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Synthesis and Characterization of a Novel Heteroditopic Macrocyclic System – Monometallic Nickel(II) and Uranyl Complexes and Their Corresponding Heterobimetallic Carbonylrhodium(I) Complexes

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A novel heteroditopic macrocyclic ligand system for selective coordination of two different transition metal ions has been obtained in the form of monometallic salen complexes of Ni^{II} (LNi, **1**) and uranyl (LUO_2, **2**). The system is characterized by the presence of a dianionic, tetradentate salen donor system (N_2O_2) derived from *cis*-1,2-diaminocyclohexane and of a neutral, tridentate 2,6-bis(alkylthiomethyl)pyridine group (NS_2). The two binding sites are connected by two oxyethyl chains. The synthetic procedure involves the coupling of the disodium salt of 2,6-bis(mercaptomethyl)pyridine with two equivalents of 3-(2-bromoethoxy)-2-(2-propenyloxy)benzaldehyde. Removal of the protecting allyl groups from the reaction product (**I**) by palladium catalysis yields the ligand synthon 2,6-bis[2-(3-formyl-2-hydroxyphenyl)oxyethyl]thiomethylpyridine (**II**). The monometallic macrocyclic complexes **1** and **2**, obtained by metal-templated synthesis from *cis*-1,2-diaminocyclohexane, ligson **II**, and the corresponding Ni^{II} or uranyl acetate salts, respectively, in the presence of barium bis(trifluoroacetate), have been fully characterized by spectroscopic techniques in solution and by X-ray diffraction analyses in the solid state. Both complexes react readily at room temperature with $[Rh(CO)_2Cl]_2$ in methanol to form the bimetallic cationic carbonyl complexes $[LNi^{II}Rh(CO)]PF_6$ (**3**) and $[LUO_2Rh(CO)]PF_6$ (**4**) upon addition of NH_4PF_6. Two conformers of complex **3** are observed in solution by IR and NMR spectroscopy, in a 5:1 ratio in [D_2]dichloromethane, which exhibit a fluxional behavior and are shown to interconvert above room temperature in [D_3]acetonitrile. The carbonylrhodium group in the bimetallic systems reacts further with methyl iodide in dichloromethane solution to form oxidative-addition products.

Introduction

Compartmental ligands characterized by at least two different binding sites are interesting synthetic targets in the field of macrocyclic chemistry[1] as heterobimetallic macrocyclic complexes can be derived from such structures and used as appropriate models in heterogeneous or homogeneous catalysis, in which cooperative effects may arise from the vicinity of two metal centers.[2] Most dinucleating macrocycles available to date contain either one ligand type incorporated into a crown ether ring,[1a,1c,3,4] or the same donor set replicated within the macrocycle,[1a,3,5] which limits, but does not exclude, selectivity toward coordination of different transition-metal ions.[6] Although heteroditopic macrocyclic frames containing nonequivalent ring cavities are a significant advantage in this respect,[7] the introduction of different binding sites implies more elaborate synthetic approaches than those used in the preparation of systems with higher symmetry.[5c,7a,7b,7e,8] Various types of heterobimetallic macrocyclic systems have been reported.[1,5c,9]

We have planned the synthesis of a heterobifunctional macrocyclic structure bearing different donor sites. The choice of the binding units has fallen on systems widely used in catalysis and in coordination chemistry, namely the dianionic tetradentate (N_2O_2) salen-type ligand and the neutral tridentate (NS_2) 2,6-bis(alkylthiomethyl)pyridine system. The classic salen [*N*,*N′*-ethylenebis(salicylideneaminato)] metal complexes and related derivatives[5a–5c,10] are nowadays finding significant applications, most notably in host–guest chemistry,[1a,8,11] in asymmetric synthesis,[12] and in supramolecular and polymer catalysis.[13] The tridentate, neutral NS_2 ligands form complexes with different transition-metal ions[14] and have been used in the preparation of homo- and heterobimetallic macrocyclic structures, including those containing rhodium(I).[15] Square planar rhodium(I) complexes are of special interest in homogeneous catalysis with regard to oxidative addition and carbonylation processes.[16]

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The combination of a hard and a soft metal center has driven the design and synthesis of binucleating systems.[17] In the case of metal carbonyl complexes, the proximity of the two metal atoms may activate a carbon monoxide group by interaction of the electrophilic metal center with the oxygen of CO.[18] In this context, we have selected a carbonylrhodium(I) group for coordination to the bis(mercaptomethyl)pyridine ligand and a uranyl or a nickel(II) metal center for the salen binding unit. The electrophilic character of the uranyl system has been well documented, especially its ability to coordinate organic carbonyl groups, such as that of urea, in its planar fifth coordination site,[19] or to act as an electrophilic catalyst for Michael additions[13a] and acyl-transfer reactions.[20] Detection of an intramolecular interaction of the $(NS_2)Rh–CO$ group with crown-ether-complexed alkaline metal ions has been attempted.[15b]

