ 72°K close to the semiconductor to metal transition temperature.

The data suggest several models: (a) columns of TTF$^+$ and TCNQ$^-$ which undergo a Jahn–Teller-type distortion at the transition temperature (Peierls distortion);[19] (b) band formation in two directions resulting in a filled band of mostly TCNQ^{2-} states[20] separated from an empty band of mostly TTF^{2+} states[14] (back charge transfer to the monocation and monoanion configuration would result in a semiconductor to metal transition arising from the decrease in the Madelung energy); (c) indirect overlap of two bands to form a semimetal; the transition to the insulating state could result from simple uncrossing of the bands or possibly to electron-hole binding to form singlet excitons on the insulating side of the transition (excitonic insulation).[21,22]

The crystal structure must be determined, however, before any of these models can be discussed in detail.

Whatever the nature of this interesting metallic state, the temperature dependence of the resistivity ($\rho = 1/\sigma$) is atypical for a model involving simple lattice scattering (for which $\rho \propto T^{+1}$) since ρ appears to have a T^{+2} dependence as shown in Figure 2. The high electrical conductivity of TTF–TCNQ provides new impetus for the formulation and preparation of organic compounds which are as electrically conducting as metals like copper, σ (298°K) = 6 × 10^5 ohm^{-1} cm^{-1}.

X-Ray crystal structure studies are in progress to aid in the understanding of the electrical and magnetic properties of the complex.

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Structure of a Planar Four-Coordinate Complex of Copper(I)

Sir:

The novel copper–copper interaction in certain copper(II) carboxylates has been the subject of a very

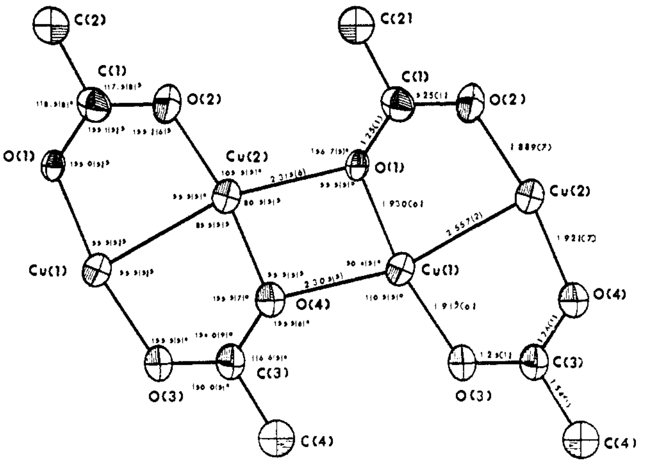

Figure 1. The structure of copper(I) acetate, $Cu(O_2CCH_3)$, showing the bridged eight-membered ring systems. The last digit in parentheses is the estimated standard deviation in the bond distances and angles.

large number of investigations whereas the behavior of copper(I) carboxylates has been almost completely neglected. Although the synthesis of copper(I) formate and acetate has been reported,[1,2] practically nothing is known about their structures or chemical properties. This is in contrast to the structures of copper(II) carboxylates which have been extensively studied and have been shown to fall into one of several well-defined groups.[3] The structure of the dimer, $[Cu(O_2CCH_3)_2 \cdot H_2O]_2$, is typical of the group in which copper–copper interactions are possible.[4] On the basis of a vapor-phase study in our laboratory of a series of copper(I) carboxylates, copper(I) acetate was found to be a dimer in the vapor phase. It was considered likely therefore, that copper–copper interactions might be present in copper(I) acetate in the solid state. An X-ray structure determination of the compound was carried out to test this expectation and the results are reported below.

Since copper(I) acetate is sensitive to air and moisture it was synthesized and crystals of the compound were grown under vacuum. A pyridine solution of anhydrous copper(II) acetate was reduced with copper metal and evaporation of pyridine from the resulting solution gave a white residue which sublimed at 120° under vacuum. The sublimate was dissolved in dry acetonitrile and the solution was filtered through a sintered glass funnel in the vacuum line. Although the copper(I) acetate in acetonitrile slowly disproportionated into copper(II) acetate and copper metal, colorless crystals that were suitable for an X-ray analysis were grown from this solution in 10–30 hr by slow evaporation of the solvent under vacuum. These crystals of copper(I) acetate were unstable in the presence of air or moisture.

