35.82; found: C 38.84, H 5.59, N 34.46. A-Et-enH · Cl: ^{1}H NMR (500 MHz, $(CD_3)_2SO$): $\delta = 2.85$ (t, NH_2-CH_2-CH_2-NH), 2.90 (t, NH_2-CH_2-CH_2-NH), 3.13 (t, NH-CH_2-CH_2-AdeN^9), 4.30 (t, NH-CH_2-CH_2-AdeN^9), 7.28 (s, NH_2), 8.24 (s, H2), 8.30 (s, H8); MS: m/z (%): 222 (100), $[M^+ - Cl]$; elemental analysis calcd for $C_9H_{16}ClN_7$: C 41.94, H 6.26, N 38.04; found: C 41.24, H 6.11, N 38.20.

1 and **2:** An equimolar aqueous solution of either G-Et-enH · Cl or A-Et-enH · Cl was added to a solution of copper nitrate in distilled water at room temperature. In each case blue crystals were isolated which were suitable for single crystal X-ray analysis. **1**: MS: m/z (%):362 (100), $[M^+]$; elemental analysis calcd for $[CuClC_9N_8O_4H_{15}]$: C 27.14, H 3.80, N 28.14; found: C 26.92, H 4.01, N 27.82. (Analyses were for pump-dried samples and correspond to an anhydrous form of **1**.) **2**: MS: m/z (%):346 (100), $[M^+]$; elemental analysis calcd for $[(CuClC_9N_7H_{15})(NO_3) \cdot H_2O]$: C 27.00, H 4.28, N 28.00; found: C 27.23, H 3.92, N 27.84.

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[6] a) Crystal data for **1**: $[C_9H_{19}CuN_7O_3][NO_3]Cl$, $M_r = 434.3$, tetragonal, space group $I4_1/a$, $a = 25.184(3)$, $c = 12.6272(15)$ Å, $V = 8008.8(16)$ Å^3, $Z = 16$, ρ_{calcd} 1.441 g cm^{-3}; $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $\mu = 1.16$ mm^{-1}, $T = 160$ K. 17849 measured reflections were corrected for absorption, 3516 were unique ($R_{int} = 0.152$, $\theta = 25.0°$); $R = 0.0946$ (F values, $F^2 > 2\sigma$), $R_w = 0.2497$ (F^2 values, all data), GOF = 1.075 for 217 parameters, residual electron density between 0.64/−0.53 e Å^3. The structure contains substantial regions of diffuse electron density modelled by the SQUEEZE procedure (A. L. Spek, PLATON, University of Utrecht, The Netherlands, **1999**) and corresponding to disordered chloride anion and approximately 6 water molecules per asymmetric unit according to total electron density and volumes. The chloride anion, required for overall charge balance and by chemical analysis results, is included in the chemical formula and derived crystal data above; addition of $6H_2O$ gives $M_r = 542.3$, $\rho_{calcd} = 1.799$ g cm^{-3}. This substantial disorder is responsible for the generally weak diffraction data. Other program used: SHELXTL (G. Sheldrick, Bruker AXS Inc., Madison, WI, USA, 1998, Version 5.1). b) Crystal data for **2**: $[C_9H_{15}ClCuN_7][NO_3] \cdot H_2O$, $M_r = 400.3$, monoclinic, space group $P2_1/c$, $a = 10.767(2)$, $b = 11.754(2)$, $c = 11.875(2)$ Å, $\beta = 100.287(4)°$, $V = 1478.7(5)$ Å^3, $Z = 4$, ρ_{calcd} 1.798 g cm^{-3}; $T = 160$ K. The very small crystal size ($0.11 \times 0.03 \times 0.02$ mm) and the relatively poor quality necessitated data collection with synchrotron radiation (SRS at Daresbury Laboratory, station 9.8, $\lambda = 0.6920$, $\mu = 1.69$ mm^{-1}). 8557 reflections were measured, 3135 were unique ($R_{int} = 0.053$, $\theta = 26.0°$); $R = 0.0529$, $R_w = 0.1425$, GOF = 0.976 for 229 parameters, residual electron density between 2.03/−0.99 e Å^3 with the largest features close to Cu. c) 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-139134 (**1**) and -139135 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Coordinated and Clathrated Molecular Diiodine in $[Rh_2(O_2CCF_3)_4I_2] \cdot I_2$[**]