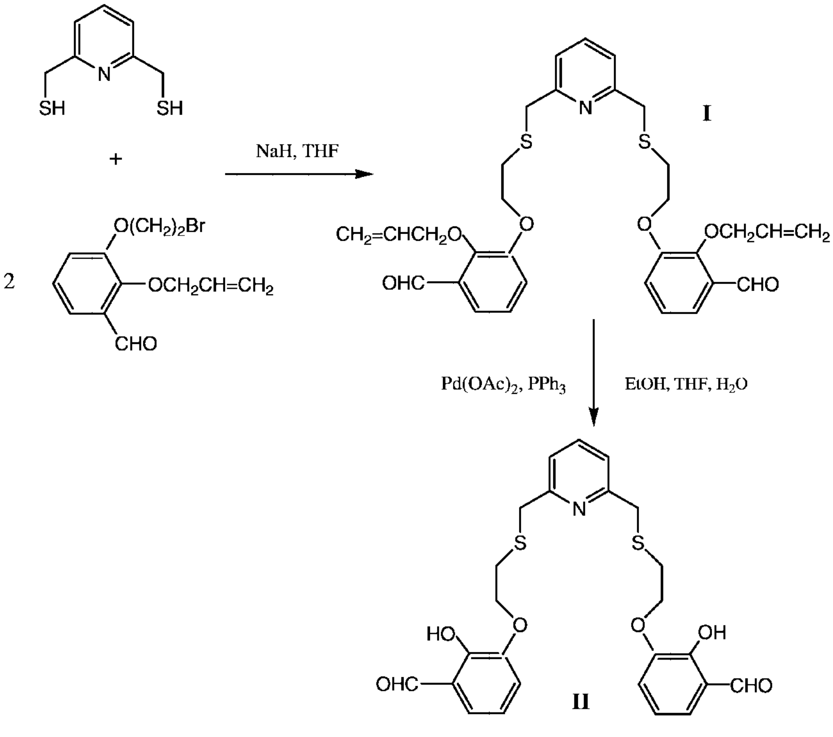
Results and Discussion

Synthesis of Monometallic Macrocyclic Complexes

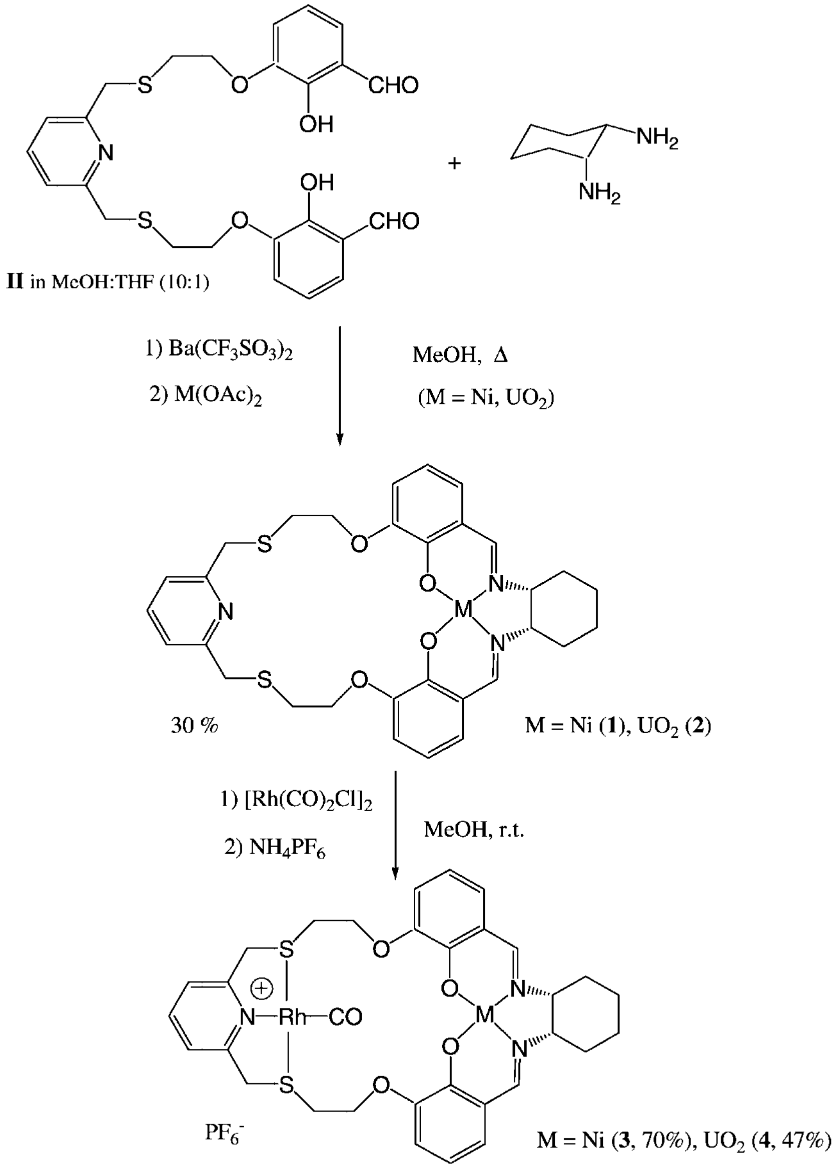
The synthetic strategy followed for the preparation of the target structure was directed by the fact that salen N_2O_2 type complexes form monometallic macrocyclic systems when a precursor molecular chain appropriately functionalized at both ends undergoes a metal-templated Schiff-base ring-closure reaction in the presence of a diamine partner and the chosen metal ion.[4b] In order to ensure the further coordination within the ring of a second metal ion, an NS_2 donor set was incorporated into the molecular chain. Therefore the synthesis of the ligand synthon **II**, which bears two terminal formyl-2-hydroxyaryl groups, was devised (Scheme 1). Following the preparation of monometallic macrocyclic complexes of Ni^{II} and UO_2, derived from **II** and *cis*-1,2-diaminocyclohexane, the reaction with $[Rh(CO)_2Cl]_2$ afforded bimetallic Ni^{II}/Rh^{I} and UO_2/Rh^{I} species (Scheme 2). The nickel and uranyl ions were selected for the preparation of the bimetallic carbonylrhodium(I) complexes due to their different electronic and coordinative properties – uranyl is oxophilic whereas nickel(II) is not.

The synthesis of the precursor for the metal-templated ring-closure involves the coupling of the disodium salt of 2,6-bis(mercaptomethyl)pyridine[21] with 3-(2-bromoethoxy)-2-(2-propenyloxy)benzaldehyde,[22] in tetrahydrofuran, to give the allyl protected bis-formyl compound **I** (yield > 50%, Scheme 1). The allyl groups of **I** are then removed by palladium catalysis, following a method described in the literature,[20] to give ligand **II** (yield > 60%), which contains the NS_2 donor set, the oxyethyl spacers, and the formyl-2-hydroxyaryl sub-units. Compounds **I** and **II** were purified by column chromatography and characterized by ^1H NMR, ^{13}C NMR, and FT-IR spectroscopy, ESI mass spectrometry, and elemental analysis. The chemical shifts of the hydrogen atoms of the aryl rings in compound **II** were identified by a NOESY experiment, which shows correlations between the OCH_2 triplet at $\delta = 4.17$ ppm and the doublet of doublets at $\delta = 6.93$ ppm, due to the aryl 4-H *ortho* to the oxyethyl chain, as well as between the formyl H atoms at $\delta = 10.08$ ppm and the doublet of doublets at $\delta = 7.20$ ppm, due to the aryl 6-H.

The synthesis of the macrocyclic structures was performed by treatment of ligson **II** with *cis*-1,2-diaminocyclohexane, in the presence of $Ba(CF_3SO_3)_2$ as template, followed by transmetalation in situ with the desired metal ace-



Scheme 1. Synthesis of the macrocyclic dialdehyde precursors **I** and **II**.



Scheme 2. Template synthesis of monometallic nickel(II) (**1**) and uranyl (**2**) macrocyclic complexes and subsequent formation of heterobimetallic nickel(II)–rhodium(I) (**3**) and uranylrhodium(I) (**4**) complexes.

tate $M(OAc)_2$ ($M = Ni, UO_2$; Scheme 2). Due to the poor solubility of **II**, which is a sticky red oil, in alcoholic solvents, the compound was added to the reaction mixture as a solution in methanol/tetrahydrofuran. The cyclization process involving the dialdehyde, the diamine, and the metal ion entails the formation of a metal–salen structure and affords the desired monometallic macrocyclic complexes **1** and **2**. Both complexes were isolated from their respective reaction mixtures as pure products by column chromatography with yields of around 30%.

The presence of Ba^{2+} as a template cation has been found to be beneficial in cyclization reactions involving a diamine and a precursor containing two formyl-2-hydroxyaryl subunits linked by a polyether chain, affording the corresponding uranyl macrocyclic complexes with yields in the range 35–50% by transmetalation.[19,23] The same template has also been used successfully in the preparation of dissymmetric azamacrocyclic ligands.[7e] However, in the present case, the yields of complexes **1** and **2** were only slightly lower upon performing the reactions in the absence of the barium salt. This fact, along with the relatively low yields of the macrocyclization reactions, may be due to the lower binding ability of the hybrid thioether chain of ligand **II** toward the barium ion with respect to a polyether chain.

Complexes **1** and **2** were characterized by FT-IR, ^1H NMR, and ^{13}C NMR spectroscopy (see Experimental Section), ESI mass spectrometry, elemental analysis, and single-crystal X-ray diffraction analyses. In the ^1H NMR spectrum of complex **1** ([D$_2$]dichloromethane), the hydrogens of the pyridine ring (py) appear as one triplet at $\delta = 7.65$ ppm (4-H) and one doublet at $\delta = 7.26$ ppm (3,5-H), while the arene protons appear as two close doublets at $\delta = 6.79$ and 6.75 ppm, due to 4,6-H, and one apparent triplet at $\delta = 6.45$ ppm, due to 5-H, thus confirming the presence of the salen and of the pyridine moieties in the expected ratio. The protons of the linking chains are also clearly identifiable. The fluxional character of the cyclohexane ring (cy) is indicated by the broad shape of the corresponding signals. One significant spectral feature is the presence of the imine CH=N protons, resulting from the coupling of the original aldehyde with the amine groups, at δ = 7.37 ppm in complex **1**. In the case of the uranyl complex **2**, the same protons appear at higher frequency, δ = 9.31 ppm, thereby indicating the stronger electron-withdrawing character of the uranyl group with respect to nickel(II). The 7-H protons of the cyclohexyl ring appear at δ = 3.45 and 4.66 ppm in complexes **1** and **2**, respectively.

In the ^{13}C NMR spectra, the imine carbon atoms are observed at δ = 159.2 and 167.2 ppm for **1** and **2**, respectively, while the infrared frequencies of the CH=N double bonds are virtually unaffected by the metal ion (1616 cm^{-1} in dichloromethane). The electropositive uranyl center affects the rest of the molecule as well, since the ^1H NMR chemical shifts of the methylene hydrogens of pyCH$_2$S and –SC*H*$_2$CH$_2$O– change from δ = 3.83 and 2.92 ppm in the nickel complex **1** to δ = 4.57–4.49 and 3.13 ppm, respectively, in complex **2**. The pyCH$_2$S hydrogen atoms exhibit AB patterns in the ^1H NMR spectra, characterized by $\Delta\nu$ = 7.1 Hz (**1**, CDCl$_3$) and 24 Hz (**2**, [D$_2$]dichloromethane), due to their diastereotopic character,[15] while the same hydrogens of complex **1** appear equivalent in [D$_2$]dichloromethane. In a NOESY spectrum of complex **1** in CDCl$_3$, the absorption at δ = 6.47 ppm exhibits a cross-peak with the imine proton at δ = 7.04 ppm and is therefore assigned to the 6-H protons, while the peaks at δ = 6.71 ppm, due to 4-H, correlate with the OCH$_2$ signal at δ = 4.08 ppm.

