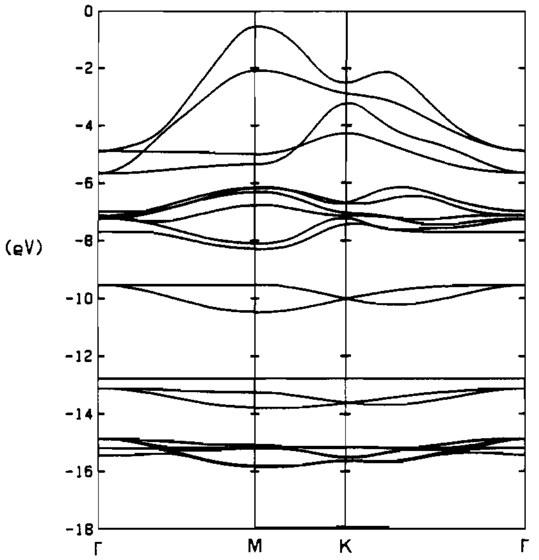

Figure 17. Energy bands for the alternative $Gd_2C_2Cl_2$ structure.

structure. The Fermi level resides in the narrow, but partially filled, π^* band. For narrow band systems, however, electron-electron repulsion may cause each band orbital to be singly occupied by electrons with parallel spin.[29] Therefore, the alternative could show properties consistent with a magnetic semiconductor, but we are unable to predict whether intercell forces would produce a ferromagnetic or an antiferromagnetic ground state.

Returning to the energy difference curve of Figure 15, the predominant dispersion in the π^* band accounts for the minimum. For lower electron counts, the curve compares occupied levels that are essentially localized on the nonmetals. Their relative energies are certainly sensitive to the magnitude of the overlap with Gd orbitals and seemingly favor the trigonal species. The fragment calculation is apparently in conflict with the solid-state results. However, on bending the dimer, we change the coordination of each carbon atom by its Gd neighbors. Nevertheless, in this layered environment with weakened Gd–C bonds, we may expect these dimeric species to become less rigidly held in their observed configuration. Beyond 28 electrons, the dispersion of π^* destabilizes the observed structure with respect to the alternative. Therefore, we may anticipate that alkali-metal intercalation would tend to realign the C_2 dimers with concomitant lengthening of the C–C distance.

Questions and Conclusions

In this paper we directed attention to the structural chemistry of $Gd_2C_2Cl_2$. We emphasized the importance of π interactions between Gd and C_2 for (1) stabilizing the observed orientation of the dimer in the octahedral holes, (2) setting the electron count at 28 electrons per formula unit, and (3) providing its metallic properties. The ionic model coupled with a qualitative MO scheme of a main-group dimer provided an indicator for the C–C bond length but gave no information about Gd-C bonding. Furthermore, we concluded that metal–metal bonding was not a major factor in these materials but did contribute to auxiliary effects, mostly in the dispersion of the bands near π^*.

The structure and bonding of $Gd_2C_2Cl_2$ raise a number of interesting questions. Are changes of the valence electron concentration possible, e.g. by intercalation reactions or by chemical substitution both in anion and cation sites? Do such changes reflect in the C–C bond length and in the orientation of the C_2 unit, which could serve as an indicator for the valence electron concentration? Are other dimeric interstitial species possible, e.g. CN, BN, and even B_2?

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Appendix

All of the calculations described in this paper used the extended Hückel method[30] both for the molecular orbital calculations on the fragments and for the tight-binding computations on the crystalline solids. The atomic parameters are listed in Table III.

The following geometrical constraints were applied: (1) the C–C distance was maintained at 1.36 Å; (2) in the observed $Gd_2C_2Cl_2$ structure, we set $d(Gd_{axial}–C)$ to 2.33 Å, $d(Gd_{basal}–C)$ to 2.65 Å, and d(Gd–Cl) to 2.81 Å. For the alternative structure, the same unit cell volume as for the observed structure was used. All lattice sums included third nearest-neighbor cells in the two directions. For the centered-rectangular cell, 72 special points were used, and for the hexagonal cell, we selected 105 special k-points, both in the irreducible wedges of their respective Brillouin zones.