Copper(I) acetate, $Cu(O_2CCH_3)$, crystallized in the monoclinic space group $P2_1/m$ with lattice constants a = 5.221 (2) Å, b = 6.259 (4) Å, c = 9.928 (4) Å, and β = 93.63 (3)°. The calculated density for four formula units per unit cell was 2.52 g cm^{-3}. It was not possible to determine the density of the crystals accurately owing to the extreme instability of the complex. The measured density was greater than 1.6 and less than 2.9 g cm^{-3}. A bar-shaped crystal (0.16 × 0.18 × 0.58 mm) which was coated with a film of polyacrylate was used for the data collection. A Picker FACS I automated diffractometer was used to collect the intensity data with Mo Kα radiation to a maximum 2θ of 53°. The intensities of the standard reflections that were monitored after every 20 reflections indicated that the compound did not decompose during the data collection. The structure was solved by Patterson and Fourier methods with 554 observed reflections. The atomic parameters and the anisotropic thermal parameters (for all atoms except the methyl carbon and hydrogen atoms) were refined by full-matrix least-squares techniques to a conventional R value of 0.044.

The molecular geometry and the most significant bond distances and bond angles are shown in Figure 1. Copper(I) acetate is a polymer in which each copper atom is bonded to two oxygen atoms from different acetate groups thereby forming eight-membered rings with long Cu–O bridges (2.30 Å). The Cu–Cu distance in the eight-membered ring is 2.56 Å which is identical with the Cu–Cu distance in copper metal.[5] It may be inferred, therefore, that there is some interaction between the copper atoms in the bridged eight-membered ring. The average of the four approximately equal Cu–O distances in this ring system is 1.91 Å. Each copper atom is coordinated to three oxygen atoms and to another copper atom, all of which are coplanar. Since all the atoms lie on crystallographic mirror planes, the nearest atoms above or below the copper atoms lie on a plane 3.13 Å away. Hence the copper atom in the planar copper(I) acetate polymer is four coordinate. Copper(I) complexes have a tendency to adopt a geometry that is four-coordinate tethrahedral[6] or three-coordinate trigonal.[7] This is the first example of a planar four-coordinate copper(I) complex. The eight-membered dimeric units have a formal resemblance to the structure of dimeric silver perfluorobutyrate[8] although the coordination polyhedron around the silver atoms is a distorted tetrahedron. The structure of copper(II) acetate[4] consists of two mutually perpendicular interpenetrating eight-membered rings. However, the Cu–Cu distance (2.64 Å) and the Cu–O distances (1.97 Å) are significantly longer in the copper(II) acetate than in the copper(I) acetate, and in the former complex the coordination polyhedron around the copper atom is a distorted octahedron.

One question of importance that has not been answered by the above X-ray structural investigation is the extent of the Cu–Cu interaction that is found in the copper(I) acetate polymer. In an attempt to provide an answer to this question we have determined the X-ray photoelectron spectrum of copper(I) trifluoroacetate, which exists as a dimer. The presence of only one oxidation state of copper implies that the Cu–Cu interaction in the eight-membered ring is not

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sufficiently great to affect the d^{10} electrons in the metal atoms.

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Structure of Dicyclopentadienylpentacarbonyldivanadium. A New Example of Grossly Unsymmetrical Carbonyl Bridging

Sir:

The molecule $(C_5H_5)_2V_2(CO)_5$[1] initially attracted our interest in connection with our studies of intramolecular carbonyl scrambling in metal carbonyls.[2-4] However, assigning a satisfactory molecular structure constituted a problem in itself. Structures had been suggested[1] but we were not satisfied that they were consistent with the reported ir spectrum (five CO stretching bands). Moreover, structures with four terminal CO groups and one bridging CO group appeared likely to incorporate also some unusual features such as 16-electron configurations for the V atoms or a triple bond between the V atoms. X-Ray study of this molecule thus promised to be of more than routine interest. The results fulfill that promise but in a remarkable and unanticipated way.

Crystals grown from methylcyclohexane at −20° belong to space group $P2_1/n$ with a = 8.246 (2) Å, b = 15.769 (5) Å, c = 11.729 (2) Å, β = 91.66 (2)°, and Z = 4. A conventional procedure employing Patterson and electron density functions and least-squares refinement, using 1149 reflections with intensities exceeding 3σ, in the range $0 < 2\theta \leqslant 43°$ (Mo Kα) led to the present agreement indices of R_1 = 0.044 and R_2 = 0.050. Hydrogen atoms were included but not refined; all other atoms were refined anisotropically.

