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[11] Characterization of porphyrin **3** was carried out by exchanging of the end groups (acid chlorides) in the product to methyl ester **4**. **4**: ^{1}H NMR ($CDCl_3$): $\delta = -2.17$ (m, 4H), 0.78 (dt, 4H), 1.38 (s, 6H), 7.75 – 8.01 (m, 28H), 9.06 (s, 8H). UV/Vis: $\lambda_{max} = 428$, 520, 559, 599 nm. Elemental analysis calcd for $C_{66}H_{50}N_4O_{10}PCl$: C 70.43, H 4.48, N 4.98; found: C 70.45, H 4.70, N 5.11.

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[14] Fluorescence lifetimes were measured using a Horiba NAES-550 time-correlated single-photon counting instrument. A solution of terephthalic acid was added to the solution of porphyrin **2** – antibody complex. The concentrations of **2**, terephthalic acid, and antibody 74-D7A combining site were set at 1.6, 3.2, and 3.2 μM, respectively. The error values are less than 0.1 ns.

Hexagonal Layered Materials Composed of $[M_2(O_2CCF_3)_4]$ (M = Ru and Rh) Donors and TCNQ Acceptors**

Hitoshi Miyasaka, Cristian S. Campos-Fernández, Rodolphe Clérac, and Kim R. Dunbar*

Multidimensional assemblies consisting of paramagnetic metal ions and polycyano organic acceptor molecules are being prepared in an effort to access molecule-based magnetic/conducting materials based on dπ – pπ electronic interactions.[1–4] Achieving high conductivity through the backbone of a metalloorganic polymer is one of the most challenging goals, and one that has been realized in only one case, namely in the $[Cu(DCNQI)_2]_\infty$ family of compounds (DCNQI = *N*,*N*′-dicyanoquinonediimine).[5] These materials consist of a three-dimensional skeleton containing tetrahedral mixed-valence Cu^I/Cu^{II} ions connected by partially reduced DCNQI radicals arranged in π-stacked columns throughout the three-dimensional network. Although the latter structural feature is a main contributor to the conducting pathway, it has been demonstrated that delocalization through the Cu – DCNQI skeleton is crucial for stabilizing the metallic state of these materials.

The use of electron-rich dimetal complexes to prepare dπ – pπ delocalized systems began in our laboratories with the isolation of the "dimer-of-dimers" $[\{Re_2Cl_4(dppm)_2\}_2(\mu\text{-TCNQ})]$ (dppm = 1,2-bis(diphenylphosphanyl)methane, TCNQ = 7,7,8,8-tetracyanoquinodimethane). This compound is the first example of a charge transfer complex of TCNQ with a metal – metal-bonded donor. The presence of the oxidized Re – Re species ($\sigma^2\pi^4\delta^2\delta^{*1}$) and reduced $TCNQ^{\bullet-}$ was confirmed by spectroscopic and magnetic studies.[6] In this 2:1 donor – acceptor system, electronic delocalization is favored through good metal dπ/organic pπ overlap; this can be represented by the resonance structures: $[Re_2^{II,III}\text{-}(TCNQ^{\bullet-})\text{-}Re_2^{II,III}]$ (1) $\rightleftharpoons Re_2^{II,III}\text{-}(TCNQ)\text{-}Re_2^{II,III}]$ (2) $\rightleftharpoons [Re_2^{II,II}\text{-}(TCNQ^{\bullet-})\text{-}Re_2^{II,III}]$ (3), with forms 1 and 3 being the main contributors.

A logical extension of the aforementioned chemistry is the construction of networks based on electron-rich Ru^{II}/Ru^{II} complexes. This idea is predicated on the notion that the dπ orbitals on Ru^{II}/Ru^{III} and the pπ orbitals of the TCNQ ligands will be energetically compatible; indeed there is ample

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[**] TCNQ = 7,7,8,8-tetracyanoquinodimethane. H.M. is a recipient of a JSPS Research Fellowship for Young Scientists.

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precedence for electronic delocalization in Ru/nitrogen donor ligand complexes.[7] In this work, we report the assembly of $[Ru_2(O_2CCF_3)_4]$ and $[Rh_2(O_2CCF_3)_4]$ with TCNQ to yield the two-dimensional compounds **1** and **2**, respectively (C_7H_8 = toluene). X-ray structural data support the conclusion that electronic delocalization is occurring within the two-dimensional (2D) network.