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Marina A. Petrukhina

The tetrakis(trifluoroacetate) dirhodium(II) molecule, $[Rh_2(O_2CCF_3)_4]$, has been shown to be a versatile, bifunctional Lewis acid, able to coordinate in solution an extraordinary variety of donor molecules to the axial positions.[1] Recent work in our laboratory employing a "solventless" synthetic technique has further extended the chemical and structural range of products to include those with aromatic and alkyne ligands, polymeric and oligomeric structures, and reaction products with dirhodium(I) units.[2] As a result of finding $[Rh_2(O_2CCF_3)_4]$ to be such an exceptionally avid

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Lewis acid we decided to see if adducts could be obtained with the elemental halogens.

We report here the interactions of I_2 with $[Rh_2(O_2CCF_3)_4]$ using a solid/vapor deposition ("solventless") technique. The resulting product is a zigzag chain polymer $\{[Rh_2(O_2CCF_3)_4I_2]\cdot I_2\}_\infty$ formed by alternating $[Rh_2(O_2CCF_3)_4]$ and I_2 molecules and having an unprecedented bidentate bridging coordination mode of molecular diiodine. Another I_2 molecule is clathrated within the channels in the structure. This unusual product further confirms the exceptional acceptor ability of the $[Rh_2(O_2CCF_3)_4]$ molecule and extends the class of halo-transition metal complexes.

We again demonstrate the utility of the solventless synthesis technique for studying weak interactions as the title compound, $[Rh_2(O_2CCF_3)_4I_2]\cdot I_2$ (**1**), was prepared by heating a mixture of unligated $[Rh_2(O_2CCF_3)_4]$ with molecular diiodine. Although we had a slight excess of $[Rh_2(O_2CCF_3)_4]$ in the initial mixture, heating that mixture to 160 °C resulted in an excess of I_2 over the dirhodium units in the gas phase, from which a product with a Rh_2:I_2 composition of 1:2 has been deposited. Interestingly, there was a tendency to form only the given composition in the solid state, as attempts to work with lower diiodine contents resulted in no crystalline product. The solid injection technique of EI mass spectroscopy applied to crystals of **1** showed only $[Rh_2(O_2CCF_3)_n]^+$ fragments, implying immediate thermal cleavage of I_2 from the product. There were indications of gradual iodine loss in the solid state even at room temperature, which prevented obtaining accurate elemental analysis data for **1**. Nevertheless, crystals appeared to be stable at low temperatures and were characterized by X-ray diffraction study.[3]

In the crystal structure of **1** the dirhodium trifluoroacetate units are linked together in a zigzag chain by interacting with neutral I_2 molecules in such a way that each Rh^{II} center has contact with one iodine atom of an I_2 molecule (Figure 1). There are two crystallographically independent dirhodium units in the cell with Rh–Rh distances of 2.417(1) and 2.415(1) Å; other characteristics of the two units are also very similar. The dirhodium fragments are linked by a diiodine bridge with the axial Rh–I contacts being only slightly different at 2.8359(9) and 2.8239(9) Å, while the Rh-Rh-I angles are close to linear (the mean value is 177.04(3)°). Such an orientation of the coordinated iodine minimizes the possible contacts with oxygen atoms of the carboxylate groups. The shortest of those, 3.44 Å, is equal to the sum of the van der Waals radii of I and O atoms. The two Rh-I-I angles have an average value of 95.31(2)°, reflecting a stereochemical activity of the lone electron pairs of the iodine atoms, and the average torsion angle for Rh-I-I-Rh is 106.6°. Another diiodine molecule is clathrated, just filling holes in the structure (Figure 2) without any close contacts to the neighboring atoms (all longer than 3.3 Å). It is disordered over two positions with site occupancies of 94.4 and 5.6%. The I–I distance in the "coordinated" I_2 molecule (2.7202(6) Å) is longer than in the "clathrated" one (2.666(2) Å). The latter is the same as the value of free diiodine in the gaseous state (2.667(2) Å).[4]

