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Addition of Mercury(II) Electrophiles to $[Ru_2(C_{10}H_8N_2)(CO)_4(P^iPr_3)_2]$ and Selective Insertion versus Addition in the Reactions of Mercury(II) Electrophiles with Trinuclear Ru_2Hg Clusters. X-ray Structures of $[Ru_2Hg(O_2CCF_3)_2(C_{10}H_8N_2)(CO)_4(P^iPr_3)_2]$ and $[Ru_2Hg_2Cl_4(C_{10}H_8N_2)(CO)_4(P^iPr_3)_2]\cdot CH_2Cl_2$ ($C_{10}H_{10}N_2$ = 1,8-Diaminonaphthalene)

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The ruthenium(I) complex $[Ru_2(C_{10}H_8N_2)(CO)_4(P^iPr_3)_2]$ (**1**) ($C_{10}H_{10}N_2$ = 1,8-diaminonaphthalene) reacts with 1 equiv of HgX_2 (X = Cl, Br, I, O_2CCH_3, O_2CPh, O_2CCH_2Cl, O_2CCF_3, SCN, ONC) to give the adducts $[(\mathbf{1})HgX_2]$, in which the Hg atoms are bonded to both Ru atoms of complex **1**. Correlations between the $^2J(^{31}P-^{199}Hg)$ coupling constants of their ^{31}P NMR spectra and the corresponding halogen electronegativities or acid pK_as have been observed. With the exception of $[(\mathbf{1})Hg(O_2CCF_3)_2]$, which does not react with any other mercury(II) salt, the compounds $[(\mathbf{1})HgX_2]$ react with HgX'_2 (X′ = Cl, Br, I, O_2CCH_3, O_2CPh, O_2CCH_2Cl) to give the insertion products $[(\mathbf{1})Hg(\mu\text{-}X')_2HgX_2]$ only when X′ is more electron-withdrawing than X; otherwise, the addition products $[(\mathbf{1})Hg(\mu\text{-}X)_2HgX'_2]$ are formed. All reactions of $[(\mathbf{1})HgX_2]$ with $Hg(O_2CCF_3)_2$ give the same substitution product $[(\mathbf{1})Hg(O_2CCF_3)_2]$. The molecular structures of $[(\mathbf{1})Hg(O_2CCF_3)_2]$ and $[(\mathbf{1})Hg(\mu\text{-}Cl)_2HgCl_2]$ have been confirmed by X-ray crystallography. $[(\mathbf{1})Hg(O_2CCF_3)_2]$: monoclinic, space group C_2/c, a = 23.730 (9) Å, b = 12.578 (4) Å, c = 14.511 (7) Å, β = 94.76 (5)°, Z = 4. $[(\mathbf{1})Hg(\mu\text{-}Cl)_2HgCl_2]\cdot CH_2Cl_2$: monoclinic, space group $P2_1/n$, a = 15.840 (7) Å, b = 12.694 (4) Å, c = 23.366 (2) Å, β = 105.74 (2)°, Z = 4.

Introduction

A recent study of the reactivity of the ruthenium(I) complex $[Ru_2(\mu\text{-}C_{10}H_8N_2)(CO)_4(P^iPr_3)_2]$ (**1**) ($C_{10}H_{10}N_2$ = 1,8-diaminonaphthalene) has revealed the presence of an electron-rich Ru–Ru bond which enables the complex to react with metallic electrophiles, such as $[AgPPh_3]^+$ or $[AuPPh_3]^+$, to give trinuclear derivatives.[1] Since the complex $[Ru_2(\mu\text{-}C_{10}H_8N_2)(CO)_6]$ does not react with metallic electrophiles,[2] it seems clear that the presence of triisopropylphosphine in complex **1** is the main reason responsible for the nucleophilic character of the Ru–Ru bond. It is also interesting to note that the doubly deprotonated 1,8-diaminonaphthalene ligand is able to hold two metal atoms very close together, as has been shown in the X-ray structures of $[Ru_2(\mu\text{-}C_{10}H_8N_2)(CO)_4(PPh_3)_2]$[3] (2.579 Å), $[Ru_2(\mu\text{-}C_{10}H_8N_2)(CO)_4\{P(OPh_3)\}_2]$[2] (2.571 Å), and $[Ru_2Ag(\mu\text{-}C_{10}H_8N_2)(CO)_4(P^iPr_3)_2(PPh_3)]^+$[1] (2.698 Å) and of some rhodium and iridium complexes.[4]

On the other hand, although the preparation of adducts between mercury compounds and complexes containing electron-rich metals has been described,[5] up to date, we only know one example of a simple addition of a mercury(II) salt to a metal–metal-bonded complex to give a product with a triangular metal arrangement: the reaction of $HgCl_2$ with $[Rh_2(C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}Ph_2PCH_2PPh_2)]$, which gives $[Rh_2HgCl_2(C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}Ph_2PCH_2PPh_2)]$;[6] in most other cases, the synthesis of compounds containing transition metal–mercury bonds involves the transformation of any of the original reagents, as occurs in the reactions of some mercury compounds with anionic complexes,[7] in the reactions of $XHgPh$[8] or $HgPh_2$[9] with hydrido complexes, or in the oxidative addition of a mercury halide to a metal complex.[10] In some cases, the reaction of metal complexes with mercury also affords mercury-containing derivatives.[11] The uptake of several equivalents of HgX_2 by neutral complexes has been described;[5,12] however, the presence of lattice HgX_2 and the formation of ionic species have been claimed as being responsible for the stability of such compounds.[12]

The present report concerns the reactivity of complex **1** with mercury(II) halides and carboxylates to give adducts which contain one or two Hg atoms. A small part of this work has been previously communicated.[13]

Experimental Section

General Data. Solvents were dried and distilled under nitrogen over sodium diphenylketyl (THF, diethyl ether) or calcium hydride (dichloromethane) prior to use. All reactions were carried out under nitrogen, using standard Schlenk techniques, although all products can be handled in air without appreciable decomposition. The complex $[Ru_2(\mu\text{-}C_{10}H_8N_2)(CO)_4(P^iPr_3)_2]$ (**1**) was prepared as described previously;[2] all other reagents were purchased and used as received. IR spectra were recorded on a Perkin-Elmer FT 1720-X spectrophotometer using 0.1-mm CaF_2 cells. NMR spectra were run on a Bruker AC-300 instrument. Microanalyses were obtained by the University of Oviedo Analytical Service. Single-crystal X-ray diffraction analyses were carried out on

