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Synthesis, characterization and thermal behavior of heterobimetallic carbonyl compounds of the type $[W(CO)_4(bipy)(CuX)](X = Cl, N_3, ClO_4$ and $BF_4)$

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Abstract—Four new heterobimetallic metal carbonyls were synthesized by the reaction of $[W(CO)_4(bipy)]$ (**1**) with copper(I) compounds leading to species with the general formula $[W(CO)_4(bipy)(CuX)]$ ($X = Cl, N_3, ClO_4, BF_4$) (**2–5**). The metal carbonyl compounds were characterized by elemental analysis, infrared and UV–visible electronic spectroscopy and thermogravimetric analysis. The IR data for **2–5** show carbonyl stretching band patterns similar to compound **1**; ie they exhibit the same number of bands. The UV–vis results show a dissociation reaction generating the starting compound **1** and CuX as consequence of a weak interaction between **1** and CuX. Thermal decomposition mechanisms as well as the thermal stability are influenced by the CuX fragments. The thermal stability decreases in the order $[W(CO)_4(bipy)] > [W(CO)_4(bipy)(CuCl)] > [W(CO)_4(bipy)(CuBF_4)]$. The X-ray results show the formation of WO_3, $CuWO_4$, Cu_2O and CuO as final decomposition products. © 1997 Elsevier Science Ltd

Keywords: tungsten; copper; carbonyl; infrared spectroscopy; thermal analysis.

The chemistry of heteronuclear metal carbonyls has been of considerable interest for over a decade [1] mainly due to structural aspects, reactivity of these compounds in respect to several classes of organic ligands and interesting electronic properties provided by the heteronuclear metal–metal bond. Group 6 metal carbonyl derivatives, particularly, have been utilized as starting material to produce heteronuclear [2] compounds. Reactions of carbonyl complexes of type $[M(CO)_4(L\text{-}L)]$ (M = Cr, Mo, W; L-L = bipy, phen, diphos) with mercuric halides [3] and halotin(IV) derivatives [4], for example, produce, *via* oxidative addition, seven-coordinated M^{II} compounds containing M—Hg and M—Sn bonds, respectively.

Similar processes using copper(I) compounds have not yet been reported, so we decided to examine these reactions using $[W(CO)_4(bipy)]$, as a part of our ongoing studies [5,6] of homo and heteronuclear metal carbonyl complexes. The heterobimetallic metal carbonyls prepared, of general formula $[W(CO)_4(bipy)(CuX)]$ ($X = Cl, N_3, ClO_4, BF_4$), were characterized by infrared and UV–vis spectroscopies and thermogravimetric analysis. The final decomposition products obtained have been characterized by X-ray powder diffractometry.

EXPERIMENTAL

General comments

All the syntheses were carried out under purified nitrogen in a Schlenk apparatus. Solvents were purified and dried by specific methods [7]. All reagents were obtained from commercial suppliers and used without any further purification. $[W(CO)_4(bipy)]$ **1** and $[Cu(CH_3CN)_4]X$,† $X = ClO_4, BF_4$, were prepared

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† In the synthesis of $[Cu(CH_3CN)_4]BF_4$, the $Cu(BF_4)_2 \cdot xH_2O$ was treated previously with $MgSO_4$.

by the appropriate methods described in the literature [8,9]. Elemental analyses were performed by Central Analítica do IQ-USP (Brazil). Copper content was determined by complexometric titration with standard EDTA solution (0.0100 M), in the presence of the indicator PAN, using a microburet METHROM model E-274.

Synthesis of heterobimetallic complexes

[W(CO)$_4$(bipy)(CuCl)] **2**. A suspension of **1** (0.50 g, 1.10 mmol) and CuCl (0.11 g, 1.12 mmol), in 20 cm^3 of dichloromethane, was stirred for 2 h. The dissolution of the suspension took place yielding a light red solid which filtered off, washed with hexane (2 × 10 cm^3) and then dried *in vacuo*. Yield: 0.376 g, 62%. Found: C, 30.0; H, 1.4; N, 5.2; Cu, 11.0. Calc. for $C_{14}ClCuH_8N_2O_4W$: C, 30.5; H, 1.4; N, 5.1; Cu, 11.5%.

