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[20] Crystallographic data for NaV$_3$(OH)$_6$(SO$_4$)$_2$: Rhombohedral, space group $R\bar{3}m$, $a = b = 7.2857(6)$, $c = 16.851(2)$ Å, $V = 774.6(1)$ Å^3, $Z = 3$, $\rho_{calcd} = 3.023$ g cm^{-3}, $F(000) = 672$, λ(Mo$_{K\alpha}$) = 0.7107 Å, crystal dimensions $0.04 \times 0.04 \times 0.01$ mm. A total of 1050 reflections were collected at $-90\,°C$ using a Siemens diffractometer equipped with a CCD detector in the θ range of 3.45° to 23.25°, of which 161 were unique ($R_{int} = 0.0351$). The structure was solved by the Patterson heavy atom method in conjunction with standard difference Fourier techniques and all heavy atoms were refined anisotropically (25 parameters). Hydrogen atoms were not included in the refinement. The least squares refinement based on F^2 converged normally giving residuals of $R = 0.0306$, $wR2 = 0.0792$. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-411658.

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Neutral Cyclooctasulfur as a Polydentate Ligand: Supramolecular Structures of [Rh$_2$(O$_2$CCF$_3$)$_4$]$_n$(S$_8$)$_m$ (*n:m* = 1:1, 3:2)**

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It is not unreasonable to suppose that the S$_8$ molecule, with two lone pairs of electrons on each atom, would be able to function as a Lewis base—even as a multidentate Lewis base. And yet, no structurally characterized example of coordination of the cyclooctasulfur ligand to a transition metal complex is reported. There are several cases in which S$_8$ rings cocrystallize with other molecules, not covalently bound but merely packed into the crystal. These solid inclusion compounds with transition metal complexes are: [Cu(C$_{12}$H$_8$N$_2$)$_2$I]I · S$_8$,[1a] [WCl$_4$S] · S$_8$[1b] and [WCl$_4$S(thf)] · S$_8$,[1c] [Co$_6$(μ-S)$_8$(CO)$_6$] · 3 S$_8$,[1d] [Cu$_4$(S$_5$)$_2$(C$_5$H$_5$N)$_4$] · S$_8$,[1e] [{Pt$_2$X(5-mpyt)$_4$}$_2$(μ-S$_4$)] · 0.5 S$_8$ (X = Cl, Br; 5-mpyt = 5-methylpyridine-2-thiolate),[1f] [M(TMTAA)$_2$] · S$_8$ (M = Cu, Ni; TMTAA = 5,7,12,14-tetramethyldibenzo[*b,i*]-1,4,8,11-tetraaza[14]annulenate),[1g] [Na-[15]crown-5]$_2$[(TaSCl$_4$)$_2$dioxane] · S$_8$.[1h]

What may well be a compound with a covalently bound S$_8$ molecule, [Re$_2$X$_2$(CO)$_6$(S$_8$)] (X = Br, I), was reported by W. Baratta and F. Calderazzo,[2] but a crystal structure was not obtained. A few years later they were able to isolate the [Re$_2$I$_2$(CO)$_6$(Se$_7$)] complex[3] and to show by X-ray crystallography that it contains an η^2-μ_2-Se$_7$ ring. They suggested that [Re$_2$X$_2$(CO)$_6$(S$_8$)] may have a similar dinuclear structure with bridging halides and an η^2-coordinated cyclooctasulfur unit. In addition, the S$_8$ molecule is known[4] to coordinate to the d^{10} silver(I) ion in [Ag(S$_8$)$_2$](AsF$_6$). As far as we know there is no other literature dealing with compounds of transition metals that contain neutral S$_8$ molecules as ligands. However, elemental sulfur is clearly a candidate (along with H$_2$ and halogens) to add coordinatively to transition metal centers, possibly as a preliminary step to the completion of an oxidative-addition process. As we have already successfully isolated and characterized a remarkable adduct of molecular diiodine with a powerful bidentate Lewis acid, dirhodium(II) tetra(trifluoroacetate), in the form of the one-dimensional (1D) chain complex [Rh$_2$(O$_2$CCF$_3$)$_4$ · I$_2$]$_\infty$,[5] we decided to extend that approach to elemental sulfur.

The preparation of products and growth of X-ray quality crystals have been achieved by using a solventless technique[6] based on a sublimation–deposition procedure, in which volatile dirhodium(II) tetra(trifluoroacetate) was employed in the presence of vapors of elemental sulfur. For the latter, the thermodynamically stable form in the vapor phase at the temperatures employed is known to be S$_8$ molecules.[7] Working with different ratios of Rh$_2$ to S$_8$ in the initial mixtures (from equimolar quantities to lower concentrations of S$_8$) we have successfully isolated two sulfur adducts of [Rh$_2$(O$_2$CCF$_3$)$_4$]. The stoichiometries of the two products [Rh$_2$(O$_2$CCF$_3$)$_4$]$_n$(S$_8$)$_m$ have been found by chemical analyses to be *n:m* = 1:1 for **1** and *n:m* = 3:2 for **2**. The new coordination compounds are relatively stable under moderate conditions, insoluble in organic solvents at room temperature, destroyed by coordinating solvents, and slowly decomposed even by noncoordinating dichloromethane to release elemental sulfur. Products **1** and **2** have been examined by X-ray crystallography.