Symmetric macrocyclic ligands containing two tetradentate salen coordination sites formed from *trans*-1,2-diaminocyclohexane, and the corresponding mono- and dinuclear nickel(II) complexes, have been reported.[24] With *trans*-1,2-diaminocyclohexane as the Schiff base counterpart, dissymmetric macrocyclic structures incorporating one nickel(II) salen unit, which acts as an intramolecular redox catalyst, and a 1,4-bis(chloromethylarene) function have been prepared by a multistep synthesis.[25] A macrocyclic compound characterized by the presence of a salen–uranyl moiety opposite a pyridine group and linked by oxyethyl chains has been reported.[23] With 1,2-phenylenediamine or *cis*-1,2-diaminocyclohexane, symmetric, dinuclear salophen or salen UO$_2$ macrocyclic complexes have been described,[26] as well as macrocyclic ligands containing 2,6-bis(alkylthiomethyl) pyridine subunits and the corresponding [Rh(CO)][PF$_6$] dinuclear complexes.[15d] However, complexes **1** and **2** are the first macrocyclic structures in which a metal–salen unit is faced by an uncomplexed tridentate donor set that is suitable for further coordination of a second transition metal ion.

X-ray Crystal Structure of Macrocyclic Nickel(II) (1) and Uranyl (2) Complexes

Single crystals of compounds **1** and **2** suitable for X-ray diffraction analysis were obtained by the "liquid diffusion" method from solutions of dichloromethane layered with heptane and kept at room temperature for several days. Selected bond angles and distances are reported in Tables 1 and 2 for complexes **1** and **2**, respectively.

Table 1. Selected bond lengths [Å] and angles [°] for the macrocyclic nickel(II) complex **1**.

Ni1–O4	1.877(4)	C26–O29	1.359(8)
Ni1–N13	1.874(5)	C27–O28	1.319(8)
Ni1–N20	1.888(5)	O29–C30	1.452(7)
Ni1–O28	1.854(4)	C30–C31	1.483(10)
O4–C6	1.295(7)	C31–S32	1.825(7)
C12–N13	1.288(8)	S32–C33	1.787(9)
N13–C14	1.501(8)	C40–S41	1.867(7)
C19–N20	1.506(8)	S41–C42	1.802(7)
N20–C21	1.281(9)	C43–O44	1.456(10)
N20–Ni1–O28	94.4(2)	C12–N13–C14	122.63(5)
N13–Ni1–O28	177.0(2)	Ni1–N13–C14	111.2(4)
N13–Ni1–N20	86.5(2)	Ni1–N20–C19	111.0(4)
O4–Ni1–O28	85.6(2)	Ni1–N20–C21	124.97(5)
O4–Ni1–N20	176.8(2)	Ni1–O28–C27	128.2(4)
O4–Ni1–N13	93.7(2)	C31–S32–C33	98.6(3)
Ni1–O4–C6	126.2(4)	C40–S41–C42	103.3(3)
Ni1–N13–C12	126.0(5)		

Table 2. Selected bond lengths [Å] and angles [°] for the macrocyclic uranyl complex **2**.

U1–O2	1.572(16)	C12–N13	1.278(21)
U1–O3	1.806(13)	N20–C21	1.278(17)
U1–O4	2.226(8)	C27–O28	1.325(15)
U1–O5	2.499(7)	C31–S32	1.806(19)
U1–N13	2.546(13)	S32–C33	1.789(16)
U1–N20	2.569(9)	C40–S41	1.771(23)
U1–O28	2.193(8)	S41–C42	1.834(22)
O4–C6	1.293(14)		
O2–U1–O3	178.4(6)	O5–U1–N13	142.7(4)
O2–U1–O28	92.8(6)	O2–U1–N20	86.1(3)
O3–U1–O28	87.9(6)	O3–U1–N20	92.8(3)
O2–U1–O4	91.1(5)	O28–U1–N20	71.6(3)
O3–U1–O4	89.0(5)	O4–U1–N20	137.1(4)
O28–U1–O4	151.3(4)	O5–U1–N20	151.4(3)
O2–U1–O5	89.5(5)	N13–U1–N20	65.8(3)
O3–U1–O5	92.1(4)	C6–O4–U1	134.8(8)
O28–U1–O5	80.5(4)	C12–N13–U1	127.8(10)
O4–U1–O5	71.1(4)	C14–N13–U1	112.5(10)
O2–U1–N13	93.1(7)	C21–N20–U1	127.4(9)
O3–U1–N13	85.4(5)	C19–N20–U1	117.2(7)
O28–U1–N13	136.4(3)	C31–S32–C33	101.9(8)
O4–U1–N13	71.6(4)	C42–S41–C40	98.0(11)

Geometry of Complex 1

The nickel atom in the N$_2$O$_2$ ligand set shows a slightly deformed square-planar conformation (Figure 1) in which the bond angles around the metal range from 85.6(4)° for O(4)–Ni(1)–O(28) to 93.7(5)° for O(4)–Ni(1)–N(13); the maximum out-of-plane deformation of the five atoms of the coordination moiety is 0.06(1) Å. The average Ni–O and Ni–N(13) bond lengths [1.865 and 1.8481 Å, respectively] compare well with the values observed in other monomeric nickel macrocyclic[24] or open complexes[27] formed from *trans*-1,2-diaminocyclohexane. The complex as a whole lies approximately on a plane, with the exception of the cyclohexane and pyridine rings, which are almost orthogonal to the mean plane of the macrocycle and in a relative *transoid* fashion. In fact, the dihedral angles formed by the mean C(6)–C(11), C(22)–C(27), C(34)–N(39) (py) and C(14)–C(19) (cy) ring planes with that of the coordinative moiety are 7.7(2)°, 2.9(3)°, 82.3(2)°, and 114.5(2)°, respectively. While the chain from O(29) to C(33) is planar and forms a dihedral angle of 4.4(2)° with the coordinative mean plane, the C(42) and C(43) carbon atoms lie 1.02(2) and 1.25(2) Å, respectively, out of the plane formed by the three remaining atoms of the chain. The water molecule is not coordinated to nickel [O(1W)···Ni = 3.99(5) Å] but is hydrogen bonded within the cavity through the oxygen of one ethylene chain [H(1W)···O(29) = 1.94(5) Å] and one of the methylene hydrogens of the opposite one [O(1W)···H(43) = 2.47(5) Å]. Other short contacts are an intramolecular H(1W)···O(28) contact [2.52(2) Å] and an intermolecular $H(12)–O(1W)^{i}$ ($i = 1 - x, y - 1/2, 3/2 - z$) contact [2.49(2) Å]. The C(14)–N(13) distance of the cyclohexyl equatorial bond is 1.501 Å, while the C(19)–N(20) distance of the axial bond is 1.506(7) Å. The molecules are connected in the crystal by van der Waals contacts. We have not been able to find other crystal structures of salen–nickel complexes obtained from *cis*-1,2-diaminocyclohexane in the literature. The conformation of the bis(alkylthiomethyl)pyridine ligand set in complex **1** is characterized by the presence of the sulfur atoms oriented outwards with exocyclic lone pairs, with C–S–C bond angles of 98.6(3)° and 103.3(3)°. The C–S bond lengths lie between 1.825 and 1.867 Å, in the usual range observed in macrocyclic structures including this uncomplexed ligand.[15d]

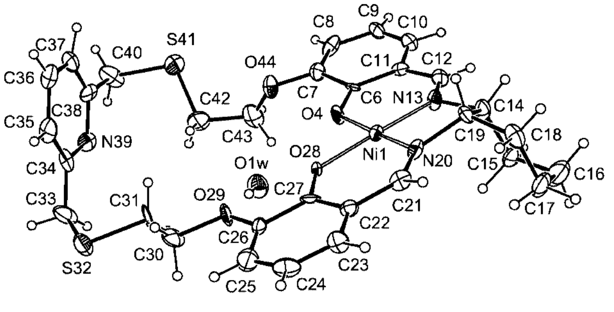


Figure 1. Molecular structure and atom-labelling scheme for the macrocyclic nickel(II) complex **1**.

