

Syntheses and structural characterization of the one dimensional polymers: <sup>1</sup><sub>∞</sub> [Rh<sub>2</sub>(OAc)<sub>4</sub>(NCPhCN)·S]; S=CH<sub>3</sub>COCH<sub>3</sub>, CH<sub>3</sub>OH, C<sub>2</sub>H<sub>5</sub>OH, C<sub>4</sub>H<sub>8</sub>O and C<sub>6</sub>H<sub>6</sub>

# Tianyan Niu, Jian Lu, Gerardo Crisci and Allan J. Jacobson\*

Department of Chemistry, University of Houston, Houston, TX 77204-5641, U.S.A.

(Received 12 January 1998; accepted 15 May 1998)

Abstract—The syntheses and characterization of five compounds obtained by the reaction of dirhodium(II)tetraacetate with 1,4-dicyanobenzene in different solvent systems are described. The structures of  $Rh_2(OAc)_4(NCPhCN)\cdot CH_3COCH_3$  (1),  $Rh_2(OAc)_4(NCPhCN)\cdot 2CH_3OH$  (2),  $Rh_2(OAc)_4(NCPhCN)\cdot C_4H_8O$  (4) and  $Rh_2(OAc)_4(NCPhCN)\cdot C_6H_6$  (5) were determined by single crystal X-ray diffraction. All structures contain one dimensional polymeric chain, comprised of dirhodiumtetraacetate units bridged by 1,4-dicyanobenzene molecules. Solvent molecules are located between the chains in each structure and three different packing arrangements of the polymer chains result from the inclusion of these different solvent molecules. Compounds 1, 2 and 3 crystallize in space group C2/c with similar cell parameters. Compound 4 also crystallizes in the same space group, but its structure is significantly different from those of 1, 2 and 3. Compound 5 crystallizes in space group  $P\overline{1}$  and contains an unusual polymer chain structure. (C) 1998 Elsevier Science Ltd. All rights reserved

*Keywords*: coordination polymer; one dimensional polymer chains; dirhodiumtetraacetate; 1,4-dicyanobenzene; synthesis; crystal structure

## INTRODUCTION

The coordination chemistry of dinuclear tetra-carboxylates of the transition metals has been a focus of several previous investigations. Adducts such as  $Cr_2(OAc)_4(py)_2$  [1] and several polymers such as:  $Cr_2(OAc)_4$ ·(pyz)<sub>2</sub>[1], Mo<sub>2</sub>(O<sub>2</sub>CCH<sub>3</sub>)<sub>4</sub>·L (L = pyrazine, 4,4'-bipyridine, 1,4-diazabicyclo[2.2.2]octane) [2],  $[Ru_2(O_2CC_2H_5)_4(phz)]BF_4$  [3] and  $Cu_2(OAc)_4(pyz)$  [4] have been studied in detail. Several reactions of the Rh(II) tetra-acetate dimer with organic or organometallic ligands have been reported [5-8]. With some ligands, for example bis(4-pyridinecarbonitrile) [9] and pyridine,  $M_2(O_2CR)_4L_2$  [10] metal cluster complexes are formed. One and two dimensional polymers with are obtained by reactions 2-(aminomethyl)pyridine [11], TCNE [12] and 4-amino-5-(aminomethyl)-2-methylpyrimidine [13] and  $K_3Co(CN)_6$  [14]. Polymers containing  $Rh_2(O_2CR)_4$  dimers with different R groups, for example,  $Rh_2(O_2 CEt)_4$  [15] or  $Rh_2(O_2CCF_3)_4$  [16, 17], bridged by suitable organic ligands have also been reported.

Although extensive studies have focused on the formation of coordination polymers of the  $Rh_2(O_2CR)_4$ dimer with linear-bidentate nitrogen ligands, the role of specific solvent molecules in the formation and crystallization of such polymers has not been investigated. In the present work, we report the syntheses and structures of compounds formed by the reaction of  $Rh_2(OAc)_4$  with 1,4-dicyanobenzene in different solvents. Five new one dimensional coordination polymers have been obtained:  $Rh_2(OAc)_4$ (NCPhCN)·CH<sub>3</sub>COCH<sub>3</sub> (1),  $Rh_2(OAc)_4(NCPhCN)$ ·2CH<sub>3</sub>OH (2),  $Rh_2(OAc)_4(NCPhCN)$ · $xC_2H_5OH$ ( $x \cong 1$ ) (3),  $Rh_2(OAc)_4(NCPhCN)$ · $xC_4H_8O$  (4) and  $Rh_2(OAc)_4(NCPhCN)$ · $C_6H_6$  (5).

The structures of 1, 2, 4 and 5 were determined by analyses of single crystal X-ray diffraction data. The polymers all consist of one dimensional chains of  $Rh_2(OAc)_4$  dimers bridged by 1,4-dicyanobenzene ligands, with the cavities between the chains filled by

<sup>\*</sup>Author to whom correspondence should be addressed.

different solvent molecules. Packing of specific solvent molecules and the chains determines the final crystal structure. For **3**, only the unit cell dimensions and space group were determined and indicate that **3** is isostructural with **1** and **2**.