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Table I. ^{31}P{^{1}H} NMR Data[a]

compound	δ, ppm	$J(^{31}P-^{199}Hg)$, Hz
[(**1**)HgCl$_2$] (**2**)	56.5	1118
[(**1**)HgBr$_2$] (**3**)	55.3	1087
[(**1**)HgI$_2$] (**4**)	52.7	1004
[(**1**)Hg(μ-Cl)$_2$HgCl$_2$] (**5**)	60.2	1168
[(**1**)Hg(μ-Br)$_2$HgBr$_2$] (**6**)	60.4	1123
[(**1**)Hg(μ-I)$_2$HgI$_2$] (**7**)	60.3	1002
[(**1**)Hg(μ-Cl)$_2$HgBr$_2$] (**8**)	60.3	1156
[(**1**)Hg(μ-Cl)$_2$HgI$_2$] (**9**)	60.1	1109
[(**1**)Hg(μ-Br)$_2$HgI$_2$] (**10**)	60.2	1076
[(**1**)Hg(O$_2$CCH$_3$)$_2$] (**11**)	54.9	1147
[(**1**)Hg(O$_2$CPh)$_2$] (**12**)	55.1	1178
[(**1**)Hg(O$_2$CCH$_2$Cl)$_2$] (**13**)	56.7	1195
[(**1**)Hg(O$_2$CCF$_3$)$_2$] (**14**)	58.1	1328
[(**1**)Hg(μ-O$_2$CCH$_3$)$_2$Hg(O$_2$CCH$_3$)$_2$] (**15**)	56.9	1162
[(**1**)Hg(μ-O$_2$CPh)$_2$Hg(O$_2$CPh)$_2$] (**16**)	59.2	1195
[(**1**)Hg(μ-O$_2$CCH$_2$Cl)$_2$Hg(O$_2$CCH$_2$Cl)$_2$] (**17**)	59.1	1242
[(**1**)Hg(μ-O$_2$CPh)$_2$Hg(O$_2$CCH$_3$)$_2$] (**18**)	59.4	1183
[(**1**)Hg(μ-O$_2$CCH$_2$Cl)$_2$Hg(O$_2$CCH$_3$)$_2$] (**19**)	58.7	1207
[(**1**)Hg(μ-O$_2$CCH$_3$)$_2$HgCl$_2$] (**20**)	59.8	1164
[(**1**)Hg(μ-O$_2$CCH$_2$Cl)$_2$HgCl$_2$] (**21**)	59.8	1198
[(**1**)Hg(μ-Cl)$_2$Hg(SCN)$_2$] (**22**)	60.7	1116
[(**1**)Hg(SCN)$_2$] (**23**)	58.7	1058
[(**1**)Hg(ONC)$_2$] (**24**)	56.3	1072

[a] Spectra recorded at 121.5 MHz in acetone-d_6; chemical shifts (δ) referred to external 85% H$_3$PO$_4$; all resonances are singlets with satellites.

an Enraf-Nonius CAD-4 diffractometer, using the graphite-monochromated Mo Kα radiation. All calculations were made on a MicroVAX 3400 computer at the University of Oviedo Computer Center.

Since the methods used to prepare the compounds were very similar, only typical procedures are described. All products were obtained in yields higher than 80%. ^{31}P{^{1}H} NMR data are reported in Table I, microanalyses (Table S-I), ^{1}H NMR (Table S-II), and IR (Table S-III) data are included in the Supplementary Material.

Preparation of [(1)HgCl$_2$] (2). Solid HgCl$_2$ (20 mg, 0.074 mmol) was added to a solution of complex **1** (58.5 mg, 0.074 mmol) in THF (5 mL), giving a pale yellow precipitate. After the mixture was stirred for 30 min, the solvent was removed under reduced pressure and the residue washed with diethyl ether (3 × 5 mL) to give complex **2** as a pale yellow solid (69 mg, 88%).

All compounds reported in this article containing one Hg atom were prepared by this procedure.

Preparation of [(1)Hg(μ-Cl)$_2$HgBr$_2$] (8). Solid HgCl$_2$ (15.2 mg, 0.056 mmol) was added to a solution of complex **1** (44.3 mg, 0.056 mmol) in THF (5 mL), giving a pale yellow precipitate. After the mixture was stirred for 30 min, solid HgBr$_2$ (20.2 mg, 0.056 mmol) was added to give a yellow solution. The solvent was removed under reduced pressure and the residue washed with diethyl ether (3 × 5 mL) to give complex **8** as a yellow solid (70 mg, 88%). The same compound was obtained when HgCl$_2$ was added to a suspension of [(**1**)HgBr$_2$] in THF.

All compounds reported in this article containing two Hg atoms were prepared by this procedure.

Reaction of [(1)HgCl$_2$] (2) with Hg(O$_2$CCF$_3$)$_2$. Solid Hg(O$_2$CCF$_3$)$_2$ (15 mg, 0.035 mmol) was added to a suspension of complex **2** (37.2 mg, 0.035 mmol) in THF (5 mL), giving a clear yellow solution. The solvent was removed under reduced pressure, and the residue washed with diethyl ether (3 × 5 mL) to give [(**1**)Hg(O$_2$CCF$_3$)$_2$] (**14**) as a yellow solid (38 mg, 89%).

Crystal Structures of Complexes 5·CH$_2$Cl$_2$ and 14. Yellow crystals of approximate dimensions 0.30 × 0.23 × 0.07 mm (**5**·CH$_2$Cl$_2$) and 0.40 × 0.23 × 0.20 mm (**14**), grown by layering diethyl ether on dichloromethane solutions of the complexes, were used for the X-ray analyses. Selected crystallographic data for both compounds are collected in Table II. Unit cell dimensions were determined from the angular settings of 25 reflections with $20° < \theta < 22°$ (**5**·CH$_2$Cl$_2$) and $15° < \theta < 17°$ (**14**). Space groups were determined from systematic absences and structure determinations: 13425 (**5**·CH$_2$Cl$_2$) and 4150 (**14**) reflections measured; *h,k,l* ranges −22,0,0 to 21,17,31 (**5**·CH$_2$Cl$_2$) and −28,0,0 to 28,14,17 (**14**); θ limits $0° < \theta < 30°$ (**5**·CH$_2$Cl$_2$) and $0° < \theta < 25°$ (**14**); ω–2θ scan technique. Intensity was checked by monitoring three standard reflections every 60 min. Empirical absorption corrections, using ψ scans,[14] were applied, μ = 78.75 cm^{-1} (**5**·CH$_2$Cl$_2$) and 43.71 cm^{-1} (**14**) (correction factors in the ranges 0.592–0.997 (**5**·CH$_2$Cl$_2$) and 0.95–1.00 (**14**)). Some double measured reflections were averaged, $R_{int} = \Sigma(I - \langle I \rangle)/\Sigma I = 0.038$ (**5**·CH$_2$Cl$_2$) and 0.040 (**14**), to give 13086 (**5**·CH$_2$Cl$_2$) and 3760 (**14**) unique reflections from which 4435 (**5**·CH$_2$Cl$_2$) and 2839 (**14**) were observed with $I > 3\sigma(I)$. Lorentz and polarization corrections were applied and data reduced to $|F_o|$ values.