$[\{Ru_2(O_2CCF_3)_4\}_2(\mu_4\text{-TCNQ})\cdot 3(C_7H_8)]_\infty$ **1**

$[\{Rh_2(O_2CCF_3)_4\}_2(\mu_4\text{-TCNQ})\cdot 3(C_7H_8)]_\infty$ **2**

Compounds **1** and **2** were synthesized from solutions of TCNQ treated with an excess of the dimetal precursor. The reaction between $[Ru_2(O_2CCF_3)_4]$ and TCNQ proceeds under refluxing conditions to afford a dark green powder. Slow cooling of the filtrate from the reaction leads to dark green crystals of **1** (yield < 10%). Infrared spectra reveal that the powder and crystals are essentially identical; the yield of the bulk powder is ~80%. There is no evidence for product formation at lower temperatures, a fact that appears to be related to a lack of lability of the axial THF ligands in $[Ru_2(O_2CCF_3)_4(thf)_2]$. In contrast, **2** was obtained directly as purplish-brown crystals by a slow diffusion of *n*-hexanes into a solution containing $[Rh_2(O_2CCF_3)_4]$ and TCNQ in toluene (yield > 80%).

Infrared spectra are useful for assigning the oxidation state of TCNQ in its compounds.[2, 8] The ν(C≡N) modes are strongly affected by the nature of the metal binding interaction as well as the redox state, but the δ(C–H) mode is sensitive mainly to the oxidation state. The infrared spectrum of **1** contains three ν(C≡N) stretches at 2203, 2155, and 2117 cm^{-1} (for **1b**; see Experimental Section) at lower energies than free TCNQ (2222 cm^{-1}), whereas compound **2** exhibits a single feature at 2237 cm^{-1}. The shift to lower energies in **1** is in accord with increased M_2–TCNQ π-backbonding for the Ru derivative. The δ(C–H) modes of $TCNQ^0$ and $TCNQ^-$ occur at ~860 cm^{-1} and between 820–825 cm^{-1}, respectively. The corresponding values for partially reduced TCNQ are known to occur at about 840 cm^{-1}.[8a,b] The new compounds exhibit δ(C–H) bending modes at 842 cm^{-1} for **1** and 844 cm^{-1} for **2**, which suggests that the TCNQ unit is partially reduced. The colors of **1** and **2** are dark green and dark purplish-brown, respectively, which is in accord with a TCNQ chromophore that is not neutral. The electronic spectral features of reduced TCNQ in the visible region typically give rise to green or dark blue colors due to an intense π–π* transition, the exact energy of which is determined by the degree of charge transfer.

Compound **1** crystallizes in the monoclinic space group *C*2/*m* with an inversion center at the midpoint of the M–M bond. The TCNQ ligands are bisected by a C_2 axis and a mirror plane which leads to only one unique Ru(1)–N(1) bond.[9] A view of one TCNQ unit surrounded by four Ru_2 units in **1** is depicted in Figure 1. All four cyano groups of TCNQ are coordinated to independent Ru_2 molecules, the result of which is a distorted hexagonal 2D network. Figure 2 shows one of the 2D sheets in **1**. The Ru–Ru distance of 2.2875(7) Å is slightly longer than the corresponding distances in

