Inorg. Chem. **2004**, *43*, 5558–5563

Inorganic Chemistry

Article

Powder Diffraction Study of a Coordination Polymer Comprised of Rigid Building Blocks: $[Rh_2(O_2CCH_3)_4 \cdot \mu^2\text{-}Se_2C_5H_8\text{-}Se,Se']_\infty$

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Received April 17, 2004

The crystal structure of a new hybrid product comprised of two rigid building blocks, namely dirhodium(II) tetraacetate, $[Rh_2(O_2CCH_3)_4]$ (**1**), and 2,6-diselenaspiro[3.3]heptane, $Se_2C_5H_8$ (**2**), has been solved ab initio using laboratory source X-ray powder diffraction (XRPD) data. The rigid body refinement approach has been applied to assist in finding an adequate model and to reduce the number of the refined parameters. Complex $[Rh_2(O_2CCH_3)_4 \cdot \mu^2\text{-}Se_2C_5H_8\text{-}Se,Se']$ (**3**) conforms to the triclinic unit cell with lattice parameters of $a = 8.1357(4)$, $b = 8.7736(4)$, and $c = 15.2183(8)$ Å, $\alpha = 77.417(3)$, $\beta = 88.837(3)$, and $\gamma = 69.276(4)°$, $V = 989.66(8)$ Å^3, and $Z = 2$. The centrosymmetric $P\bar{1}$ space group was selected for calculations. The final values of the reduced wR_p, R_p, and χ^2 were calculated at 0.0579, 0.0433, and 5.95, respectively. The structure of **3** is a one-dimensional zigzag polymer built on axial Rh···Se interactions at 2.632(6) Å. The 2,6-diselenaspiro[3.3]heptane ligand acts as a bidentate linker bridging dirhodium units via both selenium atoms. The geometrical parameters of individual groups for rigid body refinement have been obtained from X-ray powder data for dirhodium(II) tetraacetate (**1**) and from single-crystal X-ray diffraction for diselenium molecule **2**. The crystal structures of **1** and **2** are reported here for the first time. For **1** indexing based on XRPD data has resulted in the triclinic unit cell $P\bar{1}$ with lattice parameters of $a = 8.3392(7)$, $b = 5.2216(5)$, and $c = 7.5264(6)$ Å, $\alpha = 95.547(10)$, $\beta = 78.101(6)$, and $\gamma = 104.714(13)°$, $V = 309.51(5)$ Å^3, and $Z = 1$. The final values were $wR_p = 0.0452$, $R_p = 0.0340$, and $\chi^2 = 1.99$. The 1D polymeric motif built on axial Rh···O interactions of the centrosymmetric dirhodium units has been confirmed for the solid-state structure of **1**. Compound 2,6-diselenaspiro[3.3]heptane (**2**) conforms to the monoclinic space group $P2_1/c$ with the unit cell parameters of $a = 5.9123(4)$, $b = 19.6400(13)$, and $c = 5.8877(4)$ Å, $\beta = 108.5500(10)°$, $V = 648.15(8)$ Å^3, and $Z = 4$.

Introduction

Rational design of supramolecular assemblies has emerged as an innovative area of modern chemistry[1] that is driven forward by a variety of applications, such as host−guest chemistry, micro/mesoporous materials, and molecular optic/electronic devices.[2] Such complex systems tend to produce ill-defined polycrystalline solids that are often unsuitable for single-crystal diffraction studies. Future generations of supramolecules with nanoscale cavities, enclathrated molecules, or various levels of interpenetration[3] may exhibit even less efficient packing, and this would make obtaining single crystals more challenging and time-consuming. Therefore, in materials chemistry there is a current need for structural characterization of powdered products that resist crystal growth techniques. In this case, X-ray powder diffraction (XRPD) can be a unique and effective tool for structural

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10.1021/ic049497u CCC: $27.50

identification of supramolecular products. Whereas structure solution using powder diffraction data is widely used by solid-state chemists, XRPD is rarely utilized for structural characterization of coordination polymers and supramolecular systems obtained from solution.[4−6] Substantial advances[7] recently made in XRPD instrumentation techniques and computational methods should further promote in-house use of powder diffraction for solving crystal structures of such solid products. Furthermore, supramolecular materials are often comprised of preorganized building blocks of known geometries that contain heavy bonding atoms. They may also exhibit very symmetrical structures and thus have only a few independent atoms to refine. Therefore, despite their complexity, many supramolecular materials are suitable systems for powder diffraction analysis. The knowledge of geometry of molecular building blocks that constitute a hybrid product is a clear advantage as it allows the use of a rigid body refinement based on XRPD data.[8] The latter approach reduces the number of the refined parameters significantly as it only accounts for position and orientation of rigid blocks in the unit cell. In this context, the title hybrid product, $[Rh_2(O_2CCH_3)_4\cdot Se_2C_5H_8]_\infty$, comprised of two well-defined blocks has been selected as a good model for rigid body refinement using X-ray powder diffraction data.