The structure of **1** consists[8] of dirhodium(II) tetra(trifluoroacetate) units with the eight-membered S$_8$ cycles 1,3-attached to their axial positions to form a zigzag 1D chain (Figure 1). Each rhodium atom of the Rh$_2$ unit coordinates to one sulfur atom of an S$_8$ molecule; the two Rh–S distances at the ends of the dimetal unit are similar, 2.516(1) and 2.578(1) Å.

The structure of **2** is particularly interesting[9] as each S$_8$ molecule is 1,3,6-coordinated to three dirhodium complexes, while each Rh$_2$ unit binds to two different octasulfur rings.

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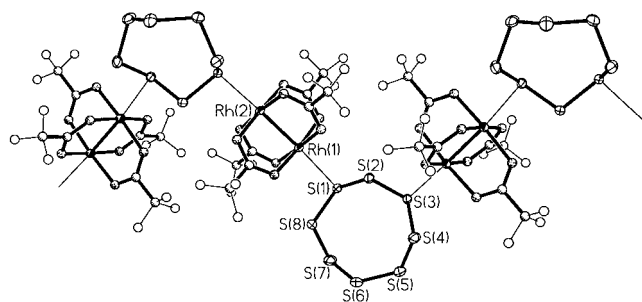
Figure 1. A fragment showing the alternating arrangement of $[Rh_2(O_2CCF_3)_4]$ and coordinated cyclooctasulfur molecules in the polymeric chain of **1**. Only rhodium and sulfur atoms are labeled for clarity. Only one orientation of each disordered CF_3 groups is depicted. The S–S bond lengths (starting from S(1), clockwise): 2.046(2), 2.067(2), 2.063(2), 2.038(2), 2.041(2), 2.047(2), 2.039(2), 2.079(2) Å.

This results in a novel, pseudo-2D architecture consisting of the octagon units (4 Rh_2 and 4 S_8 blocks, Figure 2) forming a ribbon-type extended structure (Figure 3). Alternatively, the structure of **2** can be considered as built of two polymeric chains of the monoadduct **1** stapled together by an additional $[Rh_2(O_2CCF_3)_4]$ molecule lying between each pair of facing S_8 rings, which brings the total composition to an $[Rh_2(O_2CCF_3)_4]:S_8$ ratio of 3:2. There is a much greater
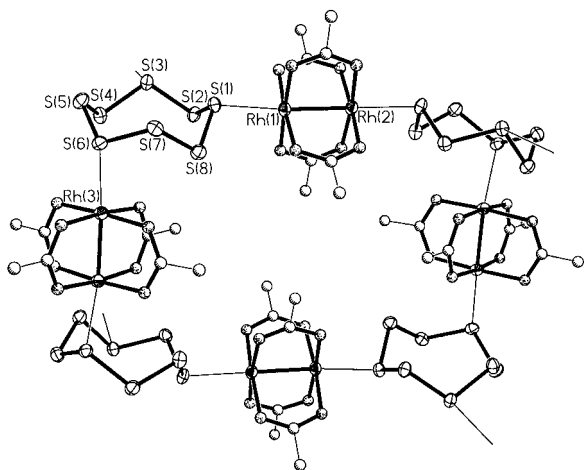

Figure 2. The elemental octagon unit built of $[Rh_2(O_2CCF_3)_4]$ and S_8 rings in the crystal structure of **2**. Only crystallographically independent rhodium and sulfur atoms are labeled. Fluorine atoms of CF_3 groups are omitted for clarity. The S–S bond lengths (starting from S(1), anticlockwise): 2.054(8), 2.034(8), 2.072(8), 2.035(9), 2.058(8), 2.061(9), 2.041(9), 2.072(8) Å.
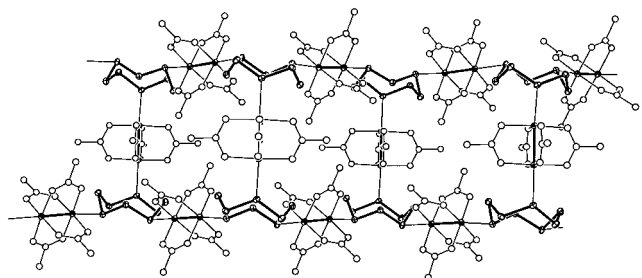

