A Two-Dimensional Polymer Formed by TCNE and Dirhodium Tetra(trifluoroacetate)

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There has already been a great deal of attention devoted to the preparation of compounds containing TCNE (tetracyanoethylene) combined with transition-metal complexes,[1] and a great variety of product types have been described. It would seem reasonable to expect that the strong electron-acceptor capacity of TCNE, coupled with its ability to serve as a ligand through two or more of its CN groups, should allow the preparation of polymeric materials, $[ML_n(TCNE)]_\infty$, that stand a good chance of displaying interesting electronic properties. To date, however, the literature records but three examples of such materials, namely, $\{[Mn(TPP)][TCNE]\}_\infty$[2] (TPP = tetraphenylphorphinato dianion) and the $\{[M(hfacac)_2][TCNE]\}_\infty$ compounds[3] (hfacac = $F_3CC(O)CHC(O)CF_3^-$ with M = Co and Cu). All of these have infinite chain structures in which μ_2,η^2-(*trans*-$C_2(CN)_4$) units are coordinated to the planar Mn(TPP) or $M(hfacac)_2$ units above and below the plane. It is clear that the size and shape of the Mn(TPP) and $M(hfacac)_2$ moieties preclude the use of the remaining two CN groups on each TCNE unit.

There have also been a few reported examples of TCNE employing one,[4] two,[5] or four[4] of its CN groups as points of ligation to form discrete molecular species. These include the $[LMn(CO)_2]_{1\text{ or }4}(TCNE)$ compounds[4] (L = MeCp or Me_5Cp), which have not been structurally characterized and $[(Ph_3P)_2Ir(CO)]_2[TCNE]$,[5] which has been structurally characterized.

We report here the preparation of the first compound in which TCNE employs all four of its CN groups to function as a μ_4-η^4 bridging group in such a way as to form infinite sheets, $[(M_xL_n)_2(TCNE)]_\infty$. The M_xL_n group is $Rh_2(O_2CCF_3)_4$, which is already well known to be a good acceptor at both of its axial positions, whereby numerous $Rh_2(O_2CCF_3)_4L_2$ compounds may be formed, many of which have been structurally characterized.[6] The compound reported here is one in which TCNE is attached to a dimetal core. The $Rh_2(O_2CCF_3)_4$ was chosen for two reasons: (1) it is extremely soluble in a variety of solvents and (2) it is a powerful acceptor with a preference for hard ligands.[7] Both of these properties arise because of the strong electron-withdrawing effect of the four CF_3 groups: molecular association is feeble because of the poor donor power of the carboxylate oxygen atoms, while the rhodium atoms have enhanced acceptor ability.

The $Rh_2(O_2CCF_3)_4$[8] (130 mg, 0.20 mmol) was dissolved in 15 mL of dichloromethane, and 25 mg of TCNE (0.20 mmol) was added to this solution. The green color of the starting material immediately changed, and a blue-black precipitate appeared. The precipitate was collected by filtration and dried under reduced pressure. Crystals suitable for X-ray crystallography were obtained by a diffusion technique in which a layer of benzene containing TCNE was placed over a CH_2Cl_2 solution of $Rh_2(O_2CCF_3)_4$. The bulk, vacuum-dried solid is stable in dry air, but the crystals contain solvent (C_6H_6) and hence disintegrate due to solvent loss when left in the open.

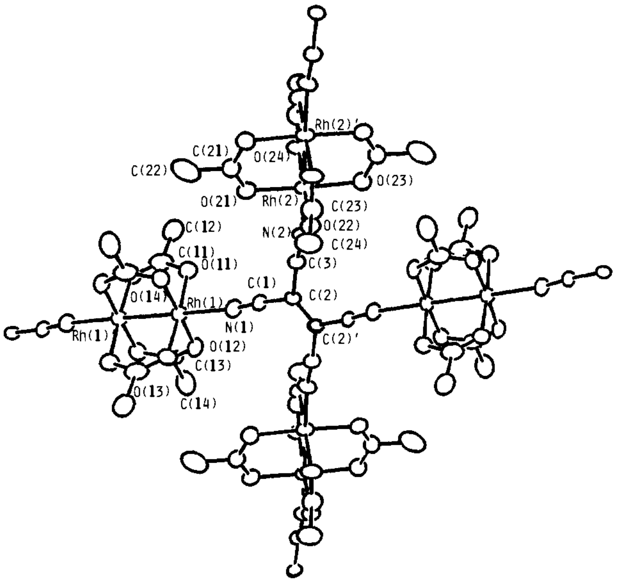

Figure 1. Drawing of one TCNE unit surrounded by four $Rh_2(O_2CCF_3)_4$ units and portions of the neighboring TCNE units. For clarity, all fluorine atoms are omitted, and the sizes of the atoms are arbitrary.

The crystalline compound has the composition $[Rh_2(O_2CCF_3)_4]_2(TCNE)(C_6H_6)_2$, and the structure was determined by conventional X-ray crystallographic methods.[9] Some difficulties were encountered due to disorder in the rotational orientations of the CF_3 groups, moderate crystal decay (23%), and the plate shape of the crystal, which necessitated absorption corrections. Figure 1 shows the crystallographically unique TCNE unit surrounded by four $Rh_2(O_2CCF_3)_4$ units. The central C=C bond, C(2)–C(2)', residues on a crystallographic inversion center. There are two crystallographically distinct $Rh_2(O_2CCF_3)_4$ units, each of which is also on a crystallographic inversion center. The Rh–Rh distances in these are not significantly different, namely, 2.392(2) and 2.399(2) Å, and are very close to the average value of 2.40 Å for $Rh_2(O_2CCF_3)_4L_2$ compounds in general.[6] The Rh–N distances are 2.16(1) and 2.19(1) Å.