In addition, dirhodium(II) tetraacetate, $[Rh_2(O_2CCH_3)_4]$, one of the building blocks in the title coordination complex, represents a good example where XRPD is the only choice for structural characterization. The solid-state structure of $[Rh_2(O_2CCH_3)_4]$ free of exogenous axial ligands has remained unknown, since the complex is nonvolatile, insoluble in noncoordinating solvents, and cannot be melted without decomposition. Herein, the structure has been solved for the first time using a direct-space XRPD analysis. To get structural parameters of the second building block, namely diselenium molecule $Se_2C_5H_8$, a single-crystal X-ray diffraction study was undertaken. The crystal structures of two building blocks, $[Rh_2(O_2CCH_3)_4]$ and $Se_2C_5H_8$, and of the hybrid coordination product are presented here. A preliminary account of this work has recently been reported.[9]

Experimental Section

General Procedures. All manipulations were carried out in a dry, oxygen-free, dinitrogen atmosphere by employing standard Schlenk techniques. The $[Rh_2(O_2CCH_3)_4]$ was purchased from Strem, recrystallized from acetone, and dried under vacuum at 65 °C for 3 days. Elemental analysis was performed by Canadian Microanalytical Service, Delta, BC, Canada. IR spectra were recorded on a Nicolet Magna 550 FTIR spectrometer using KBr pellets. NMR spectra were determined on a Varian Gemini NMR spectrometer at 300 MHz for proton and 75.1 MHz for carbon. Mass spectra were obtained on an Hewlett-Packard HP 5989/5970 GC-MS instrument at 70 eV.

Syntheses. $Se_2C_5H_8$ (2). A solution of SuperHydride ($Li(C_2H_5)_3BH$) in THF (1.0 M, 20 mL, 20.0 mmol) was added all at once to selenium powder (0.80 g, 10.0 mmol) with vigorous stirring. Gas evolution occurred and ceased within 2 min. The solution gradually turned to a heterogeneous milky white suspension. Additional THF (10 mL) was added, the suspension was stirred for 20 min, and then a solution of 1,3-dibromo-2,2-bis(bromomethyl)propane (1.94 g, 5.0 mmol) in THF (10 mL) was added. The reaction mixture was refluxed for 4 h and stirred at room temperature for an additional 12 h. The solvent was removed under vacuum, and the residue was chromatographed on neutral alumina (1:2 chloroform−hexane) to give **2** as a colorless solid. Yield: 70%. Single crystals of **2** were obtained by sublimation in a vacuum at 55 °C for 2 days. IR (KBr, cm^{-1}): 2985 m, 2925 s, 2819 w, 1429 sh, 1418 m, 1243 w, 1220 w, 1207 w, 1134 s, 1125 s, 1055 w, 1036 w, 966 w, 939 m, 874 m, 797 w, 780 w, 719 m. ^1H NMR (300 MHz, $CDCl_3$, 22 °C): δ 3.14 (s, 8H). ^{13}C NMR (75 MHz, $CDCl_3$, 22 °C): δ 28.7, 54.4. EI-MS: m/z 228 (M^+, ^{80}Se). Mp: 68(1) °C.

$[Rh_2(O_2CCH_3)_4\cdot Se_2C_5H_8]$ (3). The dirhodium complex $[Rh_2(O_2CCH_3)_4]$ (0.040 g, 0.09 mmol) was dissolved in acetone (15 mL). The hexanes solution (10 mL) containing $Se_2C_5H_8$ (0.015 g, 0.07 mmol) was added to the above acetone solution. The solutions were allowed to mix resulting in the precipitation of a brown crystalline powder, which was separated by filtration and washed vigorously

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with several portions of acetone (3 × 10 mL) and hexanes (2 × 10 mL). The product was then dried under vacuum for 3 days at 45 °C. Yield: 90%. IR (KBr, cm^{-1}): 3056 w, 3006 w, 2956 w, 2939 w, 1591 s (ν(COO)$_{asym}$), 1434 s (ν(COO)$_{sym}$), 1413 m, 1351 m, 1268 w, 1227 w, 1144 m, 1070 w, 1051 w, 956 w, 735 m, 700 m, 631 w. Anal. Calcd: C, 23.37; H, 3.02. Found: C, 23.28; H, 3.17.

