3487–3494; G. Baum, E. C. Constable, D. Fenske, C. E. Housecroft, T. Kulke, *Chem. Eur. J.* **1999**, *5*, 1862–1873; E. E. Simanek, S. Qiao, I. S. Choi, G. M. Whitesides, *J. Org. Chem.* **1997**, *62*, 2619–2621; O. Mamula, A. von Zelewsky, G. Bernardinelli, *Angew. Chem.* **1998**, *110*, 302–305; *Angew. Chem. Int. Ed.* **1998**, *37*, 289–293; R. K. Castellano, C. Nuckolls, J. Rebek, Jr. *J. Am. Chem. Soc.* **1999**, *121*, 11156–11163; T. Kondo, K.-I. Oyama, K. Yoshida, *Angew. Chem.* **2001**, *113*, 918–922; *Angew. Chem. Int. Ed.* **2001**, *40*, 894–897; C. R. Woods, M. Benaglia, F. Cozzi, J. S. Siegel, *Angew. Chem.* **1996**, *108*, 1977–1980; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1830–1833; L. J. Prins, P. Timmerman, D. N. Reinhoudt, *J. Am. Chem. Soc.* **2001**, *123*, 10153–10163.

[4] M. A. Masood, E. J. Enemark, T. D. P. Stack, *Angew. Chem.* **1998**, *110*, 973–977; *Angew. Chem. Int. Ed.* **1998**, *37*, 928–932; J.-M. Vincent, C. Philouze, I. Pianet, J.-B. Verlhac, *Chem. Eur. J.* **2000**, *6*, 3595–3599; X. Shi, J. C. Fettinger, M. Cai, J. T. Davis, *Angew. Chem.* **2000**, *112*, 3254–3257; *Angew. Chem. Int. Ed.* **2000**, *39*, 3124–3127; X. Shi, J. C. Fettinger, J. T. Davis, *J. Am. Chem. Soc.* **2001**, *123*, 6738–6739; L. J. Prins, J. Huskens, F. de Jong, P. Timmerman, D. N. Reinhoudt, *Nature* **1999**, *398*, 498–502.

[5] J. N. H. Reek, A. Kros, R. J. M. Nolte, *Chem. Commun.* **1996**, 245–247; J. A. A. W. Elemans, R. de Gelder, A. E. Rowan, R. J. M. Nolte, *Chem. Commun.* **1998**, 1553–1554; S. J. Holder, J. A. A. W. Elemans, J. J. J. M. Donners, M. J. Boerakker, R. de Gelder, J. Barberá, A. E. Rowan, R. J. M. Nolte, *J. Org. Chem.* **2001**, *66*, 391–399.

[6] C. S. Wilcox, L. M. Greer, V. Lynch, *J. Am. Chem. Soc.* **1987**, *109*, 1865–1867; S. C. Zimmerman, M. Mrksich, M. Baloga, *J. Am. Chem. Soc.* **1989**, *111*, 8528–8530; M. Harmata, C. L. Barnes, S. R. Karra, S. Elahmad, *J. Am. Chem. Soc.* **1994**, *116*, 8392–8393; F.-G. Klärner, J. Panitzky, D. Bläser, R. Boese, *Tetrahedron* **2001**, *57*, 3673–3687.

[7] a) D. Witt, J. Lagona, F. Damkaci, J. C. Fettinger, L. Isaacs, *Org. Lett.* **2000**, *2*, 755–758; b) L. Isaacs, D. Witt, J. Lagona, *Org. Lett.* **2001**, *3*, 3221–3224.

[8] Selected references: M. Fujita, J. Yazaki, K. Ogura, *J. Am. Chem. Soc.* **1990**, *112*, 5645–5647; M. Fujita, D. Oguro, M. Miyazawa, H. Oka, K. Yamaguchi, K. Ogura, *Nature* **1995**, *378*, 469–471; S.-Y. Yu, T. Kusukawa, K. Biradha, M. Fujita, *J. Am. Chem. Soc.* **2000**, *122*, 2665–2666; K. Umemoto, K. Yamaguchi, M. Fujita, *J. Am. Chem. Soc.* **2000**, *122*, 7150–7151; N. Fujita, K. Biradha, M. Fujita, S. Sakamoto, K. Yamaguchi, *Angew. Chem.* **2001**, *113*, 1768–1771; *Angew. Chem. Int. Ed.* **2001**, *40*, 1718–1721.

[9] D. Schubert, C. Tziatzios, P. Schuck, U. S. Schubert, *Chem. Eur. J.* **1999**, *5*, 1377–1383; T. M. Laue, *Methods Enzymol.* **1995**, *259*, 427–452.

[10] Coordination compounds with N and O ligands: L. D. Pettit, M. Bezer *Coord. Chem. Rev.* **1985**, *61*, 97–114; K. Matsumoto, H. Moriyama, K. Suzuki *Inorg. Chem.* **1990**, *29*, 2096–2100; T. G. Appleton, D. R. Bedgood, Jr., J. R. Hall *Inorg. Chem.* **1994**, *33*, 3834–3841.

