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Homo- and Heterobimetallic Complexes Containing 2,2′-Bipyrimidine

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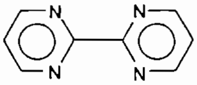
Homo- and heterobimetallic complexes of platinum(II) containing 2,2′-bipyrimidine as bridging ligand, $(C_6H_5)_2Pt(bipym)ML_2$ *(M = Pt, L =* C_6H_5*, M = Hg or Mn, L = Cl), were prepared by reacting the mononuclear chelate complex* $(C_6H_5)_2Pt(bipym)$ *with the appropriate metal salt. The homodinuclear complexes* $Cl_2M(bipym)MCl_2$ *(M = Hg or Mn) were synthesized from the reaction between* MCl_2 *and bipyrimidine. All the complexes were characterized by elemental analysis and infrared spectra, and some by proton magnetic resonance spectra. Infrared data suggest that mercury and manganese in their complexes are tetrahedrally surrounded by the donor atoms.*

Introduction

Design and synthesis of heterobimetallic complexes have been an important goal of modern inorganic chemistry [1].

In this context, 2,2′-bipyrimidine (bipym), an aromatic heterocyclic bridge,



is expected to lead to ligand bridge compounds of various complexity and various degrees of electronic interactions between metallic centers.

In the recent years only a few compounds containing bipym as a bridging ligand have been reported. Among these some have been synthesized with the aim to construct cytochrome oxidase models [2], others with the viewpoint of testing intramolecular redox processes [3,4].

Starting from *cis*-$[Pt(C_6H_5)_2(Me_2SO)_2]$ we prepared a series of homo and heterobimetallic complexes containing bipym. In the case of heterobimetallic complexes, the synthesis proceeds through the mononuclear species $[(C_6H_5)_2Pt(bipym)]$, taking advantage of the fact that phenyl groups protect the platinum atom from undesired attack.

Results and Discussion

Having in hand the suitable binucleating ligand, our preparative route was directed to obtain in successive steps a pure mononuclear chelate and its reaction product with a given metal salt. Unfortunately, our attempts to prepare mononuclear species of mercury(II) and manganese(II) failed in that the only products obtained were homobimetallic complexes $[Cl_2Hg(bipym)HgCl]_2$ and $[Cl_2Mn(bipym)MnCl_2]$.

We were able to prepare and characterize the stable mononuclear $[Pt(C_6H_5)_2(bipym)]$ from reaction of *cis*-$[Pt(C_6H_5)_2(Me_2SO)_2]$ with the stoichiometric amount of bipym in acetone. It can be seen by UV monitoring that this comes as result of the different reaction rates of the two processes, in that the formation of the first chelate ring is much faster than the attack of $[Pt(C_6H_5)_2(bipym)]$ on *cis*-$[Pt(C_6H_5)_2(Me_2SO)_2]$.

Once the mononuclear complex is obtained, heterobimetallics can be easily formed by adding equimolar quantities of the desired metal salt (Table I).

All complexes were sparingly soluble in most organic solvents, and insoluble in alcohols. $[Cl_2Mn(bipym)MnCl_2]$ is highly soluble in water, but the resulting solution is not coloured. Actually, the manganese homodinuclear compound demetallates as soon as dissolved in water, and free bipyrimidine can be evidenced by its UV absorption spectrum.

IR Spectra

Strong bands (1560, 1550 cm^{-1}) in the free 2,2′-bipyrimidine, assigned to ring stretching mode [5], remain of the same intensity upon coordination in all complexes. Another ring stretching mode, observed as a strong band at 1400 cm^{-1} in the free ligand,

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TABLE I. Analytical and Spectral Data for Some Complexes of 2,2'-Bipyrimidine.

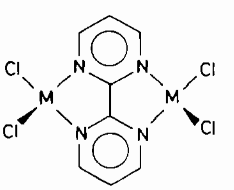
Complex	Colour	Found*				Main 2,2'-bipyrimidine modes (cm^{-1})	ν_{M-Cl} (cm^{-1})
		C	H	N	Cl		
$Pt(C_6H_5)_2$(bipym)	Red orange	47.00	3.25	10.90		1570vs, 1400vs, 1085m, 1075m, 815m	
		(47.30)	(3.15)	(11.04)			
$(C_6H_5)_2Pt$(bipym)$Pt(C_6H_5)_2$	Purple	44.20	2.94	6.42		1550vs, 1415m, 1400vs, 1090m, 1080m, 810m	
		(44.80)	(3.03)	(6.02)			
$(C_6H_5)_2Pt$(bipym)$HgCl_2$	Orange	30.60	2.07	7.25	9.05	1570vs, 1410vs, 1085w, 1075w, 850m, 840m	295ms
		(30.80)	(2.25)	(7.19)	(9.10)		
Cl_2Hg(bipym)$HgCl_2$	White	13.83	0.89	7.84	20.06	1565vs, 1410vs, 1100m, 820s	310ms
		(13.70)	(0.85)	(8.00)	(20.25)		
$(C_6H_5)_2Pt$(bipym)$MnCl_2$	Red brown	38.20	2.75	8.60	10.08	1575vs, 1425m, 1410vs, 1090w, 1080w, 840ms, 820w	255ms
		(37.90)	(2.56)	(8.84)	(11.20)		
Cl_2Mn(bipym)$MnCl_2$	Yellow	23.25	1.58	13.44	34.49	1570vs, 1400vs, 1095m 1070m, 835s	260ms
		(23.24)	(1.46)	(13.66)	(34.60)		

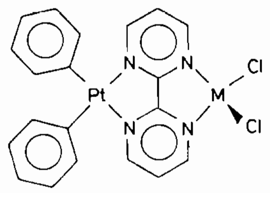
*Calculated values are given in parentheses.

appears in the complexes as a single or double band in a range of frequencies between 1400 and 1420 cm^{-1}. The band of medium intensity, due to β CH vibration in bipym (1140 cm^{-1}), appears in the complexes as two absorptions of the same intensity at lower frequencies. The antisymmetric γ-CH vibrations appear as two medium weak absorptions in bipyrimidine (830, 820 cm^{-1}), but in the complexes these appear as single absorption (double in heterobimetallics) of increased relative intensity in the same region.