X-ray Crystallographic Procedures. The XRPD data sets for **1** and **3** were collected using an automated STADI/P Stoe powder diffractometer (Cu Kα_1 radiation, $\lambda = 1.5406$ Å, Ge monochromator, linear PSD, step 0.01° 2θ, 20 °C). Peak positions were determined by profile fitting and used for indexing. The powder patterns for **1** and **3** were indexed using the ITO method by a routine incorporated in the STOE Win^{X}Pow software package.

For **1** indexing yielded a triclinic unit cell with lattice parameters of $a = 8.322(2)$, $b = 5.2151(8)$, and $c = 7.515(1)$ Å and $\alpha = 96.39(2)$, $\beta = 78.06(2)$, and $\gamma = 104.60(2)$°. The $P\bar{1}$ space group was selected for further calculations. The coordinates of the rhodium atom were found from the Patterson map to indicate that the dirhodium group resides on an inversion center (0, 0, 0). Further structure refinement was carried out with the GSAS program.[10] At the first stage, profile parameters and orientation of the [$Rh_2(O_2CC)_4$] rigid body (hydrogen atoms excluded) were refined. In the next step, the [$Rh_2(O_2CC)_4$] rigid body was rejected and independent atoms were restrained by interatomic distance and angle restraints. The final values are $wR_P = 0.0452$, $R_P = 0.0340$, and $\chi^2 = 1.99$. Thermal parameters for all atoms were fixed at 0.025 Å^2 (U_{iso}).

For **3** indexing yielded a triclinic unit cell with lattice parameters of $a = 8.124(2)$, $b = 8.768(2)$, and $c = 15.201(3)$ Å, $\alpha = 77.36(2)$, $\beta = 88.87(2)$, and $\gamma = 69.30(2)$°, and $Z = 2$. The $P\bar{1}$ space group was chosen for further calculations. The structure was then solved in three steps. In the first step, the starting model for Rietveld refinement was found using the FOX program.[11] Two types of scatterers were created, namely the [$Rh_2(O_2CC)_4$] group and the Se_2C_5 ligand (hydrogen atoms were not used for the rigid body construction). Interatomic distances and angles for individual rigid bodies **1** and **2** were taken from the corresponding X-ray powder (**1**) and single-crystal (**2**) diffraction data. Insertion of rigid bodies instead of individual atoms resulted in the reduction of the refined atomic parameters from 54 and 21 (for **1** and **2**, respectively) to 6 for each (3 positional and 3 rotational parameters). A search of the structure solution in direct space by the FOX program resulted in a reasonable structure model that was used for further Rietveld refinement. This procedure allowed us to find approximate positions of both the dirhodium group and the diselenium molecule in the unit cell. Further refinement was carried out in the GSAS program.[10] In the second step, only orientation parameters for the [$Rh_2(O_2CC)_4$] rigid body were refined since a center of this group is situated on the inversion center as determined in the first step. The Se_2C_5 group was then inserted in the unit cell. In contrast to the [$Rh_2(O_2CC)_4$] group, only soft constraints for interatomic separations were used for the ligand. After profile parameters refinement the values of the reduced wR_p, R_p and χ^2 have been calculated at 0.072, 0.055, and 8.9, respectively. This confirmed that the structural model is correct.

Whereas at the beginning of refinement a background was approximated graphically and was not refined, at the final stage it was refined as the Chebyshev polynom. This allowed us to get a better agreement between the experimental and calculated X-ray patterns. In all calculations thermal parameters for all atoms remained fixed at 0.025 Å^2 (U_{iso}). In the last step, the [$Rh_2(O_2CC)_4$] rigid body was rejected and independent atoms were restrained with deviations from starting positions for the restrained distances and angles being ±0.02 Å and ±0.5°, respectively. The final values of the reduced wR_p, R_p and χ^2 were calculated at 0.0579, 0.0433, and 5.95, respectively. The experimental, calculated, and difference X-ray patterns for **1** and **3** are shown in Figures 1 and 5, respectively. See Supporting Information for additional information.

Table 1. Crystallographic Data and Structural Refinement Parameters for [$Rh_2(O_2CCH_3)_4$] (**1**), $Se_2C_5H_8$ (**2**), and [$Rh_2(O_2CCH_3)_4 \cdot \mu_2$-$Se_2C_5H_8$-*Se*,*Se*′]$^1_\infty$ (**3**)