Table II. Crystallographic Data

	[(**1**)Hg(O$_2$CCF$_3$)$_2$]	[(**1**)Hg(μ-Cl)$_2$HgCl$_2$]·CH$_2$Cl$_2$
chemical formula	C$_{36}$H$_{50}$F$_6$HgN$_2$O$_8$P$_2$Ru$_2$	C$_{32}$H$_{50}$Cl$_4$Hg$_2$N$_2$O$_4$P$_2$Ru$_2$·CH$_2$Cl$_2$
fw	1217.47	1418.77
cryst sys	monoclinic	monoclinic
space group	*C*2/*c* (No. 15)	*P*2$_1$/*n* (No. 14)
a, Å	23.730 (9)	15.840 (7)
b, Å	12.578 (4)	12.694 (4)
c, Å	14.511 (7)	23.366 (2)
β, deg	94.76 (5)	105.74 (2)
V, Å^3	4316 (3)	4522 (2)
Z	4	4
T, K	200	293
λ, Å	0.71073	0.71073
ρ_{calcd}, g cm^{-3}	1.87	2.08
μ, cm^{-1}	43.71	78.75
cor factors (min, max)	0.95, 1.00	0.592, 0.997
$R(F_o)$[a]	0.040	0.054
$R_w(F_o)$[b]	0.042	0.054

[a] $R(F_o) = \sum||F_o/k| - |F_c||[\sum|F_o/k|]^{-1}$. [b] $R_w(F_o) = \sum w^{1/2}||F_o/k| - |F_c||[\sum w^{1/2}|F_o/k|]^{-1}$.

Table III. Positional Parameters for Selected Atoms of [(**1**)Hg(O$_2$CCF$_3$)$_2$][a]

atom	*x*/*a*	*y*/*b*	*z*/*c*
Hg(1)	0.00000	0.36934 (4)	0.25000
Ru(1)	0.05404 (3)	0.56008 (5)	0.29740 (4)
P(1)	0.12849 (9)	0.6787 (2)	0.3576 (1)
N(1)	0.0212 (3)	0.6416 (5)	0.3248 (4)
C(1)	0.0601 (3)	0.4884 (7)	0.4114 (5)
C(2)	0.1093 (4)	0.4780 (7)	0.2448 (6)
C(3)	0.0858 (4)	0.2156 (7)	0.3192 (7)
C(4)	0.1355 (6)	0.140 (1)	0.334 (1)
O(1)	0.0593 (3)	0.4508 (5)	0.4833 (4)
O(2)	0.1423 (3)	0.4278 (5)	0.2106 (5)
O(3)	0.0672 (3)	0.2312 (6)	0.2388 (5)
O(4)	0.0666 (5)	0.2542 (8)	0.3866 (6)
F(1)	0.1444 (5)	0.085 (1)	0.262 (1)
F(2)	0.1807 (4)	0.186 (1)	0.354 (1)
F(3)	0.1271 (6)	0.070 (1)	0.395 (1)

[a] The primed atoms shown in Figure 3 are related to the unprimed ones by a C_2 axis.

The structures were solved by Patterson interpretation and refined by full-matrix least-squares techniques, first with isotropic and then with anisotropic thermal parameters in the last cycles for all the non-hydrogen atoms. Solution showed a C_2 axis through the Hg(1), C(9), and C(10) atoms of **14**. Most of the hydrogen atoms of both compounds were localized in difference Fourier syntheses. All the hydrogen atoms were refined isotropically, including the positional parameters of H(1), H(61), and H(121) of **5**·CH$_2$Cl$_2$ and H(1), H(6), H(7), and H(8) of **14**; the remaining ones were left riding on their parent atoms. Maximum shift over error ratios in the last full-matrix least-squares cycles were less than 0.5 (**5**·CH$_2$Cl$_2$) and 0.1 (**14**). The final difference Fourier maps showed no peaks higher than 1.87 e Å^{-3} (**5**·CH$_2$Cl$_2$) and 0.97 e Å^{-3} (**14**) nor deeper than −1.90 e Å^{-3} (**5**·CH$_2$Cl$_2$) and −1.06 e Å^{-3} (**14**), all of them close to the Hg atoms. The SHELX-76[15] and SHELX-86[16] systems of computer programs were used. No corrections for the presence of extinction were made. Atomic scattering factors were taken from ref 17. Final atomic coordinates for selected atoms are given in Tables III and IV.

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Table IV. Positional Parameters for Selected Atoms of $[(\mathbf{1})Hg(\mu\text{-}Cl)_2HgCl_2]\cdot CH_2Cl_2$

atom	*x/a*	*y/b*	*z/c*
Hg(1)	0.05520 (5)	0.22312 (7)	0.02511 (3)
Hg(2)	−0.04398 (8)	0.29201 (9)	0.14095 (4)
Ru(1)	0.00052 (8)	0.2156 (1)	−0.09736 (5)
Ru(2)	0.18089 (8)	0.2318 (1)	−0.03754 (5)
P(1)	−0.0980 (3)	0.2104 (3)	−0.1976 (2)
P(2)	0.3238 (3)	0.2415 (3)	−0.0573 (2)
Cl(1)	−0.0848 (3)	0.1353 (4)	0.0633 (2)
Cl(2)	0.1204 (3)	0.2533 (5)	0.1357 (2)
Cl(3)	−0.0615 (4)	0.4293 (4)	0.0664 (3)
Cl(4)	−0.0746 (7)	0.2715 (7)	0.2311 (3)
N(1)	0.0998 (9)	0.324 (1)	−0.1077 (6)
N(2)	0.1112 (8)	0.1247 (9)	−0.1049 (6)
C(31)	−0.079 (1)	0.313 (2)	−0.0807 (7)
C(32)	−0.0596 (9)	0.095 (2)	−0.0755 (8)
C(41)	0.227 (1)	0.130 (1)	0.0196 (8)
C(42)	0.213 (1)	0.344 (2)	0.0167 (8)
O(31)	−0.1263 (9)	0.378 (1)	−0.0711 (7)
O(32)	−0.0865 (9)	0.022 (1)	−0.0616 (6)
O(41)	0.2537 (9)	0.066 (1)	0.0547 (7)
O(42)	0.229 (1)	0.418 (1)	0.0479 (7)

Table V. Selected Bond Lengths (Å) and Angles (deg) in $[(\mathbf{1})Hg(O_2CCF_3)_2]$