Crystal Engineering of Mixed-Metal Ru–Ag Coordination Networks by Using the *trans*-[RuCl$_2$(pyz)$_4$] (pyz = pyrazine) Building Block[**]

Lucia Carlucci, Gianfranco Ciani,[*] Francesca Porta, Davide M. Proserpio, and Laura Santagostini

In the rational development of new strategies for the crystal engineering of coordination networks[1] and of metal-based supramolecular architectures[2] the use of predetermined building blocks has assumed an increasing relevance in recent times. For example, molecular corners containing transition metals with programmed coordination angles, such as *cis*-protected $\mathrm{Pd^{II}}$ and $\mathrm{Pt^{II}}$ square-planar complexes, have been employed for the construction of frameworks and, particularly, of macromolecular polygons or polyhedral cages,[3] of potential utility for molecular recognition. We have recently employed the corner unit $[\mathrm{Cu}(2,2'\text{-bpy})]^{2+}$ (2,2'-bpy = 2,2'-bipyridine) for the self-assembly of polymeric species[4] and new architectures.[5] These building blocks generally work as acceptors and can be used with a variety of spacer ligands with different types of donor ends for the assembly of desired arrays. A different type of potentially useful metal-containing unit is represented by complexes containing ligands with *exo*-oriented donor functions. These complexes can be considered as nonconventional "ligands" in which the orientation of the donor groups can be controlled by the nature of the coordinated bases and by the coordination geometry at the metal center. Few examples of such species have been as yet reported, though they can find interesting applications for many purposes, such as the deliberate construction of *homo*- or *hetero*metallic networks with specific topologies, or the assembly of hydrogen-bonded frames, by using suitable (hydrogen-donor) organic molecules as spacers. Square-planar metal-porphyrinate complexes bearing four donor 4-pyridyl substituents on the macrocycle have been used, for instance, for the deliberate assembly of cooperite-like networks[6] and of other types of bimetallic frames.[7] Some other metal-containing "ligands" have been employed,[8] such as the anionic square-planar $[\mathrm{Pt(CN)_4}]^{2-}$[9] and digonal $[\mathrm{M(CN)_2}]^-$ (M = Ag, Au)[10] species.

We have prepared as a new building block the neutral complex *trans*-[RuCl$_2$(pyz)$_4$] (**1**; pyz = pyrazine): it was obtained by reacting [RuCl$_2$(dmso)$_4$] in toluene with a large

---

[*] Prof. G. Ciani, Dr. D. M. Proserpio
Dipartimento di Chimica Strutturale e Stereochimica Inorganica
Via G. Venezian 21, 20133 Milano (Italy)
Fax: (+39) 02-5031-4454
E-mail: davide@csmtbo.mi.cnr.it

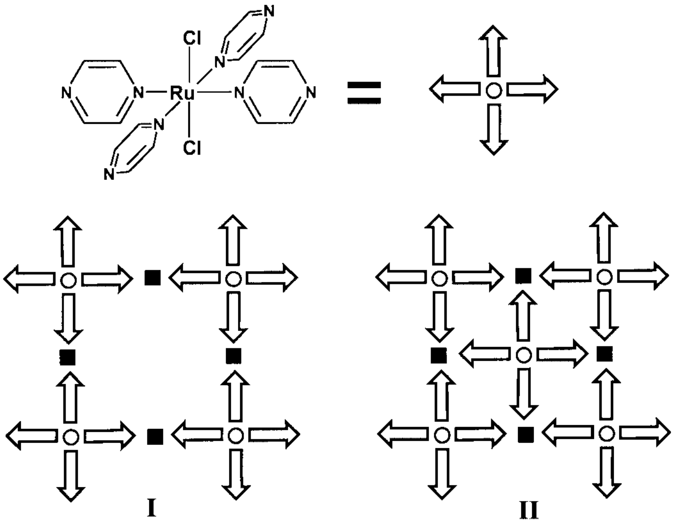
Prof. F. Porta, Dr. L. Santagostini
Dipartimento di Chimica Inorganica, Metallorganica e Analitica, and centro CNR
Via G. Venezian 21, 20133 Milano (Italy)

Dr. L. Carlucci
Dipartimento di Biologia Strutturale e Funzionale
Università dell'Insubria
Via J. H. Dunant 3, 21100 Varese (Italy)

[**] This work was supported by MURST within the project "Solid Supermolecules" 2000–2001 and by CSMTBO-CNR Center.

1433-7851/02/4111-1907 $ 20.00+.50/0

excess (tenfold) of the pyrazine ligand. Complex **1** displays four equatorial pyrazine molecules with free *exo*-oriented N-donor atoms, in square-planar orientation (see Scheme 1). It is a stable species that has many potential applications for the crystal engineering of new polymeric materials, such as bimetallic coordination networks of predictable topology, as well as hydrogen-bonded arrays. The strongly bonded axial chlorides can prevent the self-assembly of **1**, which differs from what occurs with the M^{II}—tetrapyridyl–porphyrinate building blocks.[11] On reacting **1** with digonal metal centers (d^{10} metal ions or metal complexes with two free *trans* sites) one can predict the formation of layers of square grids like **I** in Scheme 1, while square-planar metal centers can give layers such as **II** in Scheme 1. However, the axial chlorides of **1** can also play a noninnocent role, extending the array in the third dimension through interactions with the other metals.



