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Molybdenum and Tungsten Hydroxocarbonylhydrides and Hydroxocarbonylnitrosyls

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The results of an investigation on a series of molybdenum and tungsten hydroxocarbonyl complexes related to the « acidic species » formulated by Hieber as $H_3M_2(CO)_6(OH)_3$ *(*$M=Mo, W$*) are reported. By allowing these compounds to react with tertiary phosphine oxides, complexes are obtained which have been characterized as tertiary phosphine oxide adducts of tetrakis (*μ_3*-hydroxotricarbonylhydrido metal):* $\{[(HO)M(CO)_3H]_4 . 4\ OPR_3\}$*. The nitrosyl derivatives are also described and contain a similar tetrameric unit with four NO groups in place of the four hydrogen atoms and four CO groups:* $\{[(HO)M(CO)_2(NO)]_4 . 4 OPR_3\}$*. NMR and IR investigation led us to propose, for Hieber's « acidic species » and for the derived nitrosyl species, the formulae:* $\{[(HO)M(CO)_3H]_4 . 4 H_2O\}$ *and* $\{[(HO)M(CO)_2(NO)]_4 . 4H_2O\}$ *respectively.*

Introduction

Hieber and coworkers described the reaction of molybdenum and tungsten hexacarbonyls with ethanolic potassium hydroxide solutions to give the salts $K_3[M_2(CO)_6(OH)_3]$ ($M=Mo, W$)[1,2] and the products obtained by treating these salts with hydrochloric acid, formulated as $H_3M_2(CO)_6(OH)_3$. These species, which behave like moderately strong acids in aqueous solution, react with various ligands to give trisubstituted compounds $M(CO)_3L_3$ (with L= tertiary phosphine and arsine, dimethylsulphoxide etc.). From $H_3Mo_2(CO)_6(OH)_3$ with triphenylphosphine oxide Hieber obtained a compound formulated as the monomeric species $Mo(CO)_3(OPPh_3)$.[1] More recently in these laboratories some derivatise of the same class have been studied, and the derived nitrosyl species, which were formulated as dimeric: $[Mo(CO)_3L(OH)]_2$ or $[M(CO)_3L(H_2O)]_2$ and $[M(CO)_2(NO)L(OH)]_2$ ($M=Mo$, W; $L=H_2O$, OPR_3).[4]

Since the tricarbonyl compound of molybdenum in a crystal structure determination[5] was found to be tetrameric and isomorphous with their dicarbonylnitrosyl derivative, $\{[(HO)Mo(CO)_2(NO)]_4 . 4\ OPPh_3\}$, we have reinvestigated typical members of these complexes with the following aims: to ascertain their molecular complexities, to clarify the linkage of the acidic hydrogen atoms in the molecular framework, and to study the bonding properties of the hydroxo groups.

Results and Discussion

The present investigation has led to the characterization of the five types of compounds reported in Table I. All the compounds are diamagnetic both in the solid state and in solution.

Characterization of the potassium salts of tri(μ*-hydroxo) hexacarbonyldimetallate, (*$M = Mo, W$*) Compounds (I) of Table I.* These compounds, recrystallized from a water/ethanol (1/1) mixture, exist as dimers as found by X-ray analysis[6] and are formulated as the hydrated potassium salts of the anion tri(μ-hydroxo)hexacarbonyldimetallate: $K_3[M_2(CO)_6(OH)_3] . 2 H_2O$. This anion, whose structure is schematically illustrated in Figure 1a, contains two $M(CO)_3$ units connected by three μ-hydroxo groups. The intermetallic distance of 3.23 Å found in the tungsten compound

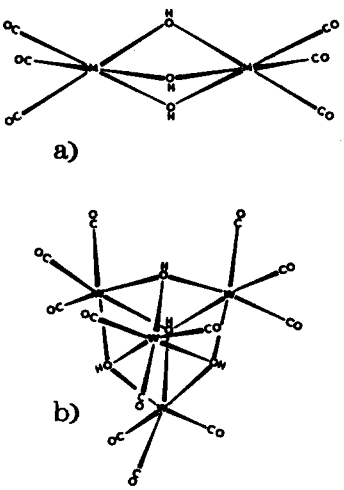

Figure 1. Schematical drawing of the structure
a) $[M_2(CO)_6(OH)_3]^{3-}$ *b*) $[(HO)W(CO)_3]_4$ determined by X-ray analysis.