Geometry of Complex 2

The uranyl moiety in complex **2** exhibits a pentagonal-bipyramidal coordination (Figure 2). Two imine nitrogen atoms [N(20), N(13)], two phenoxy oxygen atoms [O(4), O(28)], and one oxygen from a molecule of water (O5) form the pentagonal base, which is almost planar, while the two uranyl oxygen atoms occupy the apex positions, with out-of-plane deviations of 1.57 and 1.81 Å, respectively. The aromatic rings are planar and the cyclohexane ring adopts the typical chair conformation. This coordinative arrangement compares well with that found for a similar complex containing a coordinated molecule of urea in place of the water molecule.[19] The pyridine ring is oriented in such a way as to form a dihedral angle of 20.7(4)° with respect to the pentagonal planar base. When compared to the S-shaped conformation of the nickel complex **1**, complex **2** can be regarded as lying approximately on a plane including the pyridine and cyclohexyl rings. Since the two phenyl rings C(6)–C(11) and C(22)–C(27) of the salen moiety form a dihedral angle of 47.5(5)° with respect to each other, this part of the complex assumes, as a whole, a butterfly orientation. These two rings are tilted by 28.2(4)° and 19.7(4)°, respectively, with respect to the mean plane formed by the five atoms coordinated by uranium. This conformation, which is due to the relatively large ionic radius of uranium pushing apart the phenyl rings, is typical of uranyl–salen complexes and is similar to that observed in other monomeric macrocyclic uranyl systems[19,28] formed from *cis*-1,2-diaminocyclohexane. The C(14)–N(13) distance of the cyclohexyl axial bond is 1.588 Å, while the C(19)–N(20) distance of the equatorial bond is 1.464 Å. In the crystals the molecules are connected by intra- [H(18a)····N(13) = 2.53(3); O(5)····N(39) = 2.76(2); O(5)····H(40) = 2.90(1) Å], and intermolecular [$H(21A)···O(3)^{i}$ ($i = 1/2 - x, 1/2 - y, -z$) = 2.33(1); $H(30B)···O(5)^{ii}$ ($ii = -x, -y, -z$) = 2.58(1); H(40B) $···O(3)^{iii}$ ($iii = 1/2 - x, -1/2 - y, -z$) = 2.49(1) Å] van der Waals contacts involving, in particular, the water molecule. The uncomplexed bis(thiomethyl)pyridine group of the uranyl complex **2** has one exocyclic and one endocyclic sulfur atom and is characterized by C–S–C bond angles of 101.9(8)° and 98.0(9)°, respectively, and C–S bond lengths in the range 1.77–1.81 Å.

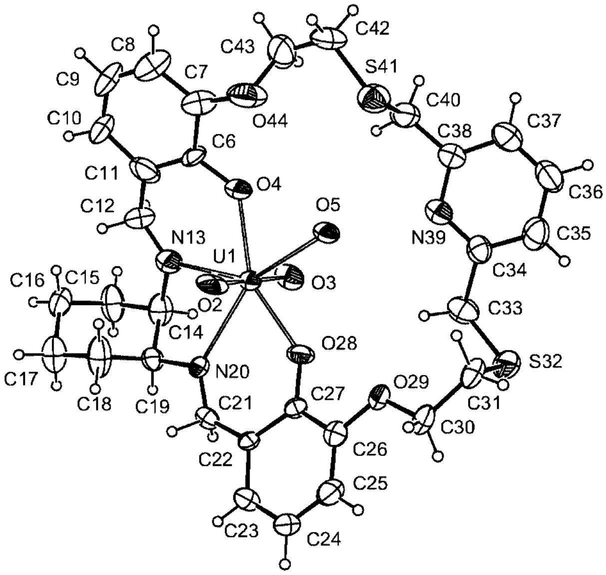


Figure 2. Molecular structure and atom-labelling scheme for the macrocyclic uranyl complex **2**.

Synthesis of Bimetallic Ni^{II}–Rh^{I} (3) and UO_2–Rh^{I} (4) Macrocyclic Complexes

A suspension of the monometallic macrocyclic nickel complex **1** in methanol was treated with a methanolic solution of $[RhCl(CO)_2]_2$ (Scheme 2). The mixing of the two compounds yielded a clear amber solution which, when analyzed after about 10 min, showed an intense IR band at 2009 cm^{-1} and the disappearance of the absorption bands (2088 and 2014 cm^{-1}) of the dicarbonylchlororhodium dimer. Addition of a methanolic solution of NH_4PF_6 caused the formation of an orange precipitate, which corresponds to the expected macrocyclic bimetallic Ni^{II}–Rh^{I} complex **3** (yield 70%). The monometallic uranyl complex **2** reacts with the dicarbonylchlororhodium dimer in a similar manner (yield 47%). Therefore, the macrocyclic metal–salen structure connected by a relatively short oxyethyl chain does not hinder the coordinative ability of the NS_2 ligand set. Both complexes **3** and **4** exhibit good solubility in organic solvents, especially in dichloromethane. This is due, presumably, to the presence of the cyclohexane ring, as a cyclohexyl group is known to increase the solubility of macrocyclic salen complexes with respect to analogous salophen derivatives.[19]

The bimetallic complexes were characterized by FT-IR, ^{1}H NMR, and ^{13}C NMR spectroscopy (**3**), FAB mass spectrometry, and elemental analyses. Complexation of the cationic carbonylrhodium group to the tridentate NS_2 ligand system is indicated by the presence of a strong split absorption at 2026–2017 cm^{-1} for complex **3** and of a band at 2020 cm^{-1} for complex **4**, both in dichloromethane. The ^{13}C NMR chemical shifts of the methylene carbons of pyCH$_2$S– and –S*C*H$_2$CH$_2$O– move from δ = 37.7 and 30.0 ppm in the monometallic nickel complex **1** to δ = 47.0 and 37.3 ppm, respectively, in the bimetallic nickel–rhodium complex **3**. The ^{13}C NMR spectrum obtained overnight from a [D$_2$]dichloromethane solution of the bimetallic uranylrhodium complex **4** is identical to that of the monometallic uranyl complex **2**, which suggests solvolysis of the (RhCO)$^+$ fragment. In analogy, decomposition by loss of CO was observed when monitoring a dichloromethane solution of complex **4** by IR spectroscopy over several hours.

In complex **3**, in addition to the two CO stretching bands in the IR spectrum, broad and split peaks appear in the ^{1}H NMR spectrum, indicating the existence of two isomers in an approximately 5:1 ratio in [D$_2$]dichloromethane. Split peaks are also observed in the ^{13}C NMR spectrum. In [D$_3$]acetonitrile solution, the three methylene groups of py–CH$_2$SCH$_2$CH$_2$O– are well separated in the region δ = 5.2–3.0 ppm (Figure 3). At room temperature, the multiplet due to the pyCH$_2$S– methylene groups is better resolved than the broad signals of the –SCH$_2$CH$_2$O– methylene chain, thus indicating rapid conformational equilibria along the carbon chain spacers and greater flexibility of the macrocyclic structure at these sites. The pyCH$_2$S– protons display a distorted AB system (δ_{Ha} = 4.80, δ_{Hb} = 4.73 ppm; $\Delta\nu$ = 22 Hz), corresponding to the coordination of the NS_2 donor set to the metal ion in a stable configuration. This pattern agrees well with that observed for the open complex [Rh(L)(CO)]PF$_6$ [L = 2,6-bis(benzylthiomethyl)pyridine] in [D$_2$]dichloromethane at –65 °C,[29b] and for the macrocyclic Rh(CO)$^+$ complexes in which a 2,6-bis(thiomethyl)pyridine subunit is linked by a polyether chain.[15c] In addition, the doubled absorptions of the –SCH$_2$CH$_2$O– groups confirm the presence of the two isomeric species observed in [D$_2$]dichloromethane. When the temperature is raised, interconversion of these isomers occurs with a coalescence temperature of 44 °C, at which both the chain methylene groups appear as single, broad peaks at δ = 3.50 and 4.55 ppm, respectively, while the multiplet of the pyCH$_2$S– protons is only slightly affected by this temperature change. The observed isomers may arise from the relative position of the metal ions with respect to the mean ligand plane – either opposite or on the same side – and interconvert by conformational changes of the oxyethylene chains, in analogy with what is observed for the symmetric bimetallic RhCO$^+$ macrocyclic complex incorporating two 2,6-bis(alkylthiomethyl)pyridine groups.[15c] Detailed variable-temperature NMR studies involving fluxional processes related to inversion at sulfur[30] and/or conformational equilibria in the macrocyclic frame have been described for mono- and bimetallic carbonylrhodium macrocyclic complexes.[15]

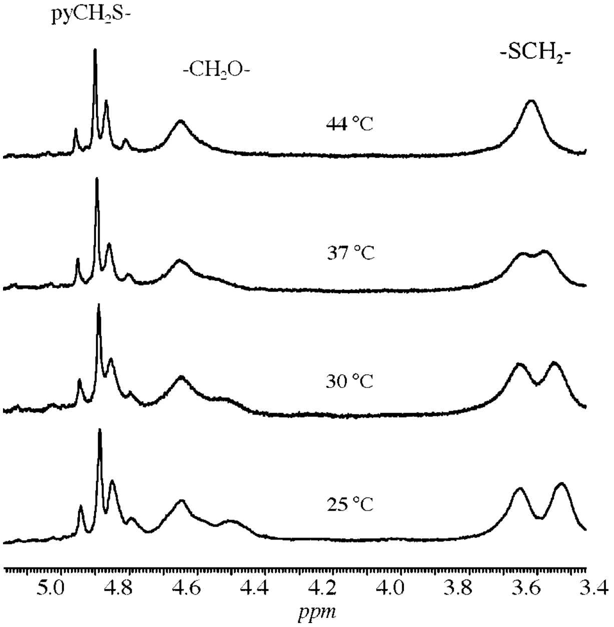


Figure 3. ^{1}H NMR spectra of the heterobimetallic Ni^{II}–Rh^{I} complex **3** in [D$_3$]acetonitrile at different temperatures, displaying the methylene groups of the pyCH$_2$SCH$_2$CH$_2$O moiety.

