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Anionic tetracarbonyl 2-carboxypiridinato or 2-carboxyquinolinato of tungsten(0). Reactions with mercury(II) derivatives

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Abstract

New anionic tetracarbonyl complexes, $[W(N,O)(CO)_4]^-$, containing (N,O)-donor ligands (2-picolinate and 2-quinaldinate) have been isolated, and their reactions with HgX_2 (X = Cl, Br, CN) studied. The reactions give either anionic or neutral compounds, containing W–Hg bonds, of the types $[W(N,O)(CO)_3(HgX)(X)]^-$ (X = Cl, Br), $[W(N,O)(CO)_3(HgBr)]_n$, $[Ph_4P]_2[\{W(N,O)(CO)_3\}_2(HgX_2)]$ (X = Cl, CN) and $[Ph_4P][W(CN)(N,O)(CO)_2Hg(CN)_2]$, depending on the reaction conditions.

Introduction

There have been few reports of complexes of Group VIB metals containing an anionic bidentate (N,O)-donor ligand such as 2-picolinate and 2-quinaldinate. Only $[M(2\text{-pic})_3]$ (M = Mo, W; 2-pic = 2-picolinate) [1,2], $[W(N,O)_4]$ (N,O = 2-picolinate, 2-quinaldinate or their derivatives) [3], $[W(2\text{-pic})(CO)_3]_n$ [1], and $[Mo(2\text{-pic})(CO)_4]^-$ [4] complexes have been reported.

Furthermore, it is now well established that neutral tetra- and tri-carbonyl complexes of molybdenum(0) and tungsten(0) readily undergo addition reactions with mercury(II) derivatives to give compounds containing M–Hg bonds [5–11], but there have been no studies of the reactions of mercury(II) salts with Mo and W carbonyl complexes [12]. Since an increase in the basicity of the carbonyl complexes favours their reactions with Lewis acids [13], we expected that the use of anionic carbonyl species would lead to an increase in the stabilities of the compounds containing M–Hg bonds.

These considerations prompted us to investigate the synthesis of new $[W(N,O)(CO)_4]^-$ species [N,O = 2-picolinate (2-pic), 2-quinaldinate (quin) (mononegative bidentate ligands)] and their reactions with mercury(II) derivatives, HgX_2 (X = Cl, Br, CN).

(*Continued on p. 303*)

Table 1

Characteristic data for the new complexes

Compound	Type	Colour	Λ_M (ohm^{-1} cm^2 mol^{-1})	Elemental analysis [c] (%)			IR data (cm^{-1})						
				C	H	N	solid state				CH_2Cl_2 solution		
							ν(C≡O)	ν_{as}(OCO)	ν_s(OCO)	ν(C≡N)	ν(C≡O)	ν_{as}(OCO)	ν(C≡N)
$[Ph_4P][W(2\text{-pic})(CO)_4]$		orange	103 [a]	53.55 (53.93)	3.65 (3.17)	1.10 (1.85)	1989 1859 1838 1794	1643	1345		2000 1875 1850 1797	1652	
$[Ph_4P][W(quin)(CO)_4]$		granite	82 [a]	54.87 (55.06)	3.12 (3.01)	0.89 (1.07)	1994 1848 1794	1640	1360 1335		1997 1867 1845 1790	1645	
$[Ni(phen)_3][W(2\text{-pic})(CO)_4]_2$		orange	103 [a]	46.30 (46.82)	2.05 (1.95)	7.33 (7.80)	2000 1857 1842 1797	1635	1347		1997 1865 1842 1792	1642	
$[Ni(phen)_3][W(quin)(CO)_4]_2$		granite	122 [a]	49.54 (50.01)	2.47 (2.34)	6.97 (7.29)	2006 1865 1804	1647	1368 1347		1988 1872 1847 1795	1645	
$[Ph_4P][W(2\text{-pic})(CO)_3(HgCl)(Cl)]$	A	orange	117 [a]	40.12 (39.61)	2.78 (2.39)	1.27 (1.40)	1975 1865	1662	1335		1987 1895 1864	1658	
$[Ph_4P][W(quin)(CO)_3(HgCl)(Cl)]$	A	orange	140 [a]	42.31 (42.30)	2.87 (2.47)	0.98 (1.33)	1970 1875 1855	1660	1355 1335		1976 1886 1851	1655	
$[Ni(phen)_3][W(2\text{-pic})(CO)_3(HgCl)(Cl)]_2$	A	orange	63 [b]	33.34 (33.74)	2.02 (1.66)	5.74 (5.83)	1963 1855	1660 1560	1340		1970 1892 1865	1665	