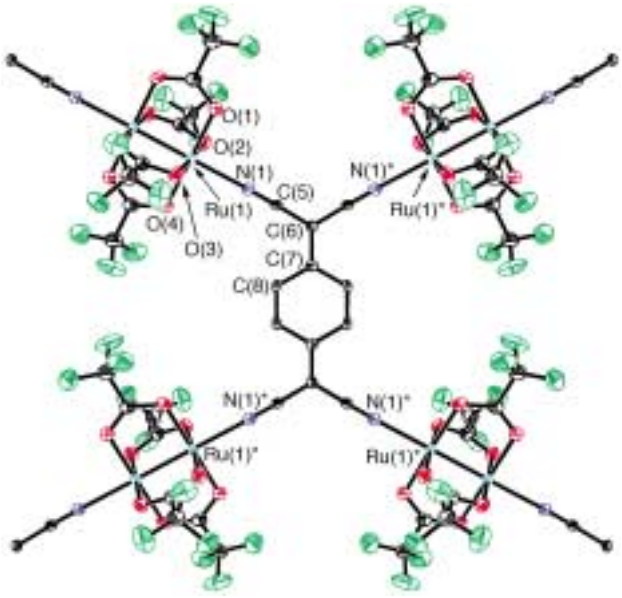

Figure 1. Structure of one TCNQ ligand coordinated to four independent $[Ru_2(O_2CCF_3)_4]$ units in **1** (ORTEP representation) with atom-numbering scheme.

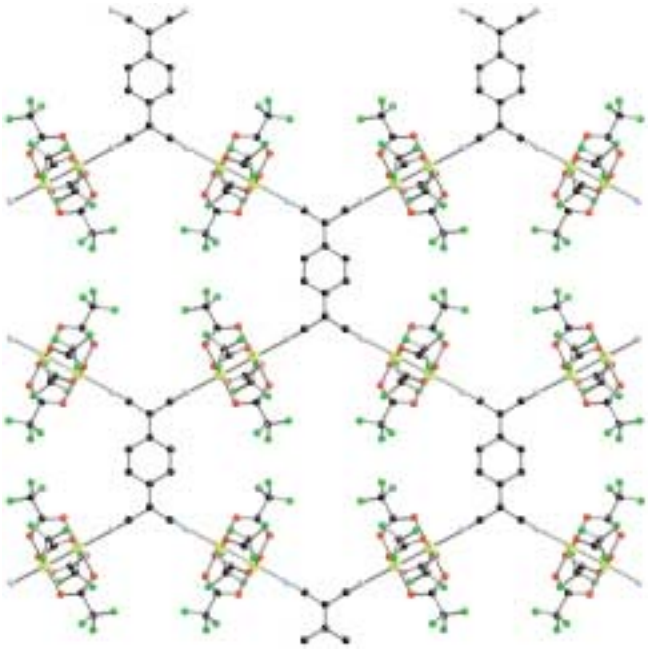

Figure 2. Perspective view of the two-dimensional network of **1**.

$[Ru_2^{II,II}(O_2CCF_3)_4(thf)_2]$[10] (2.276(3) Å) or $[Ru_2^{II,III}(O_2CCF_3)_5]$ (2.278(1) Å).[11] The Ru–N_{axial} distance is 2.277(3) Å, which is typical of such interactions.

Compound **2** is isostructural to **1**. The Rh–Rh bond length of 2.4053(8) Å is comparable to the single bond lengths found in $[Rh_2^{II,II}(O_2CCF_3)_4L_2]$ adducts (~2.40 Å).[12] The Rh–N(nitrile) distance is 2.174(4) Å, which is essentially identical to the corresponding distance in $[\{Rh_2(O_2CCF_3)_4\}_2(\mu_4\text{-TCNE})]_\infty$ (av 2.175 Å),[13] but slightly shorter than the axial interactions in $[Rh_2(O_2CCF_3)_4(MeCN)_2]$ (2.201(5) Å)[13] and $[Rh_2(O_2CCF_3)_4(L)]_\infty$ (L = 2,5-dimethyl-*N*,*N*′-dicyanoquinonediimine (DMDCNQI), 2.189(7) Å; *N*, *N*′-dicyanonaphthoquinone diimine (DCNNQI), 2.212(2) Å).[14] These differences can be ex-