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Notes

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Electrocrystallization of Poorly Conducting Charge-Transfer Complexes

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Electrocrystallization is a convenient technique for the synthesis of conducting and superconducting one-dimensional "organic metals" such as pyrene,[1] tetrathiafulvalene,[2,3] tetramethyltetraselenafulvalene,[4] and recently bis(ethylenedithio)tetrathiafulvalene complexes.[5,6] However, this method has not been exploited for poorly conducting charge-transfer complexes, which are generally prepared by cooling of saturated solutions or by metathetical methods. Precise control of the rate of crystallization,

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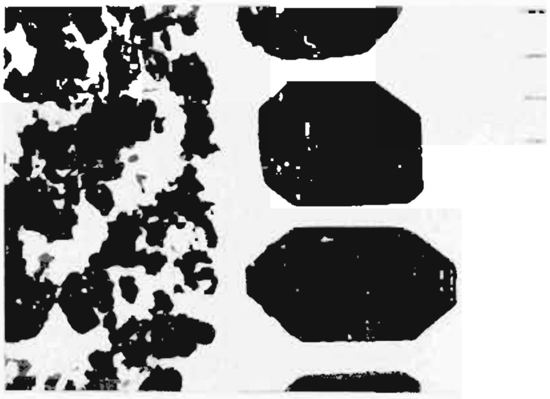

Figure 1. Photograph of **1** grown electrochemically by oxidation of $(\eta^5\text{-}C_5Me_5)_2Fe$ in the presence of $Bu_4N[TCNQ]$. The crystals on the left and right were grown at +300 and 30 μA, respectively. The scale divisions represent 1.0 mm.

and subsequently the size and quality of crystals, is generally not attainable with these two methods. Described herein is the convenient electrochemical preparation of charge-transfer complexes in which one of the constituents is introduced at a controlled rate, thereby regulating the rate of crystallization.

We have been investigating electrocrystallization of charge-transfer complexes, particularly with regard to electrochemically directed phase selectivity in potentially multiphasic systems.[7] The well-characterized decamethylferrocenium–tetracyanoquinodimethane complexes are known to form three different phases: paramagnetic $[(\eta^5\text{-}C_5Me_5)_2Fe]_2[TCNQ]_2$ (**1**),[8] metamagnetic $[(\eta^5\text{-}C_5Me_5)_2Fe][TCNQ]$ (**2**),[9] and conductive $[(\eta^5\text{-}C_5Me_5)_2Fe][TCNQ]_2$ (**3**)[10] (TCNQ = tetracyanoquinodimethane). These complexes have been prepared by conventional techniques: **1** is grown by slow cooling from acetonitrile solutions while **2** is a kinetically preferred phase and is formed upon rapid crystallization. The complex salt **3** is prepared by control of stoichiometry during crystallization. We have found that the synthesis of **1** can be accomplished by oxidation of $(\eta^5\text{-}C_5Me_5)_2Fe$ in the presence of $TCNQ^-$ anion (eq 1) or in the reverse manner by reduction of TCNQ in the presence of $[(\eta^5\text{-}C_5Me_5)_2Fe]^+$ (eq 2). Both methods are feasible since $E°\{(\eta^5\text{-}C_5Me_5)_2Fe/[(\eta^5\text{-}C_5Me_5)_2Fe^+]\}$ (−0.12 V vs. SCE) is sufficiently negative of $E°\{TCNQ/TCNQ^-\}$ (+0.19 V).

$$(\eta^5\text{-}C_5Me_5)_2Fe - e^- \xrightarrow{TCNQ^-} \mathbf{1} \qquad (1)$$

$$TCNQ + e^- \xrightarrow{[(\eta^5\text{-}C_5Me_5)_2Fe]^+} \mathbf{1} \qquad (2)$$