$[Ni(phen)_3][W(quin)(CO)_3(HgCl)(Cl)]_2$	A	orange	57 [b]	37.23 (36.82)	2.32 (1.78)	5.27 (5.54)	1958 1860	1650 1590	1365 1342	1970 1890 1835	1654
$[Ph_4P][W(2\text{-pic})(CO)_3(HgBr)(Br)]$	A	orange	125 [a]	37.22 (36.37)	2.45 (2.20)	1.05 (1.29)	1960 1857	1660	1330	1965 1886 1855	1658
$[Ph_4P][W(quin)(CO)_3(HgBr)(Br)]$	A	orange	140 [a]	39.24 (38.99)	2.51 (2.28)	1.02 (1.23)	1958 1853	1650	1334	1975 1887 1853	1650
$[W(2\text{-pic})(CO)_3(HgBr)]_n$	B	orange	19 [b]	15.83 (16.12)	0.54 (0.59)	2.08 (2.09)	1978 1870	1612 1587	1405	1982 1900 1874	1614 1590
$[W(quin)(CO)_3(HgBr)]_n$	B	granite	22 [b]	20.60 (21.67)	1.26 (0.83)	1.90 (1.94)	1978 1886 1870	1600	1405	1900 1892 1885	1600 1585(sh)
$[Ph_4P]_2[\{W(2\text{-pic})(CO)_3\}_2(HgCl_2)]$	C_1	orange	150 [b]	45.75 (46.58)	2.96 (2.82)	1.76 (1.65)	1915 1850 1800	1655	1340		
$[Ph_4P]_2[\{W(quin)(CO)_3\}_2(HgCl_2)]$	C_2	orange	155 [b]	47.81 (48.57)	3.35 (2.84)	1.59 (1.53)	1950 1915 1843 1810	1645	1350 1330		
$[Ph_4P]_2[\{W(2\text{-pic})(CO)_3\}_2Hg(CN)_2]$	I	yellow	173 [a]	47.96 (47.72)	3.29 (2.80)	3.21 (3.27)	1955 1927 1852 1817	1652	1337	1962 1935 1860 1840	1657
$[Ph_4P]_2[\{W(quin)(CO)_3\}_2Hg(CN)_2]$	I	orange	187 [a]	48.95 (50.40)	3.21 (2.87)	3.18 (3.09)	1950 1920 1850 1815	1640	1350 1330	1960 1932 1854 1832	1648

continued

Table 1 (continued)

Compound	Type	Colour	Λ_M (ohm^{-1} cm^2 mol^{-1})	Elemental analysis ^{c} (%)			IR data (cm^{-1})						
				C	H	N	solid state				CH$_2$Cl$_2$ solution		
							ν(C≡O)	ν_{as}(OCO)	ν_s(OCO)	ν(C≡N)	ν(C≡O)	ν_{as}(OCO)	ν(C≡N)
[Ph$_4$P][W(2-pic)(CO)$_2$(CN)Hg(CN)$_2$]	II	yellow	98 ^{a}	41.31 (42.89)	2.59 (2.45)	5.90 (5.71)	1935 1847	1660	1332	2090 2030	1940 1858	1660	2115 2100 2030
[Ph$_4$P][W(quin)(CO)$_2$(CN)Hg(CN)$_2$]	II	orange	106 ^{a}	43.38 (45.49)	2.82 (2.53)	5.65 (5.44)	1935 1842	1665	1355 1335	2105 2030	1942 1850	1650	2105 2030

^{a} Acetone (10^{-3} M). ^{b} DMF (10^{-3} M). ^{c} Calculated values in parentheses.

Table 2. Electronic spectra of the complexes (br = broad, sh = shoulder)

Compound	Solid, λ_{max} (nm)							Solution ^{a}, λ_{max} (nm) (ϵ ^{b})
[Ph$_4$P][W(2-pic)(CO)$_4$]		740	485				265	440 (1.167×10^3)
[Ph$_4$P][W(quin)(CO)$_4$]			525(br)		315(sh)		270	450 (1.443×10^3) 410 (1.435×10^3)
[Ni(phen)$_3$][W(2-pic)(CO)$_4$]$_2$	780		500			290		435 (1.472×10^3)
[Ni(phen)$_3$][W(quin)(CO)$_4$]$_2$	780		550(br)	390(sh)	325(sh)		280	450 (0.987×10^3) 400 (1.150×10^3)
[Ph$_4$P][W(2-pic)(CO)$_3$(HgCl)(Cl)]		740	410		320(sh)		270	385 (1.440×10^3)
[Ph$_4$P][W(quin)(CO)$_3$(HgCl)(Cl)]			470(br)		330(sh)	290	270	410 (1.673×10^3)
[Ni(phen)$_3$][W(2-pic)(CO)$_3$(HgCl)(Cl)]$_2$	785		405		330	300	270	385 (1.859×10^3)
[Ni(phen)$_3$][W(quin)(CO)$_3$(HgCl)(Cl)]$_2$	790		460(br)		330(sh)	290	270	415 (1.220×10^3)
[Ph$_4$P][W(2-pic)(CO)$_3$(HgBr)(Br)]		740	420				280	
[Ph$_4$P][W(quin)(CO)$_3$(HgBr)(Br)]			445(br)		320(sh)		280	
[W(2-pic)(CO)$_3$(HgBr)]$_n$		750	475				285	^{c}
[W(quin)(CO)$_3$(HgBr)]$_n$			520(br)				290	^{c}
[Ph$_4$P]$_2$[{W(2-pic)(CO)$_3$}$_2$(HgCl$_2$)]		750	470				275	^{c}
[Ph$_4$P]$_2$[{W(quin)(CO)$_3$}$_2$(HgCl$_2$)]			510(br)		310(sh)		280	^{c}
[Ph$_4$P]$_2$[{W(2-pic)(CO)$_3$}$_2$Hg(CN)$_2$]		710	460			290		
[Ph$_4$P]$_2$[{W(quin)(CO)$_3$]$_2$Hg(CN)$_2$]			490(br)		315(sh)		275	
[Ph$_4$P][W(2-pic)(CO)$_2$(CN)Hg(CN)$_2$]		710	460			300		
[Ph$_4$P][W(quin)(CO)$_2$(CN)Hg(CN)$_2$]			500(br)		315(sh)		280	