[W(CO)$_4$(bipy)(CuN$_3$)] **3**. To a solution of 0.05 g (0.77 mmol) of NaN$_3$, partially solubilized in 20 cm^3 of methanol/dichloromethane (1 : 1), 0.38 g (0.70 mmol) of **2** was added. The mixture was stirred for 2 h at room temperature, its colour changing gradually from light red to light orange. The resulting light orange solid was filtered off, washed thoroughly with diethyl ether, and dried *in vacuo*. Yield: 0.261 g, 67%. Found: C, 29.8; H, 1.5; N, 12.1; Cu, 11.0. Calc. for $C_{14}CuH_8N_5O_4W$: C, 30.2; H, 1.4; N, 12.6; Cu, 11.3%.

[W(CO)$_4$(bipy)(CuClO$_4$)] **4**. To a suspension of 0.36 g (1.10 mmol) of [Cu(CH$_3$CN)$_4$]ClO$_4$ in 20 cm^3 of dichloromethane, 0.50 g (1.10 mmol) of **1** was added. The mixture was stirred for 2 h at room temperature to give an orange solid which was filtered off, washed with diethyl ether, and then dried *in vacuo*. Yield: 0.344 g, 51%. Found: C, 27.9; H, 1.4; N, 4.8; Cu, 10.1. Calc. for $C_{14}ClH_8N_2CuO_8W$: C, 27.4; H, 1.3; N, 4.6; Cu, 10.2%.

[W(CO)$_4$(bipy)(CuBF$_4$)] **5**. Heterobimetallic metal carbonyl **5** was obtained using a work-up similar to that used for **4**. 0.50 g (1.10 mmol) of **1** reacts with 0.34 g (1.10 mmol) of [Cu(CH$_3$CN)$_4$]BF$_4$ to give **5** as an orange solid. Yield: 0.364 g, 55%. Found: C, 28.4; H, 1.4; N, 4.6; Cu, 10.9. Calc. for $BC_{14}CuF_4H_8N_2O_4W$: C, 27.9; H, 1.3; N, 4.6; Cu, 10.5%.

Instrumental

Infrared spectroscopy. Infrared spectra (IR) were recorded on a Nicolet FTIR-730 spectrophotometer in the spectral range 4000–400 cm^{-1} with the samples in the form of potassium bromide pellets or in acetone solution using a cell of KBr.

UV–vis electronic spectroscopy. Electronic spectra were measured on a Hewlett Packard 8552-A diode-array spectrophotometer, in the range 600–250 nm, in dichloromethane solution (1.00 × 10^{-3} M) with a quartz cell (1 cm), under an atmosphere of prepurified dinitrogen. The dissociation and decomposition reactions were followed by scanning the spectra from time to time.

Thermogravimetric analysis. Thermogravimetric analysis (TG) was carried out under dynamic flow of dry synthetic air (25 cm^3 min^{-1}) and a heating rate of 20°C min^{-1}, using a TGS-2 Perkin-Elmer thermoanalyser.

X-ray diffractometry. The X-ray diffractograms were obtained with an HGZ 4/B horizontal diffractometer (G.D.R.) equipped with a proportional counter and pulse height discriminator. The Bragg-Bretano arrangement was adopted using Cu-K_α radiation (λ = 1.541 Å) and setting of 34 kV and 20 mA. The peaks were identified using ASTM data files [10].

RESULTS AND DISCUSSION

The reaction of the metal carbonyl [W(CO)$_4$(bipy)] (**1**) with copper(I) compounds in the molar ratio 1 : 1 occurs without elimination of CO ligands, leading to 1 : 1 adducts of the general formula [W(CO)$_4$ (bipy)(CuX)] (X = Cl, N$_3$, ClO$_4$ and BF$_4$) (**2**–**5**). The elemental analysis results are in agreement with the proposed formula. These heterobimetallic metal carbonyl complexes show in the solid state a partial stability to environmental air. All attempts to obtain a single crystal of the new heterobimetallic compounds, for X-ray diffraction studies, failed. These compounds are not stable in solution, generating in a dissociation process the starting metal carbonyl **1** and CuX (X = Cl, N$_3$, ClO$_4$ and BF$_4$). The compounds **2**–**5** were characterized by IR and UV–vis spectroscopies and thermogravimetric analysis (TG). The results obtained with these techniques are presented below.