For example, a divided H-cell (medium-porosity fritted-glass separator) was assembled containing a nearly saturated methylene chloride solution prepared from microcrystalline **1**, with 0.04 M $(\eta^5\text{-}C_5Me_5)_2Fe$ (0.40 mmol) and 0.05 M $Bu_4N[TCNQ]$ in the working compartment and 0.05 M $Bu_4N[TCNQ]$ in the other compartment. A platinum-wire electrode (1.0 cm × 0.1 cm) was placed in each compartment and a constant current of +300 μA applied across the cell at 25 °C. After 24 h (2.7×10^{-4} faradays) the mixture was filtered to yield 95 mg of purple, X-ray-quality crystals of **1** (67% Faradaic yield). When the electrolysis was performed at +30 μA, flat, octagonal single crystals of **1** were formed in similar yields that were greater than 10× larger (0.5 × 0.2 cm) than those grown at the higher current density (Figure 1). Crystallization occurred primarily at the electrode since the concentration of the complex initially exceeded its saturation limit in this region. This suggests that nucleation occurs at the electrode surface, followed by crystal growth on those nuclei. The particle size of precipitates is related to the relative supersaturation of the system, as shown in eq 3, where Q is the momentary concentration

$$\text{relative supersaturation} = \frac{Q - S}{S} \qquad (3)$$

of the complex and S is its equilibrium solubility under the crystallization conditions.[11] Thus, crystal size is inversely related to the degree of relative supersaturation that exists during the crystallization process. The size dependence on current for **1** is explained by the formation of more nucleation sites at higher current, equivalent to the situation of high degree of supersaturation (analogous to rapid mixing in metathesis routes). At lower currents the degree of relative supersaturation is smaller and crystal growth on a smaller number of nuclei is favored. Therefore, electrocrystallization can be exploited as a technique for "controlled metathesis" in the preparation of these complexes. Since the current can be precisely regulated, the rate of crystallization can be reproducibly controlled.

Since **2** is conventionally prepared by rapid crystallization, it seemed reasonable that its synthesis could be accomplished by electrocrystallization at large currents (>1 mA). However, black fibrous crystals of **3** formed concurrently with **1** under these conditions. Since **3** can be prepared from solutions containing $TCNQ^-$ and TCNQ, it is likely that the complex salt was observed due to concurrent generation of TCNQ with $[(\eta^5\text{-}C_5Me_5)_2Fe]^+$ owing to the more positive electrode potential at the high current density. Furthermore, constant-potential electrolysis via eq 2 afforded fibrous black crystals of **3** when the applied potential was $E = E°$ for the $TCNQ/TCNQ^-$ couple (i.e. $[TCNQ] = [TCNQ^-]$) whereas more negative potentials gave **1**. Similar behavior observed in the synthesis of $[(\eta^6\text{-}C_6Me_6)_2M][TCNQ]_2$ and $[(\eta^6\text{-}C_6Me_6)_2M][TCNQ]_4$ (M = Fe, Ru) charge-transfer complexes was attributed to the potential-dependent concentration of TCNQ at the electrode during crystallization.[7] In this case, constant-potential electrocrystallization afforded quantitative yields of X-ray-quality crystals of the poorly conducting 1:2 phases $[(\eta^6\text{-}C_6Me_6)_2M][TCNQ']_2$ (M = Fe, Ru; TCNQ′ = TCNQ, $(TCNQ)F_4$, $(TCNQ)Cl_2$). However, these complexes differ from **1** in that they need not be prepared from presaturated solutions owing to their negligible solubility.