### **EXPERIMENTAL**

### Reagents and apparatus

Rhodium(II)acetate (STREM Chemical) and 1,4dicyanobenzene (Aldrich) were used as received. Acetone, methanol, ethanol, benzene and tetrahydrofuran (THF) were dried over molecular sieves (4 Å). Infrared data were collected on a Galaxy FTIR 5000 series spectrometer, using the KBr pellet method. X-ray powder diffraction measurements were carried out using a Scintag XDS 2000 automated powder diffractometer (Cu K $\alpha$  radiation,  $\theta$ – $\theta$ , flat plate geometry). The Cerius 2 program [18] was used to simulate X-ray powder diffraction patterns from the single crystal X-ray data. Thermogravimetric analyses were carried out by using a TA Instruments 2100 thermal analyzer in a flowing nitrogen atmosphere at a heating rate of 1°C/min.

#### Syntheses

# *Rh*<sub>2</sub>(*OAc*)<sub>4</sub>(*NCPhCN*)·*CH3COCH3* (*1*). Rh<sub>2</sub>(OAc)<sub>4</sub> (10 mg, 0.023 mmol) and 1,4-dicyanobenzene (5 mg, 0.039 mmol) were dissolved in 25 ml acetone. The solution was stirred for 30 min and then slowly evaporated. Dark red crystals in the form of long columns or thin plates crystallized from the solution after 6 d. IR bands (cm<sup>-1</sup>): 3443 (s), 3092 (w), 3046 (w), 2986 (w), 2934 (w), 2396 (w), 2301 (w), 2234 (m), 1588 (s), 1506 (w), 1437 (s), 1417 (s), 1358 (m), 1279 (w), 1051 (w), 924 (w), 845 (m), 702 (s), 629 (w), 561 (m).

 $Rh_2(OAc)_4(NCPhCN)\cdot 2CH_3OH$  (2). A solution of 1,4-dicyanobenzene (15.2 mg, 0.119 mmol) in THF (30 ml) was added to a suspension of  $Rh_2(OAc)_4$  (35 mg, 0.08 mmol) in methanol (40 ml). The mixture was stirred for about 1 h at room temperature. Slow evaporation produced small, red rod-shaped crystals in about 1 week in 95.9% yield. The compound is insoluble in water, but soluble in acetonitrile, THF and methanol. IR bands (cm<sup>-1</sup>): 3443 (s), 3090 (w), 3044 (w), 2930 (w), 2233 (w), 1591 (s), 1435 (s), 1416 (s), 1385 (m), 1352 (w), 1277 (w), 1219 (w), 1051 (w), 858 (w), 812 (w), 702 (m), 629 (w), 565 (w).

 $Rh_2(OAc)_4(NCPhCN) \cdot C_2H_5OH$  (3). The same procedure was used as described above for **1**, with ethanol replacing acetone. The dark red crystals were irregular multifaceted prisms. IR bands (cm<sup>-1</sup>): 3447 (s), 3435 (s), 3098 (w), 3054 (w), 2363 (w), 2234 (m), 1588 (s), 1506 (w), 1437 (s), 1418 (s), 1358 (m), 1277 (w), 1051 (w), 922 (w), 845 (m), 704 (s), 629 (w), 598 (w), 561 (m).

 $Rh_2(OAc)_4(NCPhCN) \cdot C_4H_8O$  (4). The reaction was carried out as described above for 1, using THF as the solvent in place of acetone. Dark red diamondshaped plates formed in 7 days. IR bands (cm<sup>-1</sup>): 3495 (s), 3422 (s), 3100 (w), 3054 (w), 2971 (w), 2930 (w), 2855 (w), 2361 (w), 2234 (m), 1935 (w), 1588 (s), 1506 (w), 1437 (s), 1416 (s), 1356 (m), 1279 (w), 1057 (m), 845 (s), 799 (w), 698 (s), 629 (w), 596 (w), 561 (s).

 $Rh_2(OAc)_4(NCPhCN) \cdot C_6H_6$  (5). A solution of 1,4dicyanobenzene (5 mg, 0.039 mmol) in 10 ml THF was added to a suspension of Rh<sub>2</sub>(OAc)<sub>4</sub> (10 mg, 0.023 mmol) in 10 ml benzene. The solid dissolved completely after being stirred for 1 h. Two distinct habits of lilac coloured crystals were observed after a week of slow evaporation. The majority of the product consisted of very large multifaceted blocks, while the remainder were square columns. A square column crystal was used for the data collection since the large blocks appeared to be polycrystalline. Subsequently, a small fragment cut from a large block verified that it was indeed the same phase as the crystal used for data collection. IR bands (cm<sup>-1</sup>): 3449 (s), 3424 (s), 3096 (w), 3054 (w), 3005 (w), 2926 (w), 2390 (w), 2234 (m), 1588 (s), 1437 (s), 1416 (s), 1385 (m), 1356(m), 1279(w), 1045(w), 845(m), 696(s), 629(w), 598(w), 561(m).

All of the compounds show the expected IR stretching frequencies from the  $Rh_2(OAc)_4$ ·dicyanobenzene polymer and the specific solvent molecule. Coordination of the dicyanobenzene is indicated by a CN stretching frequency at 2234 cm<sup>-1</sup>, which is slightly blue-shifted from the CN stretching frequency (2232 cm<sup>-1</sup>) of neat 1,4-dicyanobenzene.