Scheme 1.

We report here on three new self-assembled networks obtained from **1** with different silver salts ($AgCF_3SO_3$ and $AgNO_3$), that is $[RuCl_2(pyz)_4Ag](SO_3CF_3)$ (**2**), $[RuCl_2(pyz)_4Ag_2(SO_3CF_3)_2] \cdot C_2H_2Cl_4 \cdot 0.5\,n\text{-}CH_3(CH_2)_3OH$ (**3**) and $[RuCl_2(pyz)_4Ag]NO_3$ (**4**). The latter two species exhibit interesting mineralomimetic 3D structures[12] that can be related to the prototypical lattices of rutile and rock salt, respectively.

The reactions of **1** with $AgCF_3SO_3$ afford different products depending on the molar ratio of the reagents and on the solvent system. Slow diffusion of a solution of the silver salt in MeOH into a solution of **1** in CH_2Cl_2 (molar ratio 1:1) gave dark red crystals of **2**. On the other hand, when $AgCF_3SO_3$ in *n*-butanol is diffused into a solution of **1** in 1,1,2,2-tetrachloroethane (TCE), using a 2:1 molar ratio of the reagents, brown-red crystals separated, corresponding to compound **3**.

The crystal structures[13] of these species revealed the formation of polymeric bimetallic frames. Compound **2** consists of 2D double layers containing molecular square units with alternate Ru and Ag corners (Figure 1 top; Ru ⋯ Ag edges 7.21–7.26 Å). Two of the pyrazine ligands of the original Ru building block act as terminal ligands, while the other two form bridges to two silver atoms (Ru–N in the range 2.06–2.09 Å; Ag–N 2.37–2.38 Å). The squares are joined together through chloride bridges, two per metal corner, that connect the octahedral Ru centers to the distorted tetrahedral Ag corners (Ru ⋯ Ag contacts 4.48–4.59 Å). The chloride bridges are asymmetric and markedly bent (mean Ru–Cl 2.40 Å, mean Ag–Cl 2.56 Å, and mean Ag-Cl-Ru 132°). The resulting 2D array is a double layer structure schematically shown in Figure 1 (center) and displays parallel channels running in the [010] direction, perpendicular to the Ru_2Ag_2 squares (see Figure 1 bottom), that contain half of the triflate anions. The network topology of this double honeycomb[14] layer (4^36^3) is, to our knowledge, unprecedented. The double layers stack in the [100] direction (with AAA... sequence) and exhibit strong π–π interlayer interactions involving pairs of dangling pyz ligands (distance 3.33 Å, offset 1.69 Å).[15] The interlayer regions contain the remaining triflate anions.

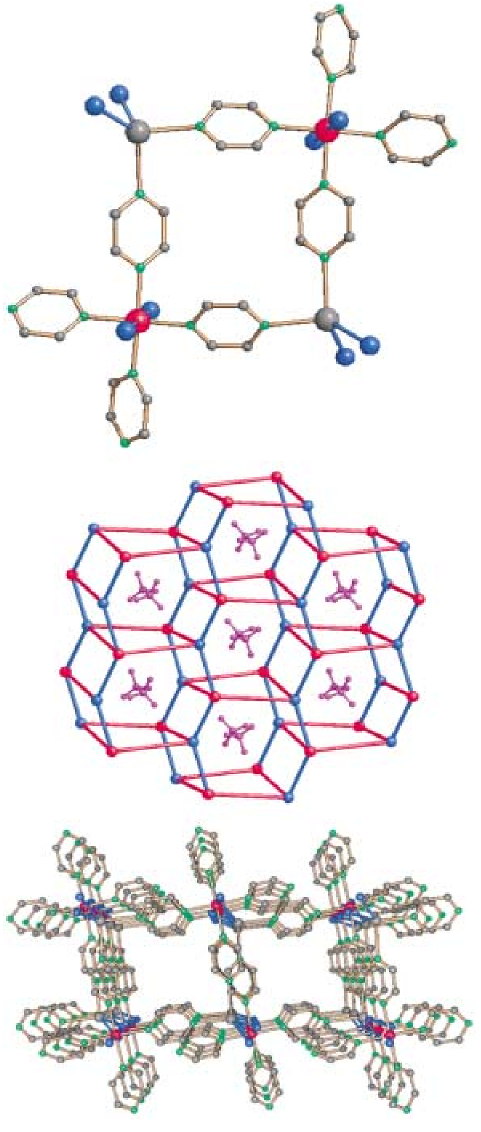


Figure 1. Structure of compound **2**: top: a square Ru_2Ag_2 unit; center: a schematic view of the double honeycomb layer, with the square units in red and the Cl bridges in blue; bottom: a lateral view of the layer showing the channels along the [010] direction.