The structure is shown in Figure 1. Other dimensions are 1.40 Å for the average ring C–C bond; 2.22 (1) and 2.26 (1) Å for the mean distances of V(1) and V(2) to ring carbon atoms and 1.93 (1) Å for the V(2)–C(12) distance. Each vanadium atom is bonded to one h^5-C_5H_5 ring and to one or two ordinary terminal CO groups.[5]

The remaining two CO groups have an anomalous relationship to the two vanadium atoms. The V(1)–C(14)–O(4) and V(1)–C(15)–O(5) chains are nearly, but not exactly linear (angles of 169°), the V(1)–C(14) and V(1)–C(15) bonds are somewhat shorter than the other V–CO bonds, and the C(14)–V(2) and C(15)–V(2) distances, 2.40 and 2.44 Å, respectively, are too short to be regarded as mere nonbonded contacts.

There does not appear to be any straightforward way to specify the electronic structure of this molecule. For V(1), the V atom itself, the h^5-C_5H_5 group, and the three CO groups contribute a total of 16 electrons to the valence shell orbitals of the metal atom. For V(2), the V atom itself, the h^5-C_5H_5 group, and the two CO groups contribute a total of 14 electrons. It is clear that there are three important interactions between these two [$C_5H_5V(1)(CO)_3$ and $C_5H_5V(2)(CO)_2$] parts of the molecule. There is obviously a metal-metal bond; however, the order of this bond is uncertain. It seems to us that the V(1)–V(2) distance is shorter than would be expected for a simple single bond but also too long to be a full triple bond. It exceeds the recently reported length (2.22 Å) of an Fe–Fe double bond,[6a] as well as that (2.28 Å) of a Cr–Cr triple bond,[6b] but this may be due mainly to the greater intrinsic size of the vanadium atoms. The second and third interactions are between V(2) and the carbonyl groups C(14)–O(4) and C(15)–O(5): these are doubtless weak, but the C–V distances involved leave no doubt that they are real, bonding interactions. In short, C(14)–O(4) and C(15)–O(5) are not simply terminal CO groups, but are grossly unsymmetrical bridging carbonyl groups.

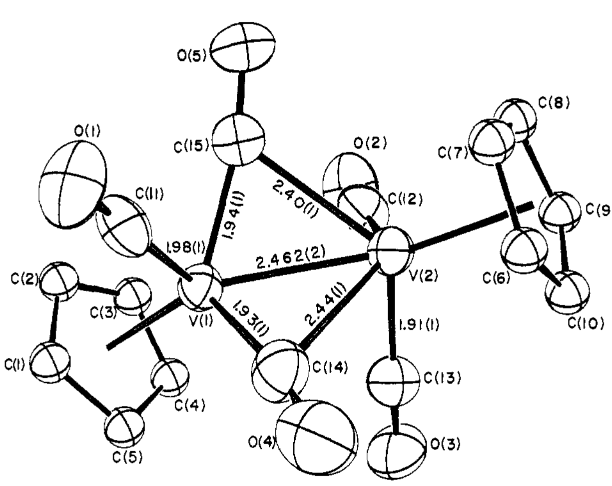

Figure 1. A view of the $(C_5H_5)_2V_2(CO)_5$ molecule, showing some important bond lengths and bond angles. Thermal parameters for the cyclopentadienyl carbon atoms have been arbitrarily reduced for clarity. See text for other important distances.

Grossly unsymmetrical carbonyl bridges are relatively rare but have been observed in at least ten compounds[7] before, the first such observation having been in the $Fe_4(CO)_{13}{}^{2-}$ ion[8] and the most recent in $H_2Ru_4(CO)_{13}$.[9] The exact nature and function of such bridges are not clear. The present compound displays them under relatively uncomplicated circumstances, and may thus help to increase our understanding of these points. Detailed discussion must be reserved for a later paper, however.

Only slightly unsymmetrical CO bridges have been observed in other molecules, *e.g.*, in both $Fe_3(CO)_{11}PPh_3$ isomers.[10] Markedly unsymmetrical NO bridges have also been observed in $(h^5\text{-}C_5H_5)_2Mn_2(NO)_3NO_2$.[11]

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