#### Structure determinations

For 1, 3 and 5, X-ray data were collected using a Nicolet R3m/V automatic diffractometer (graphite-monochromated Mo-K $\alpha$  radiation). Data for 2 and 4 were collected using an Enraf-Nonius CAD-4, four circle diffractometer also with Mo-K $\alpha$  radiation.

Α crystal of 1 with dimensions  $0.10 \times 0.35 \times 0.45$  mm was mounted on a glass fiber and transferred to the diffractometer. The crystal was cooled to 223 K in a stream of cold nitrogen gas. Lattice parameters were determined from the angles of 25 reflections in the range  $16.3^{\circ} < 2\theta < 30.3^{\circ}$ . Crystal data and details of the data collection and refinement are presented in Table 1. Data were collected in  $\omega$ -2 $\theta$ mode. Intensity data for 2386 reflections (2121 unique) were collected in the range  $4^\circ < 2\theta < 50^\circ$ . Two standard reflections were monitored after every two h or every 100 data collected and these showed a 12% linear decay over the course of the experiment. A normalization factor as a function of X-ray exposure time was applied to account for this. During data reduction, Lorentz and polarization corrections and a semi-empirical absorption correction based on ten

Solvent	Acetone (1)	Methanol (2)	Ethanol (3) <sup>d</sup>	THF (4)	Benzene (5)
Formula	$C_{19}H_{22}N_2O_9Rh_2$	$C_{18}H_{24}N_2O_{10}Rh_2$		$C_{20}H_{24}N_2O_9Rh_2$	$C_{22}H_{22}N_2O_8Rh_2$
FW	628.21	634.24		642.23	648.24
a (Å)	23.122(7)	23.113(3)	23.336(8)	22.735(5)	8.062(2)
b (Å)	12.382(7)	12.290(3)	12.248(4)	8.162(10)	8.400(2)
<i>c</i> (Å)	8.518(3)	8.503(1)	8.527(3)	14.660(8)	10.354(2)
α (°)	90	90	90	90	95.16(2)
β (°)	97.82(2)	97.54(2)	98.223	116.16(2)	99.14(2)
γ (°)	90	90	90	90	118.18(2)
Ζ	4	4	4	4	1
$V(\text{\AA}^3)$	2416	2395	2412	2442	599
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
Space group	C2/c (No. 15)	C2/c (No. 15)	C2/c (No. 15)	C2/c (No. 15)	<i>P</i> 1 (No. 2)
$T(\mathbf{K})$	223	298	223	298	223
$\lambda$ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
$D_{\text{calc.}} (\text{g cm}^{-3})$	1.727	1.760		1.747	1.796
$\mu$ (Mo-K $\alpha$ ) (mm <sup>-1</sup> )	1.415	1.431		1.402	1.426
<i>F</i> (000)	1248	1280		1280	322
Data collection, $\theta$ (°)	2.96 to 25.05	2.97 to 24.98		2.00 to 27.91	2.80 to 25.05
Index ranges	$-27 \leq h \leq 27$	$-27 \leq h \leq 26$		$-29 \leq h \leq 26$	$0 \leq h \leq 9$
	$0 \leq k \leq 14$	$0 \leq k \leq 14$		$0 \leq k \leq 10$	$-9 \leq k \leq 8$
	$-10 \leqslant l \leqslant 0$	$0 \leq l \leq 10$		$0 \leq l \leq 19$	$-12 \le l \le 11$
Reflections collected	2280	2269		2714	2112
Independent reflections	2121	1964		2714	2102
Number of parameters	147	143		150	198
$R(F)^{a} (\%)^{c}$	5.86	4.75		3.39	1.77
$wR2(F)^{\rm b} (\%)^{\rm c}$	15.75	13.14		9.38	4.32
$\Delta \rho_{\text{max.}}, \Delta \rho_{\text{min}} \text{ (eÅ}^{-3})$	1.784, -2.343	1.128, -1.396		0.740, -1.188	0.527, -0.353
Goodness-of-fit $(F^2)$	1.057	1.124		1.049	0.993

Table 1. Crystallographic data for 1, 2, 3, 4 and 5

<sup>a</sup>  $R = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|$ .

<sup>b</sup> wR2 =  $[\Sigma[w(F_0^2 - F_c^2)^2] / \Sigma[w(F_0^2)^2]]^{1/2}$ .

 $^{\mathrm{c}}[F_0 > 4\sigma(F_0)].$ 

<sup>d</sup>Only unit cell determined.

reflections having  $\chi$  values between 70 and 90° were applied. The structure was solved in space group C2/c by direct methods and standard difference Fourier techniques using SHELXS-96 [19]. Refinement on  $F^2$ was carried out by full-matrix least-squares procedures using SHELXL-96 beta [19]. All nonhydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in calculated positions riding on their carrier atoms, with fixed isotropic thermal parameters related to the value of the equivalent isotropic thermal parameter of their carrier atoms by a factor of 1.5 for the methyl hydrogen atoms and a factor of 1.2 for the other hydrogen atoms. Weights were optimized in the final refinement cycles.