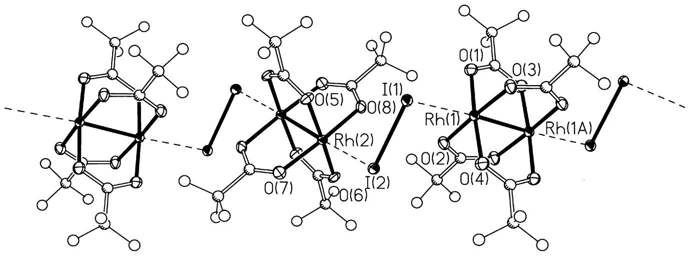


Figure 1. Fragment showing the alternating arrangement of $[Rh_2(O_2CCF_3)_4]$ and coordinated diiodine molecules in the crystal structure of **1**. Atoms are represented by thermal ellipsoids at the 40% probability level. Carbon and fluorine atoms are shown as spheres of arbitrary radii and are not labeled for clarity. Axial contacts to Rh atoms are drawn as dashed lines. Only one orientation of disordered CF_3 groups is depicted.

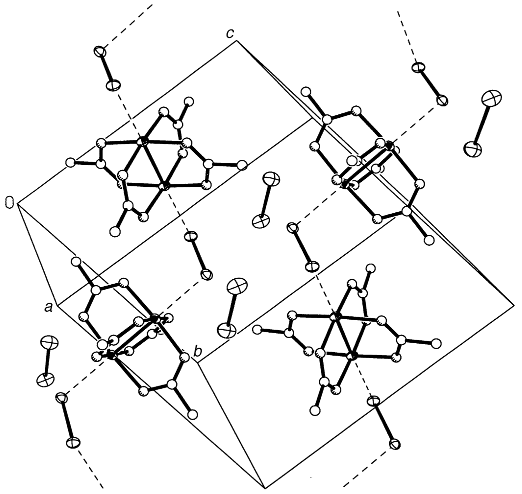
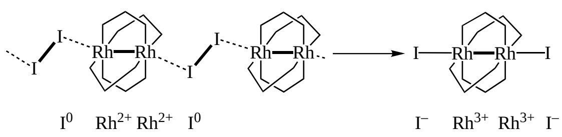


Figure 2. Packing diagram of **1** showing the displacement of both coordinated and clathrated diiodine molecules. Fluorine atoms of CF_3 groups are omitted for clarity. Axial interactions to dirhodium units are drawn as dashed lines. Only the major orientation of clathrated I_2 molecules is depicted.

The bridging coordination mode of I_2 found here is without precedent. There are numerous examples of iodine adducts of transition metal complexes, but most of them have the I_2 forming a part of a polyiodide anion—for instance I_3^-, I_5^-, I_4^{2-}—in both terminal and bridging modes.[5, 6] An example of a complex in which the reactive neutral halogen, I_2, is coordinated directly to a transition metal is the iodine–platinum(II) complex $[PtI\{o,o'\text{-}(Me_2NCH_2)_2C_6H_3\}(\eta^1\text{-}I_2)]$[7a] where there is a linear Pt-I-I arrangement with a long Pt–I distance of 2.895(1) Å. This platinum–iodine bonding resulted in an elongation of the I–I bond distance from 2.667(2) Å in "free" diiodine[4] to 2.822(1) Å. A number of similar Pt–I_2 compounds with the same type of ligand $C_6H_3\{CH_2NR^1R^2\}_2$ bearing various substituents R^1 and R^2 on the N atom have been reported having the same η^1-coordination mode.[7b] In all these Pt-I-I complexes, there is a linear arrangement, which is in sharp contrast to the bent (95°) structure in the present case. It has been suggested[7a] that in the Pt compounds the metal is donating to the σ* orbital of the I_2 molecule, whereas in **1** we believe that the I_2 molecule is functioning as an electron-pair donor to the rhodium atoms. There appears to be no close analogue to the bridging bidentate coordination mode of molecular diiodine to a transition metal atom found in **1**.

Another interesting synthetic aspect of this result is the resistance of the dirhodium trifluoroacetate unit toward oxidation by I_2 at temperatures above 150 °C. Analogous reactions with different concentrations of Br_2 and $PhI \cdot Cl_2$ (as a dichlorine source) have been attempted over a wide range of temperatures (100–180 °C), but no crystalline products were formed under the conditions used. These reactions most probably resulted in the oxidation of $[Rh_2(O_2CCF_3)_4]$ and formation of nonvolatile materials. The oxidation of dirhodium carboxylates by Br_2 is known to take place in solutions at ambient temperatures.[8] The unique halo-metal complex **1** represents a model for probable intermediates during the early stages of oxidative addition reactions by halides (Scheme 1).