The structure of compound **3** consists of a single 3D bimetallic network of alternating six-connected Ru centers and three-connected Ag centers in the ratio 1:2. The Ru complexes use in this case all the pyrazine ligands and the two chloride ions for bridging to six different silver atoms. The structure can be rationalized considering that the Ru building blocks form with the silver atoms simple 2D undulated layers of square meshes (Figure 2, top and center), with Ru-pyz-Ag-pyz-Ru edges (Ru···Ag contacts of 7.17 Å, Ru–N 2.05–2.08 Å, Ag–N 2.29–2.33 Å), similar to those expected (see **I** in Scheme 1). However, these layers are not isolated but interconnected through Ru-Cl-Ag bridges (Ru···Ag 4.44 Å) and superimposed to give the overall 3D network schematically illustrated in Figure 2, bottom. The coordination geometry at the silver atoms is distorted tetrahedral, involving two pyrazine ligands, one bridging chloride, and a terminal O-bonded triflate ligand. As in **2** the chloride bridges are asymmetric and bent (mean Ru–Cl 2.40 Å, mean Ag–Cl 2.51 Å, and Ag-Cl-Ru 134°). The topology of this network, based on six- and three-connected nodes in the ratio 1:2, is the same of the prototypical rutile,[12, 14] with Ru in the place of Ti and Ag in the place of O (see Figure 3, bottom left). Few other examples of coordination networks with this topology have been previously reported.[16] The channels along [101] (Figure 3, top) contain solvated molecules of TCE and butanol (that are lost on heating the bulk samples above 120 °C). It is like that the templating effect of these guest solvents can also prevent interpenetration. Note that the void spaces in the framework, evaluated without the solvated molecules, represent about the 30 % of the cell volume.

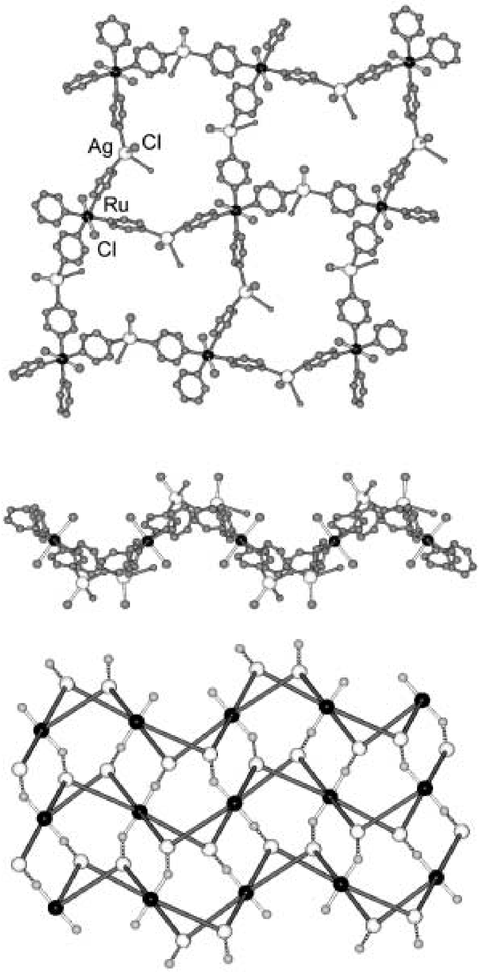


Figure 2. Two views, perpendicular (top) and lateral (center), of the undulated layers of Ru_4Ag_4 meshes contained in the 3D structure of compound **3**. The linkage of these layers (dashed) operated by the Cl bridges is also schematically shown (bottom).

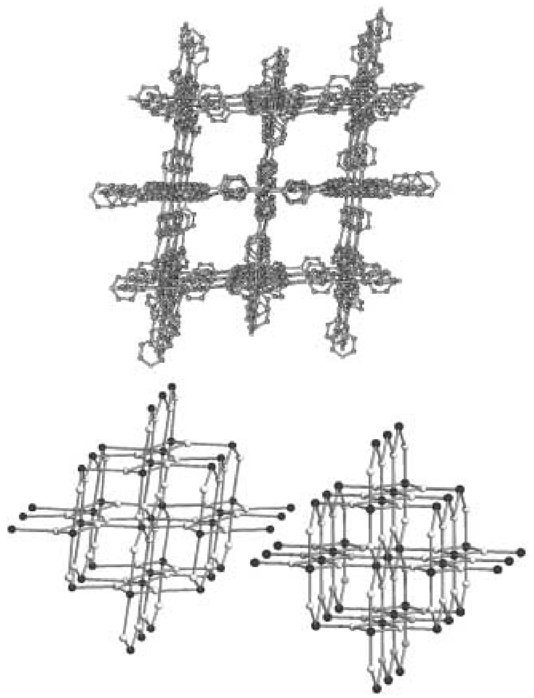


Figure 3. The 3D network in **3** down the [101] direction (top), and its schematic view (bottom left) compared with the structure of rutile (bottom right).

