

SUPPLEMENTARY INFORMATION

Experimental Details

General Data. All of the manipulations were carried out in a dry, oxygen-free, dinitrogen atmosphere by employing standard Schlenk techniques. 1,3-Dicyanobenzene, anhydrous dichloromethane and benzene were purchased from Aldrich and used as received. Rhodium(II) trifluoroacetate was prepared according to the literature procedures.¹ IR spectra were recorded on a Nicolet Magna 550 FTIR spectrometer using KBr pellets. Thermogravimetric measurements were carried out under nitrogen at a heating rate of 5°C/min using a TGA 2050 Thermogravimetric Analyzer, TA Instruments, Inc. Elemental analysis was performed at Maxima Laboratories Inc., Ontario, Canada.

Synthesis of $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4 \cdot (1,3\text{-C}_6\text{H}_4(\text{CN})_2)]$

1) Solution reaction. Rhodium(II) trifluoroacetate (0.132 g, 0.20 mmol) was dissolved in dichloromethane (5 mL) to form a green solution and 1,3-dicyanobenzene (0.026 g, 0.20 mmol) was dissolved in benzene (5 mL). The latter was then carefully layered on a top of the dichloromethane solution using a thin (OD 22 mm) Schlenk tube. Violet crystals **1** appeared in three days and accumulated at the bottom of the tube. Yield: *ca.* 60 %. IR (KBr, cm^{-1}): 3081w, 3043w, 2962w, 2907w, 2275w, 2239w, 1664s, 1478w, 1460w, 1194s, 1166sh, 860m, 816w, 786w, 738m, 678w, 544w.

2) Removal and Reintroduction of Solvent Molecules. Freshly prepared crystals of **1** (2.562 mg) were subjected to TGA measurements (Fig. 1). Crystals started to loose dichloromethane at room temperature, but heating was required to completely remove benzene and residual dichloromethane. The evacuation of both solvents is fully completed at 85 °C, weight loss of

0.404 mg is equivalent to 15.8% (calcd. weight loss of CH_2Cl_2 and C_6H_6 based on the crystal structure of **1** is 18.6%). Product starts to decompose at temperatures above 225 °C to leave an unidentified residue (6.4%).

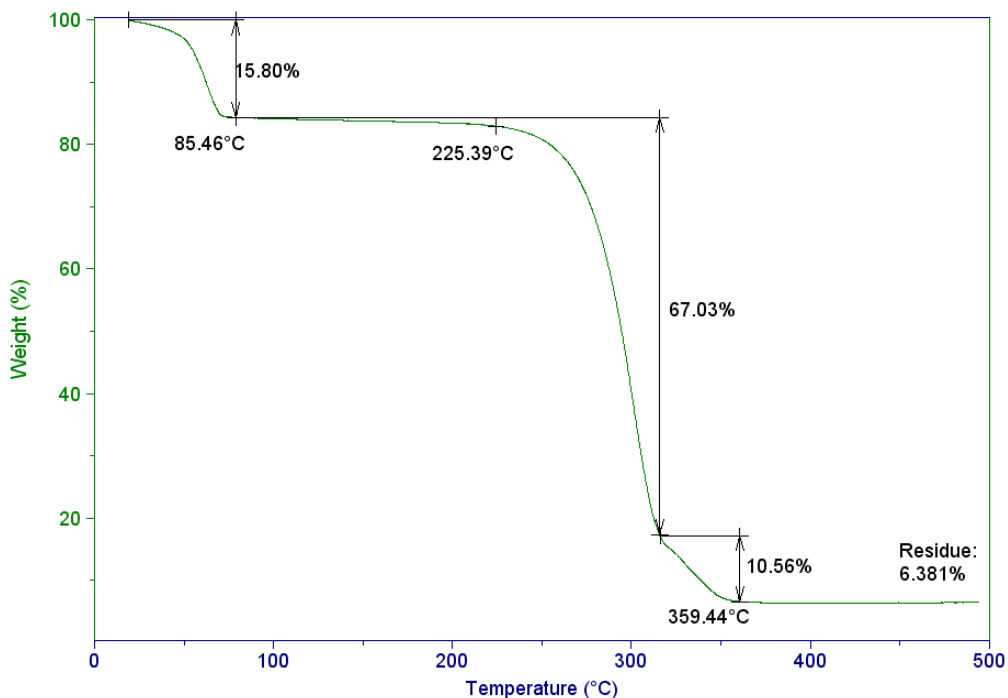


Fig. 1 TGA of **1**.