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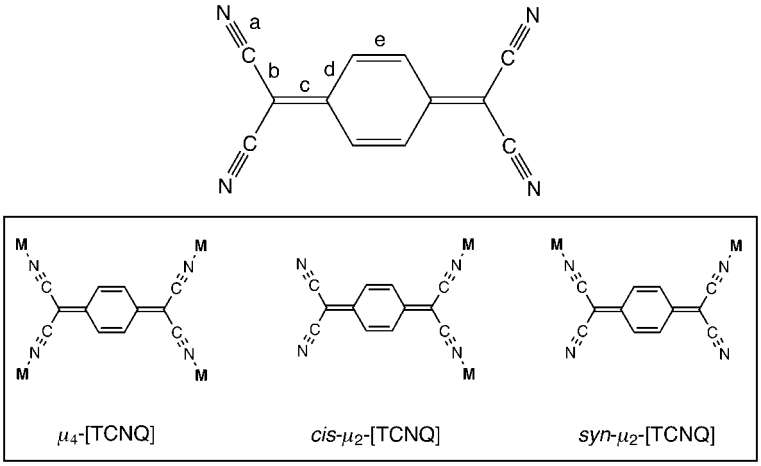
plained by the fact that the nitrile ligands in $[Rh_2(O_2CCF_3)_4(CH_3CN)_2]$ and $[Rh_2(O_2CCF_3)_4(L)]_\infty$ (L = DMDCNQI, DCNNQI) behave as σ donors, whereas in **2** and $[\{Rh_2(O_2CCF_3)_4\}_2(\mu_4\text{-TCNE})]_\infty$, M–L π-back-donation is occurring.

In the context of electronic issues, the most important structural features in TCNQ complexes are the bond lengths within the TCNQ ligand. These are listed in Table 1 for **1** and **2** along with data for previously reported compounds. The C≡N bond length is affected mainly by M–N coordination, but the C–C distances within the TCNQ ring are good indicators of the oxidation state. The bond lengths for "free" $TCNQ^0$ and $TCNQ^-$ were determined by averaging the data for a number of compounds. The bond lengths within the TCNQ units are nearly the same in **1** and **2** (Table 1). Interestingly they are intermediate between the values for $TCNQ^0$ and $TCNQ^-$, which is an indication of partially reduced TCNQ. The degree of charge transfer from a donor to TCNQ has been estimated by Kistenmacher et al., from the relationship $\rho = A[c/(b+d)] + B$ ($A = -41.667$ and $B = 19.833$ are determined from neutral TCNQ[15] ($\rho = 0$) and RbTCNQ[16] ($\rho = -1$)).[17] The values of c, b, and d are TCNQ

Table 1. Important structural features in TCNQ complexes.



Compound	Charge	a	b	c	d	e	b + d	c/(b + d)	ρ[a]	Ref.
Noncoordinated TCNQ										
TCNQ	0	1.140(1)	1.441(4)	1.374(3)	1.448(4)	1.346(3)	2.889	0.476	0	[15]
$CsTCNQ_3$	0	1.140(4)	1.428(4)	1.371(5)	1.444(4)	1.341(5)	2.872	0.477	− 0.04	[16]
	− 1	1.152(3)	1.419(3)	1.410(4)	1.427(3)	1.355(4)	2.846	0.495	− 0.81	
RbTCNQ	− 1	1.153(7)	1.416(8)	1.420(1)	1.423(3)	1.373(1)	2.839	0.500	− 1	[18]
$(TMPD)(TCNQ)_2$	− 1/2	1.17(1)	1.427(3)	1.395(2)	1.434(2)	1.354(2)	2.861	0.488	− 0.50	[19]
$(TPP)(TCNQ)_2$	− 1/2	1.17(1)	1.428(3)	1.396(2)	1.434(2)	1.354(2)	2.862	0.488	− 0.50	[20]
$[Pd(MeCN)_4](TCNQ)_4$										
	− 1/2	1.138(2)	1.428(2)	1.388(4)	1.428(2)	1.356(5)	2.856	0.486	− 0.42	[21]
	− 1/2	1.138(2)	1.428(4)	1.393(8)	1.426(3)	1.358(11)	2.854	0.488	− 0.50	
	− 1/2	1.139(3)	1.428(2)	1.384(1)	1.430(1)	1.355(5)	2.858	0.484	− 0.33	
Coordinated TCNQ										
cis-μ_2-[TCNQ]	− 1	1.147(9)	1.401(10)	1.404(8)	1.43(2)	1.365(8)				
		1.129(8)	1.407(10)	1.421(7)	1.43(1)					
		[1.138]	[1.404]	[1.4125]	[1.43]	[1.365][b]	2.834	0.498	− 0.93[c]	[1a]
	− 1	1.160(4)	1.421(4)	1.431(4)	1.419(4)	1.365(4)				
		1.151(4)	1.416(4)	1.425(4)	1.423(4)					
		[1.1555]	[1.4185]	[1.428]	[1.421]	[1.365][b]	2.840	0.503	− 1.13[c]	[1a]
syn-μ_2-[TCNQ]	− 1	1.147(2)	1.415(2)	1.419(2)	1.429(2)	1.365(2)				
		1.147(2)	1.417(2)	1.419(2)	1.430(2)					
		[1.147]	[1.416]	[1.419]	[1.4295]	[1.365][b]	2.846	0.499	− 0.96[c]	[1a]
μ_4-[TCNQ]	− 1	1.141(9)	1.412(8)	1.389(11)	1.341(8)	1.378(10)				
		1.138(11)	1.411(8)	1.414(11)	1.424(8)					
		[1.1395]	[1.4115]	[1.4015]	[1.3825]	[1.378][b]	2.794	0.502	− 1.08[c]	[2]
	− 1	1.138(9)	1.405(13)		1.424(9)	1.358(13)				
		1.146(9)	1.47(8)	1.422(8)	1.431(9)					
		[1.142]	[1.4375]	[1.422]	[1.4275]	[1.358][b]	2.865	0.496	− 0.83[c]	[22]
	0	1.126(8)	1.453(8)	1.361(9)	1.451(8)	1.337(9)				
		1.148(8)	1.431(9)							
		[1.137]	[1.442]	[1.361]	[1.451]	[1.337][b]	2.893	0.470	0.25[c]	[23]
1		1.132(4)	1.431(4)	1.393(6)	1.435(4)	1.349(6)	2.866	0.486	− 0.42	this work
2		1.131(6)	1.436(5)	1.409(9)	1.432(5)	1.358(8)	2.868	0.491	− 0.63	this work