The Hg–Cl and Mn–Cl stretching frequencies both in homo and in heterobimetallic complexes lie around 300 and 250 cm^{-1} respectively. These values are important in order to assess the effective coordination around mercury and manganese [6, 7], since the common structure for the complexes MCl_2D_2 (D = non-halogen donor atom) can be tetrahedral or octahedral. Generally, the four coordinate species have ν(M–Cl) between 345 and 200 cm^{-1}, whereas the six-coordinate ones usually have ν(M–Cl) below this range.

A tetrahedral complex MCl_2D_2 has point group symmetry C_{2v} and should give rise to two vibrations involving M–Cl, both infrared active. Our compounds give only one broad infrared band, but it is known that the two bands from M–Cl stretching often cannot be resolved. On this basis we can formulate the following structures for both homo and heterobimetallic complexes of mercury and manganese:





Nuclear Magnetic Resonance

Because of the low solubility of the complexes, we were not able to obtain ^1H NMR spectra. Only mercury(II) compounds exhibited in d_6-Me_2SO a solubility large enough to obtain reasonable spectra.

With respect to uncoordinated bipyrimidine the symmetrical complex Cl_2Hg(bipym)$HgCl_2$ shows a similar pattern, *i.e.*, a doublet corresponding to β-hydrogens (τ = 9.0 ppm relative to TMS as internal standard, 0.2 ppm downfield with respect to free ligand), and a triplet corresponding to γ-hydrogens (τ = 7.75 ppm, 0.3 ppm downfield with respect to free bipyrimidine). In the complex $(C_6H_5)_2Pt$(bipym)$HgCl_2$ the presence of two different metals makes the β-hydrogens chemically non-equivalent. This is evident from the resulting spectrum, which shows two multiplets centred at τ = 9.15 and τ = 8.60 ppm. The γ-hydrogens are present as a multiplet centred at τ = 7.75 ppm.

Experimental

IR spectra were recorded as mulls with nujol and hexachlorobutadiene on a Perkin Elmer 457 spectrometer. NMR spectra were recorded on a Hitachi Perkin Elmer R 24 B 60 MHz instrument. 2,2'-bipyrimidine was purchased from Lancaster Synthesis and used without further purification. *cis*-$Pt(C_6H_5)_2(Me_2SO)_2$ was prepared starting from Pt(COD)$(C_6H_5)_2$ [8].

Preparation of Compounds

Diphenyl(2,2'-bipyrimidine)platinum(II)

A solution containing 1 mmol (505 mg) of *cis*-$[Pt(C_6H_5)_2(Me_2SO)_2]$ in acetone was added dropwise to a stirred solution containing an equimolar quantity of bipym (158 mg). The solution became red-orange and upon concentration gave $[Pt(C_6H_5)_2(bipym)]$ as a red-orange microcrystalline powder (yield = 60%).

μ-(2,2′-bipyrimidine)tetraphenyldiplatinum(II)

To an acetone solution containing 2,2′-bipyrimidine (0.5 mmol, 79 mg), were added 505 mg (1 mmol) of *cis*-$[Pt(C_6H_5)_2(Me_2SO)_2]$. The solution first became red-orange (mononuclear species) and then red-purple (binuclear species). Upon concentration, $[(C_6H_5)_2Pt(bipym)Pt(C_6H_5)_2]$ precipitated as purple microcrystalline powder (yield = 55%).

Diphenylplatinum(II)-μ-(2,2′-bipyrimidine)dichloromercury(II)

505 mg (1 mmol) of *cis*-$[Pt(C_6H_5)_2(Me_2SO)_2]$, dissolved in acetone, were reacted with the stoichiometric amount of bipym (158 mg). The mixture was allowed to react for ½ h, and then 271 mg (1 mmol) of $HgCl_2$ were added. $[(C_6H_5)_2Pt(bipym)HgCl_2]$ precipitated immediately as an orange-yellow microcrystalline powder (yield = 63%).

μ-(2,2′-bipyrimidine)tetrachlorodimercury(II)

To an acetone solution containing 2,2′-bipyrimidine (79 mg, 0.5 mmol), were added 271 mg (1 mmol) of $HgCl_2$. $[Cl_2Hg(bipym)HgCl_2]$ precipitated as a white compound in quantitative yield.

Diphenylplatinum(II)-μ(2,2′-bipyrimidine)dichloromanganese(II)

1 mmol of *cis*-$[Pt(C_6H_5)_2(Me_2SO)_2]$ was transformed into $[Pt(C_6H_5)_2(bipym)]$. To the resulting red-orange solution was added 197 mg (1 mmol) of $MnCl_2 \cdot 4H_2O$. $[(C_6H_5)_2Pt(bipym)MnCl_2]$ precipitated immediately as a red-brown microcrystalline powder (yield = 58%).

μ-(2,2′-bipyrimidine)tetrachlorodimanganese(II)

To an acetone suspension of $MnCl_2 \cdot 4H_2O$ (197 mg, 1 mmol), were added 79 mg of bipym (1 mmol). The yellow compound obtained was analyzed for $Cl_2Mn(bipym)MnCl_2 \cdot H_2O$. Water was removed on heating for 12 h at 90 °C. The yield was almost quantitative.

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