^{a} In acetone solution (10^{-4} M). ^{b} ϵ values in dm^3 mol^{-1} cm^{-1}. ^{c} Insoluble in acetone.

Results and discussion

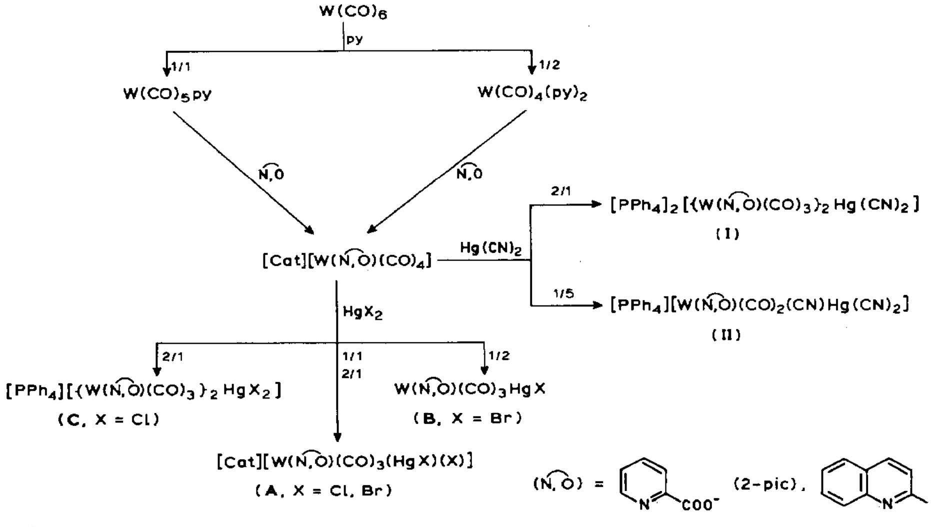
The reactions described in this paper are shown in Scheme 1. Characteristic data for new compounds are listed in the Tables 1 and 2. Most of the new complexes are fairly unstable, and some of them are insoluble in common solvents.

I. Reaction of [W(CO)$_5$(2-Mepy)] or [W(CO)$_4$(py)$_2$] with 2-picolinate and 2-quinaldinate anions. Formation of the species [Cat]$^+$[W(N,O)(CO)$_4$]$^-$ (N,O = 2-pic, quin)

The [W(CO)$_4$(py)$_2$] (py = pyridine) and [W(CO)$_5$(2-Mepy)] (2-Mepy = 2-methylpyridine) complexes were found to react with the potassium salts of the 2-picolinic and 2-quinaldinic acids to give the hexacoordinated anionic tungsten(0) complexes K[W(N,O)(CO)$_4$]. Sometimes traces of the pentacarbonyl species K[W(N,O)(CO)$_5$] were detected. The new compounds are microcrystalline, very unstable solids, which decompose even when stored at low temperatures under an inert atmosphere in the absence of light.

The [Ph$_4$P]$^+$ or [Ni(phen)$_3$]$^{2+}$ cations have been used previously to stabilize anionic carbonyl species of Group VIB [4,14], and we chose to isolate the [Ph$_4$P][W(N,O)(CO)$_4$] and [Ni(phen)$_3$][W(N,O)(CO)$_4$]$_2$ species, which are more stable than the potassium salts, although they do slowly decompose to give decarbonylation products. The stability in solid state and solution increase in the following sequence: $K^+ <$ [Ni(phen)$_3$]$^{2+}$ $<$ [Ph$_4$P]$^+$ and quin < 2-pic.

The new anionic complexes isolated are soluble in polar solvents and behave as 1/1 ([Ph$_4$P]$^+$ derivatives) or 2/1 ([Ni(phen)$_3$]$^{2+}$ derivatives) electrolytes in freshly prepared acetone solutions. The low values of molar conductivity in some cases are attributed to the low ionic mobilities of the large ions present in the solution. The [Ph$_4$P][W(N,O)(CO)$_4$] complexes are diamagnetic and the [Ni(phen)$_3$]$^{2+}$ derivatives have μ_{eff} 2.90 BM, corresponding to a Ni^{2+} ion in octahedral environment.