A systematic investigation of the role of the solvents in driving the formation of **2** or **3** has been carried out. Binary combinations of the solvents TCE, *n*-butanol, methanol and CH_2Cl_2 were used for the syntheses of **2** (Ru/Ag = 1/1) and **3** (Ru/Ag = 1/2). The nature of the synthesised bulk products was recognized by superimposing their XRPD spectra with the patterns calculated using the atomic positions of single crystal. It was pointed out that methanol and TCE are essential in driving the formation of the 2D (**2**) and 3D (**3**) species, respectively. In particular it was also observed that solid samples of **3** left in methanol are transformed into **2** after a few hours.

Slow diffusion of $AgNO_3$ dissolved in MeCN into a solution of **1** in CH_2Cl_2 (molar ratio ca. 4:1) produces red crystals of another species, (**4**), that, in spite of the fact that its stoichiometry is similar to that of **2**, shows a quite different structure.[13] This species contains a 3D network with alternate six-connected Ru and Ag octahedral centers. We can describe the structure as comprising 2D layers like **II** in Scheme 1 (Ru···Ag 7.27 Å), that are superimposed with a translation of [½ ½ *z*] (in an *ABAB* stacking sequence) in such a way that the Ru-bonded chlorides can form bridges to the silver atoms of the two adjacent layers (Ru···Ag 5.28 Å, Figure 4, top). Though both metals display octahedral enviroments, these are significantly different (Ru–N 2.06 versus Ag–N 2.40 Å; Ru–Cl 2.40 versus Ag–Cl 2.88 Å). All the bridges (Ru-pyz-

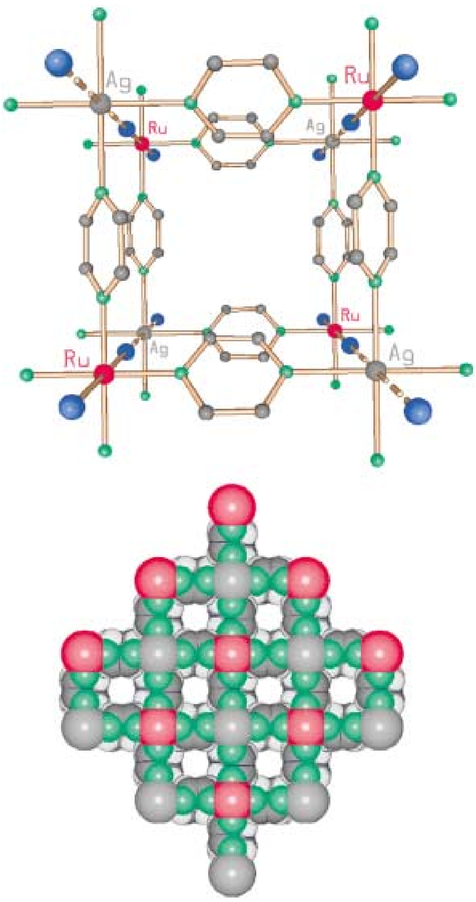


Figure 4. Structure of compound **4**: top: a single cage; bottom: the sphere-packing view of the network down the tetragonal axis.

Ag and Ru-Cl-Ag) in these species (**2**–**4**) are asymmetric, with longer distances to the silver atoms, but the asymmetry of the Ru-Cl-Ag (exactly linear) bridges in **4** is particularly pronounced (also taking into account the increased coordination number of Ag). The Ag–Cl interactions are rather weak and highly ionic in nature (see, for example, the Ag–Cl value of 2.77 Å in AgCl). The octahedral coordination for silver is unusual but we have already described a similar situation in $[Ag(pyz)_3]SbF_6$ that contains an "octahedral" network with the α-polonium topology.[17] Because of the alternation of the two metal atoms in **4** a more proper reference lattice, rather than α-polonium, is NaCl. The centers of the cells (of dimensions 7.27 × 7.27 × 5.28 Å, free internal volume of about 53 $Å^3$) are all occupied by statistically distributed nitrate anions with half occupancy. A view of the packing in **4**, showing the channels along the tetragonal axis is given in Figure 4, bottom. It is worth noting that the framework of **4** has the same composition as that of **2**. This "network isomerism" is clearly related to the different dimensions of the counterions. While the nitrate anions can be accomodated in the cells of **4** the bulkier triflate anions cannot occupy such cavities, thus determining the different framework topology of **2**, where much larger cells (of dimensions ca. 7.2 × 7.3 × 8.4 Å, free internal volume of ca. 122 $Å^3$) are present (see Figure 1, center), each containing a triflate anion with full occupancy. We have also obtained the $[RuCl_2(pyz)_4Ag]BF_4$ species, though only as polycrystalline samples. The BF_4^- ions, that are only sligthly bulkier than the nitrates, can still be accomodated inside the smaller cells, as evidenced by the XRPD pattern that is almost the same as that of **4**.