[a] $\rho = A[c/(b+d)] + B$ with $A = -41.667$ and $B = 19.833$.[17, 24] [b] Average value. [c] Estimated from the average values.

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bond lengths defined in Table 1.[18–24] The charges for **1** and **2** estimated from the Kistenmacher relation are -0.42 and -0.63, respectively. These values point to partially reduced TCNQ bridges in these compounds, which agrees with the aforementioned IR data in the δ(C–H) region.

A packing diagram for **1** is shown in Figure 3. Each two-dimensional sheet is separated by 6.6 Å, which allows for toluene molecules to reside between the layers. One type of C_7H_8 molecule π-stacks with TCNQ ligands in one-dimensional columns along the *c* axis (phenyl–phenyl distance is about 4.2 Å and the nitrile–phenyl distance is about 3.3 Å). The remaining two independent toluene molecules occupy the one-dimensional channels that run throughout the crystal.

Magnetic measurements performed on powder samples of **1** and **2** were measured between 1.8 and 300 K. As expected, **2** was found to be diamagnetic, but **1** possesses a moment of 0.678 $cm^3 K mol^{-1}$ at 300 K (expressed as $\chi_M T$) which continuously decreases with cooling. A large zero-field splitting arising from the $S=1$ $Ru_2^{II,II}$ units ($D \sim 300\ cm^{-1}$) contributes to the reduced moments observed at low temperatures,[25] but the moment at room temperature is already significantly less than the expected value of $\chi_M T = 2.0\ cm^3 K mol^{-1}$ for two isolated $S=1$ spin centers. These data are in accord with a relatively strong antiferromagnetic interaction through the TCNQ bridges, which is an indication of electronic communication. Attempts are underway to grow sufficiently large crystals so that single-crystal conductivity and magnetic measurements can be performed.

In summary, two-dimensional networks that consist of $[M_2(O_2CCF_3)_4]$ molecules connected to each other by μ_4-TCNQ ligands exhibit appreciable M–L π-backbonding. This situation can be described by the resonance structures depicted in Figure 4.