Scheme 1

	Solvent	$(\widehat{\mathrm{N,O}})$ Ligand	Molar ratio (W/Hg)		
			2/1	1/1	1/2
HgX_2	Acetone	2-pic	A	A	B
		2-quin	A	A	B
	CH_2Cl_2	2-pic	A	A	B
		2-quin	A	A	B
	THF	2-pic	C_1	A	product mixture
		2-quin	C_2	A	

Type **A**: $[\mathrm{W}(\widehat{\mathrm{N,O}})(\mathrm{CO})_3(\mathrm{HgX})(\mathrm{X})]^-$

Type **B**: $[\mathrm{W}(\widehat{\mathrm{N,O}})(\mathrm{CO})_3(\mathrm{HgX})]_n$

Type **C**: $[\{\mathrm{W}(\widehat{\mathrm{N,O}})(\mathrm{CO})_3\}_2(\mathrm{HgCl_2})]^{2-}$

Scheme 2

The IR spectra of $[W(N,O)(CO)_4]^-$ complexes in the carbonyl stretching region are typical of *cis*-$[M(CO)_4L_2]$ compounds [15]; the ν(CO) frequencies are slightly lower than those for the neutral complexes $[W(CO)_4(N,N)]$ [7] [N,N = bipy, phen, dmp (2,9-dimethyl-1,10-phenanthroline)]. The ν(CO) frequencies of 2-picolinate derivatives are generally lower than those of quinaldinate complexes, suggesting that the 2-picolinate is a stronger donor than the quinaldinate ligand. Depending on the cation used, small changes in the ν(CO) vibrations are observed; such behaviour has been observed previously for complexes of the type $[Cat][Mo(CN)(CO)_3(bipy)]$ (Cat = K^+, $[Ni(phen)_3]^{2+}$) [14].

The ν_{as}(OCO) and ν_s(OCO) frequencies of the carboxylate group, and also the difference between these two values, indicate that this group is unidentate [16].

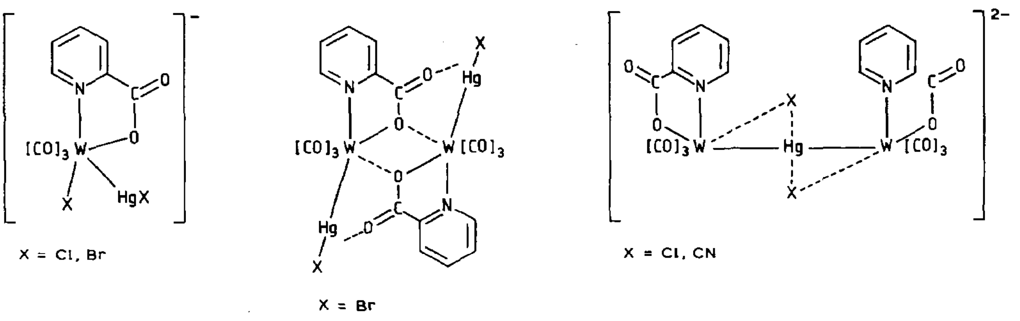
A (N,O)-bidentate coordination of the 2-pic and quin ligands in the $[W(N,O)(CO)_4]^-$ complexes, similar to that previously described [1,2,4], is proposed.

II. Reactions of [Cat][W(N,O)(CO)$_4$] complexes with HgX$_2$ (X = Cl, Br, CN)

II.I. Reactions with HgX$_2$ (X = Cl, Br)

The reactions of the $[W(N,O)(CO)_4]^-$ species with HgX_2 (X = Cl, Br) give three types of product depending on the solvent and molar ratio used. The products have been characterized by spectroscopic, analytical, magnetic, and conductivity data (see Tables 1 and 2). Scheme 2 shows which compounds are obtained under various conditions.

II.1.1. Reactions in acetone. The reactions in acetone with a 2/1 or 1/1 W/Hg molar ratio all yield complex (A), which is characterized as a tungsten(II) heptacoordinate anionic species of formula $[W(N,O)(CO)_3(HgX)(X)]^-$ (X = Cl, Br), similar to those described for neutral complexes with (N,N)-donor ligands [6,7] (Fig. 1). The $[W(N,O)(CO)_3(HgX)(X)]^-$ species are diamagnetic, and the new compounds isolated behave as 1/1 or 2/1 electrolytes depending on the cation present. The IR spectra in the ν(CO) region are consistent with a *fac*-distribution of the three CO



A B C,I

Fig. 1. Probable formulae of the new complexes.

groups, and the ν(CO) frequencies are in the range observed for $[M(CO)_3(N,N)(HgX)(X)]$ (M = Mo, W) [7]. The ν_{as}(OCO) and ν_s(OCO) bands of the 2-picolinate or quinaldinate ligands are in the same region as those of the starting complexes, which suggests that there is (N,O)-coordination (Table 1).

When the reaction is carried out with a 1/2 W/Hg molar ratio, a different species is formed. The IR spectra of these products have the ν_{as}(OCO) band of the carboxyl group at lower frequencies than those of the complexes of type **A**.