Scheme 1. Schematic representation of oxidative addition reactions of halides with $[Rh_2(O_2CCF_3)_4]$, with **1** as a model for probable intermediates.

Experimental Section

All experimental manipulations involving the synthesis of the starting materials were carried out under dry, oxygen-free argon by employing Schlenk techniques. The unligated form of $[Rh_2(O_2CCF_3)_4]$ was obtained using literature procedures.[9] The EI/DP mass spectra were acquired using a VG Analytical 70S high-resolution, double focusing, sectored (EB) mass spectrometer.

The title compound **1** was prepared by heating a mixture of $[Rh_2(O_2CCF_3)_4]$ (65 mg, 0.10 mmol) and freshly sublimed I_2 (20 mg, 0.08 mmol) at 150–160 °C for 5–6 days in a sealed evacuated Pyrex ampoule. Dark (red-violet on grinding) crystals of **1** were collected in the "cold" zone of the tube where the temperature was set about 5 °C lower; yield: 34 mg (29.2 %). MS (300 °C): *m/z* (%): 657 (38, $[Rh_2(O_2CCF_3)_4]^+$), 544 (47, $[Rh_2(O_2CCF_3)_3]^+$), 431 (65, $[Rh_2(O_2CCF_3)_2]^+$), 318 (9, $[Rh_2(O_2CCF_3)]^+$), 127 (100, $[I]^+$)

The use of FeI_2 as a slow release source of I_2, and lower concentrations of molecular I_2 produced no crystalline iodine-containing products.

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[3] Crystallographic data for **1** ($C_8F_{12}I_4O_8Rh_2$): $M_r = 1165.50$, red-violet block, 0.45 × 0.25 × 0.18 mm, triclinic, space group $P\bar{1}$, $a = 10.4259(3)$, $b = 10.671(1)$, $c = 11.924(3)$ Å, $\alpha = 80.35(3)$, $\beta = 89.82(1)$, $\gamma = 68.80(1)^\circ$, $V = 1216.9(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 3.181$ g cm^{-3}, $\mu = 6.553$ mm^{-1}, $2\theta_{max} = 50.14^\circ$, Nonius FAST area detector system, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $T = -60$ °C, 8002 reflections measured, data corrected for Lorentz and polarization effects, absorption correction (transmission coefficients 0.109–0.286), direct method solution (SHELXTL V.5), full-matrix refinement on F^2 (SHELXL-93), $R1$ (on F_o) = 0.040, $wR2$ (on F_o^2) = 0.1121 for 316 parameters and 37 restraints, 4061 independent reflections, $R1$ (on F_o) = 0.0381, $wR2$ (on F_o^2) = 0.1094 for 3874 reflections with $I > 2\sigma(I)$, highest residual peak 1.51 e$^-$ Å^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no.CCDC-138682 (entries carrying the suffix *x* represent disordered atoms). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Thermosensitive, Reversibly Cross-Linking Gels with a Shape "Memory"

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Smart polymers/gels are materials that undergo a sharp and reversible change in their microstructure when subjected to an external stimulus such as temperature, pH, ionic strength, solvent composition. When triggered, this change can be seen on a macroscopic level either as phase separation, or else in the case of gels, an order-of-magnitude volume change.[1] The ability of smart materials to change their physical properties according to their environment makes them desirable for a multitude of applications, including drug delivery devices,[2] supports for biocatalysts,[3, 4] bioseparations,[5] and biosensors. The external trigger for a thermosensitive polymer is temperature. The polymer is soluble in water at temperatures below the lower critical solution temperature (LCST) as a result of a thermodynamic balance of the four fundamental forces between the polymeric material and the water.[6]

The polymer-enriched phase formed above the LCST could be either in the form of a compact polymer precipitate or as a physically cross-linked gel. The latter occurs with linear polymer chains where there is an increased physical interaction between neighboring chains.[7, 8] This type of self-

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