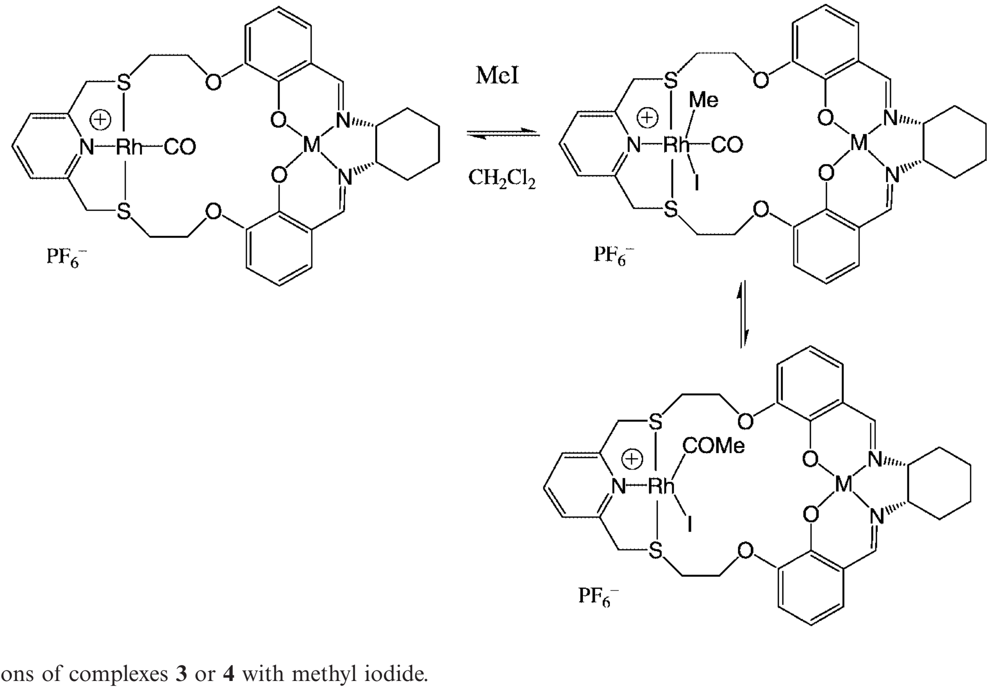
The CO stretching band of the complex [Rh(L)(CO)]PF$_6$, in which L is the “open” NS_2 ligand 2,6-bis(benzylthiomethyl)pyridine, is observed at 2019 cm^{-1} in dichloromethane.[29] A comparison with the macrocyclic systems reported here shows that the carbonylrhodium group is not perturbed by the adjacent metal centers. It is worth mentioning that during the synthesis of the bimetallic complexes the intermediate chloride species shows a carbonyl band at 2009 cm^{-1} for the nickel–rhodium complex **3** and 2015 cm^{-1} for the uranylrhodium complex **4**, in methanol, indicating a small effect of the salen–metal ion on the carbonylrhodium group. The dinuclear [2+2] symmetric carbonylrhodium macrocyclic complexes incorporating two 2,6-bis(alkylthiomethyl)pyridine sub-units linked by (CH$_2$)$_n$ chains (n = 5–10) exhibit CO stretching values in the range

1991–2009 cm^{-1} (KBr).[15d] The values of 2013 and 2012 cm^{-1} observed in the solid state (KBr) for the heterobimetallic complexes **3** and **4**, respectively, indicate a larger triple-bond character than in the homobimetallic systems. This suggests reduced electron density on rhodium, and hence reduced back-donation from rhodium to carbonyl, rather than an intramolecular CO···M contact in the heterobimetallic complex, which would have lowered the carbonyl stretching frequency.

We have recently described that the monometallic complex [Rh(L)(CO)]PF_6 reacts with MeI to give an intermediate methylrhodium(III) iodide species $[Rh(L)(CO)(Me)I]^+$ and an isolable acylrhodium(III) complex [Rh(L)(COMe)I]PF_6 as the result of consecutive oxidative addition/migratory insertion reactions.[29a] This was the first report of the organometallic reactivity of a carbonylrhodium complex of the neutral tridentate 2,6-bis(substituted thiomethyl) pyridine system. The product of oxidative addition is observed as a relatively stable intermediate that accumulates in solution and exhibits a strong infrared band at 2106 cm^{-1} (acetonitrile). We therefore tested the reactivity of both complexes **3** and **4** toward methyl iodide (3.5 M) in solution in dichloromethane (Scheme 3). In the case of the nickel–rhodium complex **3**, the reaction solution, when stirred for 5 h at 40 °C, gave an abundant red precipitate, which, analyzed in [D$_3$]acetonitrile, exhibits a strong carbonyl band at 2128 cm^{-1} due to the methylrhodium species, thus indicating the conversion of complex **3** into the product of oxidative addition of methyl iodide. In the case of the macrocyclic uranylrhodium complex **4**, the solution was stirred for 6 h at room temperature in order to minimize the spontaneous loss of CO. After removal of excess MeI and solvent, the spectrum showed the presence of starting material (2001 cm^{-1}), the oxidative-addition intermediate (2116 cm^{-1}), and the migratory-insertion product at 1676 cm^{-1}. Due to the smaller absorptivity of the acyl moiety with respect to the parent terminal Rh^I and Rh^{III} complexes, it can be deduced that the acyl product is more abundant than both the substrate and the methylrhodium(III) intermediate. The presence of the acyl derivative from the bimetallic UO_2/Rh^I complex suggests an easier migratory-insertion reaction than in the corresponding nickel complex. It appears that the IR frequencies of the carbonyl group in the $[Rh(CO)(Me)I]^+$ moiety are affected by the different environments in the two heterobimetallic complexes and in the open system.

Conclusions

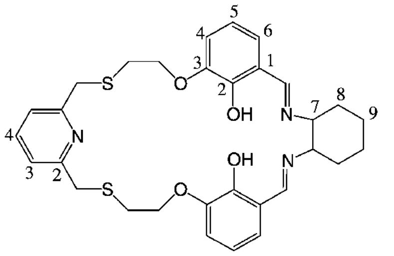
The synthesis of a novel macrocyclic ligand system containing a neutral, tridentate NS_2 donor set and a tetradentate, dianionic N_2O_2 unity has been described, in particular the isolation and structural characterization of the corresponding monometallic salen complexes of Ni^{II} and of UO_2 obtained from *cis*-1,2-diaminocyclohexane. These are the first examples of macrocycles in which a different uncoordinated ligand set (NS_2) faces the salen–metal group. Both monometallic compounds react with $[RhCl(CO)_2]_2$ to yield heterobimetallic, cationic complexes characterized by the presence of the $[(NS_2)RhCO]^+$ fragment. This synthetic method allows the sequential and selective coordination of two different metal ions onto a dissymmetric ligand frame using conventional procedures. The uranyl group enhances the lability of the CO ligand with respect to nickel(II). In fact, the UO_2–Rh^I complex decomposes slowly by loss of CO and solvolysis of the $Rh(CO)^+$ fragment. The Ni^{II}–Rh^I complex, which is more stable, exists in solution as two conformational isomers. The $[Rh–CO]^+$ fragment of both bimetallic complexes undergoes oxidative addition of MeI.



Scheme 3. Reactions of complexes **3** or **4** with methyl iodide.