II.1.2. Reactions in dichloromethane. The reactions with $HgBr_2$ in CH_2Cl_2 were monitored by IR spectroscopy, and various reaction times and reagent concentrations were used (Fig. 2a). The choice of $HgBr_2$ as reagent stems from the higher stability in solution of $HgBr_2$ derivatives. The initial concentration of the $[Ph_4P][W(N,O)(CO)_4]$ complexes in CH_2Cl_2 was ca. 10^{-4} *M*. As for the reactions in acetone, the reaction with $[W(2\text{-pic})(CO)_4]^-$ are faster than those with the analogous quin complexes. Use of a W/Hg ratio < 1/1 produces a mixture of the type **A** product with the starting carbonyl complex, but none of the latter remains if the W/Hg molar ratio is 1/1; under these conditions the reaction is almost immediate. Addition of further $HgBr_2$ in the direction of a W/Hg ratio of 1/2 leads to the formation of a new species **B** along with one of type **A**, and **B** is the sole product, formed within a few minutes, at a 1/2 ratio.

The compounds of type **B** can be isolated (see Experimental section). They are reddish-brown diamagnetic solids, with analytical and conductivity data consistent with the formulation $[W(N,O)(CO)_3(HgBr)]$. The pattern of their ν(CO) absorptions in the infrared spectrum is similar to that of the type **A** complexes, which is consistent with presence of a W–HgX bond in compounds **B** also.

On the other hand, the shift of ν_{as}(OCO) by 60 cm^{-1} to lower frequencies can be attributed to the interactions in the two oxygens of the carboxylate group. Dorsett [1] suggests the formation of a polymer, $[W(2\text{-pic})(CO)_3]_n$, in which the (N,O)-ligand provides an oxygen bridge between two tungsten atoms. In our case a similar coordination mode for the (N,O)-ligand is proposed, possibly together with inter- or intra-molecular interactions of the other oxygen atom (C=O) with HgBr. Heptacoordination around the W^{II} atom is consistent with all data obtained (Fig. 1).

We tried to confirm the structure of complex **B** by treating it with N-donor ligands such as pyridine (py) and acetonitrile. The reaction with py occurs with partial decomposition and deposition of Hg metal but an unstable yellow solid can