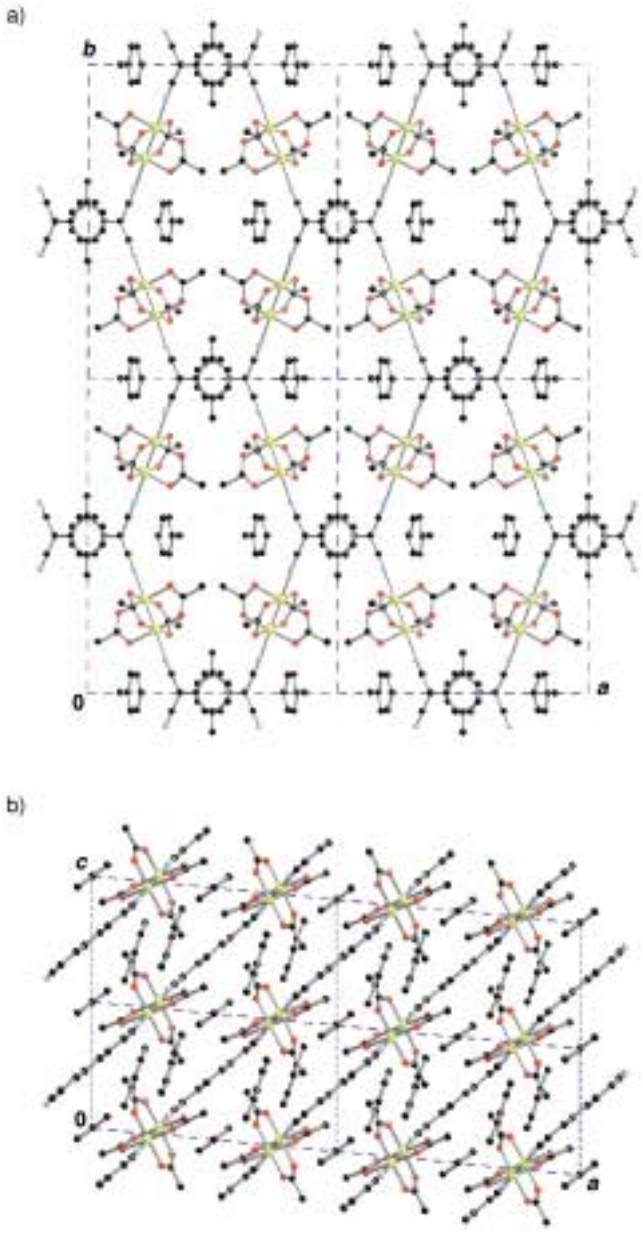

Figure 3. Packing diagram view of a) **1** along the *c* axis and b) along the *b* axis, showing the alternating $\pi-\pi$ stacked columns and the one-dimensional channels along the *c* axis. The fluorine atoms were omitted for the sake of clarity.

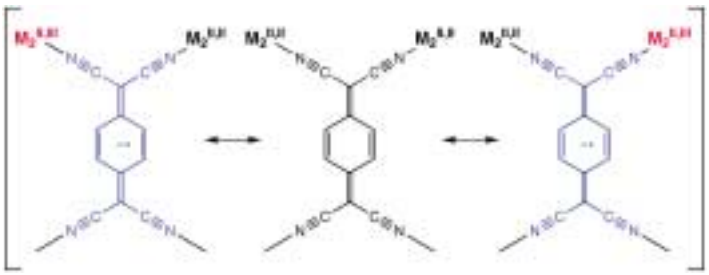

Figure 4. Resonance structures of a one-electron delocalized system for the (2:1) donor–acceptor assemblies.

Experimental Section

1: All synthetic procedures were performed anaerobically. TCNQ (20 mg, 0.1 mmol) was added to a solution of $[Ru_2(O_2CCF_3)_4(thf)_2]$ (160 mg, 0.2 mmol) in toluene (40 mL), and the brown suspension was refluxed for 1 h at 120 °C. The resulting dark green precipitate was separated from the hot solution, washed with toluene (20 mL), and dried in vacuo (**1a**, yield > 80 %). The hot filtrate was cooled to room temperature and allowed to stand undisturbed for two days during which time a crop of X-ray quality, dark green crystals was obtained (**1b**, yield < 10 %). IR (Nujol): for **1a**: $\tilde{\nu}$ = 2207 (sh), 2159 (m), 2120 (sh)ν(C≡N); 842 cm^{-1} (w) δ(C-H); for **1b**: $\tilde{\nu}$ = 2203 (sh), 2155 (m), 2117 (sh) ν(C≡N); 842 cm^{-1} (w) δ(C–H).