Experimental Section

General Methods: Reactions involving air- and moisture-sensitive compounds were carried out under nitrogen using standard Schlenk line techniques. Tetrahydrofuran was distilled from Na/K alloy, acetonitrile from phosphorus pentoxide, and methanol from magnesium turnings. ^{1}H, ^{13}C, and 2-D NOESY NMR spectra were obtained with a Bruker AM-300 spectrometer. Chemical shifts are reported in ppm relative to tetramethylsilane with (for ^{1}H NMR) chloroform (δ = 7.24 ppm) or dichloromethane (δ = 5.32 ppm) or (for ^{13}C NMR) $CDCl_3$ (δ = 77.0 ppm), [D$_2$]dichloromethane (δ = 53.1 ppm) or [D$_3$]acetonitrile (δ = 118.2 ppm) as internal standards. IR spectra were recorded for KBr pellets or in 0.1-mm CaF_2 solution cells with a FT-IR Nicolet 510 instrument using the Omnic 4 software. ESI mass spectra were recorded with a Fisons Instruments VG-Platform Benchtop LC-MS (positive ions). FAB mass spectra were obtained with *m*-nitrobenzyl alcohol as matrix on a VG-Quattro Instrument of the University of Tor Vergata, Roma. Elemental analyses were performed by the Servizio di Microanalisi of the Department of Chemistry, Università La Sapienza, Roma. The compounds 3-(2-bromoethoxy)-2-(2-propenyloxy)benzaldehyde[22] and 2,6-bis(mercaptomethyl)pyridine[21,29a] were prepared according to literature procedures. Commercial $[RhCl(CO)_2]_2$ was purified by sublimation before use. Silica gel 60 was used for preparative column chromatography, unless stated otherwise. Other chemicals were used as supplied commercially.



2,6-Bis{[2-[3-formyl-2-(propenyloxy)phenyl]oxyethyl]thiomethyl}pyridine (I): Sodium hydride (80% dispersion in mineral oil; 438 mg, 14.6 mmol) was introduced into a 250-mL, three necked flask and washed three times with dry hexane under nitrogen. Tetrahydrofuran (50 mL) and a tetrahydrofuran solution of 2,6-bis(mercaptomethyl)pyridine (1.24 g, 7.3 mmol) were introduced by cannula, and the mixture was stirred for 15 min. 3-(2-Bromoethoxy)-2-(2-propenyloxy)benzaldehyde (4.13 g, 14.5 mmol) was added dropwise to the resulting solution. After 12 h at reflux, the reaction mixture was poured into water and chloroform, and extracted with chloroform (3 × 50 mL). The combined organic layers were washed with 0.5 M NaOH (3 × 30 mL), twice with water, then dried with sodium sulfate. After filtration, evaporation of the solvent under vacuum afforded 3.9 g of crude product, which appeared in a TLC analysis (silica/chloroform) as the most intense spot with a retention factor of 0.11–012, preceded and followed by weaker spots. Purification by column chromatography with chloroform as eluent gave pure **I** as a yellow, sticky oil in 54% yield. ^{1}H NMR ($CDCl_3$): δ = 10.38 (s, 2 H, CHO), 7.60 (t, J = 7.7 Hz, 1 H, py 4-H), 7.38 (pseudo-t, J = 4.7 Hz, 2 H, aryl 5-H), 7.23 (d, J = 7.7 Hz, 2 H, py 3,5-H), 7.05 (pseudo-d, J = 4.7 Hz, 4 H, aryl 4,6-H), 6.08–5.94 (m, 2 H, =CH), 5.34–5.18 (m, 4 H, =CH_2), 4.65–4.62 (m, 4 H, OCH_2), 4.11 (t, J = 6.7 Hz, 4 H, $OC\mathit{H}_2CH_2S$), 3.85 (s, 4 H, pyCH_2S), 2.92 (t, J = 6.5 Hz, 4 H, $OCH_2C\mathit{H}_2S$) ppm. ^{13}C NMR ($CDCl_3$): δ = 190.17 (CHO), 158.06 (py C-2), 151.72, 151.20 (Ar C-2, C-3), 137.49 (py C-4), 133.03 (CH=), 130.06 (Ar C-1), 123.94, 121.24, 119.15, 118.82 (py C-3 and Ar C-4, C-5, C-6), 119.34 (=CH_2), 75.07 ($O\mathit{C}H_2CH=CH_2$), 67.98 (OCH_2), 38.01 (pyCH_2S), 30.41 ($OCH_2\mathit{C}H_2S$) ppm. FT-IR (dichloromethane): $\tilde{\nu}_{max}$ = 1687 cm^{-1} (C=O). ESI (acetonitrile): m/z = 580.7 [M + 1]$^+$, 602.4 [M + Na]$^+$, 618.8 [M + K]$^+$. $C_{31}H_{33}NO_6S_2\cdot H_2O$ (597.74): calcd. C 62.29, H 5.90, N 2.34, S 10.73; found C 62.62, H 5.64, N 2.64, S 10.82.

2,6-Bis{[2-(3-formyl-2-hydroxyphenyl)oxyethyl]thiomethyl}pyridine (II): Formic acid (0.28 mL, 7.5 mmol), triethylamine (freshly distilled from over sodium; 1.0 mL, 7.5 mmol), triphenylphosphane (49 mg, 0.19 mmol), palladium acetate (10 mg, 0.046 mmol), and compound **I** were dissolved in 11 mL of ethanol/water/tetrahydrofuran (5:1:5). The yellow solution was kept under reflux for 2 h, then the solvents were removed in vacuo. The residue was extracted with water (50 mL) and chloroform (3 × 50 mL). The combined extracts were washed with water (3 × 50 mL) and dried with sodium sulfate. Evaporation in vacuo gave 667 mg of crude product as a sticky, red oil. Purification of this material was carried out by column chromatography using a mixture of petroleum ether and acetone (2:1, v/v) to afford pure **II** in 60% yield. Compound **II** appears as the most intense spot in a TLC analysis from hexane/acetone (1:1) with R_f = 0.56. When the reaction was performed under more dilute conditions, the deallylation process was slower and incomplete. On the other hand, longer reaction times produced decomposition of the expected product. ^{1}H NMR ($CDCl_3$): δ = 11.14 (s, 2 H, OH), 10.08 (s, 2 H, CHO), 7.71 (t, J = 7.7 Hz, 1 H, py 4-H), 7.41 (d, J = 8.0 Hz, 2 H, py 3,5-H), 7.20 (dd, ^3J = 7.7, ^4J = 1.5 Hz, 2 H, Ar 6-H), 6.93 (dd, ^3J = 7.8, ^4J = 1.3 Hz, 2 H, Ar 4 H), 6.82 (pseudo-t, J = 7.9 Hz, 2 H, Ar 5-H), 4.17 (t, J = 6.2 Hz, 4 H, $OC\mathit{H}_2CH_2S$), 4.01 (s, 4 H, pyCH_2S), 2.76 (t, J = 6.1 Hz, 4 H, $OCH_2C\mathit{H}_2S$) ppm. ^{13}C NMR ($CDCl_3$): δ = 194.50 (CHO), 157.93 (py C-2), 151.56 (Ar C-3), 146.99 (Ar C-2), 137.99 (py C-4), 132.08 (Ar C-1), 128.53 (Ar C-5), 123.31, 122.21, 119.22 (py C-3 and Ar C-4, C-6), 69.99 (OCH_2), 37.39 (SCH_2py), 29.14 ($OCH_2\mathit{C}H_2S$) ppm. FT-IR (tetrahydrofuran): $\tilde{\nu}_{max}$ = 1658 cm^{-1} (C=O). ESI (acetonitrile): m/z = 500.4 [M + 1]$^+$, 522.3 [M + Na]$^+$. $C_{25}H_{25}NO_6S_2\cdot H_2O$ (517.62): calcd. C 58.01, H 5.26, N 2.71, S 12.39; found C 58.56, H 5.60, N 2.45, S 11.15.