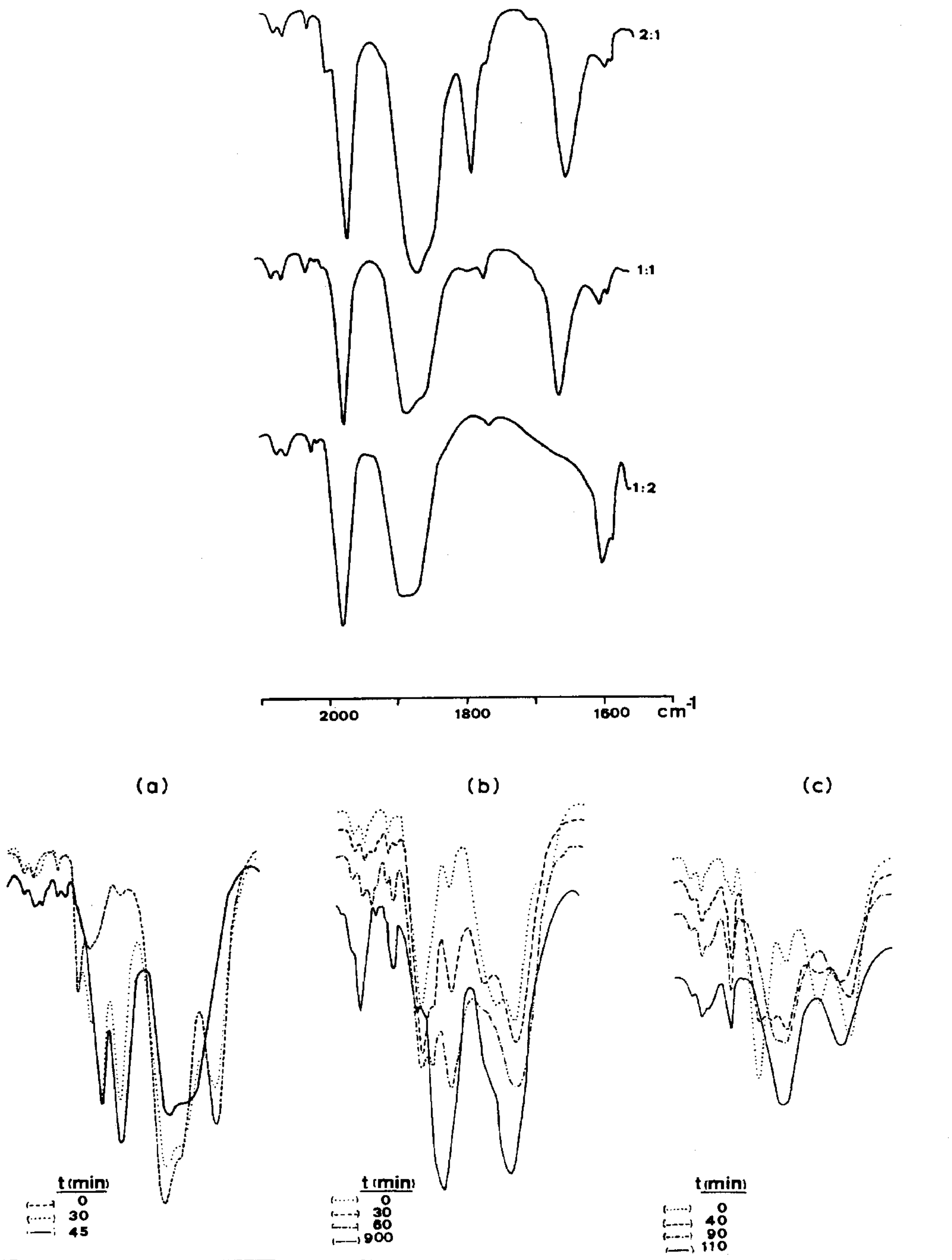


Fig. 2. (a) ν(CO) and ν_{as}(OCO) bands in CH_2Cl_2 solutions of reactions of $[W(quin)(CO)_4]^-$ with HgX_2 in 2/1, 1/1 and 1/2 molar ratios. (b) Monitored ν(CO) bands in CH_2Cl_2 solutions of reactions of $[W(2\text{-pic})(CO)_4]^-$ with $Hg(CN)_2$ in a (2/1), b (1/1), c (1/5) molar ratios.

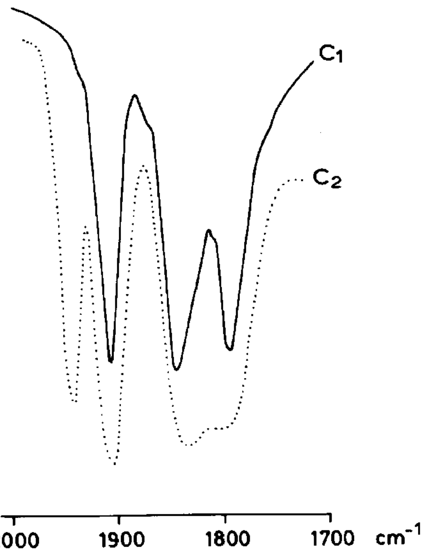


Fig. 3. ν(CO) bands in the compounds of the type C.

be isolated in very low yield. The IR spectrum of this product shows the presence of coordinated pyridine with a shift of the ν(CO) to lower frequencies than in the complex **B**, and an increase in the ν_{as}(OCO) frequencies of the carboxylate group (1660 cm^{-1}). These data indicate the formation of a complex of the type $[W(N,O)(CO)_3(py)(HgBr)]$ by cleavage of a carboxylate bridge. Analogous results were observed in the IR spectrum of the solution obtained from the reaction in acetonitrile.

II.1.3. Reactions in THF. Reactions of the $[W(N,O)(CO)_4]^-$ species with $HgCl_2$ in THF in 2/1 ratio give products of type **C**, $[Ph_4P]_2[\{W(N,O)(CO)_3\}_2(HgCl_2)]$. However, reaction under the same conditions of $[W(Diket)(CO)_4]^-$ (Diket = diketonate) with $HgCl_2$ gives $[W(Diket)(CO)_3(HgCl)_2]^-$ [12].

In type **C** complexes, differences in the IR spectrum in the ν(CO) region are observed, depending on the (N,O) ligand. The quin derivative (type C_2) shows a pattern of ν(CO) bands analogous to that observed for several compounds [10,17,18] in which there are two $M(CO)_3$ units for each Hg atom; the splitting of the bands is assigned to "skew" configuration similar to that described by Fischer and Noack for the $[CpMo(CO)_3]_2Hg$ complex [19]. In contrast, the IR spectrum of $[Ph_4P]_2[\{W(2\text{-pic})(CO)_3\}_2(HgCl_2)]$ (type C_1) shows three sharp bands of ν(CO) vibrations; a "trans" disposition of the tricarbonyl groups in the complex could account for this [19].

The two complexes are diamagnetic and 2/1 electrolytes in acetone. The 2-pic or quin ligands act as anionic (N,O)-donor ligands.

When the reaction is carried out in 1/1 ratio, the same complexes than those obtained in acetone are isolated. However, in 1/2 ratio a products mixture is obtained.

II.2. Reactions of [Cat][W(N,O)(CO)$_4$] complexes with Hg(CN)$_2$

The reactions in CH_2Cl_2 were also monitored by IR spectroscopy (Fig. 2b). When a 2/1 W/Hg ratio is employed, a type I compound is formed. Addition of further $Hg(CN)_2$ produces a new compound (type II). The rate of reaction depends on the amount of $Hg(CN)_2$ added. Thus, for a 1/5 W/Hg ratio the final compound is obtained after 1.45 h. Use of any ratio (1/1 to 1/5) gives the same final product type.

Analytical, spectroscopic, and conductivity data are consistent with the formulation of the compounds I as $[Ph_4P]_2[\{W(N,O)(CO)_3\}_2Hg(CN)_2]$. These complexes are unstable to air and decompose even when stored at low temperatures under inert atmosphere and absence of light. They are diamagnetic solids, soluble in polar solvents such as CH_2Cl_2 and acetone in which much decomposition is observed. The conductivity values of freshly prepared solutions are characteristic of 2/1 electrolytes. The IR spectra are consistent with "skew" dimeric arrangement of the $W(CO)_3$ moieties around to the W–Hg–W bond [19], and a (N,O) coordination of the 2-pic or quin ligand. No ν(CN) bands are seen (such behaviour has been observed previously for $Hg(CN)_2nL$ adducts [20]) but the Raman spectra show two weak bands at ca. 2050 and 2140 cm^{-1} attributable to $\nu(C{\equiv}N)$ vibrations. Heptacoordination around the W^0 atom and the presence of a W–Hg–W bond are consistent with all the data obtained (Fig. 1).