	1	**2**	**3**
formula	$Rh_2O_8C_8H_{12}$	$Se_2C_5H_8$	$Rh_2Se_2O_8C_{13}H_{20}$
fw	442.00	226.03	668.03
space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a (Å)	8.3392(7)	5.9123(4)	8.1357(4)
b (Å)	5.2216(5)	19.6400(13)	8.7736(4)
c (Å)	7.5264(6)	5.8877(4)	15.2183(8)
α (deg)	96.547(10)		77.417(3)
β (deg)	78.101(6)	108.5500(10)	88.837(3)
γ (deg)	104.714(13)		69.276(4)
V (Å^3)	309.51(5)	648.15(8)	989.66(8)
Z	1	4	2
radiatn	Cu Kα_1	Mo Kα	Cu Kα_1
λ (Å)	1.5406	0.710 73	1.5406
D_{calc} (g cm^{-3})	2.371	2.316	2.242
μ (mm^{-1})	21.892	11.283	18.029
T (K)	293(2)	173(2)	293(2)
2θ range (deg)	7−65	4−56	4−70
data collcn mode	transmn		transmn
R indices	$R_p{}^a = 0.0340$ $wR_p{}^b = 0.0452$ $\chi^{2\,c} = 1.99$	$R1^d = 0.0292^e$ $wR2^f = 0.0829^e$ $GOF^g = 1.075$	$R_p{}^a = 0.0433$ $wR_p{}^b = 0.0579$ $\chi^{2\,c} = 5.95$

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

A single-crystal data set was collected for **2** at −100(2) °C (Bruker KRYO-FLEX) on a Bruker APEX CCD X-ray diffractometer equipped with graphite-monochromated MoKα radiation ($\lambda = 0.710\,73$ Å). The frames were integrated with the Bruker SAINT software package, and the data were corrected for absorption using the program SADABS. The structure was solved and refined using the Bruker SHELXTL (version 6.1) software package in the space group $P2_1/c$ with $Z = 4$ for the formula unit $Se_2C_5H_8$. All hydrogen atoms were found in difference Fourier maps and were refined independently. The final anisotropic full-matrix least-squares procedures on F^2 for 97 parameters converged at $R1 = 0.0292$ and $wR2 = 0.0829$ for 1414 reflections with $I > 2\sigma(I)$ ($R1 = 0.0305$ and $wR2 = 0.0839$ for total 1506 reflections) and a goodness-of-fit value of 1.075.

Crystallographic data and X-ray experimental conditions for **1**−**3** are listed in Table 1. Selected distances and angles for **1**−**3** are given in Table 2.

Results and Discussion

In general, isolation of dimetal carboxylate complexes without exogenous ligands from solution presents a challenge to synthetic chemists.[12] In the case of volatile complexes sublimation−deposition from the gas phase provides a solvent-free environment for crystallization of “unligated” metal carboxylates. For example, volatile dirhodium(II) trifluoroacetate and pivalate [$Rh_2(O_2CR)_4$] (R = CF_3[13a] and CMe_3[13b]) have been isolated from the gas phase in the form

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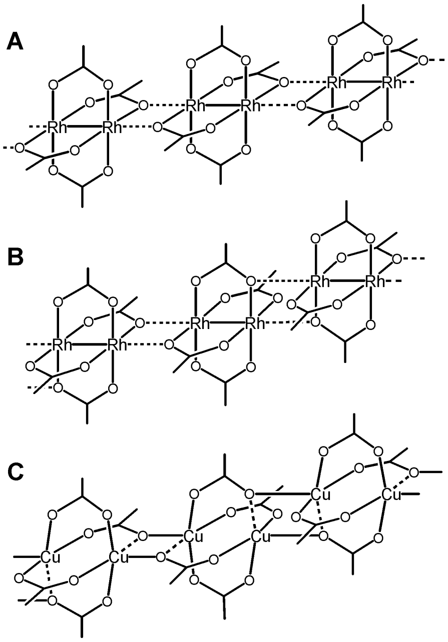
Table 2. Selected Distances (Å) and Angles (deg) in [$Rh_2(O_2CCH_3)_4$]·(**1**)$Se_2C_5H_8$ (**2**), and [$Rh_2(O_2CCH_3)_4$·($Se_2C_5H_8$)]$^1_\infty$ (**3**)

	1	**2**	**3**
Rh−Rh	2.415(3)[b]		2.398(2)
Rh−O_{acet}[a]	2.041(2)		2.045(3)
Rh···O_{ax}	2.506(2)		
Rh−Se[a]			2.625(6)
Rh−Rh−O_{acet}[a]	84.3(6)		85.7(5)
Rh−Rh−Se[a]			177.6(5)
Se−C[a]		1.978(3)	2.000(5)
C−C[a]		1.536(4)	1.55(2)
C−Se−C[a]		72.0(1)	72.9(2)
Se−C−C[a]		91.4(1)	91.2(3)
C−C−C		98.1(2)−119.1(2)	100.0(3)−126.8(2)

[a] Averaged. [b] Estimated standard deviations calculated by Rietveld refinement may be significantly smaller than those obtained by integrated intensity refinement of the same data set. For details see: Scott, H. G. *J. Appl. Crystallogr.* **1983**, *16*, 159.