Hg(1)–Ru(1)	2.780 (1)	Ru(1)–Ru(1′)	2.808 (1)
Hg(1)–O(3)	2.373 (7)	Ru(1)–P(1)	2.420 (2)
Ru(1)–N(1)	2.124 (6)	Ru(1)–C(1)	1.879 (8)
Ru(1)–C(2)	1.880 (9)	C(3)–O(3)	1.23 (1)
C(3)–O(4)	1.22 (1)		
Ru(1)–Hg(1)–Ru(1′)	60.67 (4)	Hg(1)–Ru(1)–Ru(1′)	59.66 (4)
Ru(1)–Hg(1)–O(3)	110.5 (2)	Ru(1)–Hg(1)–O(3′)	156.0 (2)
O(3)–Hg(1)–O(3′)	85.9 (3)	Ru(1)–N(1)–Ru(1′)	82.4 (2)
Ru(1′)–Ru(1)–P(1)	141.88 (7)	Hg(1)–Ru(1)–P(1)	158.4 (1)
N(1)–Ru(1)–N(1′)	70.7 (2)		

Table VI. Selected Bond Lengths (Å) and Angles (deg) in $[(\mathbf{1})Hg(\mu\text{-}Cl)_2HgCl_2]\cdot CH_2Cl_2$

Hg(1)–Ru(1)	2.758 (1)	Hg(1)–Ru(2)	2.775 (2)
Ru(1)–Ru(2)	2.827 (2)	Hg(1)–Cl(1)	2.834 (6)
Hg(1)–Cl(2)	2.537 (4)	Hg(2)–Cl(1)	2.652 (5)
Hg(2)–Cl(2)	2.685 (5)	Hg(2)–Cl(3)	2.427 (6)
Hg(2)–Cl(4)	2.301 (9)	Ru(1)–N(1)	2.15 (1)
Ru(1)–N(2)	2.15 (1)	Ru(2)–N(1)	2.14 (1)
Ru(2)–N(2)	2.14 (1)	Ru(1)–P(1)	2.434 (4)
Ru(2)–P(2)	2.433 (5)	Ru(1)–C(31)	1.88 (2)
Ru(1)–C(32)	1.94 (2)	Ru(2)–C(41)	1.86 (2)
Ru(2)–C(42)	1.88 (2)		
Ru(1)–Hg(1)–Ru(2)	61.5 (1)	Hg(1)–Ru(2)–Ru(1)	59.0 (1)
Hg(1)–Ru(1)–Ru(2)	59.6 (1)	Ru(1)–Hg(1)–Cl(1)	105.1 (1)
Hg(1)–Ru(1)–P(1)	159.6 (1)	Hg(1)–Ru(2)–P(2)	160.0 (1)
Ru(2)–Hg(1)–Cl(1)	156.4 (1)	Ru(1)–Hg(1)–Cl(2)	171.2 (1)
Ru(2)–Hg(1)–Cl(2)	112.3 (1)	Cl(1)–Hg(1)–Cl(2)	82.9 (2)
Cl(1)–Hg(2)–Cl(2)	83.7 (2)	Cl(1)–Hg(2)–Cl(3)	95.0 (2)
Cl(2)–Hg(2)–Cl(3)	91.2 (2)	Cl(1)–Hg(2)–Cl(4)	117.9 (2)
Cl(2)–Hg(2)–Cl(4)	118.0 (3)	Cl(3)–Hg(2)–Cl(4)	136.7 (3)
Ru(2)–Ru(1)–P(1)	140.8 (1)	Ru(1)–Ru(2)–P(2)	141.0 (1)
Ru(1)–N(1)–Ru(2)	82.5 (5)	Ru(1)–N(2)–Ru(2)	82.5 (4)

Selected bond lengths and angles are given in Tables V and VI.

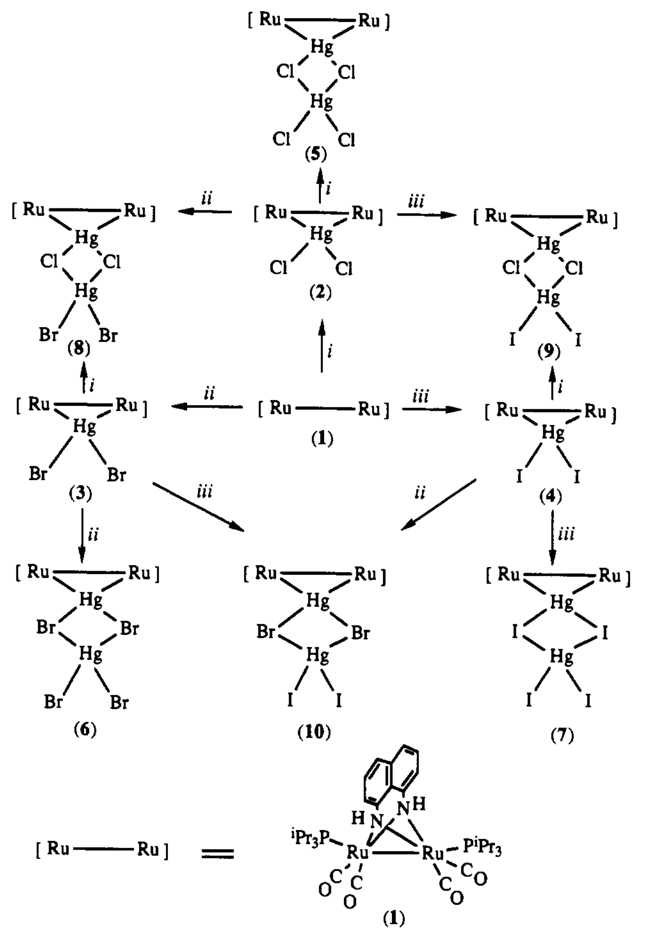
Results

The reactions described in this work are summarized in Schemes I–III. The main analytical tool used for the characterization of the compounds has been ^{31}P NMR spectroscopy, whose results are collected in Table I. Single-crystal X-ray diffraction studies were undertaken for the compounds $[(\mathbf{1})Hg(O_2CCF_3)_2]$ and $[(\mathbf{1})Hg(\mu\text{-}Cl)_2HgCl_2]\cdot CH_2Cl_2$; their results are presented in Tables II–VI. These will be introduced in the appropriate places in the sections which follow.