The data collection and refinement of **5** were carried out in the same way as for **1**. A lilac square column with dimensions  $0.08 \times 0.12 \times 0.40$  mm was used. Twenty-five reflections in the range  $18^{\circ} < 2\theta < 42^{\circ}$ were centered, giving a triclinic cell. Intensity data were collected in the  $\omega$ -2 $\theta$  mode with a range of  $4 < 2\theta < 50^{\circ}$ . A semi-empirical absorption correction based on  $\psi$  scans was applied to the data during data reduction. The structure was determined and refined in space group  $P\bar{1}$  using the same programs as 1.

For 2 and 4, suitable crystals with dimensions  $0.31 \times 0.11 \times 0.10$  and  $0.15 \times 0.3 \times 0.3$  mm, respectively, were mounted with epoxy glue on the tip of a glass fiber and transferred to the diffractometer. 25 reflections were used to determine the unit cell and data were collected using the  $\omega$ -2 $\theta$  scan method in both cases. Intensities were corrected for Lorentz and polarization effects, as well as for absorption ( $\psi$ scans). Intensities of three standard reflections showed no variations greater than those predicted by counting statistics. In both cases, space group C2/c was chosen and confirmed by successful structure refinement. The structure solution and refinement were carried out similarly as the other compounds. For 3, only the unit cell dimensions and space group were determined (223 K). Selected bond distances and angles for 1, 2, 4 and 5 are given in Table 2.

A			
Acetone (1)			
Rh(1)-O(4)	2.029(4)	Rh(1)-O(1)	2.031(4)
Rh(1)-O(3)	2.035(5)	Rh(1)-O(2)	2.049(5)
Rh(1)-N(1)	2.239(5)	$Rh(1)-Rh(1)^{a}$	2.3910(10)
O(1)–C(1)	1.267(8)	$O(2)-C(2)^{a}$	1.273(8)
O(3) - C(2)	1.250(8)	$O(4) - C(1)^{a}$	1.266(8)
N(1) - C(11)	1 128(8)	C(1) - C(3)	1 498(9)
C(2) $C(4)$	1.511(11)	C(1) C(3)	1.490(9)
C(2)=C(4)	1.311(11)	C(11) = C(12)	1.446(6)
C(12)-C(14)	1.382(9)	C(12) - C(13)	1.409(10)
$C(13)-C(14)^{b}$	1.353(10)		
O(4) <b>P</b> h(1) $O(1)$	175 8(2)	O(4) <b>Ph</b> (1) $O(3)$	89.6(2)
O(4) = RI(1) = O(1)	1/3.0(2)	O(4) = RI(1) = O(3)	00.4(2)
O(1) = KII(1) = O(3)	90.4(2)	O(4) = RII(1) = O(2)	90.4(2)
O(1) - Rh(1) - O(2)	89.2(2)	O(3) - Rh(1) - O(2)	1/5.8(2)
O(4) - Rh(1) - N(1)	91.2(2)	O(1)-Rh(1)-N(1)	93.1(2)
O(3)-Rh(1)-N(1)	91.4(2)	O(2)-Rh(1)-N(1)	92.9(2)
$O(4)-Rh(1)-Rh(1)^{a}$	87.92(13)	$O(1)-Rh(1)-Rh(1)^{a}$	87.85(12)
$O(3)-Rh(1)-Rh(1)^{a}$	87.76(12)	$O(2)-Rh(1)-Rh(1)^{a}$	88.01(12)
$N(1)-Rh(1)-Rh(1)^{a}$	178.7(2)		
C(1) = O(1) = Rh(1)	119 8(4)	$C(2)^{a} - O(2) - Rh(1)$	118 7(4)
C(2) = O(3) = Rh(1)	120.2(4)	$C(1)^{a} - O(4) - Rh(1)$	110.0(1) 110.0(4)
C(2) = O(3) = KII(1) C(11) = N(1) = Bh(1)	178 1(5)	C(1) = O(4) = Kii(1) $O(1) = C(1) = O(4)^{a}$	119.9(4) 124.5(6)
C(11)=N(1)=Rn(1)	1/8.1(5)	$O(1)=O(1)=O(4)^{-1}$	124.5(6)
$O(3)-C(2)-O(2)^{a}$	125.2(7)	N(1)-C(11)-C(12)	179.1(7)
CH <sub>3</sub> OH ( <b>2</b> )			
Rh–O(3)	2.024(4)	Rh–O(1)	2.033(4)
Rh–O(2)	2.049(5)	Rh–O(4)	2.050(4)
Rh–N	2.236(4)	Rh–Rh <sup>°</sup>	2.3910(8)
O(1)-C(11)	1.248(7)	O(2)-C(13)	1.265(7)
$O(3) = C(11)^{c}$	1 262(7)	$O(4) = C(13)^{\circ}$	1 246(7)
N = C(1)	1 122(7)	C(1) - C(2)	1.2(7)
$\Gamma(-C(1))$	1.122(7) 1.275(9)	C(1) = C(2) C(2) = C(2)	1.402(7)
C(2) = C(4)	1.373(8)	C(2)=C(3)	1.591(9)
C(3) = C(4)	1.392(8)	C(11) - C(12)	1.519(8)
C(13) - C(14)	1.499(9)		
O(3)-Rh-O(1)	175.48(14)	O(3)-Rh-O(2)	90.1(2)
O(1) = Rh = O(2)	89 4(2)	O(3) = Rh = O(4)	90.1(2)
O(1) - Rh - O(4)	90.0(2)	O(2) - Rh - O(4)	1754(2)
O(2) Ph N	01.3(2)	O(1) Rh $O(4)$	173.4(2)
O(3)-RI-N	91.3(2)	O(1)-RII-N	93.2(2)
O(2)-Rh-N	92.4(2)	O(4)-Rn-N	92.1(2)
O(3)-Rh-Rh <sup>c</sup>	87.76(11)	O(1)-Rh-Rh <sup>c</sup>	87.74(11)
O(2)–Rh–Rh <sup>c</sup>	87.95(11)	$O(4)$ – $Rh$ – $Rh^{c}$	87.50(11)
N–Rh–Rh <sup>c</sup>	179.00(13)	C(11)–O(1)–Rh	119.5(4)
C(13)–O(2)–Rh	119.2(4)	$C(11)^{c}-O(3)-Rh$	119.6(3)
C(13)°-O(4)-Rh	120.1(4)	C(1)–N–Rh	177.8(5)
N-C(1)-C(2)	179.2(7)	$O(1)-C(11)-O(3)^{c}$	125.5(5)
$O(4)^{c} - C(13) - O(2)$	125.1(6)		
	12011(0)		
THF ( <b>4</b> )			
$P_{h}(1) O(4)$	2 029(3)	Ph(1) O(2)	2.030(3)
R(1) = O(4)	2.029(3)	Ri(1) = O(2)	2.039(3)
Rn(1)=O(1)	2.040(3)	Rn(1)=O(3)	2.040(3)
Rh(1)-N(1)	2.226(3)	$Rh(1)-Rh(1)^{a}$	2.3830(10)
O(1) - C(1)	1.263(4)	O(2) - C(2)	1.265(5)
$O(3)-C(1)^{a}$	1.258(4)	$O(4) - C(2)^{a}$	1.253(4)
N(1)-C(11)	1.140(5)	C(1)–C(4)	1.489(5)
C(2)–C(3)	1.506(6)	C(11)-C(12)	1.434(4)
C(12)-C(13)	1.374(5)	C(2)–C(14)	1.388(5)
$C(13) - C(14)^{e}$	1.376(5)	O(21)–C(21)	1.401(11)
$C(21)-C(22)^{g}$	1.306(13)	$C(22)-C(22)^{f}$	1.42(2)
		(22) (22)	
O(4)-Rh(1)-O(2)	175.98(9)	O(4)-Rh(1)-O(1)	89.47(12)
O(2)-Rh(1)-O(1)	89.94(11)	O(4)-Rh(1)-O(3)	90.45(12)
O(2)-Rh(1)-O(3)	89.86(11)	O(1)-Rh(1)-O(3)	176.06(9)
O(4)-Rh(1)-N(1)	91.37(12)	O(2)-Rh(1)-N(1)	92.64(12)