Chart 1



of single crystals. The determination of the solid-state structure of [$Rh_2(O_2CCF_3)_4$] revealed a 1D polymeric motif involving intermolecular Rh···O interactions of the centrosymmetric dirhodium units (Chart 1A). The intermolecular bonding involves trans-positioned carboxylate groups on each dimer so that the system of metal and bridging oxygen atoms constitutes a flat ribbon. A different motif, a so-called "Venetian blind" type, was found in the solid-state structure of [$Rh_2(O_2CCMe_3)_4$], in which axial interactions involve cis rather than trans carboxylate bridges (Chart 1B). While A and B types are known for some other metal(II) carboxylates, a unique structure has been found in copper(II) trifluoroacetate, [$Cu_2(O_2CCF_3)_4$] (Chart 1C).[14] The latter type is somewhat similar to type B but is characterized by the intermolecular Cu···O contacts being shorter than some of intramolecular Cu−O distances.

In contrast to trifluoroacetate and pivalate, the structural characterization of rhodium(II) acetate without any exogenous ligands is lacking. Dirhodium(II) tetraacetate itself can only be obtained in the form of powder, since it is not volatile, decomposes before melting, and is insoluble in noncoordinating solvents. While single-crystal X-ray diffraction has been used extensively to characterize a great number of the dirhodium tetraacetate adducts (a total of 83 based on the Cambridge Crystallographic Database[15] search), powder diffraction seemed the only possible choice to obtain direct structural information for **1**. The structural characterization of rhodium acetate is important, since distinctly different properties of [$Rh_2(O_2CCH_3)_4$] may have been associated with the structural differences between **1** and other known dirhodium carboxylates.

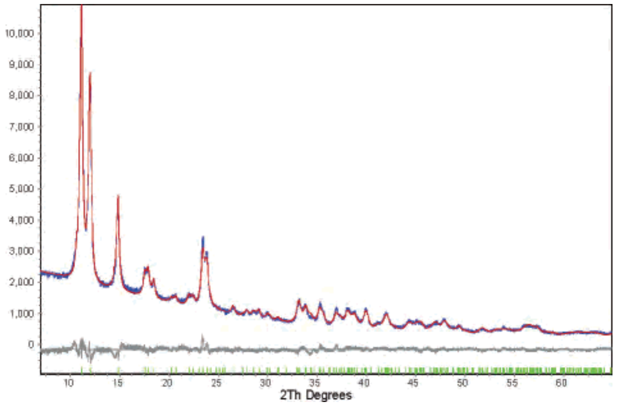


Figure 1. Rietveld plot of the powder diffraction pattern for [$Rh_2(O_2CCH_3)_4$] (**1**) at 293 K. The observed pattern (blue), the best calculated fit (red), and the difference profile (gray) are given. The green lines at the bottom show allowed peak positions.

In this work, the XRPD data were collected for the polycrystalline sample of **1** (Figure 1) and an analysis of the X-ray pattern clearly indicated that it is isostructural to dimolybdenum(II) tetraacetate.[16] It is noteworthy that the quality of X-ray powder spectra depends on the crystallinity of a sample. Poor crystallinity results in the broadening of the peaks and contributes to the difficulties in peak separation due to additional overlaps. This may affect correct indexing of a diffraction pattern and makes the extraction of valuable information from a powder spectrum very problematic. We found that annealing of the commercially available rhodium(II) acetate under vacuum for prolonged time (2 weeks) at temperatures well below decomposition (110 °C) significantly improves its crystallinity (Figure 2).

After the successful indexing of powder data for **1**, the structure of [$Rh_2(O_2CCH_3)_4$] was refined using the GSAS program.[10] The Rietveld plot for **1** showed a good correspondence between the model and the observed data (Figure 1). The final values $wR_p = 0.0452$, $R_p = 0.0340$, and $\chi^2 = 1.99$ indicate reliable refinement (Table 1). The 1D polymeric structural motif built on axial Rh···O interactions of the centrosymmetric dimers (Chart 1A), known for some dimetal tetracarboxylates,[13a] has now been confirmed for **1** (Figure 3).

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(13) (a) Cotton, F. A.; Dikarev, E. V.; Feng, X. *Inorg. Chim. Acta* **1995**, *237*, 19−26. (b) Dikarev, E. V. Unpublished results.

(14) (a) Karpova, E. V.; Boltalin, A. I.; Korenev, Yu. M.; Troyanov, S. I. *Russ. J. Coord. Chem.* **2000**, *26*, 361−366. (b) Cotton, F. A.; Dikarev, E. V.; Petrukhina, M. A. *Inorg. Chem.* **2000**, *39*, 6072−6079.

(15) See http://www.ccdc.cam.ac.uk/ for details.