Type II compounds are paramagnetic species formulated as $[Ph_4P][W(CN)(N,O)(CO)_2Hg(CN)_2]$. Their IR spectra show an intense ν_{as}(OCO) band characteristic of a (N,O) coordination of 2-pic or quin ligands. Two ν(CO) vibrations are to higher frequencies than those for the tungsten(0) dicarbonyl complexes [21], but they are in the same region as those from the molybdenum(II) dicarbonyl complexes [22,23]. Two bands (ca. 2040 and 2120 cm^{-1}) are assigned to $\nu(C{\equiv}N)$ vibrations of CN groups possibly bonded to different metals. Low values have also been noted for cyanomercury derivatives containing M–Hg bonds [8,9,24], and attributed to an increase in the ionic nature of the interaction and the negative charge on the nitrogen atom; furthermore cyano complexes of molybdenum give $\nu(C{\equiv}N)$ bands in the 2130–2030 cm^{-1} region [25]. Consequently, there may be interactions between mercury and CN via nitrogen in these compounds. A "pseudo-bridged" behaviour of the CN ligands is suggested [24]. The Raman spectrum for 2-pic derivative shows the presence of two $\nu(C{\equiv}N)$ bands, at 2048 and 2157 cm^{-1}. Its ^{13}C NMR spectrum shows two signals, at δ 121 and 116 ppm, which are consistent with the presence of two different cyanide groups; the signals corresponding to the CO and $[Ph_4P]^+$ groups appear at 206 and ca. 134 ppm, respectively. The magnetic moment (2.1 BM) is consistent with the presence of W^I in the type II compounds.

Electronic spectra

The electronic spectra in acetone solution (325–900 nm) and the diffuse reflectance (900–190 nm) were recorded for new derivatives (Table 2). The nature of the absortion maxima was assigned by comparison with data reported in the literature [26,27]. Bands in 400–540 nm range were assigned to $M \rightarrow L_{\pi^*(CO)}$ charge transfer transitions. The values for these maxima vary with the type of compounds, the changes perhaps being due to the nature of the groups bonded to mercury and to the environment around the tungsten. The increase in the energy of the $M \rightarrow L_{\pi^*(CO)}$ transition with respect to that for the $[W(N,O)(CO)_4]^-$ complexes is consistent with an increase in the formal oxidation state of tungsten upon metal–metal bond formation. Small differences are observed depending on the nature of the ligand and the cation.

For the complexes with $[Ni(phen)_3]^{2+}$, the reflectance diffuse spectra show a weak band at ca. 785 nm, which is attributed to the $^3A_{2g} \rightarrow {}^3T_{2g}$ transition of this complex [28].

Experimental

All reactions were carried out under oxygen-free dry nitrogen. Analytical grade solvents were used. The $[W(CO)_5(2\text{-Mepy})]$, $[W(CO)_4(py)_2]$, and $[Ni(phen)_3]Cl_2$ complexes were prepared as previously described [29,14]. C, H, and N analyses were carried out by Elemental Micro-Analysis Ltd. Laboratories (Devon). IR spectra were recorded on a Perkin–Elmer 1300 spectrophotometer with KBr pellets and CH_2Cl_2 solutions. Conductance measurements were performed on acetone solutions at room temperature with a Philips conductivity bridge PW9506120 and a PW9510160 conductivity cell. Electronic spectra were recorded in a Kontron Uvikon 820 spectrophotometer equipped with a reflectance attachment. The magnetic susceptibilities were determined by the Faraday method.

Preparation of potassium 2-picolinate and quinaldinate

The 2-picolinic or quinaldinic acid (65 mmol) was added to a solution of KOH (0.3479 g.; 65 mmol). The suspension was stirred and a pearl-coloured white solid was formed. This was filtered off, washed with ethanol, and dried in vacuo over P_2O_5 (96% yield).

Preparation of [Cat][W(N,O)(CO)$_4$] complexes (N,O = 2-pic, quin)

K[W(N,O)(CO)$_4$] complexes. A suspension of the potassium salt of the (N,O) ligand (0.5 mmol) in acetone was added with stirring to a solution of $[W(CO)_5(2\text{-Mepy})]$ or $[W(CO)_4(py)_2]$ (0.5 mmol) in acetone. The mixture was refluxed for 30 min (2-pic derivative) or 45 min (quin derivative). The reddish solution was cooled to 0 °C and filtered. Addition of cold light petroleum (b.p. 40–60 °C) to the filtrate produced an oil. After decantation of the supernatant solution, the residual solvent was evaporated from the oil and then cold diethyl ether was added to give an orange (2-pic complex) or dark-brown (quin complex) solid, which was washed with diethyl ether and dried in vacuo (ca. 30–40% yield).