Table 2. Selected bond distances (Å) and angles (°) for  $1,\,2,\,4$  and 5

(continued)

Table 2—continued						
O(1)-Rh(1)-N(1)	93.97(12)	O(3)–Rh(1)–N(1)	89.96(11)			
$O(4)-Rh(1)-Rh(1)^{a}$	88.17(8)	$O(2)-Ph(1)-Rh(1)^{a}$	87.84(7)			
$O(1)-Rh(1)-Rh(1)^{a}$	88.13(8)	$O(3)-Rh(1)-Rh(1)^{a}$	87.94(7)			
$N(1)-Rh(1)-Rh(1)^{a}$	177.85(8)	C(11)-N(1)-Rh(1)	168.7(3)			
$O(3)^{a}-C(1)-O(1)$	125.7(3)	$O(3)^{a}(C1)-C(4)$	117.8(3)			
O(1)-C(1)-C(4)	116.6(3)	$O(4)^{a}(C2)-O(2)$	125.7(3)			
$O(4)^{a}-C(2)-C(3)$	117.9(4)	O(2)–C(2)–C(3)	116.3(4)			
N(1)-C(11)-C(12)	178.2(4)	C(21) <sup>f</sup> -O(21)-C(21)	106.4(13)			
C(22) <sup>g</sup> -C(21)-O(21)	106.4(9)	$(C21)^{h}$ -C(22)-C(22) <sup>f</sup>	106.0(8)			
Benzene (5)						
Rh–O(3) <sup>i</sup>	2.0348(14)	Rh–O(4)	2.0360(14)			
Rh–O(1)	2.0360(12)	Rh–O(2) <sup>i</sup>	2.0369(13)			
Rh-N(1)	2.237(2)	$\mathbf{R}\mathbf{h}$ - $\mathbf{R}\mathbf{h}^{\mathrm{i}}$	2.3887(4)			
O(1)-C(1)	1.264(2)	O(2)–C(1)	1.260(2)			
O(3)-C(3)	1.263(2)	O(4)–C(3)	1.265(2)			
N(1)-C(5)	1.137(3)	C(1)–C(2)	1.502(2)			
C(3)-C(4)	1.503(3)	C(5)–C(6)	1.446(3)			
C(6)-C(8) <sup>b</sup>	1.380(3)	C(6)–C(7)	1.389(3)			
C(7)–C(8)	1.382(3)	$C(9)-C(11)^{j}$	1.336(10)			
C(9)-C(10)	1.399(10)	C(10)–C(11)	1.371(10)			
C(9')-C(10')	1.340(11)	$C(9')-C(11')^{j}$	1.407(11)			
C(10')-C(11')	1.399(11)					
O(3) <sup>i</sup> -Rh-O(4)	176.01(5)	O(3) <sup>i</sup> -Rh-O(1)	89.84(5)			
O(4)-Rh-O(1)	90.44(5)	$O(3)^i$ -Rh- $O(2)^i$	89.82(5)			
$O(4)-Rh-O(2)^{i}$	89.63(5)	$O(1)$ -Rh- $O(2)^i$	175.98(5)			
$O(3)^i - Rh - N(1)$	98.32(6)	O(4)-Rh- $N(1)$	85.65(6)			
O(1)-Rh-N(1)	92.03(5)	$O(2)^{i}$ -Rh-N(1)	91.99(5)			
O(3) <sup>i</sup> -Rh-Rh <sup>i</sup>	87.90(4)	O(4)–Rh–Rh <sup>i</sup>	88.13(4)			
O(1)-Rh-Rh <sup>i</sup>	187.97(4)	O(2) <sup>i</sup> –Rh–Rh <sup>i</sup>	88.01(4)			
N(1)-Rh-Rh <sup>i</sup>	173.78(4)	C(1)–O(1)–Rh	119.18(11)			
C(1)-O(2)-Rh <sup>i</sup>	119.17(11)	C(3)–O(3)–Rh <sup>i</sup>	119.39(12)			
C(3)-O(4)-Rh	119.06(12)	C(5)–N(1)–Rh	150.6(2)			
O(2)–C(1)–O(1)	125.7(2)	O(3)–C(3)–O(4)	125.5(2)			
N(1)-C(5)-C(6)	176.2(2)					