IR spectra

The frequencies (cm^{-1}) of the more significant bands that appear in the spectra of the new products are given in Table 1, together with those of the starting metal carbonyl compound. In general, the CO stretching vibrations are the most characteristic ones for the carbonyl compounds and allow a clear distinction of the adducts from products arising as a result of oxidative addition reactions. Thus, the general pattern of bands observed in the νCO region of the IR spectra of **1**–**5** are similar, i.e., they all show four bands suggesting, therefore, a C_{2v} symmetry around the tungsten atom. Furthermore, the formation of compounds *via* an oxidative-addition can be discarded considering that, in this way, their IR spectra would show only three νCO bands displaced toward higher frequencies in comparison to **1**, due to the lowering in the electronic density on the tungsten atom as a result of its oxidation. The foregoing suggestion is reinforced by the IR spectra of the heterobimetallic metal carbonyls recorded immediately after dissolution in acetone and under N$_2$ which are identical to that of the starting

Table 1. IR spectral data[a] (cm^{-1}) for carbonyl metal complexes

Compound	$\nu(C—H_{ar})$	$\nu(CO)$	$\nu(C—N)$	$\nu(C—C)$
$[W(CO)_4(bipy)]$		2005(m)		
	3115(w)	1969(s)	1608(w)	1469(m)
	3090(w)	1909(s)		1440(m)
		1810(s)		
$[W(CO)_4(bipy)(CuCl)]$		2001(m)		
	3111(w)	1902(s)	1606(w)	1480(m)
	3080(w)	1862(s)		1440(m)
		1800(s)		
$[W(CO)_4(bipy)(CuN_3)]$[b]		2005(m)		
	3120(w)	1925(s)	1604(w)	1475(m)
	3092(w)	1880(s)		1439(m)
		1796(s)		
$[W(CO)_4(bipy)(CuClO_4)]$[c]		2016(m)		
	3115(w)	1900(s)	1605(w)	1470(m)
	3084(w)	1827(s)		1431(m)
		1789(s)		
$[W(CO)_4(bipy)(CuBF_4)]$[d]		2000(m)		
	3110(w)	1907(s)	1615(w)	1485(m)
	3080(w)	1832(s)		1443(m)
		1789(s)		

[a] s = Strong; m = medium; w = weak; sh = shoulder.
[b] $\nu_{as}N_3 = 2065\ cm^{-1}$.
[c] $\nu_{as}(Cl—O)$ = 1103(sh), 1080(s) cm^{-1}.
[d] $\nu_{as}(B—F)$ = 1158(m), 1003(s), 965(m) cm^{-1}.

compound **1** in the range of the CO stretching frequencies. This point allows us to confirm the formation of the adducts. In addition, it is noteworthy that for **2–5** three νCO bands are shifted to lower frequencies, a feature that may be suggestive of CO groups semi-bridging the tungsten and copper atoms.

The IR spectrum of **3** evidences that the chlorine atom is being displaced by the pseudo-halogen N_3^-. This fact is confirmed by the appearance of a single strong absorption band at 2065 cm^{-1}, assignable [11] to the asymmetric stretching $\nu_{as}(N_3)$.

In the IR spectra of the compounds **4** and **5**, absorption bands assignable to $\nu(C{\equiv}N)$ (2300–2200 cm^{-1}) are not observed. This fact indicates that acetonitrile ligands have been removed from the coordination sphere of the copper atom. Moreover, the IR spectrum of compound **4** shows two absorption bands at 1103 and 1080 cm^{-1} assignable to the $\nu_{as}Cl—O$ vibrational mode [12], indicating the presence of a monodentate perchlorate group coordinated to copper. For compound **5** there are three absorption bands at 1158, 1003 and 965 cm^{-1}, assignable to the $\nu_{as}B—F$ vibrational mode [13], indicating a bidentate coordination of the BF_4 group to the copper atom.