These results demonstrate that electrocrystallization can be used to prepare charge-transfer complexes that exhibit negligible conductivity. Electrochemical growth of insulating materials is commonly accompanied by the formation of resistive films that passivate the electrode.[12] Further electrodeposition occurs only if the film suppors charge propagation or is sufficiently porous to allow diffusion of the solution to the substrate beneath the film.[13] For example, these properties allow electrodeposition of redox polymers such as poly(vinylferrocene)[14] and polymerized (vinylbipyridine)ruthenium.[15] Formation of crystals on the working electrode did not hinder further crystallization in either of the above cases, suggesting that the crystalline habit of the charge-transfer complexes allowed transport of solution to the electrode so that crystal growth could occur. Indeed, the crystals only loosely adhered to the electrode surface; if the electrode was disturbed during the growth process, the crystals fell to the cell bottom and new crystals formed on the electrode.

Electrocrystallization of charge-transfer complexes that contain redox-active components requires that one of the components of

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the desired complex be electrochemically inactive under the electrocrystallization conditions. In addition to the complexes described above, this requirement is met by most charge-transfer complexes since the difference in redox potentials between the individual components, ΔE, is generally positive. That is, neutral donors are usually oxidized at less positive potentials than the acceptor anions, and neutral acceptors are usually reduced at less negative potentials than the donor cations. The observation that crystallization of the moderately soluble charge-transfer complex **1** can be electrochemically induced in saturated solutions illustrates that electrocrystallization is not limited to molecular solids with negligible solubility, as is the case for most one-dimensional conductors formed in "conventional" electrocrystallization[2-6] where presaturation of the medium is not required. Only the degree of solubility is different, and in conventional systems saturation may be reached very quickly due to the negligible solubility of the complexes.

These results demonstrate the generality of electrocrystallization as a convenient technique for the preparation of high-quality crystalline charge-transfer complexes. The ability to precisely control the crystallization process may eventually lead to electronic materials with unique or superior characteristics.

Registry No. **1**, 71035-23-9; **2**, 64679-24-9; **3**, 64679-25-0; $(C_5Me_5)_2Fe$, 12126-50-0; $Bu_4N[TCNQ]$, 34481-16-8; $[(C_6Me_6)_2Ru][TCNQ]_2$, 104507-52-0; TCNQ, 1518-16-7; $[(C_6Me_6)_2Fe][TCNQ]$, 71357-00-1; $[(C_6Me_6)_2Fe][TCNQ]_4$, 104507-53-1; $[(C_6Me_6)_2Ru][TCNQ]_4$, 104531-38-6; $[(C_6Me_6)_2Fe][(TCNQ)F_4]_2$, 104507-54-2; $[(C_6Me_6)_2Ru][(TCNQ)F_4]_2$, 104507-55-3; $[(C_6Me_6)_2Fe][(TCNQ)Cl_2]_2$, 104507-57-5; $[(C_6Me_6)_2Ru][(TCNQ)Cl_2]_2$, 104507-58-6.

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Heats of Reaction of $[Mo(CO)_2Cp^*]_2$ ($Cp^* = C_5H_5$, $C_5(CH_3)_5$, C_9H_7) with CO, $HC{\equiv}CH$, and $C_6H_5C{\equiv}CH$. Thermochemical Investigation of the Molybdenum–Molybdenum Triple Bond

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The chemistry of complexes that contain formal metal–metal multiple bonds has been the subject of detailed investigations by a number of groups[1] and remains one of the most intriguing areas of transition-metal chemistry. The most widely studied organometallic system is the series of complexes $[M(CO)_2C_5H_5]_2$, where M = Cr, Mo, W.[2] In order to achieve a noble gas configuration, these compounds can be viewed as having a metal–metal triple bond. The carbonyl groups are "semibridging" as shown in Figure 1. Theoretical calculations have suggested that understanding the nature of these dimers does not require postulation of a metal–metal multiple bond.[3]

As part of a program of solution thermochemical study of organometallic complexes, we have reported studies of ligand exchange,[4] hydrogen activation,[5] and carbonyl insertion[6] for the group VI (group 6[26]) metals. We now extend this to an investigation of the complexes $[Mo(CO)_2Cp^*]_2$ ($Cp^* = C_5H_5$, $C_5(CH_3)_5$, C_9H_7).