2: TCNQ (20 mg, 0.1 mmol) was added to a solution of $[Rh_2(O_2CCF_3)_4]$ (132 mg, 0.2 mmol) in toluene (30 mL) to give a light green suspension which was heated at 80 °C for 2 h. During this time, the solution color changed from green to reddish brown. The resulting solution was cooled to room temperature, reduced in volume to 20 mL and treated with dichloromethane (30 mL). After filtration, the solution was layered in a narrow Schlenk tube with *n*-hexanes (30 mL), which led to the formation of dark purplish-brown single crystals after one week. IR (Nujol): $\tilde{\nu}$ = 2237 (m, br) ν(C≡N), 1539 (m) ν(C–O), 844 cm^{-1} (w) δ(C–H).

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[9] Crystal data for $[\{Ru_2(O_2CCF_3)_4\}_2(TCNQ)\cdot 3(C_7H_8)]_\infty$ (**1**): $C_{49}H_{28}N_4O_{16}F_{12}Ru_4$, monoclinic, space group $C2/m$, $a = 16.682(3)$, $b = 20.881(4)$, $c = 8.6120(17)$ Å, $\beta = 95.47(3)^\circ$, $V = 2986.2(10)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.736$ g cm^{-3}, $\mu = 1.10$ mm^{-1}, $F(000) = 1524.00$, $R1$ ($wR2$) = 0.0350 (0.0843) ($I > 2\sigma(I)$), $R1$ ($wR2$) = 0.1536 (0.0961) (all data), GOF = 0.940. Crystal data for $[\{Rh_2(O_2CCF_3)_4\}_2(TCNQ)\cdot 3(C_7H_8)]_\infty$ (**2**): $C_{49}H_{28}N_4O_{16}F_{12}Rh_4$, monoclinic, space group $C2/m$, $a = 16.793(3)$, $b = 20.806(4)$, $c = 8.4450(17)$ Å, $\beta = 95.54(3)^\circ$, $V = 2936.9(10)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.774$ g cm^{-3}, $\mu = 1.21$ mm^{-1}, $F(000) = 1532.00$, $R1$ ($wR2$) = 0.0471 (0.1202) ($I > 2\sigma(I)$), $R1$ ($wR2$) = 0.0689 (0.1360) (all data), GOF = 0.997. Data were collected on a Bruker SMART CCD diffractometer in the range $1.57 < 2\theta < 28.32$ for **1** and $1.56 < 2\theta < 28.26$ for **2** at 110(2) K with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å). Of the 18164 and 9188 unique reflections, 3747 and 3548 were unique for **1** and **2**, respectively. The structures were solved by direct methods (SHELXS-97)[26] and refined by full-matrix least-squares calculations on F^2 (SHELXL-97).[27] The non-hydrogen atoms were refined anisotropically, while hydrogen atoms were refined isotropically. Full-matrix least-squares refinement was based on 3747 reflections ($I > 2.00\sigma(I)$) for **1** and 3548 reflections ($I > 2.00\sigma(I)$) for **2**. The highest peaks in the final difference map were 1.272 and 1.546 e$^-$ Å^{-3} for **1** and **2**, respectively. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-145608 (**1**) and CCDC-145609 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
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Supramolecular Chemistry of Anionic Cobalt(III) Bis(dicarbollide) and Cyclotriveratrylene in the Solid State and the Gas Phase**

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Despite the fundamental role played by anionic species in many natural processes the supramolecular chemistry of anions has been one of the least explored aspects of supramolecular chemistry.[1] While the neutral, isomeric icosahedral carboranes *o*, *m*, *p*-$C_2B_{10}H_{12}$, for instance, are emerging as versatile components in supramolecular systems, forming hydrogen-bonded complexes [2] and host–guest species with a range of host molecules and assemblies,[3–9] studies on the supramolecular chemistry of anionic carboranes, or indeed anionic boranes, are limited. The most significant example of the binding of a borane anion in a supramolecular system is that of the divalent anion $[B_{10}H_{10}]^{2-}$ which forms a host–guest

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