Figure 3. The pseudo-2D ribbon-type structure of **2**. Two infinite chains of $[Rh_2(O_2CCF_3)_4(S_8)]_\infty$ (**1**) are further connected by additional dirhodium tetra(trifluoroacetate) molecules. Atom labels are omitted for clarity. Fluorine atoms of CF_3 groups are also omitted.

variation in the Rh–S contacts in this structure, with one relatively short distance of 2.484(6) versus two longer ones, 2.507(6) and 2.567(6) Å. The average Rh–S distance of 2.547(1) in **1** is slightly longer than that in **2** (2.519(6) Å). The Rh-Rh-S angles are close to linear, averaging to 176.63(4)° in **1** and 174.6(2)° in **2**.

About each coordinated sulfur atom, in both **1** and **2**, there is a trigonal-pyramidal conformation with angles spanning the range 102–113°, which reflects a stereochemical activity of the lone electron pair. As far as the S_8 moiety as a whole is concerned, it retains its crown conformation in both **1** and **2**. The mean values for the S–S distances and S-S-S valence angles in the sulfur molecule are nearly identical in both adducts: 2.053(2) Å and 107.1(1)° in **1**, and 2.053(8) Å and 107.2(4)° in **2**, respectively. These data for the coordinated cyclo-S_8 ligands are in good agreement with the mean values for the S–S bond lengths (2.046(3) Å) and the S-S-S bond angles (108.2(6)°) reported for elemental orthorhombic sulfur.[10] At the same time, the coordination of neutral sulfur atoms to rhodium centers of $[Rh_2(O_2CCF_3)_4]$ is relatively strong: the $Rh^{2+}–S^0$ distances in **1** and **2** are identical to the $Rh^{2+}–S^{2-}$ bonds found[11] for axial binding of doubly coordinated S atoms in dialkylsulfides by dirhodium(II) tetracarboxylates.

There are no significant contacts in **1** and **2** between sulfur atoms and carboxylate oxygen atoms (all longer than 3.2 Å). However, in the structure of **2** there are some long solid-state interactions between sulfur atoms of neighboring S_8 molecules; the shortest ones are 3.49 and 3.61 Å, which are comparable with the van der Waals radius sum estimate.[12]

Reactions involving elemental sulfur typically proceed with the cleavage of one or more S–S bonds. We have succeeded in the isolation and characterization of the first transition metal complexes with coordinated neutral cyclooctasulfur moieties. The employment of a two-ended Lewis acid, $[Rh_2(O_2CCF_3)_4]$, and a potentially multidentate eight-membered sulfur Lewis base as structural units has resulted in the formation of novel extended supramolecular structures. What is more interesting is the fact that the S_8 rings function as bidentate and tridentate donor bridges thus allowing the formation of 1D and 2D architectures.

Cyclic S_8 molecules are known[13] to be involved in thermal conversion reactions consisting of ring opening or dissociation followed by the formation of smaller intermediate species S_x ($x < 8$). It seems likely that these pathways can be dominant at temperatures much higher than those employed here for the preparation of **1** and **2**. We are interested in continuing this study, as we believe that there may exist more such adducts than have yet been detected, and that dirhodium tetra(trifluoroacetate) as a powerful acceptor and a thermally stable unit can be used to trap these reactive sulfur intermediates. Work is also in progress to extend this study to elemental selenium and phosphorus as well as to other metal trifluoroacetates.

Experimental Section

All experimental manipulations were carried out under dry, oxygen-free argon by employing Schlenk techniques. The unligated form of

[Rh$_2$(O$_2$CCF$_3$)$_4$] was obtained using a literature procedure.[14] Sulfur powder, 99.98%, was purchased from Aldrich. The IR spectra were recorded on a Perkin-Elmer 16PC FT-IR spectrophotometer using KBr pellets. Elemental analysis was done by Canadian Microanalytical Services, Ltd.

1: [Rh$_2$(O$_2$CCF$_3$)$_4$] (0.066 g, 0.10 mmol) was mixed with sulfur powder (0.026 g, 0.10 mmol based on the S$_8$). The mixture was sealed in an evacuated Pyrex tube and the tube was placed in a furnace at 140 °C. The tube was kept at that temperature for about a week, and then slowly (over 24 h) cooled to room temperature. Several dozen dark violet crystals of **1** deposited in the "cold" zone of the tube, where the temperature was about 5 °C lower. Elemental analysis (%) calcd for S$_8$C$_8$F$_{12}$O$_8$Rh$_2$: C 10.51, S 28.00; found: C 10.35, S 28.35; IR (KBr): $\tilde{\nu} = 1650.0$ (s), 1244.6 (m), 1192.5 (s), 1169.5 (s), 861.7 (m), 804.1 (w), 784.4 (w) 739.8 (m) cm^{-1}.