Heating of the crystals **1** (0.076 g) under vacuum at 85°C for 2 days has yielded a purple powder **2** (0.064 g, weight loss 15.7%). No weight gain has been detected when powder **2** (0.064 g) was exposed to the mixture of dichloromethane and benzene at room temperature for 48 hours. The powder X-ray analysis revealed that the XRPD pattern for the desolvated powder **2** differs significantly from that calculated for single crystals **1** (Fig. 2).

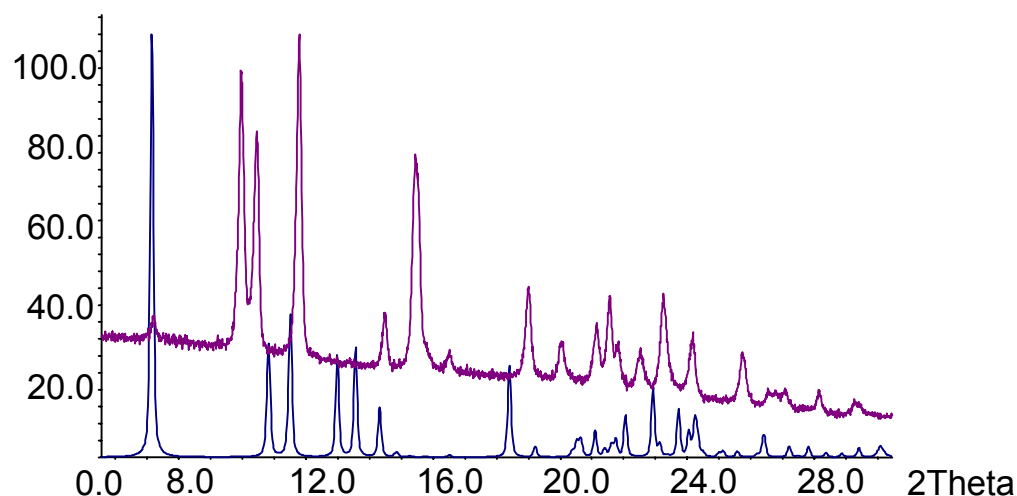


Fig. 2 Simulated X-ray powder pattern (blue) based on the structure of **1** at 173 K and observed pattern for the desolvated powder **2** (purple) at room temperature.

3) Solid-state reaction. A stoichiometric mixture of 1,3-dicyanobenzene (0.026 g, 0.20 mmol) and emerald-green rhodium(II) trifluoroacetate (0.132 g, 0.20 mmol) was sealed in an evacuated glass ampule. The container was then placed in an electric furnace at 70 °C. The mixture started to turn purple-violet in a few hours. The reaction was completed in about 5 days to yield a uniform fine powder of the product quantitatively formed in the ampule. The product was washed with benzene and dichloromethane, and then dried in vacuum at 50°C for two days. The powder X-ray analysis revealed the absence of starting materials in the product and unambiguously confirmed that it was identical to **2** obtained by removal of solvent from single crystals **1**, as described above. Yield 99%. Anal. Calcd.: C, 24.32; N, 3.55; H, 1.02. Found: C, 24.84; N, 3.55; H, 0.80. IR (KBr, cm^{-1}): 3117w, 3083w, 3044w, 2280w, 1664s, 1462w, 1404w, 1194s, 1166sh, 911w, 860m, 816w, 788m, 738m, 678w, 548w.

X-ray Crystallographic Procedures

Single-crystal X-ray study. A single crystal of **1** selected from the solution reaction was used for structural determination. The X-ray intensity data were measured at 173(2) K (Bruker

KRYOFLEX) on a Bruker SMART APEX CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube ($\lambda = 0.71073 \text{ \AA}$) operated at 1800 W power. The crystal was mounted on a goniometer head with silicone grease. The detector was placed at a distance of 6.140 cm from the crystal. A total of 1850 frames were collected with a scan width of 0.3° in ω and an exposure time of 20 s/frame. The frames were integrated with the Bruker SAINT software package² using a narrow-frame integration algorithm to a maximum 2θ angle of 56.58° (0.75 \AA resolution). The final cell constants are based upon the refinement of the XYZ-centroids of 6738 reflections above $20\sigma(I)$. Analysis of the data showed negligible decay during data collection. Data were corrected for absorption effects using the empirical program SADABS³ (min/max apparent transmission is 0.8062 / 0.9355). The structure was solved and refined by full-matrix least-squares procedures on $|F^2|$ using the Bruker SHELXTL (version 6.12) software package.⁴ The coordinates of rhodium atoms for the structure were found in direct method E maps. The remaining atoms were located after an alternative series of least-squares cycles and difference Fourier maps. All the hydrogen atoms were included in idealized positions for structure factor calculations. Benzene and dichloromethane solvent molecules were found to exhibit a two-fold disorder. The fluorine atoms of all CF_3 groups were disordered over three rotational orientations. Anisotropic displacement parameters were assigned to all non-hydrogen atoms, except for the disordered fluorine atoms and atoms of the solvent molecules. Relevant crystallographic data are summarized in Table 1.