Discussion

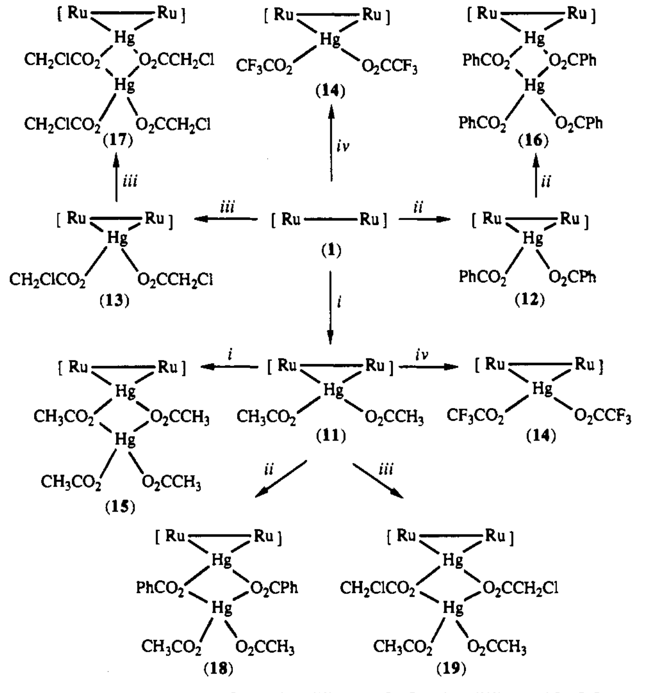
Complex **1** reacted with 1 equiv of HgX_2 (X = Cl, Br, I, O_2CCH_3, O_2CPh, O_2CCH_2Cl, O_2CCF_3) in tetrahydrofuran (THF), at room temperature, to give the adducts $[(\mathbf{1})HgX_2]$ (Schemes I and II) in nearly quantitative yields. The triangular arrangement of the Ru_2Hg framework in the complexes was indicated by IR and ^{31}P NMR spectroscopies. Their IR spectra in the ν(CO) region were almost identical, showing three ab-

Scheme I[a]



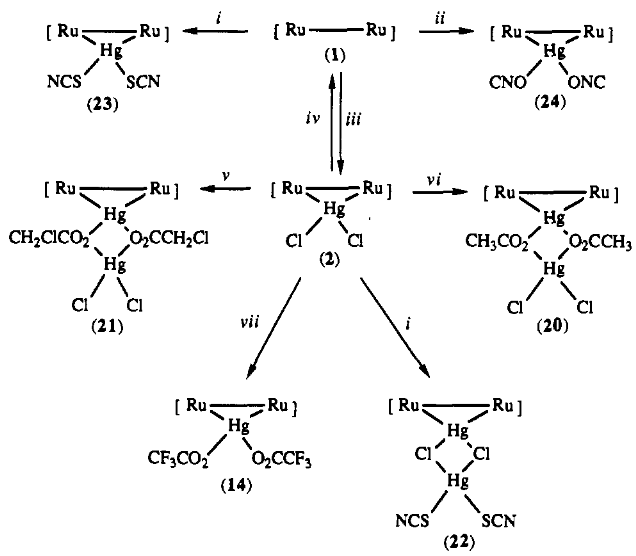
[a] Reagents: (i) $HgCl_2$; (ii) $HgBr_2$; (iii) HgI_2.

Scheme II[a]



[a] Reagents: (i) $Hg(O_2CCH_3)_2$; (ii) $Hg(O_2CPh)_2$; (iii) $Hg(O_2CCH_2Cl)_2$; (iv) $Hg(O_2CCF_3)_2$.

Scheme III[a]



[a] Reagents: (i) $Hg(SCN)_2$; (ii) $Hg(ONC)_2$; (iii) $HgCl_2$; (iv) $HgPh_2$; (v) $Hg(O_2CCH_2Cl)_2$; (vi) $Hg(O_2CCH_3)_2$; (vii) $Hg(O_2CCF_3)_2$.

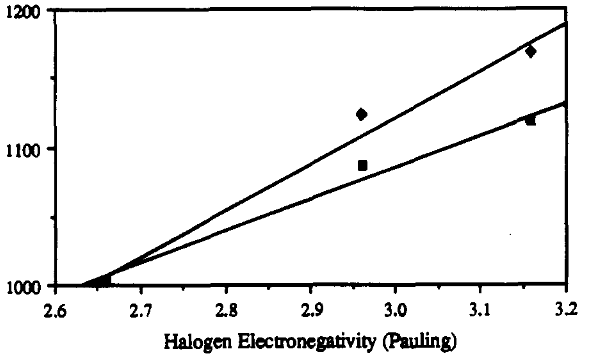


Figure 1. Correlations between the observed $^2J(^{31}P-^{199}Hg)$ coupling constants and halogen electronegativities for the complexes $[(\mathbf{1})HgX_2]$ (■) and $[(\mathbf{1})Hg(\mu\text{-}X)HgX_2]$ (◆) (X = I, Br, and Cl, from left to right).

sorptions (C_{2v} symmetry) (ca. 2036 m, 2021 m, and 1977 s cm^{-1}; THF) at higher wavenumbers than those of complex **1** (1991 s, 1953 m, and 1918 s cm^{-1}; THF). Their ^{31}P MNR spectra (Table I) were singlets with satellites due to coupling to ^{199}Hg (17% natural abundance). It is interesting to note that the $^2J(^{31}P-^{199}Hg)$ values varied almost regularly with the electronegativity of the halogens (Figure 1) and with the pK_a of the carboxylic acids (Figure 2), ranging from 1004 Hz for $[(\mathbf{1})HgI_2]$ to 1118 Hz for $[(\mathbf{1})HgCl_2]$ or from 1147 Hz for $[(\mathbf{1})Hg(O_2CCH_3)_2]$ to 1328 Hz for $[(\mathbf{1})Hg(O_2CCF_3)_2]$, indicating that the electron density on the Ru atoms is significantly affected by the nature of the ligands bonded to the Hg atoms. Correlations between $^1J(P-M)$ and the electronegativity of the substituents attached to the phosphorus[18] or to the metal[19] have been observed previously.[20]

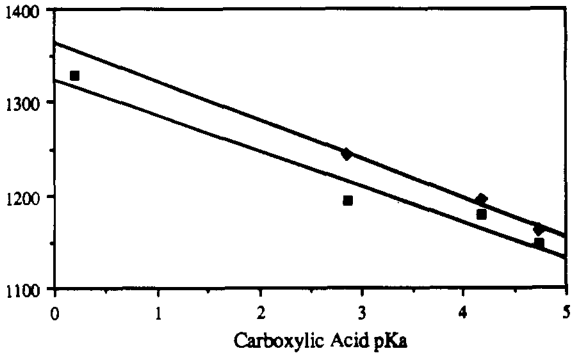


Figure 2. Correlations between the observed $^2J(^{31}P-^{199}Hg)$ coupling constants and carboxylic acid pK_as for the complexes $[(\mathbf{1})Hg(O_2CR)_2]$ (■) and $[(\mathbf{1})Hg(\mu\text{-}O_2CR)_2Hg(O_2CR)_2]$ (◆) (R = CF_3, CH_2Cl, Ph, and CH_3, from left to right).