(16) (a) Cotton, F. A.; Mester, Z. C.; Webb, T. R. *Acta Crystallogr.* **1974**, *B30*, 2768−2770. (b) ICDD PDF-2 No. 46−913.

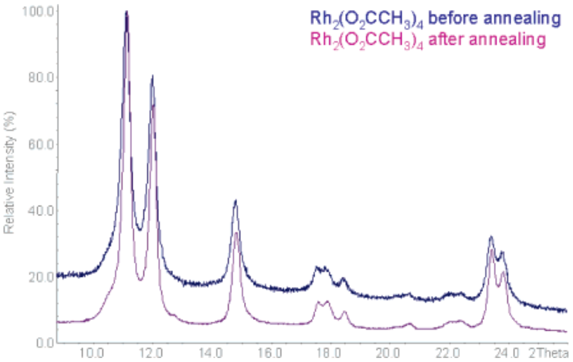


Figure 2. Effect of annealing on the crystallinity of the rhodium acetate sample.

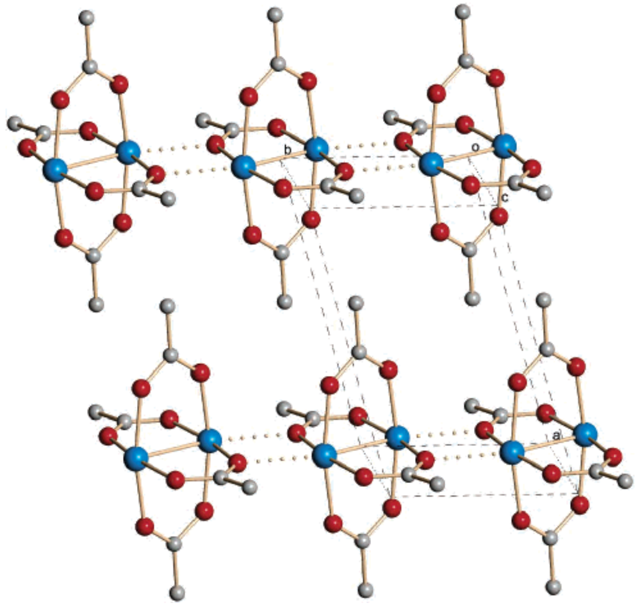


Figure 3. Ball-and-stick representation of the solid-state packing in the structure of **1**. Atomic color scheme: Rh = blue; O = red; C = gray.

The major geometric characteristics of the molecular structure of $[Rh_2(O_2CCH_3)_4]$ have been obtained: the Rh−Rh distance was found at 2.415(3), while the Rh···O contact is 2.51 Å. The major difference between the isostructural molybdenum[16] and rhodium acetates is that for the former metal−metal distance is considerably shorter (Mo−Mo, 2.0934(8) Å), while intermolecular Mo···O contacts of 2.645(4) Å are longer. On the other hand, the Rh−Rh and Rh···O distances in **1** are longer than the corresponding distances in dirhodium(II) trifluoroacetate (2.3813(8) and 2.337(4) Å, respectively).

As a part of our coordination chemistry study of selenium-containing molecules of natural or synthetic origin,[17] we have recently turned to dispiro ligands of the composition $X_2C_5H_8$ (X = Se or S/Se). These ligands are of interest for self-assembling reactions as molecular rigid rods since sulfur-containing molecules exhibited[18] substantial through-bond interactions in mixed-valent metal complexes. So far only S-donor molecules have been examined in coordination reactions,[18,19] while ligating properties of Se or mixed S/Se analogues have not been studied. An early reference[20] to the preparation of 2,6-diselenaspiro[3.3]heptane (**2**) should be mentioned, although a different synthetic approach has been used in this work to prepare this compound, which has also been more fully characterized than before. As the ligand structure remained unknown, prior to coordination reactions, we obtained crystals of $Se_2C_5H_8$ by deposition from the gas phase at ca. 55 °C and determined its molecular structure using the single-crystal X-ray diffraction data. The diselenium dispiro molecule built around the tetrahedral carbon atom is nonplanar with the angles around the central C(5) atom ranging from 98.1(2) to 119.1(2)° (Figure 4). The Se−C distances are averaged to 1.978(3), while the average C−C distances are 1.536(4) Å. The C−Se−C angles at the donor selenium atoms of 72.03(11)° are acute.