[Ph$_4$P][W(N,O)(CO)$_4$] complexes. $[W(CO)_5(2\text{-Mepy})]$ or $[W(CO)_4(py)_2]$ (1.0 mmol) and the potassium 2-picolinate or quinaldinate (1.0 mmol) were refluxed in acetone (15 ml) until CO evolution ceased (30–45 min). The solution was allowed to cool to room temperature and then filtered. $[Ph_4P]Br$ (1.0 mmol) was added and the mixture was stirred for some minutes. Diethyl ether was added and the solution again filtered. The filtrate was diluted with cold hexane (150 ml) and the solid that separated was filtered off, washed with cold hexane/diethyl ether, and dried in vacuo. $[Ph_4P][W(2\text{-pic})(CO)_4]$ (orange, 85% yield) $[Ph_4P][W(quin)(CO)_4]$ (reddish-brown, 80% yield).

[Ni(phen)$_3$][W(N,O)(CO)$_4$]$_2$ complexes. The complexes were prepared as described above, except that a solution of $[Ni(phen)_3]Cl_2$ in a 2/1 ratio (W complex/Ni complex) in 20 ml of distilled and degassed water was used. More distilled water

was added until the precipitation was complete. The solid obtained was washed with cold hexane and dried in vacuo. (yield: ca. 85%).

Reactions of the [Cat][W(N,O)(CO)$_4$] complexes

Reaction of the [W(N,O)(CO)$_4$]$^-$ species with HgX$_2$ (X = Cl, Br) in 1/1 W/Hg ratio. Formation of the species [W(N,O)(CO)$_3$(HgX)(X)]$^-$. Method A. In a typical experiment, $HgCl_2$ (0.004 mmol) was added to a stirred solution in acetone of $[Ni(phen)_3][W(2\text{-pic})(CO)_4]_2$ (0.002 mmol). Stirring was continued for 10 min, and the solution filtered trough Celite. The filtrate was treated with cold light petroleum (b.p. 40–60 ° C) and the precipitate formed was filtered off, washed with cold light petroleum and diethyl ether, and dried in vacuo (55% yield). In the case of $[Ph_4P]^+$ derivatives, the precipitation was carried out with diethyl ether.

Method B. A mixture of $[Ph_4P][W(N,O)(CO)_4]$ (0.1 mmol), $HgCl_2$ (0.1 mmol) and dry THF (12 ml) was stirred for 15 min, then the solution was filtered through Celite. The filtrate was stirred for 1 h and a large volume of light petroleum (150 ml, b.p. 40–60 ° C) was added, to give a orange precipitate that was filtered off, washed with light petroleum, and dried in vacuo (90% yield).

Reaction of the [Ph$_4$P][W(N,O)(CO)$_4$] complexes with HgCl$_2$ in 2/1 ratio. Formation of the species [Ph$_4$P]$_2$[{W(N,O)(CO)$_3$}$_2$(HgCl$_2$)]. These complexes were prepared by reaction of $HgCl_2$ (0.1 mmol) and $[Ph_4P][W(N,O)(CO)_4]$ (0.2 mmol) in dry THF (15 ml). After 10 min stirring the mixture was filtered and the filtrate was stirred for 1 h. The solid formed was filtered off, washed with THF, and dried in vacuo (80% yield).

Reaction of [Ph$_4$P][W(N,O)(CO)$_4$] complexes with HgBr$_2$ in 1/2 ratio. Formation of [W(N,O)(CO)$_3$(HgBr)]$_n$. A mixture of $HgBr_2$ (0.2 mmol), the tungsten complex (0.1 mmol), and CH_2Cl_2 (10 ml) was stirred 3 min then filtered through Celite and the filtrate was stirred for 40 min. The solid formed was filtered off, washed with CH_2Cl_2, and dried in vacuo (60% yield).

Reaction of [Ph$_4$P][W(N,O)(CO)$_4$] complexes with Hg(CN)$_2$ in 2/1 W/Hg ratio. Formation of [Ph$_4$P]$_2$[{W(N,O)(CO)$_3$}$_2$Hg(CN)$_2$]. A mixture of $Hg(CN)_2$ (0.035 mmol), $[Ph_4P][W(N,O)(CO)_4]$ (0.070 mmol) and CH_2Cl_2 (10 ml) was kept at 40 ° C for 45 min then filtered through Celite. Addition of light petroleum (30 ml, b.p. 40–60 ° C) to the filtrate produced a precipitate, which was washed with cold light petroleum and dried in vacuo (60% yield).

Reaction of [Ph$_4$P][W(N,O)(CO)$_4$] with Hg(CN)$_2$ in 1/5 ratio. Formation of [Ph$_4$P][W(CN)(N,O)(CO)$_2$Hg(CN)$_2$]. A mixture of $[Ph_4P][W(N,O)(CO)_4]$ (0.01 mmol), $Hg(CN)_2$ (0.05 mmol) and CH_2Cl_2 (10 ml) was stirred for 2 h, then filtered. Addition of light petroleum (30 ml, b.p. 40–60 ° C) to the filtrate produced a solid, which was filtered off, washed with cold light petroleum and dried in vacuo (70% yield).

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