In conclusion, the results here described show that **1** is a useful and stable building block for the construction of networks that exhibit some predictable structural features. In these silver species also the two *trans*-chlorides of the Ru complex are involved in the networking process, but this can be prevented by using other types of metal-based centers. Investigations are in progress on other bimetallic frames based on **1**, with potential electronic properties, and on architectures assembled by joining these building blocks through hydrogen-bond bridges.

Experimental Section

1: A brown solution of pyrazine (1280 mg, 16.0 mmol) and $[RuCl_2(dmso)_4]$ (200 mg, 0.413 mmol) in toluene (20 mL) was refluxed for 3.5 h to give a brown precipitate. This was filtered off, washed with toluene, and dried in vacuo for 2 h. Yield: 190 mg; 90%. M.p. 165–170 °C; elemental analysis calcd (%) for $C_{16}H_{18}Cl_2N_8ORu$: C 37.6, H 3.56, N 22.0, Ru 19.8; found: C 37.1, H 3.50, N 21.5, Ru 19.7.

2: A solution of $AgSO_3CF_3$ (7.50 mg, 0.0290 mmol) in MeOH (9.5 mL) was added dropwise to a red-brown solution of **1** (13.9 mg, 0.0270 mmol) in CH_2Cl_2 (14 mL). After 45 min a precipitate was collected and filtered off. This crude amorphous solid was treated with MeOH (15 mL) under magnetic stirring for 45 min, then filtered off, washed with further MeOH, and dried in vacuo for 3 h, to obtain a microcrystalline brown powder of **2**. Yield: 16 mg, 79%. Elemental analysis calcd (%) for $C_{17}H_{16}AgCl_2F_3N_8O_3RuS$: C 27.2, H 2.15, N 14.9, Ru 13.5, Ag 14.4; found: C 27.3, H 2.70, N 13.6, Ru 13.3, Ag 13.9; IR (KBr): $\tilde{\nu} = 1261$, 1035 $\nu(SO_3)$, 1583 ν(ring), 809, 630 cm^{-1} δ(CH); UV/Vis spectroscopy of a solid sample: $\lambda_{max} \approx 400$ nm, shoulders at 480 and 620 nm. TGA measurements show a weight loss of 22% between 120 and 280 °C, probably due to the loss of two pyrazine molecules (21.4%). A second higher weight loss (about 50%) is observed in the range 310–570 °C corresponding to the complete decomposition of the polymer to give a residue of metallic ruthenium and silver. Dark red crystals were obtained by slow diffusion of a solution of $AgSO_3CF_3$ in MeOH (6.5 mL, 2.8×10^{-3} M) into a brown solution of $[RuCl_2(pyz)_4]$ in CH_2Cl_2 (2 mL, 1.8×10^{-3} M).

3: A solution of $AgSO_3CF_3$ (21.1 mg, 0.0820 mmol) in n-$CH_3(CH_2)_3OH$ (14 mL) was added dropwise to a brown-red solution of **1** (21.0 mg, 0.0410 mmol) in TCE (18.6 mL). The brown-red microcrystalline product was filtered off after 1 h, washed with n-butanol, and dried in vacuo for 3 h. Yield: 44.7 mg, 90%. Elemental analysis calcd (%) for $C_{22}H_{23}Ag_2Cl_6F_6N_8O_{6.5}RuS_2$: C 21.8, H 1.91, N 9.25, Ru 8.34, Ag 17.8; found: C 21.1, H 1.90, N 9.50, Ru 7.70, Ag 18.9; IR (KBr): $\tilde{\nu} = 1261$, 1034 $\nu(SO_3)$, 1585 ν(ring), 810, 638 cm^{-1} δ(CH). UV/Vis spectroscopy of a solid sample: $\lambda_{max} = 380$ nm, shoulders at 500 and 600 nm. TGA measurements confirm the presence of the solvents in the lattice; two weight losses between 120 and 235 °C (calcd (found) [%]: 23.4 (21.0)) due to the losses of ½ n-butanol, 1 tetrachloroethane, and 1 pyrazine per formula unit, and a successive strong weight loss in the broad range 235–600 °C leading to the complete decomposition of the polymer to give a metallic residue (ca. 27%) of ruthenium and silver. Brown-red crystals were obtained by slow diffusion of a solution of $AgSO_3CF_3$ in n-$CH_3(CH_2)_3OH$ (5.5 mL, 5.8×10^{-3} M) into a brown solution of $[RuCl_2(pyz)_4]$ in TCE (4 mL, 1.9×10^{-3} M). An XRPD spectrum of the massive product **3** fit the profile derived from the crystal structure.