X-ray powder diffraction. The X-ray powder diffraction data for the structure solution and refinement of **2** were collected on an automated STADI-P (STOE) diffractometer (transmission mode, Cu $K_{\alpha 1}$ -radiation, $\lambda = 1.5406 \text{ \AA}$, Ge-monochromator, linear-PSD, step 0.01° , 2θ , 20° C). The sample was ground in dried vaseline oil and placed between two mylar foils. Prior to

indexing the pattern fitting procedure using the Win^XPow software⁵ was performed in the range of 5-35° 2 θ to determine the correct peak positions. The obtained peak list was used for indexing by the TREOR program.⁶ The first 30 peaks were indexed in the *I*-centered monoclinic unit cell with the lattice parameters $a = 17.681(6)$, $b = 16.863(8)$, $c = 8.317(5)$ Å, $\beta = 110.99(2)^\circ$, $V = 2479.7(14)$ Å³ ($F_{30} = 23.9$). Additionally, an estimated average volume per the dirhodium unit and the 1,3-dicyanobenzene ligand allowed us to determine Z as 4. Analysis of the systematic extinctions suggested the *I*2/*a* space group. For further calculations the standard *C*2/*c* setting with the transformed cell parameters of $a = 19.411(20)$, $b = 16.879(19)$, $c = 8.348(4)$ Å and $\beta = 114.91(2)^\circ$ was used.

The unit cell parameters and space group were further tested using Pawley's fit.⁷ The structural motif was found by the grid search method⁸ varying the five degrees of freedom. The rigid geometries of dirhodium(II,II) tetrakis(trifluoroacetate) and 1,3-dicyanobenzene were built up in accordance with the literature data for the single crystal structures of pure compounds.^{1,9} The crystal packing consideration suggests the two moieties occupy two elements of symmetry. Assuming that the mid of the dirhodium unit occupies the inversion center (1/4, 1/4, 1/2) and 1,3-dicyanobenzene is situated on the two-fold axis (1/2, y , 1/4), and varying three orientational parameters for the former moiety, and one translational and one orientational parameter for the latter one, the solution was found in a standard run of grid search. The final bond-restrained Rietveld refinement was carried out with the program MRIA¹⁰ using a split-type pseudo-Voigt peak profile function¹¹ and a symmetrized harmonics expansion texture formalism¹² up to the 4th order. The following constraints and restraints were applied: (i) the two isotropic displacement parameters were refined in total, one parameter for the Rh atom and one common parameter for six independent fluorine atoms; (ii) the rigid restraints were applied to the intramolecular bond

lengths and contacts in the dirhodium trifluoroacetate and 1,3-dicyanobenzene moieties. The strength of the restraints was a function of an interatomic separation and, for intramolecular bond lengths, corresponded to an r.m.s. deviation of 0.01 Å; (iii) additional soft restraints were applied to the planarity of the 1,3-dicyanobenzene moiety. Hydrogen atoms were positioned geometrically with the C–H distance of 0.93 Å. The diffraction profiles and the differences between the measured and calculated profiles after the final bond-restrained Rietveld refinement are shown in the text.

Recent reviews highlighting the progress of the XRPD method and programming are listed in the *Reference Section*.¹³ The characteristic parameters for the π - π ligand-solvent or ligand-ligand aromatic interactions in the structures of **1** and **2**, based on the criteria of Janiak,¹⁴ are presented in Table 2. A fragment of the 1D chain in **1** with labeling is shown in Fig. 3.