2: [Rh$_2$(O$_2$CCF$_3$)$_4$] (0.066 g, 0.10 mmol) was mixed with elemental sulfur (0.016 g, 0.063 mmol based on the S$_8$). The mixture was sealed in an evacuated Pyrex tube and the tube was placed in a furnace at 130 °C. The tube was kept at that temperature for about a week, and then slowly (over 24 h) cooled to room temperature. Several dark violet crystals of **2** deposited not far from the "hot" zone of the tube along with some dark brown polycrystalline solid. Red crystals of free sulfur accompanied the powdered product in the hot zone; these were mechanically separated under the microscope. Elemental analysis (%) calcd for S$_{16}$C$_{24}$F$_{36}$O$_{24}$Rh$_6$: C 11.59, S 20.63; found: C 11.36, S 20.80; IR (KBr): $\tilde{\nu} = 1653.0$ (s), 1258.7 (m), 1234.4 (m), 1190.2 (s), 1142.8 (w), 1130.6 (w), 1094.2 (w), 1075.4 (w), 1050.1 (m), 1018.1 (w), 861.3 (m), 823.8 (w), 785.2 (w), 737.7 (m), 688.0 (w) cm^{-1}.

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[8] Crystallographic data for **1** (S$_8$C$_8$F$_{12}$O$_8$Rh$_2$): $M_r = 914.38$, dark violet block, $0.25 \times 0.08 \times 0.05$ mm, monoclinic, space group $P2_1/c$, $a = 9.1826(5)$, $b = 16.605(1)$, $c = 16.5885(4)$ Å, $\beta = 92.267(4)°$, $V = 2527.4(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.403$ g cm^{-3}, $\mu = 2.090$ mm^{-1}, $2\theta_{max} = 50.18°$. Nonius FAST area detector system, Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $T = -60$ °C, 14 915 reflections measured, data corrected for Lorentz and polarization effects, solution by direct methods (SHELXTL V.5), full-matrix refinement of F^2 (SHELXL-93), R_1 (on F_o) = 0.0585, $wR2$ (on F_o^2) = 0.1125 for 355 parameters and 48 restraints, 4439 independent reflections, R_1 (on F_o) = 0.0496, $wR2$ (on F_o^2) = 0.1009 for 3868 reflections with $I \geq 2\sigma(I)$, highest residual peak 0.96 e Å^{-3}.

[9] Crystallographic data for **2** (S$_{16}$C$_{24}$F$_{36}$O$_{24}$Rh$_6$): $M_r = 2486.66$, dark violet plate, $0.25 \times 0.08 \times 0.03$ mm, monoclinic, space group $C2/c$, $a = 30.93(2)$, $b = 15.911(4)$, $c = 16.762(8)$ Å, $\beta = 121.83(4)°$, $V = 7009(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.357$ g cm^{-3}, $\mu = 2.018$ mm^{-1}, $2\theta_{max} = 45.02°$. Nonius FAST area detector system, Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $T = -60$ °C, 15 755 reflections measured, data corrected for Lorentz and polarization effects, solution by direct methods (SHELXTL V.5), full-matrix refinement of F^2 (SHELXL-93), R_1 (on F_o) = 0.1430, $wR2$ (on F_o^2) = 0.2462 for 436 parameters and 60 restraints, 4484 independent reflections, R_1 (on F_o) = 0.1047, $wR2$ (on F_o^2) = 0.2165 for 3314 reflections with $I \geq 2\sigma(I)$, highest residual peak 1.36 e Å^{-3}. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-154796 (**1**) and CCDC-154797 (**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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A Ligand-Modulated Padlock Oligonucleotide for Supercoiled Plasmids**

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Supramolecular structures involving a circular oligonucleotide catenated to a double-stranded nucleic acid have been recently described.[1–3] The formation of these structures involves the recognition of a specific region of the DNA by the oligonucleotide through either triple-helix formation[1, 2] or strand displacement.[3] The oligonucleotide can be circularized first and then loaded onto a linear DNA fragment[1] or circularized around the DNA target after triplex formation.[2] In the latter case, the catenated structure can be established on a circular supercoiled DNA. In both cases, the circular oligonucleotide may be able to move along the DNA, whereas in the method developed by Kuhn et al.,[3] sliding does not occur, as the oligonucleotide is threaded between complementary strands of DNA before circularization around the displaced DNA single strand takes place. In the method that we previously described,[2] the linear oligonucleotide is wound around the double-stranded DNA sequence through sequence-specific triple-helix formation, and then circularized by using a template oligonucleotide and T4 DNA ligase. When the target sequence was located on a plasmid, the circular oligonucleotide became catenated to the plasmid. However, it was shown to slide more than 600 bp away from

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