4: A solution of $AgNO_3$ (38.4 mg, 0.230 mmol) in MeCN (10 mL) was added under magnetic stirring to a red-brown solution of **1** (30.4 mg, 0.0590 mmol) in CH_2Cl_2 (25 mL). The microcrystalline product was completely precipitated within 30 min, then filtered off, washed with MeCN, and dried in vacuo for 3 h. Yield: 36 mg, 92%. Elemental analysis calcd (%) for $C_{16}H_{16}AgCl_2N_9O_3Ru$: C 29.0, H 2.44, N 19.0, Ru 15.3, Ag 16.3; found: C 28.7, H 2.30, N 19.0, Ru 15.5, Ag 15.6; IR (KBr): $\tilde{\nu} = 1357$ $\nu(NO_3)$, 1583 ν(ring C), 811, 635 cm^{-1} δ(CH). An XPS survey analysis shows peaks of $Ru_{3p3/2}$, Ag_{3d}, N_{1s}, Cl_{2p} (respectively at the binding energy (BE) values of 461.5, 367.2, 399.2, and 197.1 eV) and elemental molar ratios respectively equal to 1.0:1.07:7.63:2.10, that fit with the experimental elemental analysis. TGA measurements show a weight loss of about 33 % in the range 130 – 270 °C due to the loss of three pyrazine molecules, followed by a two-step demolition (range 270 – 600 °C) leading to the metals (ca. 32 %). An XRPD spectrum of the massive product **4** was found to be identical to a simulated profile achieved from the single-crystal structure. Red crystals were obtained by slow diffusion of a solution of $AgNO_3$ in MeCN (3.5 mL, 7.1×10^{-3} M) into a brown solution of $[RuCl_2(pyz)_4]$ in TCE (3 mL, 1.9×10^{-3} M), by using pure MeCN (1.5 mL) as a spacer between the two solutions.

Received: December 27, 2001 [Z18436]

---

[1] a) B. F. Hoskins, R. Robson, *J. Am. Chem. Soc.* **1990**, *112*, 1546; b) R. Robson, B. F. Abrahams, S. R. Batten, R. W. Gable, B. F. Hoskins, J. Liu, *Supramolecular Architecture*, American Chemical Society, New York, **1992**, chap. 19; c) C. L. Bowes, G. A. Ozin, *Adv. Mater.* **1996**, *8*, 13; d) M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2001** *34*, 319; e) M. Munakata, L. P. Wu, T. Kuroda-Sowa, *Adv. Inorg. Chem.* **1999** *46*, 173; f) A. J. Blake, N. R. Champness, P. Hubberstey, W. S. Li, M. A. Withersby M. Schröder, *Coord. Chem. Rev.* **1999**, *183*, 117; g) P. J. Hagrman, D. Hagrman, J. Zubieta, *Angew. Chem.* **1999**, *111*, 2798; *Angew. Chem. Int. Ed.* **1999**, *38*, 2638; h) B. Moulton, M. J. Zaworotko *Chem. Rev.* **2001**, *101*, 1629.

[2] See, for example: S. Leininger, B. Olenyuk P. J. Stang, *Chem. Rev.* **2000**, *100*, 853; M. Fujita, *Acc. Chem. Res.* **1999**, *32*, 53; M. Fujita, K. Umemoto, M. Yoshizawa, N. Fujita, T. Kusukawa, K. Biradha, *Chem. Commun.* **2001**, 509.

[3] a) M. Fujita, J. Yazaki K. Ogura, *J. Am. Chem. Soc.* **1990**, *112*, 5645; b) M. Fujita K. Ogura, *Coord. Chem. Rev.* **1996**, *148*, 249; c) M. Fujita, O. Sasaki, T. Mitsuhashi, T. Fujita, J. Yazaki, K. Yamaguchi K. Ogura, *Chem. Commun.* **1996**, 1535.

[4] L. Carlucci, G. Ciani, A. Gramaccioli, D. M. Proserpio S. Rizzato, *CrystEngComm* **2000**, 29.

[5] L. Carlucci, G. Ciani, D. M. Proserpio S. Rizzato, *Chem. Commun.* **2001**, 1198.

[6] B. F. Abrahams, B. F. Hoskins, D. M. Michail R. Robson, *Nature* **1994**, *369*, 727.

[7] C. V. K. Sharma, G. A. Broker, J. G. Huddleston, J. W. Baldwin, R. M. Metzger R. D. Rogers, *J. Am. Chem. Soc.* **1999**, *121*, 1137.

[8] a) A. Kamiyama, T. Noguchi, T. Kajiwara, T. Ito, *Angew. Chem.* **2000**, *112*, 3260; *Angew. Chem. Int. Ed.* **2000**, *39*, 3130. b) A series of interesting polymers based on M(2-pyrazinecarboxylate)$_2$ building blocks has been recently reported: Y. B. Dong, M. D. Smith, H. C. zur Loye, *Inorg. Chem.* **2000**, *39*, 1943; Y. B. Dong, M. D. Smith, H. C. zur Loye, *Angew. Chem. Int. Ed.* **2000**, *112*, 4441; *Angew. Chem. Int. Ed.* **2000**, *39*, 4271; Y. B. Dong, M. D. Smith, H. C. zur Loye, *Solid State Sci.* **2000**, *2*, 335; Y. B. Dong, M. D. Smith, H. C. zur Loye, *Solid State Sci.* **2000**, *2*, 861; D. M. Ciurtin, M. D. Smith, H. C. zur Loye, *Chem. Commun.* **2002**, 74.