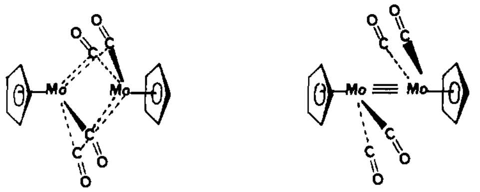

Figure 1. Limiting forms depicting the bonding in $[Mo(CO)_2C_5H_5]_2$. See ref 2c for crystal structure and ref 3 for discussion of the bonding.

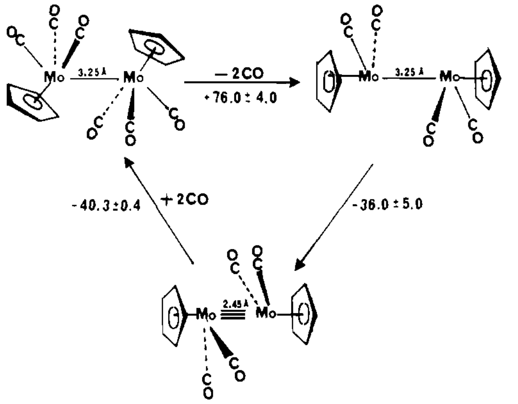

Figure 2. Scheme for estimation of the Mo–Mo interaction in $[Mo(CO)_2C_5H_5]_2$.

Table I. Heats of Reaction and Heats of Solution of $[Mo(CO)_2Cp^*]_2$ Complexes[a]

complex	ligand	ΔH_{exptl}[b]	ΔH_{reacn}[c]
$[Mo(CO)_2C_5H_5]_2$	CO	−36.5 ± 0.3	−40.3 ± 0.4
$[Mo(CO)_2C_5H_5]_2$	$HC{\equiv}CH$	−30.1 ± 1.7	−33.9 ± 1.8
$[Mo(CO)_2C_5H_5]_2$	$C_6H_5C{\equiv}CH$	−27.8 ± 0.7	−31.6 ± 0.8
$[Mo(CO)_2C_5(CH_3)_5]_2$	CO	−29.4 ± 0.5	−32.9 ± 0.7
$[Mo(CO)_2C_9H_7]_2$	CO	−26.6 ± 0.7	−31.4 ± 0.7

[a] $Cp^* = C_5H_5$, $C_5(CH_3)_5$, C_9H_7. [b] All values, in kcal/mol, refer to the heat of reaction of the crystalline complex with the excess ligand in toluene solution. Experimental errors are the standard deviation on, typically, five separate determinations. [c] The heat of reaction with all components, in solution, incorporates the experimental values for the heats of solution in toluene of $[Mo(CO)_2C_5H_5]_2 = +3.8 \pm 0.1$, $[Mo(CO)_2C_5(CH_3)_5]_2 = +3.5 \pm 0.2$ and $[Mo(CO)_2C_9H_7]_2 = +4.8 \pm 0.1$ kcal/mol. The heat of solution in THF of $[Mo(CO)_2C_5H_5]_2$ is $+2.8 \pm 0.2$ kcal/mol.

There are three relevant thermodynamic investigations of purely inorganic molybdenum–molybdenum multiple-bonded systems. In the temperature range 2600–3000 K, mass spectrometric investigation of reaction 1 led to a Mo–Mo bond strength estimate of 97 ± 5 kcal/mol.[7] A formal bond order of six has been

$$Mo_2(g) \rightarrow 2Mo(g) \tag{1}$$

postulated for the diatomic molecule Mo_2.[8] The molybdenum(II) carboxylate $[Mo_2(O_2CR)_4]$ was investigated by solution calori-

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