Symmetry transformations used to generate equivalent atoms:<sup>a</sup>-x+1/2, -y+1/2, -z; <sup>b</sup>-x+1, -y+1, -z+1; <sup>c</sup>-x+1/2, -y+3/2, -z; <sup>d</sup>-x+1, -y+2, -z+1; <sup>e</sup>-x+1, -y, -z+1; <sup>f</sup>-x+1, y, -z+1/2; <sup>g</sup>-x+1, y-1, -z+1/2; <sup>h</sup>-x+1, y+1, -z+1/2; <sup>i</sup>-x, -y+1, -z+2; <sup>j</sup>-x, -y, -z+1.

## **RESULTS AND DISCUSSION**

#### Preparation

The characteristics of the compounds obtained from the reaction of rhodium(II)acetate dimer with 1,4-dicyanobenzene vary with the different solvents used. Two methods were used for the synthesis of the five compounds. **1**, **3** and **4** were synthesized with only one type of solvent. The solvent served to dissolve the starting materials and was subsequently incorporated into the structure within a channel formed by stacking of the polymer chains. For **2** and **5**, two types of solvents were involved in the synthesis. One served to dissolve the starting material and the other one was incorporated into the structure. THF was used as the solvent but was not observed in the final structures. Excess 1,4-dicyanobenzene was used in all of the five reactions. The structure and composition of the final products were insensitive to changes in the stoichiometry of the reactants.

## Structures

All of the polymeric structures contain one dimensional chains comprised of rhodiumacetate dimers bridged by 1,4-dicyanobenzene (see Fig. 1 for 1). Each compound has different solvent molecules located between the polymer chains and each solvent causes significant variations in the crystal structures that are adopted.

Figure 1 shows the local coordination of compound 1 with the atoms labelled. Figures 2 and 3 show different views of the spatial relationship between the linear chains. In Fig. 2, the acetate ligands have been omitted



Fig. 1. Ortep drawing of the local coordination of 1 with thermal ellipsoids at the 50% probability level, the solvent acetone is not shown.

for clarity. The dinuclear  $Rh^{4+_2}$  carboxylate core remains intact, with a Rh–Rh distance of 2.391(1)Å. The Rh–O distances range from 2.029(4) to 2.049(5)Å. The octahedral coordination sphere of Rh is completed by axial coordination to the nitrogen atom of the organic ligand at a distance of 2.239(5)Å. The Rh–N–C linkage is nearly linear, with an angle of 178.1(5)°. The chains stack together with an average separation of 3.8Å, Fig. 2. The phenylrings from the alternating chains are not parallel to each other and the closest contact between adjacent phenylrings is 3.559Å (Cl2 from one ring and Cl4 from another ring). Adjacent chains are oriented at an angle of 56.3° with respect to each other when projected on the **ab**  plane, Fig. 3. Part of the extended structure of **1** is shown in Fig. 3. The intersections of the chains define channels in the structure that are occupied by the solvent molecules.

The acetone molecules in 1 are severely disordered and are difficult to locate in difference maps. One acetone molecule was refined with an occupancy factor of 0.276, while four additional atom sites designated as carbon were also located and refined with fixed occupancies of 0.3. From thermogravimetric analysis data (see Section 3.3), one acetone molecule per dirhodium unit is present.