[9] R. W. Gable, B. F. Hoskins R. Robson, *J. Chem. Soc. Chem. Commun.* **1990**, 762.

[10] See, for example: T. Soma, T. Iwamoto, *Angew. Chem.* **1994**, *106*, 1746; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1665; B. F. Hoskins, R. Robson, N. V. Y. Scarlett, *Angew. Chem.* **1995**, *107*, 1317; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1203.

[11] I. Goldberg, *Chem. Eur. J.* **2000**, *6*, 3863.

[12] a) M. Schindler, F. C. Hawthorne, W. H. Baur, *Acta Crystallogr. Sect. B* **1999**, *55*, 811; b) M. O'Keeffe, M. Eddaoudi, Hailian Li, T. Reineke, O. M. Yaghi, *J. Solid State Chem.* **2000**, *152*, 3.

[13] Crystal data for **2**, $C_{17}H_{16}AgCl_2F_3N_8RuS$: monoclinic, space group $P2/c$ (no. 13), $a = 16.7527(12)$, $b = 8.4254(6)$, $c = 17.0204(13)$ Å, $\beta = 97.417(3)^\circ$, $V = 2382.3(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.089$ Mg m^{-3}, final *R1* value 0.0662 for 3138 independent reflections ($I > 2\sigma(I)$). Crystal data for **3**, $C_{22}H_{23}Ag_2Cl_6F_6N_8O_{6.5}RuS$: monoclinic, space group $P2_1/c$ (no. 14), $a = 18.837(2)$, $b = 15.021(2)$, $c = 14.950(2)$ Å, $\beta = 109.520(10)^\circ$, $V = 3987.0(9)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.018$ Mg m^{-3}, final *R1* value 0.0655 for 3337 independent reflections ($I > 2\sigma(I)$). Crystal data for **4**, $C_{16}H_{16}AgCl_2N_9O_3Ru$: tetragonal, space group $P4/nnc$ (no. 126), $a = b = 10.2793(4)$, $c = 10.5587(5)$ Å, $V = 1115.67(8)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.971$ Mg m^{-3}, final *R1* value 0.0406 for 574 independent reflections ($I > 2\sigma(I)$). The data collections were performed at room temperature for **2** and **3** and at 193 K for **4** on a Bruker SMART CCD area detector diffractometer, by using $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), by the ω-scan method, within the limits $1 < \theta < 25^\circ$ for **2**, $1 < \theta < 23^\circ$ for **3**, and $1 < \theta < 30^\circ$ for **4**. Empirical absorption corrections (SADABS) were applied. The structures were solved by direct methods (SIR97) and refined by full-matrix least-squares on F^2 (SHELX-97). Anisotropic thermal factors were assigned to all the non-hydrogen atoms but to the chlatrate *n*-butanol molecules in **3** and the nitrate anion in **4**. Disordered triflate anions were found in **2** and a suitable 50 % – 50 % double model was refined. A similar treatment was applied to the disordered chlatrate *n*-butanol molecule in **3**. The nitrate anions in **4** are statistically distributed on all the *c* Wyckoff positions with half occupancy. All the diagrams were generated by using the SCHAKAL 97 program. CCDC-175850 (**2**), CCDC-175851 (**3**), and CCDC-175852 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

[14] M. O'Keeffe, B. G. Hyde, *Crystal Structures I. Patterns and Symmetry*, Mineralogical Society of America, Washington, DC, **1996**.

[15] For a discussion of the π – π interactions see: C. Janiak, *J. Chem. Soc. Dalton Trans.* **2000**, 3885.

[16] P. Jensen, D. J. Price, S. R. Batten, B. Moubaraki K. S. Murray, *Chem. Eur. J.* **2000**, *6*, 3186, and references therein.

[17] L. Carlucci, G. Ciani, D. M. Proserpio, A. Sironi, *Angew. Chem.* **1995**, *107*, 2037; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1895.

Synthesis of Metal Nanoparticles by Using Polyoxometalates as Photocatalysts and Stabilizers**

Aristidis Troupis,* Anastasia Hiskia, and
Elias Papaconstantinou*

Formation of colloidal metal nanoparticles is a topic of great interest from a fundamental and practical point of view.[1–4] Metal nanoparticles have been obtained by thermal,[3, 5] photochemical,[6] radiolytic,[7] electrochemical,[8] or sonochemical methods,[9] by using various reagents.

Polyoxometalates (POMs) are well-defined metal – oxygen cluster anions.[10, 11] Their redox chemistry is characterized by

---

[*] A. Troupis, Dr. E. Papaconstantinou, Dr. A. Hiskia
Institute of Physical Chemistry
NCSR Demokritos
153 10 Athens (Greece)
Fax: (+30) 16511766
E-mail: atroup@chem.demokritos.gr, epapac@mail.demokritos.gr

A. Troupis
Chemical Engineering Department
National Technical University
157 80 Athens (Greece)

[**] We thank the Ministry of Development, General Secretariat of Research and Technology of Greece, for supporting part of this work. We also thank Dr. A. Travlos for help with the TEM images.