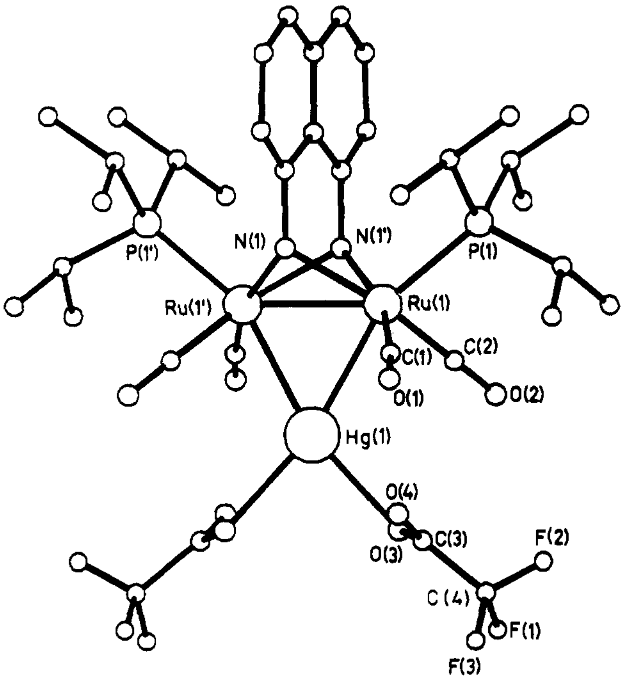


Figure 3. View of the molecular structure of the complex $[(\mathbf{1})Hg(O_2CCF_3)_2]$.

The X-ray structure of $[(\mathbf{1})Hg(O_2CCF_3)_2]$ (**14**) is depicted in Figure 3. The complex has a crystallographically imposed C_2 symmetry with the axis perpendicular to the Ru–Ru bond passing through the Hg atom. The Ru atoms are bridged by both N atoms of the doubly deprotonated 1,8-diaminonaphthalene ligand, Ru(1)–N(1) = 2.124 (6) Å, in such a way that the Ru_2N_2 framework is in a butterfly arrangement with the two wings forming a dihedral angle of 100.5 (2)° and with the body spanned by the Hg atom, Ru(1)–Hg(1) = 2.780 (1) Å. The Ru(1)–Ru(1') separation, 2.808 (1) Å, is longer than those found in $[Ru_2(\mu\text{-}C_{10}H_8N_2)(CO)_4(PPh_3)_2]^3$ (2.579 Å), $[Ru_2(\mu\text{-}C_{10}H_8N_2)(CO)_4\{P(OPh_3)\}_2]^2$ (2.571 Å), $[Ru_2Ag(\mu\text{-}C_{10}H_8N_2)(CO)_4(P^iPr_3)_2(PPh_3)]^{+1}$ (2.698 Å), and other ligand-bridged ruthenium(I) dimers,[21] as a consequence of having a bulky Hg atom bridging the two Ru atoms,[22] but it is still rather short. Each Ru atom is heptacoordinated, surrounded by two carbonyl ligands, the two N atoms of the bridging ligand, the P atom of a triisopropylphosphine ligand, the other Ru atom, and the Hg atom. The distortion in the octahedral arrangement caused by the presence of the Ru–Ru bond is evidenced specially by the angles Hg(1)–Ru(1)–P(1), 158.4 (1)°, and N(1)–Ru(1)–N(1'), 70.7 (2)°, which differ significantly from the theoretical 180 and 90°, respectively. The carbonyl groups are approximately trans to the N atoms and the P^iPr_3 ligands are trans to the Hg atom. The rather short Ru–Ru separation must be caused by the strain imposed by the bridging ligand, which also determines a very narrow Ru(1)–N(1)–Ru(1') angle, 82.4 (2)°. The coordi-

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(19) Yamasaki, A.; Fluck, E. *Z. Anorg. Allg. Chem.* **1973**, *396*, 297. Grim, S. O.; Pui, J. L.; Keiter, R. L. *Inorg. Chem.* **1974**, *13*, 342.

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(22) The presence of a large bridgehead atom lengthens considerably the bridged M–M distance: Churchill, M. R.; Lashewycz, R. A. *Inorg. Chem.* **1979**, *18*, 3261.

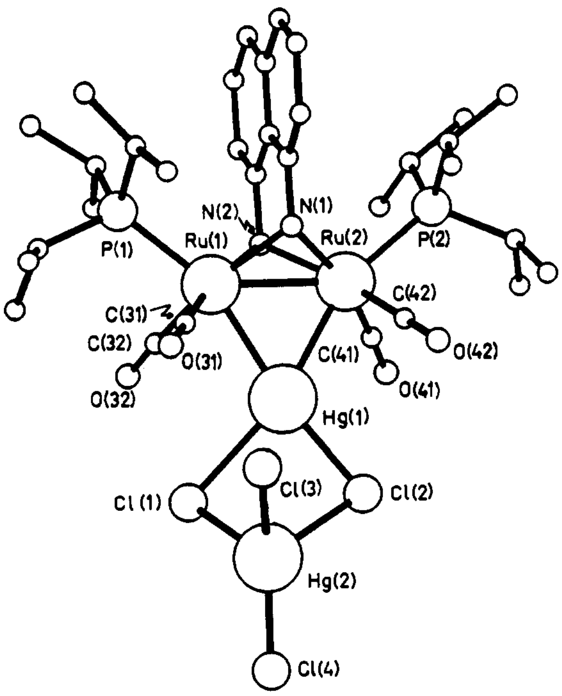

Figure 4. View of the molecular structure of the complex $[(\mathbf{1})Hg(\mu\text{-}Cl)_2HgCl_2]$.

nation geometry of the Hg atom can be considered as either distorted square planar or as distorted tetrahedral. Although there exist many examples in the literature[7-9] in which a μ_4-Hg atom shows considerable deviation from tetrahedral coordination (i.e. dihedral angles of 45–65°) the dihedral angle between the Ru(1)–Hg(1)–Ru(1′) and O(3)–Hg(1)–O(3′) planes of **14**, 35.0 (2)°, indicates that the coordination of the Hg atom is closer to square planar than to tetrahedral. A three-center, two-electron bridging system probably describes the bonding mode of the Lewis acid $Hg(O_2CCF_3)_2$ to the two Ru atoms, although theoretical calculations are needed to fully define the situation.

The reactions of 1 equiv of HgX'_2 (X′ = Cl, Br, I) with the complexes $[(\mathbf{1})HgX_2]$ led to the isolation of yellow solids (Scheme I). Similarly, the reactions of $Hg(O_2CR')_2$ (R′ = CH_3, Ph, CH_2Cl) with $[(\mathbf{1})Hg(O_2CR)_2]$ (R ≠ CF_3) also led to the isolation of new compounds (Scheme II). Although their IR spectra did not differ significantly from those of the parent complexes, their microanalyses and ^{31}P NMR spectra confirmed the incorporation of a second mercury halide or carboxylato fragment.