The arrangement of the polymer chains in the structure of **2** is the same as in **1**. Adjacent chains are oriented at an angle of  $56.0^{\circ}$  with respect to each other, when projected on the **ab** plane. This angle is essentially the same as observed in **1** ( $56.3^{\circ}$ ). The average Rh–O, Rh–N and Rh–Rh bond distances in the two compounds are the same within errors. The methanol solvent molecules in **2** are also disordered. The positions of two methanol molecules could be refined, albeit with high thermal parameters. The exact number of methanol molecules could not be determined from the X-ray data, however thermogravimetric analysis indicates that two methanol molecules per dirhodium unit are present.

In 4, the THF solvent molecules are ordered and a significant change in the arrangement of the polymeric chains [Fig. 4(a)–(c)] is observed. In 1 and 2 the chains are nearly linear, but in 4 the C–N–Rh angle is reduced to  $168.7(3)^{\circ}$ . The Rh–Rh–N and N–C–C angles in 4 are still close to  $180^{\circ}$ . The N–Rh distance [2.226(3)Å]



Fig. 2. View of the structure of **1** showing the stacking of the chains. For clarity, the acetate groups of the Rh dimer are not shown.



Fig. 3. Projection of the structure of 1 along c. Disordered acetone molecules are shown between the chains.



Fig. 4. (a) View of the structure of **4** showing the stacking of the chains and the THF molecules. For clarity, the acetate groups of the Rh dimer are not shown. (b) Local coordination of **4** showing the attraction between oxygen of the THF and the phenylrings in the chains. For clarity, the acetate groups of the Rh dimer are not shown. The dotted lines indicate the closest contact between the THF and phenylrings. (c) View of the structure of **4** showing the attraction between oxygen of the THF and the phenylrings in the chains. For clarity, the acetate groups of the Rh dimer are not shown. The dotted lines indicate the closest contact between the the closest contact between the THF and the phenylrings in the chains. For clarity, the acetate groups of the Rh dimer are not shown. The dotted lines indicate the closest contact between the THF and phenylrings.

is similar to the distance in 1 and 2. The change in angle at the N atom, however, imparts a slight zigzag geometry to the chains as can be seen in Fig. 4. The stacking of the polymer chains in 4 is similar to that observed in 1 and 2, but the alternating chains make

an angle of  $39.50^{\circ}$  (projected on **ab** plane). The arrangement of THF molecules between adjacent chains suggests a weak interaction through the oxygen lone electron pairs. This interaction may be responsible for reducing the dihedral angle between the



chains by ~  $17^{\circ}$ . The distances between the THF oxygen atom and the chains (O21–C14 and O21–C12) are 3.381 and 3.434 Å, respectively. The bridging geometry is symmetric because THF lies on a crystallographic two-fold axis.

A different structure is observed when benzene molecules are trapped between the polymer chains. Crystals of **1**, **2**, **3** and **4** all have the same dark red color, while crystals of **5** are lilac. In **5**, all of the chains in the crystal are parallel to each other (Figure 5). Every polymeric chain zigzags as in **4**, with a C–N–Rh angle of  $150.6(2)^{\circ}$ , which is much further from linear than the corresponding angle in **4** [168.7(3)°]. The benzene molecules that sandwich each phenylring in the chain are parallel to each other and are separated by a distance of 8.461 Å. The phenylring in the chain and the benzenering are not parallel and the closest contact between them is 3.483 Å (C6–C9), while the distance from C5 of the cyanide group to C9 of the benzenering is 3.352 Å. The spacing between the phenylrings is too large to imply any strong electronic interaction. The benzene molecules are disordered over two different positions, rotated at roughly 30° to each other about a common crystallographic inversion center. Analysis of the isotropic thermal parameters showed a 50% occupancy for each orientation.

4086



Fig. 5. (a) View of the structure of **5** showing the stacking of the chains and the benzene molecules. For clarity, the acetate groups of the Rh dimer are not shown and only one position of the disordered benzene molecule is shown. (b) Local coordination of **5** showing the attraction between the benzene molecules and the phenylrings in the chains. The dotted lines indicate the closest contact between the benzene molecule with the chains. (c) View of the structure of **5** along *a* showing the stacking of the chains.

All five crystal structures have solvent "channels" leading directly to the surface: 1, 2, 3 and 4 have channels along the c axis, while 5 has a channel along a. In TGA measurements on heating, acetone, methanol and ethanol are all removed near their boiling points. However, THF and benzene are lost at temperatures significantly higher than their boiling points and the removal of the solvent molecules is not well resolved in temperature from the temperature at which the dicyanobenzene molecules are removed. The TGA data suggest some weak interaction between the solvent molecules and the frameworks of 4 and 5.

The structure of **4**, suggests some interaction between the oxygen lone pair electrons in THF and the chains, whereas in **5** the benzene molecules may have some  $\pi$ - $\pi$  interactions with the phenylrings in the chain.