Nickel(II) Complex 1: Separate solutions of *cis*-1,2-diaminocyclohexane (0.115 mL, 0.96 mmol) in 70 mL of methanol and dialdehyde **II** (475 mg, 0.95 mmol) in 70 mL of methanol/tetrahydrofuran were added simultaneously, within 1 h, to a refluxing solution of $Ba(CF_3SO_3)_2$ (430 mg, 0.99 mmol) in 250 mL of dry methanol. The solution of **II** was prepared by dissolving compound **II** in 10 mL of tetrahydrofuran, followed by addition of methanol up to the desired volume. After 30 min, $Ni(CH_3COO)_2\cdot 4H_2O$ (249 mg, 1.0 mmol) was added. The solution turned brown and was kept at reflux for 50 min, then cooled to room temperature. The solvent was removed under vacuum, and the residue was extracted with dichloromethane. The organic solution was washed with saturated aqueous solutions of sodium sulfate (3 × 100 mL), sodium hydrogen carbonate (1 × 100 mL), and sodium chloride (1 × 100 mL), then dried with sodium sulfate. After filtration and removal of the solvent under vacuum, the crude product was separated into two equal portions, each of which was purified by column chromatography over alumina deactivated with 3% of water. Initial elution with dichloromethane separated two yellow bands of a material which was not identified. Continued elution with dichloromethane/methanol (at first 150:1, then 100:1) moved a long, brown band, which left the product as a red-brown solid (93 mg from the first portion of crude material and 90 mg from the second; combined yield 30%). ^{1}H NMR ([D$_2$]dichloromethane): δ = 7.65 (t, J = 8 Hz, 1 H, py 4-H), 7.37 (s, 2 H, CH=N); 7.26 (d, J = 8 Hz, 2 H, py 3,5-H), 6.79 (dd, ^3J = 8.2, ^4J = 1.5 Hz, 2 H, Ar 4-H), 6.75 (dd, ^3J = 7.6, ^4J = 1.5 Hz, 2 H, Ar 6-H), 6.45 (pseudo-t, J = 7.8 Hz, 2 H, Ar

5-H), 4.05 (t, J = 7.8 Hz, 4 H, –CH$_2$OAr), 3.83 (s, 4 H, pyCH$_2$S), 3.45 (br. s, 2 H, cy 7-H), 2.92 (d, J = 7.9 Hz, 4 H, –CH$_2$CH_2S), 2.29 (br. m, 2 H, cy 8-H), 1.93 (s, 2 H, H$_2$O), 1.69 (br. m, 2 H, cy 8-H), 1.41 (m, 4 H, cy 9-H) ppm. ^{1}H NMR (CDCl$_3$): δ = 7.61 (t, J = 7.5 Hz, 1 H, py 4-H); 7.25 (d, J = 8 Hz, 2 H, py 3,5-H), 7.04 (s, 2 H, ArCHN), 6.71 (d, J = 7.4 Hz, 2 H, Ar 4-H), 6.47 (d, J = 7.6 Hz, 2 H, Ar 6-H), 6.30 (pseudo-t, J = 7.7 Hz, 2 H, Ar 5-H), 4.08 (m, 4 H, –CH$_2$OAr), 3.84 and 3.81 (AB system: $\Delta\nu$ = 7.1 Hz, 4 H, pyCH$_2$S), 3.56 (br. s, 2 H, cy 7-H), 2.89 (m, 4 H, SCH_2CH$_2$O), 2.32 (s, 2 H, H$_2$O), 2.21 (br. m, 2 H, cy 8-H$_a$), 1.60 (br. m, 2 H, cy 8-H$_b$), 1.35 (br. m, 4 H, cy 9-H) ppm. ^{13}C NMR (CDCl$_3$): δ = 159.2 (CH=N), 158.6 (py C-2), 155.9, 149.1 (Ar C-2, C-3), 137.6 (py C-4), 125.4, 121.4, 120.8, 117.1, 113.5 (py C-3 and Ar C-1, C-4, C-5, C-6), 67.6 (CH$_2$OAr), 67.4 (br. s, cy C-7), 37.7 (pyCH$_2$S), 30.0 (CH$_2$S), 27.32 (C-8), 20.9 (C-9) ppm. ESI (acetonitrile): clusters centered at m/z = 635 [**1** + H$^+$], 657 [**1** + Na$^+$]. FT-IR (KBr): $\tilde{\nu}_{max}$ = 1614 cm^{-1} (vs, C=N), 1572, (py) 1543, 1470, 1446 (vs, Ar), 1322, 1229 (s),1085, 1002, 864, 739 (s). Analytically pure material was obtained by precipitation upon addition of pentane to a solution in dichloromethane. C$_{31}$H$_{33}$N$_3$NiO$_4$S$_2$·H$_2$O (652.45): calcd. C 57.07, H 5.41, N 6.44; found C 57.38, H 4.64, N 6.15.

Uranyl Complex 2: Separate solutions of *cis*-1,2-diaminocyclohexane (0.068 mL, 0.576 mmol) in 50 mL of methanol and dialdehyde **II** (288 mg, 0.576 mmol) in 50 mL of methanol/tetrahydrofuran were added simultaneously, within 1 h, to a refluxing solution of Ba(CF$_3$SO$_3$)$_2$ (251 mg, 0.576 mmol) in 200 mL of dry methanol. The solution of **II** was prepared by dissolving compound **II** in 5 mL of tetrahydrofuran, followed by addition of methanol up to the desired volume. After 30 min, UO$_2$(CH$_3$COO)$_2$·2H$_2$O (244 mg, 0.576 mmol) was added. The solution was kept at reflux for 30 min, then cooled to room temperature. The solvent was removed under vacuum, and the residue was extracted with dichloromethane. The organic solution was washed with saturated aqueous solutions of sodium sulfate (3 × 100 mL), sodium hydrogen carbonate (1 × 100 mL), and sodium chloride (1 × 100 mL), then dried with sodium sulfate. After filtration and removal of the solvent under vacuum, the crude product was purified by column chromatography. Elution was first performed using dichloromethane, which slowly separated a yellow band. Subsequent elution with dichloromethane/methanol (500:1) separated out a second yellow band from the top of the column. Neither of these materials was the expected product and they were not identified. A red band was eluted with dichloromethane/methanol (100:1), and collected as a red powder after removal of solvent. Pure uranyl macrocycle **2** was obtained by precipitation with hexane from a concentrated dichloromethane solution (140 mg, 29% yield). ^{1}H NMR ([D$_2$]dichloromethane): δ = 9.31 (s, 2 H, CH=N), 7.79 (t, J = 7.6 Hz, 1 H, py 4-H), 7.49 (d, J = 7.6 Hz, 2 H, py 3,5-H), 7.24 and 7.22 (two dd, ^3J = 6.5, ^4J = 1.4 Hz, 2 H + 2 H, Ar 4-H and 6-H), 6.70 (pseudo-t, J = 7.8 Hz, 2 H, Ar 5-H), 4.66 (br. m, 2 H, cy 7-H), 4.57 and 4.49 (AB system, $\Delta\nu$ = 24 Hz, 4 H, pyCH$_2$S), 4.48 (t, J = 5.1 Hz, 4 H, –CH$_2$OAr), 3.13 (t, J = 5.1 Hz, 4 H, –CH$_2$S), 2.44 (m, 2 H, cy 8-H), 1.99 (m, 2 H, cy 8-H), 1.75 (m, 4 H, cy 9-H) ppm. ^{13}C NMR ([D$_2$]-dichloromethane): δ = 167.2 (CH=N), 159.4 (py C-2), 157.5, 149.7 (Ar C-2, C-3), 138.48 (py C-4), 126.0, 123.3, 122.1, 116.8, 116.0 (py C-3 and Ar C-1, C-4, C-5, C-6), 71.14 (cy C-7), 69.76 (–CH$_2$OAr), 38.32 (pyCH$_2$S), 31.58 (CH$_2$S), 27.36 (C-8), 21.42 (C-9) ppm. ESI (methanol): positive, cluster centered at m/z = 847 [**2** + H$^+$]. FT-IR (KBr): $\tilde{\nu}_{max}$ = 1612 cm^{-1} (vs, C=N), 1594 (py), 1522, 1466, 1451, 1309, 1246, 1223, 1086, 898 (s, UO$_2$), 738. FT-IR (dichloromethane): $\tilde{\nu}_{max}$ = 1616 cm^{-1} (vs, C=N), 1597, 1575 (py), 1555, 1456 (vs). C$_{31}$H$_{33}$N$_3$O$_6$S$_2$U·2H$_2$O (881.80): calcd. C 42.22, H 4.23, N 4.77; found C 42.77, H 4.16, N 4.62.