The way in which the second mercury-containing fragments are attached to the parent compounds was indicated by the X-ray structure of $[(\mathbf{1})Hg(\mu\text{-}Cl)_2HgCl_2]\cdot CH_2Cl_2$ ($\mathbf{5}\cdot CH_2Cl_2$) (Figure 4). The structure shows an $HgCl_2$ fragment attached through the Hg atom to both Ru atoms of the original complex **1**, Hg(1)–Ru(1) = 2.758 (1), Hg(1)–Ru(2) = 2.775 (2), and Ru(1)–Ru(2) = 2.827 (2) Å, and to the Hg atom of the second $HgCl_2$ fragment through both Cl atoms, Hg(1)–Cl(1) = 2.834 (6), Hg(1)–Cl(2) = 2.537 (4), Hg(2)–Cl(1) = 2.652 (5), Hg(2)–Cl(2) = 2.685 (5), Hg(2)–Cl(3) = 2.427 (6), and Hg(2)–Cl(4) = 2.301 (9) Å. The coordination around Hg(1) is closer to square planar than that found in $[(\mathbf{1})Hg(O_2CCF_3)_2]$, the dihedral angle between the planes Ru(1)–Ru(2)–Hg(1) and Cl(1)–Hg(1)–Cl(2) being only 22.2 (1)°, whereas that around Hg(2) is approximately tetrahedral. The Hg(1)···Hg(2) distance, 3.587 (1) Å, is out of the bonding range and is comparable to that found in the complex $[cis\text{-}Ru(CO)_4\{Ru_3Hg(\mu_3\text{-}C_2{}^tBu)(CO)_9\}_2]$, 3.55 Å.[7b] All the other structural parameters are comparable to those of $[(\mathbf{1})Hg(O_2CCF_3)_2]$, described above. Many compounds containing Hg atoms in a tetrahedral environment are known,[23] but mercury compounds with a distorted square-planar coordination are less common.[7-9]

The relative positions (bridging or terminal) of the halide or carboxylato ligands in the complexes containing two different mercury(II) halide or carboxylato fragments (Scheme I and II) were deduced from the values of their $^2J(^{31}P\text{-}^{199}Hg)$ coupling constants (Table I), which are related to the electron-withdrawing effect[24] of the ligands attached to the Hg atoms. Since the electron-withdrawing effect of the bridging ligands should affect the coupling constant to a greater extent than that of the terminal ones, and since the higher that effect is the greater is the coupling constant, the observed data clearly indicate that the most electron-withdrawing ligands always occupy bridging positions.

The mixed-ligand compounds $[(\mathbf{1})Hg(\mu\text{-}O_2CR)_2HgCl_2]$ (R = CH_3, Ph, CH_2Cl) (Scheme III) were prepared either by reaction of $[(\mathbf{1})Hg(O_2CR)_2]$ with $HgCl_2$ or by reaction of $[(\mathbf{1})HgCl_2]$ with $Hg(O_2CR)_2$. This result also confirms that the most electron-withdrawing ligands (in this case, the carboxylates) always occupy bridging positions.

Since $Hg(O_2CCF_3)_2$ is a better Lewis acid than all other mercury(II) salts used in this work, it was expected to give insertion instead of substitution reactions when treated with $[(\mathbf{1})HgX_2]$ (X = Cl, Br, I, O_2CCH_3, O_2CPh, O_2CCH_2Cl). However, all these reactions gave the same product: $[(\mathbf{1})Hg(O_2CCF_3)_2]$ (some examples are shown in Schemes II and III). Most probably, the uncoordinated oxygen atoms of the trifluoroacetato groups of $[(\mathbf{1})Hg(O_2CCF_3)_2]$ are not basic enough to react with any other mercury(II) compound due to the high electron-withdrawing effect of the CF_3 group.

Complex **1** also reacted with mercury(II) thiocyanate and fulminate[25] to give the corresponding adducts (Scheme III). Complex **1** did not react with $HgPh_2$ or ClHgPh; in fact, the reaction of $[(\mathbf{1})HgCl_2]$ with $HgPh_2$ afforded a mixture of complex **1** and ClHgPh. We also tried the reactions of complex **1** with mercury(II) fluoride, cyanide, cyanate, chromate, sulfate, and nitrate, but the high insolubility of these reagents in organic solvents prevented their reaction or the isolation of pure products.

Throughout this article, the reactions leading to $[(\mathbf{1})Hg(\mu\text{-}X')_2HgX_2]$ from $[(\mathbf{1})HgX_2]$ and HgX'_2 (only when X′ is more electron-withdrawing than X) have been clasified as insertion reactions only from a formal point of view. In fact, the mechanism operating in such reactions remains unknown. Considering the possibility of X′ exchange with X followed by addition of $[(\mathbf{1})HgX'_2]$ to HgX_2, we tried the reactions of $[(\mathbf{1})HgBr_2]$ with [PPN]Cl and of $[(\mathbf{1})HgCl_2]$ with $[PPN]O_2CCF_3$, but no exchange was observed by ^{31}P NMR spectroscopy.

Concluding Remarks

This article reports the formation and structural characterization of the first carbonyl compounds linked to Hg_2X_4 groups. The simple addition of mercury(II) salts to metal–metal-bonded ruthenium compounds does not seem to have been described before. Correlations between the nature of the ligands bonded to mercury and the $^2J(^{31}P\text{-}^{199}Hg)$ coupling constants have been observed and have been used to determine that the addition of HgX'_2 (X′ = Cl, Br, I, O_2CCH_3, O_2CPh, O_2CCH_2Cl) to the complexes $[(\mathbf{1})HgX_2]$ (X = Cl, Br, I, O_2CCH_3, O_2CPh, O_2CCH_2Cl) gives rise to the insertion products $[(\mathbf{1})Hg(\mu\text{-}X')_2HgX_2]$ when X′ is more electron-withdrawing than X; otherwise, the addition products $[(\mathbf{1})Hg(\mu\text{-}X)_2HgX'_2]$ are obtained.

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Registry No. **1**, 133288-27-4; **2**, 133288-28-5; **3**, 133288-29-6; **4**, 133288-30-9; **5**, 133288-31-0; $\mathbf{5}\cdot CH_2Cl_2$, 133288-38-7; **6**, 133288-32-1; **7**, 133288-33-2; **8**, 133288-34-3; **9**, 133288-35-4; **10**, 133288-36-5; **11**, 139199-84-1; **12**, 139199-85-2; **13**, 139199-86-3; **14**, 139199-87-4; **15**,

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[23] See, for example: Brown, D. L.; Ibers, J. A. *Inorg. Chem.* **1976**, *15*, 2794. Bycroff, B. M.; Cotton, J. D. *J. Chem. Soc., Dalton Trans.* **1973**, 1867.