The most important, and indeed unique, structural feature of this compound is that there are sheets formed by quasirectangular 30-membered rings (molecular hogwire?) that lie approximately in the *ab* planes and are stacked along the *c* axis. This is shown in Figure 2. The layers are separated by about 9.5 Å, which is attributable to the steric requirements of the CF_3 groups. Nevertheless, there are lacunae between the layers, each of which is occupied by two molecules of benzene. In this way, a very satisfactory packing is achieved, with the mean volume per atom being equal to 18.2 Å^3.

In seeking a simple molecule with which to compare this polymer, we looked for a dinitrile adduct of $Rh_2(O_2CCF_3)_4$. Curiously, in spite of the enormous number of $Rh_2(O_2CR)_4L_2$ compounds that have been prepared and structurally characterized, no nitrile adduct of $Rh_2(O_2CCF_3)_4$ has been reported.

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(1) A useful reference list can be found in ref 3 and need not be repeated here.

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(9) The compound crystallizes in space group $P\bar{1}$ with a = 12.500(5) Å, b = 12.609(4) Å, c = 9.951(3) Å, α = 95.15(3)°, β = 99.23(4)°, γ = 74.77(5)°, V = 1492 Å^3, and Z = 1, which gives a calculated density of 1.750 g cm^{-3}. Data were collected on a AFC5R Rigaku diffractometer at 20 °C employing Cu Kα radiation. With 2557 reflections having intensities greater than 3σ, 288 parameters were refined to convergence with R = 0.081, R_w = 0.103, and the largest residual peak in the final difference electron density map had a height of 1.3 e/Å^3.

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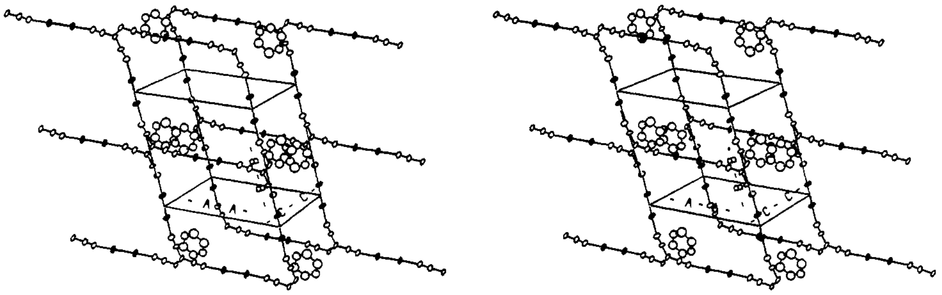

Figure 2. Stereoview of the packing of the nets. The $Rh_2(O_2CCF_3)_4$ groups are represented only by the Rh_2 units. The unit cell is outlined and the clathrated benzene molecules are also shown (without hydrogen atoms).

We therefore prepared red-purple $Rh_2(O_2CCF_3)_4(CH_3CN)_2$ and determined its structure.[10]

The Rh-Rh distance is 2.4178(6) Å, and the Rh-N distance is 2.201(5) Å. Both are slightly longer than their counterparts in $\{[Rh_2(O_2CCF_3)_4]_2(TCNE)\}_\infty$. The C=C, C—CN and C—N distances are 1.31(1), 1.45(2), and 1.13(2) Å, respectively, which, in view of the esds, are not significantly different from those in TCNE itself.

The existence of a significant π interaction between the $Rh_2(O_2CCF_3)_4$ and $C_2(CN)_4$ moieties is indicated by the frequencies of the CN stretching modes, 2230 and 2210 cm^{-1}, in the infrared spectrum. These are lower, by 30 and 20 cm^{-1}, respectively, than those in the spectrum of pure TCNE, whereas when a nitrile behaves as a simple σ donor there is a significant rise in ν_{CN} for kinematic reasons. This is illustrated by the case of $Rh_2(O_2CCF_3)_4(CH_3CN)_2$, where bands are observed at 2310 and 2285 cm^{-1}, whereas in uncoordinated CH_3CN[11] ν_{CN} is at 2250 cm^{-1}. The very dark color (blue-black) of $\{[Rh_2(O_2CCF_3)_4]_2(TCNE)(C_6H_6)_2\}_\infty$, compared to those of the starting materials (light green and colorless) or even compared to that of $Rh_2(O_2CCF_3)_4(CH_3CN)_2$ (red-purple), is also indicative of significant π delocalization.

The isolation of this first compound in which TCNE employs all four CN groups to create a two-dimensional net suggests that the use of a dinuclear species such as $Rh_2(O_2CCF_3)_4$, where the two receptor sites are colinear but separated, may be a critical steric requirement. It will be of interest to see if this feature, plus the effect of the CF_3 groups in rendering the metal atoms strongly Lewis acidic, can be exploited in other cases, i.e., by employing other $M_2(O_2CCF_3)$ units. Such work is now in progress.

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(10) The compound crystallizes in space group $P2_1/n$ with a = 8.872(3) Å, b = 8.374(1) Å, c = 15.260(3) Å, β = 100.41(2)°, V = 1115.2(4) $Å^3$, and Z = 2. Data were collected on a Nicolet P3/F diffractometer at 20 °C with monochromated Mo Kα radiation. With 1532 reflections having intensities greater than 3σ, 163 parameters were refined to convergence with R = 0.032, R_w = 0.038, and the largest residual peak had a height of 0.69 e/$Å^3$.

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