Ni^{II}–Rh^{I} Complex 3: In a Schlenk tube, 52.1 mg (0.082 mmol) of the macrocyclic nickel complex **1** was suspended in 3 mL of dry methanol and stirred under argon at room temperature. [RhCl(CO)$_2$]$_2$ (16 mg, 0.041 mmol) dissolved in 2 mL of methanol was then added with a cannula from another Schlenk tube into the suspension of **3** to afford a clear, amber solution. An infrared analysis of the solution after 10 min showed the presence of an intense peak at 2009 cm^{-1}, and the absence of the 2088 and 2014 cm^{-1} bands of the dicarbonylchlororhodium dimer. Addition of a methanolic solution (2 mL) of NH$_4$PF$_6$ (85 mg) caused the formation of an orange solid, and the mixture was stirred for a few minutes. The solid was then allowed to deposit and the solvent was decanted off. The precipitate was washed twice with cold methanol and vacuum-dried to leave 42 mg of an orange powder. Addition of 0.5 mL of pentane to the reaction solution caused the precipitation of an additional 10 mg of solid. Both materials were characterized by intense infrared absorptions near 2020 cm^{-1} in dichloromethane solution. Overall yield 70%. The compound is moderately air-sensitive, as indicated by the slow decay of intensity of the carbonyl infrared band upon standing in air. ^{1}H NMR ([D$_2$]dichloromethane): δ = 7.98 (t, J = 7 Hz, 4-H py) and 7.86 (m due to the minor isomer, 1 H, py 4-H), 7.59 (d, J = 8 Hz, 2 H, py 3,5-H), 7.31 and 7.38 (2 × s due to the minor isomer, 2 H, CH=N), 6.83 (d, J = 7 Hz, 2 H, Ar 4-H), 6.68 (br. s, 2 H, Ar 6-H), 6.40 (br. s, 2 H, Ar 5-H), 4.72–4.50 (br. m, 8 H, pyCH$_2$S and –CH$_2$OAr), 3.47 and 3.68 (2 × m, due to the minor isomer, 4 H, CH$_2$S; 5:1 ratio), 3.22 (br. s, 2 H, cy C-7), 2.24, 1.76, 1.39 (br. m, 8 H, cy 8,9-H) ppm. ^{13}C NMR ([D$_3$]acetonitrile, peaks of the major isomer): δ = 161.8 (ArCHN), 161.4 (py C-2), 154.9, 147.8 (Ar C-2, C-3), 140.2 (py C-4), 127.5, 122.1, 121.9, 119.0, 115.3 (py C-3 and Ar C-1, C-4, C-5, C-6), 69.7 (br. s, cy C-7), 68.4 (–CH$_2$OAr), 47.0 (pyCH$_2$S), 37.3 (–CH$_2$S), 27.8 (C-8), 21.4 (C-9) ppm. FT-IR (dichloromethane): $\tilde{\nu}_{max}$ 2026, 2017 cm^{-1} (vs, CO), 1618 (s, C=N), 1606 (w, py), 1545, 1470, 1446. FT-IR (KBr): $\tilde{\nu}_{max}$ = 2013 cm^{-1} (CO), 1618 (C=N), 1544, 1444, 1321, 1230, 840, 741, 558. FAB: clusters centered at m/z =765.3 [**3** + H$^+$] and 737 [**3** + H$^+$ – CO]. C$_{32}$H$_{33}$F$_6$N$_3$NiO$_5$PRhS$_2$·3H$_2$O (964.36): calcd. C 39.85, H 4.08, N 4.36; found C 39.54, H 3.52, N 4.40.

UO$_2$–Rh^{I} Complex 4: The monometallic uranyl complex **2** (60.6 mg, 0.070 mmol) was suspended in 9 mL of methanol in a Schlenk tube and stirred at room temperature. A yellow solution of [RhCl(CO)$_2$]$_2$ (13.6 mg, 0.035 mmol) in 4 mL of methanol was then added with a cannula and the suspension changed into a clear red-orange solution. After 20 min, the infrared analysis of the solution showed an intense absorption at 2015 cm^{-1} and the absence of the bands due to the starting rhodium dimer. A methanolic solution (3 mL) of NH$_4$PF$_6$ (155 mg) was added to the reaction flask, causing the immediate formation of a red-brown powder. After stirring for a few minutes the precipitate was allowed to settle, then the solution was decanted off. The solid was washed twice with cold methanol and vacuum-dried to give 17 mg of a brown-red powder. A second crop precipitated out of the mother solution upon standing under argon for a few hours (15 mg). Both crops were characterized by an intense infrared absorption at 2015 cm^{-1} in dichloromethane. Yield: 42%. As in the case of complex **3**, this material is moderately air sensitive. FT-IR (dichloromethane): $\tilde{\nu}_{max}$ = 2020 cm^{-1} (s, CO), 1616 (vs, C=N), 1556, 1453; (KBr): $\tilde{\nu}_{max}$ = 2011 cm^{-1} (CO), 1614 (C=N), 1553, 1450, 1400, 1306, 1230, 1085, 997, 890 (UO$_2$), 844, 745, 558. FAB: clusters centered at m/z = 976.7 [**4**$^+$] and 949 [**4**$^+$ – CO]. C$_{32}$H$_{33}$F$_6$N$_3$O$_7$PRhS$_2$U (1121.7): calcd. C 34.27, H 2.97, N 3.75; found C 34.32, H 3.67, N 3.32.

Crystal Structure Determination of the Macrocyclic Nickel Complex 1: The data were collected on a Philips PW1100 diffractometer using Mo-K_α radiation (λ = 0.71069 Å), controlled by a local program.[31] The preliminary cell parameters were obtained from least-squares plots of the (θ,χ,φ) angular values of 25 reflections (θ range = 7.3–12.7°) accurately centered on the diffractometer. The intensity of one standard reflection, recorded for every 100, showed a decomposition of about 29%. The recorded data (θ range = 3–27°) were corrected for this decay, for polarization, and for Lorentz effects. The absorption correction was performed with the method of Walker and Stuart,[32] using a program written by Gluzinski.[33] The low quality of the employed crystal resulted in the low number of observed reflections. The structure was solved by direct methods with SIR97,[34] and refined full-matrix anisotropic least-squares methods with SHELX97.[35] Most of the H atoms were found in a difference Fourier map, and the remainder were put in their theoretical positions, refined by a few cycles with isotropic thermal parameters, and then blocked in the refined positions. The ORTEP drawings were produced with the ORTEP-3 program.[36]

Crystal Structure Determination of the Macrocyclic Uranyl Complex 2: The data were collected on a Bruker AXS Smart CCD diffractometer with Mo-K_α radiation (λ = 0.71069 Å) (θ range = 3–29°). Auto-indexing was performed with an algorithm operating on difference vectors derived from the input reflections. During the data collection the specimen decomposed by about 23%. Data reduction, absorption, and decomposition corrections, structure solution and refinement were all performed with the programs contained in SHELXTL-NT V5.1.[37] The small dimensions of the employed crystal and its low quality resulted in a small number of observed reflections. All the non-hydrogen atoms were refined anisotropically. While most of the hydrogen atoms were found in a difference Fourier map, the remainder ones were put in their geometrical positions, refined by a few cycles with isotropic thermal parameters, and then blocked in the refined positions. The hydrogen atoms of the water molecule were not localized. Experimental crystallographic information for both complexes **1** and **2** are reported in Table 3.

Table 3. Selected crystallographic details for complexes **1** and **2**.

	1	2
Formula	$C_{31}H_{33}N_3NiO_4S_2\cdot H_2O$	$C_{31}H_{33}N_3O_6S_2U\cdot H_2O$
Formula weight	652.45	863.79
Crystal color	amber	red
Crystal shape	prism	prism
Size [mm]	0.29 × 0.34 × 0.39	0.09 × 0.15 × 0.20
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$C2/c$
a [Å]	15.866(3)	23.788(2)
b [Å]	11.983(4)	13.353(1)
c [Å]	16.505(2)	21.737(2)
β [°]	106.98(4)	112.24(3)
Cell volume [Å^3]	3001.17	6390.91
$\mu_{\text{calcd.}}$ [cm^{-1}]	8.25	49.91
Temperature [K]	293(2)	293(2)
Z	4	8
h, k, l ranges	–20/19, 0/15, 0/21	–30/14, –15/16, –28/28
No. collected reflns.	7085	19496
No. indep. reflns.	6261	6843
R_{int}	0.08	0.14
No. reflns. obsd. [$I > 2\sigma(I)$]	1828	2730
Final R factor	0.067	0.058
Final R_w factor	0.147	0.132
GOF	0.69	0.78

CCDC-253882 (for **1**) and -253883 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): ^{1}H NMR, ^{13}C NMR, and FT-IR spectra of complexes **1**–**4**. FT-IR spectra of the products of oxidative addition of methyl iodide to complexes **3** and **4**.

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