[24] The electron-withdrawing effect is directly related to halogen electronegativity and to carboxylic acid K_a.

[25] *Caution*! Mercury(II) fulminate is a known explosive and should be handled with care. All mercury compounds are known to be harmful.

139199-88-5; **16**, 139242-65-2; **17**, 139199-89-6; **18**, 139199-90-9; **19**, 139199-91-0; **20**, 139199-92-1; **21**, 139199-93-2; **22**, 139242-66-3; **23**, 139242-67-4; **24**, 139242-68-5; ^{199}Hg, 14191-87-8; Hg, 7439-97-6; Ru, 7440-18-8.

Supplementary Material Available: Tables of analytical (Table S-I), ^{1}H NMR (Table S-II), and IR data (Table S-III), complete positional parameters, bond distances, bond angles, thermal parameters for the non-hydrogen atoms, hydrogen atom positions with their isotropic thermal parameters, and complete crystal data for both structures (17 pages); tables of structure factors (52 pages). Ordering information is given on any current masthead page.

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and Laboratorium voor Polymeer-Chemie, University of Groningen, Nijenborg 16, 9747 AG Groningen, The Netherlands

Stereoregular Coordination Polymers Formed on Binding of Peptide-Based Polydentate Ligands to Silver(I) and Copper(I). X-ray Structure of ([Ag{*N*-[*N*-((5-methyl-2-thienyl)methylidene)-L-methionyl]histamine}]$^+$[O_3SCF_3]$^-$·MeOH)$_\infty$ and a Solution Structure Study[1]

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From the 1:1 metal salt to ligand reactions of $Ag^IO_3SCF_3$ or $Cu^IO_3SCF_3$ with the polydentate donor ligand system *N*-[*N*-((5-R-thienyl)methylidene)-L-methionyl]histamine (=(5R)Th-Met-Histam; R = H, Me, Me_3Si) stable coordination complexes have been obtained. The solid-state structure of [Ag{(5Me)Th-Met-Histam}](OTf) was determined. ([$C_{16}H_{22}N_4S_2Ag$]$^+$[O_3SCF_3]$^-$·CH_4O)$_\infty$ crystallizes in the orthorhombic space group $P2_12_12_1$, with $a = 11.339$ (1) Å, $b = 13.122$ (1) Å, and $c = 17.451$ (1) Å. The complex cation has a polymeric structure that results from each ligand molecule stretching out over three different Ag(I) cations. Each Ag(I) center is sp^2 hybridized and trigonally coordinated by an imidazole N [2.218 (4) Å], an imine N [2.378 (5) Å], and a methionine S atom [2.509 (2) Å]. There is an additional weak interaction with an amide O atom [2.568 (4) Å], which is situated above the trigonal plane. A more distant thiophene S atom lies on the other side of the plane [3.081 (2) Å]. Viewed from S to O along an axis perpendicular to the trigonal plane the configuration of all Ag(I) centers is *R*; this defines a Δ-helix structure for the polymeric cation. By use of a combination of spectroscopic techniques (^{19}F, ^{109}Ag, and ^{1}H NMR, UV, CD, and optical rotation) and other measurements (vapor pressure osmometry and conductivity), it is established that the complexes [Ag{(5R)Th-Met-Histam}](OTf) (R = H, Me, Me_3Si) in solution have an oligomeric structure that is similar to the polymeric structure of [Ag{(5Me)Th-Met-Histam}](OTf) in the solid state. The average chain length of the oligomer is a function of complex concentration and temperature; for the (5Me)Th-Met-Histam complex at 318 K the chain length varies from 1 unit in dilute solution to at least 11 units at a concentration of 0.14 mol·L^{-1}. Comparison of the X-ray structure conformations of (5Me)Th-Met-Histam as a free molecule and as ligand in this Ag(I) complex shows that, apart from one rotation, the changes are minimal. The self-assembly process, which affords the polycationic Ag(I) coordination complexes through a simultaneous, configurationally unique arrangement of different ligating sites from three separate sources around each cationic nucleus, manifests a degree of self-organization that has so far not often been encountered in synthetic coordination chemistry. The Cu(I) complexes have structures that are comparable to those of their Ag(I) counterparts, although the average chain length under identical conditions may be less. An intramolecular electron shift equilibrium mechanism, involving Cu(I)–imidazole and Cu(II)–imidazole$^{\bullet-}$ transitions, is proposed to explain the line broadening present in the ^{1}H NMR spectra of the Cu(I) complexes.

Introduction

The field of supramolecular chemistry, as defined among others by Lehn,[2] is a rapidly growing area. An aspect of the "chemistry beyond the molecules", involves the concept of molecular self-assembly, i.e., the formation of specifically organized aggregates from small basic building blocks. Self-assembly is an important feature in living nature,[3] e.g., the double helix formation of nucleic acids, yet the number of examples in synthetic chemistry is still limited. Recently Lehn and co-workers have reported on "helicates", coordination complexes of the group 11 cations Ag(I) or Cu(I) with oligobipyridines, whose structures turn out to be inorganic double helices.[3,4]

We had already reported extensively on a similar double-helix effect that occurs in binuclear Ag(I) and Cu(I) coordination complexes of the neutral N_4 donor ligand (pyridine-2-CH=N)$_2$(*R*),(*S*)-1,2-cyclohexane.[5] In these dicationic complexes with an [$M_2\{N_4\}_2$]$^{2+}$ stoichiometry the ligand acts as a bis(N_2-bidentate) donor. In the free ligand the conformation of the chiral cyclohexanediyl bridging group enforces a more or less perpendicular arrangement of both chelating functions, and upon complexation of this ligand a helical structure results with both metal centers having either the Δ or the Λ configuration.[6]

The related N_2S_2 donor ligand,[7] in which thiophene replaces pyridine, gives rise to a dicationic [$M_2\{N_2S_2\}_2$]$^{2+}$ complex similar

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(1) (a) Part of this work has been presented at the fourth International Conference on Bioinorganic Chemistry (ICBIC-4, MIT, Cambridge, MA, July 24–28, 1989): (a) Modder, J. F.; van Koten, G.; Vrieze, K.; Spek, A. L. *J. Inorg. Biochem.* **1989**, *36*, 234. (b) Part of this work was also presented in a preliminary communication: Modder, J. F.; van Koten, G.; Vrieze, K.; Spek, A. L. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1698–1700. (c) Modder, J. F. Ph.D. thesis, University of Amsterdam, The Netherlands, 1991.

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