UV–vis electronic spectra

The electronic spectra of the heterobimetallic metal carbonyl compounds **2–5**, recorded immediately after dissolving solid samples in dichloromethane and under N_2 are identical to that of $[W(CO)_4(bipy)]$ [14]. All of them show two bands at 256 and 298 nm which, because of their high intensity and locations, are assigned to CT transitions $\pi^*(CO) \leftarrow d\pi$ (W), one band at 352 nm corresponding to $\pi \rightarrow \pi^*$ transition of bipyridine ligand and one broad band at 484 nm assigned to MLCT (d-π^*bipy). In the light of the results presented above, the existence of a dissociation process of these heterobimetallic metal carbonyl compounds in solution, leading to the starting metal carbonyl **1** and CuX, could be confirmed (see Scheme 1). Scanning spectra from time to time showed after 30 min, a decrease in the intensity of the corresponding bands assigned to CT transitions, indicating the decomposition of **1**. The solution reactions may be represented as follows:

$$\begin{tikzcd}
{[W(CO)_4(bipy)(CuX)]} \arrow[r, "\text{very fast}", "CH_2Cl_2,\ N_2"'] & {[W(CO)_4(bipy)] + CuX} \arrow[d, "\text{slow}"] \\
{X = Cl,\ N_3,\ ClO_4,\ BF_4} & \text{decomposition products}
\end{tikzcd}$$

Scheme 1.

The results of UV–vis spectroscopy are in agreement with IR data; i.e. the formation of adducts which show a weak interaction between $[W(CO)_4(bipy)]$ and CuX (X = Cl, N_3, ClO_4, BF_4). In order to get more information about these compounds in the solid state, we utilized thermogravimetric analysis and the results obtained from this technique are presented below.

Thermogravimetric analysis

The thermal analysis has become in the past few years an important tool for studies of metal carbonyl compounds [15]. In the present work the application of the thermogravimetric analysis has its main purpose in revealing the influence of the CuX moiety (X = Cl, BF_4) on the initial decomposition temperature and on the thermal decomposition mechanisms. The heterobimetallic compounds **3** and **4** exhibit an explosive character, so it was not possible to carry out a study of these complexes by thermogravimetry. Table 2 lists the steps, initial and final temperatures (°C), partial and total weight losses (%) for the thermal decompositions of **1**, **2** and **5**, in dry air atmosphere. The TG curves for these compounds, under dry air atmosphere, are shown in Fig. 1.

The metal carbonyl **1** is stable up to 170°C beyond which a first mass loss takes place corresponding to, by mass calculation, the loss of two CO groups and the uptake of O_2. In the temperature range of 230–540°C the loss of another two CO groups and the combustion of bipyridine ligand is observed. A constant mass was reached at 540°C and the residue was identified as WO_3 (ASTM card file 5-388) [10].

The TG curve of **2** evidences that its thermal degradation starts above 140°C. The first decomposition step suggests, by mass calculation, the loss of four CO groups and the uptake of O_2. In the second step (178–273°C) a consumption of O_2, associated with a mass gain occurs, followed by a third step (273–529°C) corresponding to the pyrolysis of bipyridine ligand. A constant mass was reached at 529°C and the final decomposition product was identified as a mixture of WO_3, $CuWO_4$, CuO and Cu_2O in a ratio of approximately 4 : 4 : 2 : 1 (ASTM card file: 5-388; 21-307; 5-667; 5-661, respectively) [10].

Table 2. Thermal analysis data for compounds **1**, **2** and **5**

Compound	Step	T_i (°C)	T_f (°C)	Δm (%)
[W(CO)$_4$(bipy)]	1	170	230	8.85
	2	230	310	22.56
	3	310	540	17.26
				(48.67)
[W(CO)$_4$(bipy)(CuCl)]	1	140	178	13.55
	2	178	273	−1.20
	3	273	529	30.72
				(43.07)
[W(CO)$_4$(bipy)(CuBF$_4$)]	1	45	200	13.31
	2	200	468	34.82
				(48.13)

T_i = initial temperature; T_f = final temperature; Δm = mass variation; total percentage mass losses are shown in parentheses for each compound.