#### Thermogravimetric analysis

Each of 1, 2, 3, 4 and 5 was heated to  $400^{\circ}$ C in nitrogen to determine the solvent contents and thermal stabilities (Figure 6). For 1, the first two weight losses at  $T < 118^{\circ}$ C corresponded to the loss of one

T. Niu et al.



Fig. 5—continued.

molecule of acetone (observed 9.67%, calculated 9.25%). From 118 to  $175^{\circ}$ C, a second weight loss corresponded to removal of one dicyanobenzene molecule (observed 21.99%, calculated 20.40%). The final weight loss occurred between 227 and 246°C and corresponded to the loss of the four acetate groups. No further decomposition was observed above 246°C. X-ray powder diffraction confirmed that the black residue was pure Rh (observed 31.20%, calculated 32.76%). Interestingly the original shape of the crystal was preserved after decomposition.

The thermal decomposition behaviors of 2 and 3 were similar to that of 1. In both cases, the loss of solvent molecules was completed at relatively low temperature ( $62^{\circ}C$  for 2 and  $113^{\circ}C$  for 3). The weight losses corresponding to the loss of dicyanobenzene molecules and the four acetate groups occurred in similar temperature ranges in 2 and 3 and they were not significantly different from those of 1. The solvent losses indicated a composition of two methanol molecules per dirhodium unit per unit cell in 2 and one ethanol molecule per dirhodium unit per unit cell in 3.

Compound 4 showed no thermal decomposition until 100°C. This temperature is significantly higher than observed for 1, 2 and 3, which lose solvent molecules immediately on heating. The removal of THF and the dicyanobenzene molecules were not well resolved in temperature but the sum of the losses (observed 31.35%, calculated 31.18%) indicated only one THF molecule per formula unit. The weight loss corresponding to the four acetate groups was similar to the value observed for the other compounds. The thermal decomposition of **5** showed three-steps in the weight loss below  $178^{\circ}$ C, the total weight loss corresponded to the removal of one benzene and one dicyanobenzene molecule (observed 31.81%, calculated 31.82%). The remaining weight losses was similar to other compounds.

# 4. CONCLUSIONS

Five new one dimensional coordination polymers formed by dirhodium(II)tetraacetate bridged by 1,4dicyanobenzene have been synthesized and characterized. Each compound has a different solvent molecule filling the cavities between the polymeric chains. The type of solvent apparently plays an important role in the crystallization process and determines the separation and orientation of the polymeric chains. We are currently investigating other solvents that can be introduced between the chains and further work will focus on studying the extensions to 2D and 3D polymers by using multifunctional organic bridging ligands.

*Acknowledgements*—We thank the National Science Foundation (DMR-9214804) and the Robert A. Welch Foundation for support of this work and Dr James Korp for help with crystallography.

4088



Fig. 6. Thermogravimetric analysis data for  $1 \ \mbox{(a)}, \, 4 \ \mbox{(b)}$  and  $5 \ \mbox{(c)}.$ 

## REFERENCES

- Cotton, F. A. and Felthouse, T. R., *Inorg. Chem.*, 1980, **19**, 328–331.
- Handa, M., Yamada, K., Nakao, T. and Kasuga, K., Chem. Lett., 1993, 1969–1972.
- Cotton, F. A. and Kim, Y., Ren, T., *Inorg. Chem.*, 1992, 31, 2723–2726.
- 4. Morosin, B., Hughes, R. C. and Soos, Z. G., Acta Cryst. B, 1975, 31, 762.
- Cotton, F. A., Deboer, B. G., Pipal, M. D. and Ucko, D. A., *Acta Cryst. B*, 1971, **27**, 1664.
- Christoph, G. G. and Koh, Y.-B., J. Am. Chem. Soc., 1979, 101, 1422.
- 7. Koh, Y. B. and Christoph, G. G., *Inorg. Chem.*, 1979, **18**, 1122.
- Cotton, F. A. and Felthouse, T. R., *Inorg. Chem.*, 1980, **19**, 323–328.
- Cotton, F. A. and Felthouse, T. R., Acta. Cryst. C, 1984, 40, 42–45.
- Koh, Y. B. and Christoph, G. G., *Inorg. Chem.*, 1978, 17, 2590–2596.
- Crawford, C. A., Day, E. F., Streib, W. E., Huffman, J. C. and Christou, G., *Polyhedron*, 1994, **13**, 2943–2993.
- 12. Cotton, F. A. and Kim, Y., Lu, J., *Inorg. Chim. Acta*, 1994, **221**, 1–4.
- Aoki, K. and Yamazaki, H., J. Am. Chem. Soc., 1984, 106, 3691–3692.
- 14. Lu, J., Harrison, W. T. A. and Jacobson, A. J., *Chem. Commun.*, 1996, 399–400.
- Cotton, F. A. and Felthouse, T. R., *Inorg. Chem.*, 1981, **20**, 600–608.
- Cogne, A., Grand, A. and Rey, P., Subra, R., J. Am. Chem. Soc., 1989, 111, 3230–3238.
- Cotton, F. A. and Kim, Y., J. Am. Chem. Soc., 1993, 115, 8511–8512.
- Cerius2, Version 2.0. BIOSYM/Molecular Simulations, 1995.
- Sheldrick, G. M., SHELXS-96 beta and SHELXL-96 beta, Program Package for Structure Solution and Refinement. Universität Göttingen, Göttingen, 1996.