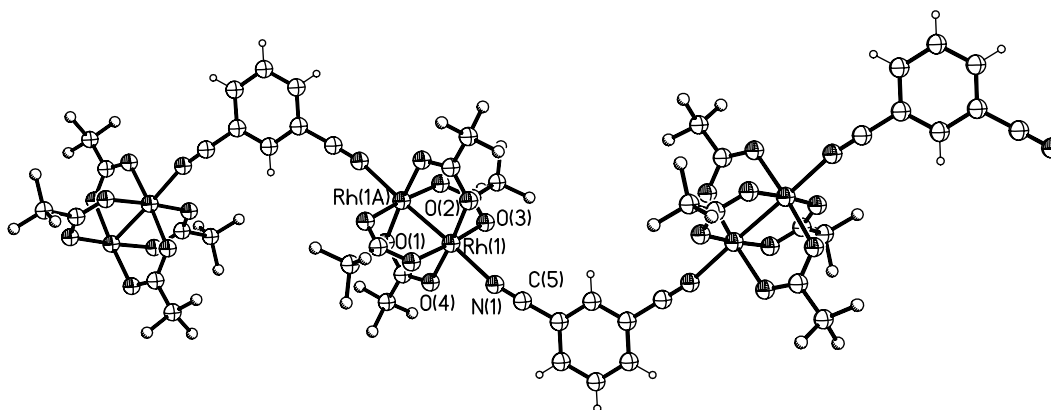


Fig. 3 A perspective drawing of a fragment of the 1D chain **1** with labeling. Atoms are represented by thermal ellipsoids at the 40% probability level. Fluorine and hydrogen atoms are shown as spheres of arbitrary radii. Only one orientation of the disordered CF₃ groups is depicted. Only metal, oxygen, and nitrogen atoms are labeled for clarity.

Table 1. Crystallographic data and structural refinement parameters for $\{[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4] \cdot (1,3\text{-C}_6\text{H}_4(\text{CN})_2)\} \cdot 1.75\text{C}_6\text{H}_6 \cdot 0.5\text{CH}_2\text{Cl}_2$ (**1**) and $\{[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4] \cdot (1,3\text{-C}_6\text{H}_4(\text{CN})_2)\}$ (**2**).

	1	2
formula	$\text{C}_{27}\text{H}_{15.5}\text{ClF}_{12}\text{N}_2\text{O}_8\text{Rh}_2$	$\text{C}_{16}\text{H}_4\text{F}_{12}\text{N}_2\text{O}_8\text{Rh}_2$
fw	965.18	786.03
crystal system	orthorhombic	monoclinic
space group	<i>Pnma</i>	<i>C2/c</i>
<i>a</i> (Å)	16.3302(10)	19.411(20)
<i>b</i> (Å)	24.7253(15)	16.879(19)
<i>c</i> (Å)	8.7079(5)	8.348(4)
α (deg)	90	90
β (deg)	90	114.91(2)
γ (deg)	90	90
<i>V</i> (Å ³)	3516.0(4)	2481(4)
<i>Z</i>	4	4
radiation	Mo $K\alpha$	Cu $K\alpha_1$
λ (Å)	0.71073	1.5406
D_{calcd} (g·cm ³)	1.823	2.105
μ (mm ⁻¹)	1.126	12.060
T (K)	173(2)	293(2)
2 θ range (deg)	4.96 – 56.64	6.00 – 65.00
data collcn mode		transmission
<i>R</i> indices	$R1^{\text{a}} = 0.0550^{\text{d}}$ $wR2^{\text{b}} = 0.1405^{\text{d}}$ $\text{GOF}^{\text{c}} = 1.090$	$R_{\text{p}}^{\text{e}} = 0.0324$ $wR_{\text{p}}^{\text{f}} = 0.0426$ $\chi^2^{\text{g}} = 1.246$

^a $R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. ^b $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$. ^c $\text{GOF} = [\Sigma[w(F_o^2 - F_c^2)^2] / (N_{\text{obs}} - N_{\text{params}})]^{1/2}$, based on all data. ^d for reflections with $I > 2\sigma(I)$. ^e $R_{\text{p}} = \Sigma(|I_o - I_c|) / \Sigma I_o$. ^f $wR_{\text{p}} = [\Sigma w(I_o - I_c)^2 / \Sigma w I_o^2]^{1/2}$. ^g $\chi^2 = \Sigma w(I_o - I_c)^2 / (N_{\text{obs}} - N_{\text{var}})$.

Table 2. Weak π - π interaction observed in the solid state packing of **1**, **2** and 1,3-dicyanobenzene⁹ between the arene rings of C₆H₄(CN)₂ (L) and C₆H₆ (S).