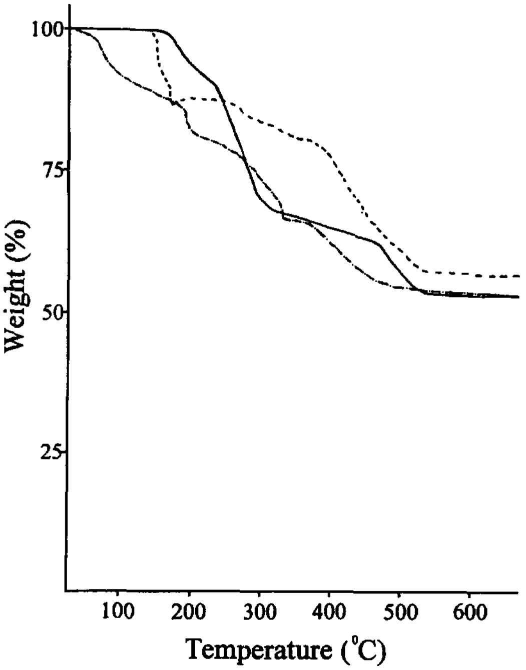

Fig. 1. TG curve of [W(CO)$_4$(bipy)] (——), [W(CO)$_4$(bipy)(CuCl)] (– – –) and [W(CO)$_4$(bipy)(CuBF$_4$)] (–·–·–) in dry air.

The thermal decomposition of **5** starts at 45°C with a mass loss attributable to, as observed for **2**, the loss of four CO groups and the uptake of O_2. Between 200 and 468°C, a mass loss occurs which was attributed to the pyrolysis of the bipyridine. A constant mass was reached at 468°C and the final residue was identified as a mixture of WO_3, $CuWO_4$, CuO and Cu_2O in a ratio of approximately 4 : 4 : 2 : 1.

Summarizing the above results it was seen that the complexes **1**, **2** and **5** liberate CO groups at the beginning of the decomposition process. However, the loss of these ligands occurs in two steps for **1** and one step for **2** and **5**, suggesting in these latter cases that the thermal degradation processes are faster than **1**. Moreover, the initial decomposition temperatures of **2** and **5** are smaller than that of its precursor **1**, probably due to the influence of the fragment CuX (X = Cl, BF_4), which causes the destabilization of the heterobimetallic metal carbonyl compounds. Thus, taking into account the initial temperature of the decomposition processes, it was possible to establish the following thermal stability order: [W(CO)$_4$(bipy)] > [W(CO)$_4$(bipy)(CuCl)] > [W(CO$_4$(bipy)(CuBF$_4$)]. The lower thermal stability of **2** and **5** as compared with **1** can be reasonably explained by the presence in the adducts, of CO groups interacting with the metallic atoms. This point is supported by the available IR data.

It is also verified by X-ray phase analysis of the final decomposition product that the presence of the copper atom in the complex leads to the formation of $CuWO_4$ besides the generation of copper oxides. In addition it was observed that the chlorine atom and BF_4 group have no influence on the composition and on the proportion of the final decomposition products. Another important point to emphasize is that despite the thermal degradation processes occurring in an oxidizing atmosphere, some copper atoms remain in the copper(I) form.

In conclusion, the results of the present work have shown that the reaction of $[W(CO)_4(bipy)]$ with copper(I) compounds leads to a new class of heterobimetallic carbonyl compounds without elimination of CO ligands. The IR and UV–vis spectra indicate that in solution these heterobimetallic compounds undergo a dissociation process with the recurrent formation of starting metal carbonyl and CuX. The thermal analysis results have demonstrated that interaction of **1** and CuX promotes the thermal destabilization of the heterobimetallic complexes. Current studies involving these heterobimetallic metal carbonyl compounds are under way to better elucidate the structural and electronic parameters. These heterobimetallic metal carbonyl compounds in solid state present luminescent properties when excited by UV radiation ($\lambda_{exc} = 400$ nm). Preliminary results, obtained from emission and excitation spectroscopy, show that the emission maximum band of these complexes is dependent on CuX fragments.

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