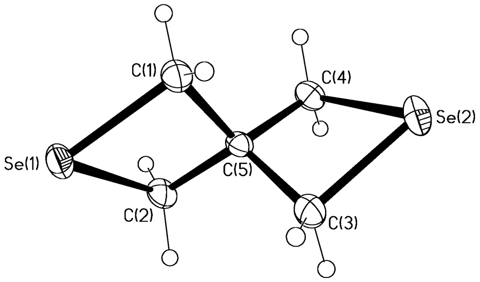
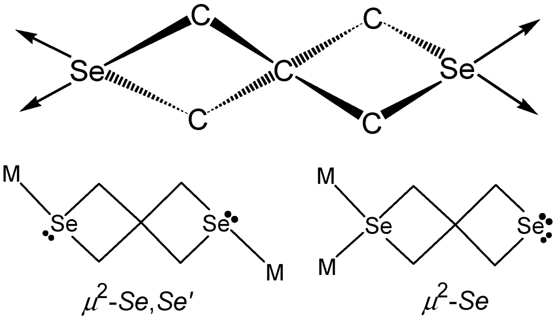


Figure 4. Perspective drawing of diselenium dispiro molecule (**2**). Atoms are represented by thermal ellipsoids at the 40% probability level. Hydrogen atoms are shown as spheres of arbitrary radius.

Chart 2



From the coordination point of view, the bidentate ligand **2** is rigid but not directional. Each Se-donor atom has two lone electron pairs and therefore may exhibit two different bridging modes (Chart 2). Both should result in the formation of polymeric structures with bidentate Lewis acidic metal complexes. The μ^2-Se coordination of dimethyl selenide by two rhodium(II) centers has recently been observed in complex $[Rh_2(O_2CCF_3)_4{\cdot}SeMe_2]$.[17a]

For a system containing bidentate ligand **2** and a two-ended Lewis acid **1**, several attempts to grow crystals of the hybrid product having sufficient size and quality failed. Only

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[17] (a) Dikarev, E. V.; Petrukhina, M. A.; Li, X.; Block, E. *Inorg. Chem.* **2003**, *42*, 1966−1972. (b) Dikarev, E. V.; Becker, R. Y.; Block, E.; Shan, Z.; Haltiwanger, R. C.; Petrukhina, M. A. *Inorg. Chem.* **2003**, *42*, 7098−7105.

[18] Stein, C. A.; Taube, H. *J. Am. Chem. Soc.* **1981**, *103*, 693−695. (b) Stein, C. A.; Lewis, N. A.; Seitz, G. *J. Am. Chem. Soc.* **1982**, *104*, 2596−2599. (c) Baker, A. D.; Scharfman, R.; Stein, C. A. *Tetrahedron Lett.* **1983**, *24*, 2957−2960. (d) Rendell, A. P. L.; Bacskay, G. B.; Hush, N. S. *J. Am. Chem. Soc.* **1988**, *110*, 8343−8354. (e) Lewis, N. A.; Taveras, D. V *Adv. Chem. Series* **1990**, *No. 226*, 197−210.

[19] Abel, E. W.; Orrell, K. G.; Poole, M. C.; Sik, V. *Polyhedron* **1999**, *18*, 1345−1353.

[20] Backer, H. J.; Winter, H. J. *Rec. Trav. Chim.* **1937**, *56*, 492−509.

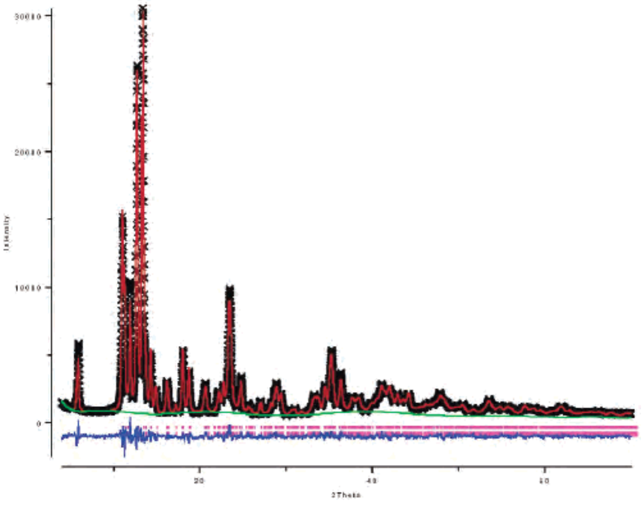

Figure 5. Rietveld plot of the powder diffraction pattern for [$Rh_2(O_2CCH_3)_4\cdot Se_2C_5H_8$] (**3**) at 293 K. The observed pattern (black crosses), the best calculated fit (red), the refined background curve (green), and the difference profile (blue) are given. The violet lines at the bottom show allowed peak positions.

microcrystalline powders precipitated out of the solution mixtures. Spectroscopic methods indicated the presence of both building groups in the product. A 1:1 composition of the dirhodium complex to the diselenium ligand and the absence of interstitial solvent molecules have been confirmed in **3** by elemental analysis. Since geometries of both building blocks, [$Rh_2(O_2CCH_3)_4$] and $Se_2C_5H_8$, used for the preparation of the hybrid product are now known, application of the rigid body refinement approach using X-ray powder data is now feasible. Importantly, chemical analysis confirmed the purity of the hybrid microcrystalline sample. The issue of purity is crucial when one attempts to use powder diffraction data for indexing followed by a direct structural solution.