Compound	Aromatic rings ^a	Dihedral angle [°]	Intercentroid distance [Å]	Interplanar distance ^b	Ring slippage ^c	Shortest C–C distance [Å]
1	L-S ₁	40.4(7)	4.44(2)	3.27 (2)	20.2	3.42
		40.4(7)	4.31(2)	3.35(2)	9.5	3.50
	L _a -S ₂	29.1(6)	4.06(2)	3.38(2)	2.9	3.36
		L _b -S ₂	40.3(7)	4.50(3)	3.37(2)	19.3
2	L-L	0	4.18(7)	3.33(7)	37.2	3.33
L	L-L	0	3.87(1)	3.47(1)	26.4	3.48

^aL_a, L_b refer to C₆H₄(CN)₂ in chains having two different orientations and S₁, S₂ are two crystallographically independent C₆H₆ molecules in **1**. ^bThe shortest estimated distance between carbon atom of one ring and the partner ring. ^cAngle between the centroid of the first ring and the normal to the second ring plane.

Table 3. Selected bond distances [Å] and angles [°] for **1** and **2**.

	1	2
Rh(1)-Rh(1A)	2.4137(6)	2.398(9)
Rh(1)-O(1)	2.031(3)	2.03(4)
Rh(1)-O(2)	2.042(3)	2.03(4)
Rh(1)-O(3)	2.038(3)	2.03(4)
Rh(1)-O(4)	2.040(3)	2.05(4)
Rh(1)-N(1)	2.197(4)	2.20(5)
N(1)-C(5)	1.133(6)	2.03(4)
Rh(1A)–Rh(1)–N(1)	179.50(12)	177(1)
Rh(1)–N(1)–C(5)	175.6(4)	168(3)

References for Supplementary Information

- (1) F. A. Cotton, E. V. Dikarev and X. Feng. *Inorg. Chim. Acta*, 1995, **237**, 19.
- (2) *SAINTE*, version 6.02; Bruker AXS, Inc.: Madison, WI, 2001.

- (3) *SADABS*; Bruker AXS, Inc.: Madison, WI, 2001.
- (4) *SHELXTL*, version 6.10; Bruker AXS, Inc.: Madison, WI, 2001.
- (5) Win^xPow software, v.1.1 STOE&Cie GmbH, 2001.
- (6) P.-E. Werner, L. Eriksson and M. Westdahl, *J. Appl. Cryst.*, 1985, **18**, 367.
- (7) G. S. Pawley, *J. Appl. Cryst.*, 1981, **14**, 357.
- (8) V. V. Chernyshev and H. Schenk, *Z. Kristallogr.*, 1998, **213**, 1.
- (9) J. Janzak and R. Kubiak, *J. Mol. Struct.*, 2000, **553**, 157.
- (10) V. B. Zlokazov and V. V. Chernyshev, *J. Appl. Crystallogr.*, 1992, **25**, 447.
- (11) H. Toraya, *J. Appl. Cryst.*, 1986, **19**, 440.
- (12) M. Ahtee, M. Nurmela, P. Suortti, M. Järvinen, *J. Appl. Cryst.*, 1989, **22**, 261.
- (13) D. M. Poojary and A. Clearfield, *Acc. Chem. Res.*, 1997, **30**, 414; K. D. M. Harris, M. Tremayne and B. M. Kariuki, *Angew. Chem. Int. Ed.*, 2001, **40**, 1626; V. V. Chernyshev, *Russ. Chem. Bull.*, 2001, **50**, 2273; A. D. Bond and W. Jones, *Acta Crystallogr., Sect. B*, 2002, **58**, 233; K. D. M. Harris, R. L. Johnston, G. W. Turner, E. Tedesco, E. Y. Cheung and B. M. Kariuki, *Mol. Cryst. Liq. Cryst. Sci. Technol.*, 2002, **389**, 123; M. A. Neumann, F. J. J. Leusen, G. E. Engel, S. Wilke and C. Conesa-Moratilla, *Int. J. Modern Physics, Sect. B*, 2002, **16**, 407; C. Giacovazzo, A. Altomare, C. Cuocci, A. G. Moliterni and R. Rizzi, *J. Appl. Crystallogr.*, 2002, **35**, 422; *Structure Determination from Powder Diffraction Data*, ed. W. I. F. David, K. Shankland, L. B. McCusker and C. Baerlocher, Oxford University Press, New York, 2002, pp. 1-337; K. D. M. Harris, *Crystal Growth & Design*, 2003, **3**, 887; W. I. F. David, K. Shankland and A. J. Markvardsen, *Crystallogr. Rev.*, 2003, **9**, 3; V. Brodski, R. Peschar and H. J. Schenk, *J. Appl. Crystallogr.*, 2003, **36**, 239.
- (14) C. Janiak, *J. Chem. Soc., Dalton Trans.*, 2000, 3885.