A high-quality set of XRPD experimental data was collected for **3**, and the indexing was successfully accomplished in the triclinic system (Table 1). The unit cell parameters seemed reasonable from the calculated volume/non-hydrogen atom for a 1:1 composition in **3** (19.8 Å^3) and consistent with one crystallographically independent Rh_2 unit and one diselenium ligand. Moreover, the crystallographic volumes/molecule of **1** and **2** add up nearly perfectly to give the volume/molecule of **3**. A detailed account of procedures for both structure solution and refinement is given in the Experimental Section. The final fit to the experimental diffraction pattern for **3** is shown in Figure 5. The final values of the reduced wR_p, R_p, and χ^2 calculated at 0.0579, 0.0433, and 5.95, respectively, indicate that accurate structural information has been obtained from the powder diffraction experiment for **3**.

The solid-state structure of **3** is an infinite 1D polymer comprised of the alternating units **1** and **2** (Figure 6). The structure is built on intermolecular Rh$\cdots$Se interactions of the rhodium atoms from two crystallographically independent centrosymmetric [$Rh_2(O_2CCH_3)_4$] units to two different selenium ends of $Se_2C_5H_8$. The average axial Rh$\cdots$Se distance of 2.63 Å is similar to that in [$Rh_2(O_2CCF_3)_4\cdot(SeMe_2)$][17a] averaged to 2.59 Å. Two Rh−Rh−Se bond angles of 176.7 and 178.5° in **3** are close to linear. The dihedral angle between the two neighboring Rh−Rh units is 89.6°, and the −Rh−Rh−Se−Se− moiety defines a semispiral chain structure. A comparison of geometrical parameters of 2,6-diselenaspiro[3.3]heptane in free (**2**) and complexed (**3**) forms (Table 2) confirms that coordination does not cause any significant distortions in the structure of ligand. The above data clearly show that not only have the details of the solid-state structure been determined but also that the geometrical parameters found for **3** are of sufficient resolution and are comparable with those routinely extracted from single-crystal diffraction studies.

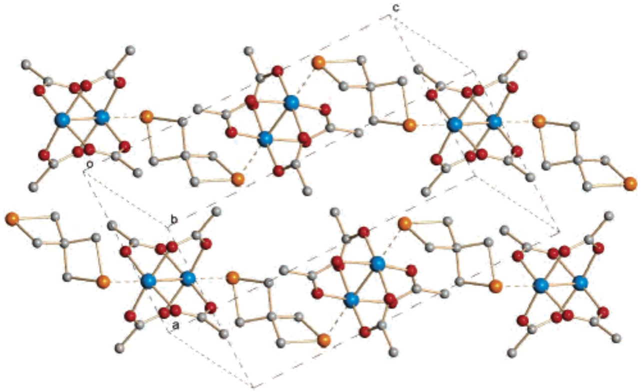

Figure 6. Ball-and-stick representation of the solid-state packing in the structure of **3**. Atomic color scheme: Rh = blue; O = red; C = gray; Se = orange.

In conclusion, this study illustrates the potential of the XRPD technique for direct structural characterization of insoluble coordination polymers that resist single-crystal growth techniques. When the hybrid structures contain well-defined building units as in **3**, the use of appropriate rigid bodies results in a significant reduction in the number of refined parameters and thus facilitates identification of an adequate structural model. Furthermore, accurate geometrical characteristics of coordination polymers can be obtained in the absence of single crystals when good quality X-ray powder data are available. The XRPD technique should become an invaluable tool for structural characterization of complex hybrid systems that cannot be isolated in the form of single crystals, which should greatly assist in future developments of supramolecular chemistry.

Acknowledgment. This work has been funded by the National Academy of Sciences under the COBASE (Collaboration in Basic Science and Engineering) Program supported by Contract No. INT-0002341 from the National Science Foundation (M.P.). We also acknowledge the support of the donors of the American Chemical Society Petroleum Research Fund Grants 39039-G3 (M.P.) and 38450-AC1 (E.B.) and the National Science Foundation Grants NSF CHE-01300985 (E.D.) and NSF CHE-9906566 (E.B.). R.S. is grateful to the ICDD (Grant-in-Aid 91-05APS) and to Dr. R. B. Von Dreele for fruitful discussions during structure refinement.

Supporting Information Available: Three X-ray crystallographic files, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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