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[2] W Hieber, K. Englert, and K. Rieger, Z. *Anorg. Allg. Chem.*, *300*, 304 (1959).

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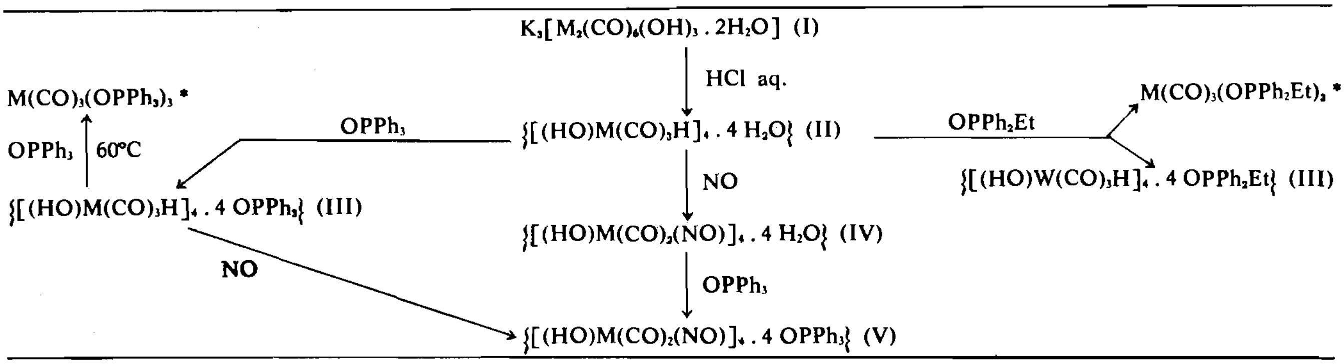
Table I.



M=Mo,W.; * M=Mo, Ref. 4.

Table II. Infrared data for compounds(I)[a] in the range 4000-600 cm^{-1}

	νH$_2$O	νOH	νCO	δH$_2$O	δMOH	ρH$_2$O
(I) $K_3[Mo_2(CO)_6(OH)_3].2H_2O$	3660(m) 3540(s) 3300(br)	2950(w) 2920(m) 2850(w)	1855(vs) 1680(vs)	1580(s)	1150(w,br)	760(m) 660(m)
$K_3[W_2(CO)_6(OH)_3].2H_2O$	3570(s) 3300(br)	2950(w) 2930(m) 2855(w)	1840(vs) 1700(vs,br)	1600(vs,br)	1150(w,br)	780(m) 670(m)

[a] In fluorolube mull supported between sodium chloride plates vs=very strong; m=medium; w=weak; sh=shoulder; br=broad

is considered to be non-bonding, the diamagnetism of the compound and the inert-gas rule are obeyed without requiring a metal-metal bond. Nuclear magnetic resonance spectra in D_2O, in agreement with this structure, show signals of H_2O protons and signals at 3.38 ppm (M = Mo) and 4.10 ppm (M = W), lower than the H_2O protons signal, which are attributed to the protons of the OH bridging groups. Moreover the infrared spectra exhibit two strong and rather broad bands in the region 1860-1680 cm^{-1} due to the stretching of the CO groups in agreement with the two IR active stretching modes expected for the six carbonyls from the idealized D_{3h} symmetry of the anion ($A_2'' + E'$). Other band assignments are reported in Table II.

Characterization of the triphenylphosphine oxide adducts of tetrakis(μ_3-hydroxotricarbonylhydridometal) and tetrakis(μ_3-hydroxodicarbonylnitrosylmetal), (M = Mo, W) Compounds (III) and (V) of Table I. X-ray analysis of typical members of the title compounds[5,7] have shown the presence of tetranuclear species $[(HO)M(CO)_3]_4$ and $[(HO)M(CO)_2(NO)]_4$ with the metal atoms at the corners of a tetrahedron, linked by four μ_3-hydroxo groups (see Figure 1b). The phosphine oxide molecules are found to be bonded to the bridging OH groups by hydrogen bonds. In both cases, the intermetallic distance are 3.43-3.49 Å which excludes the presence of metal-metal bonds. However the diamagnetism of compounds (III) does not agree with the formulation, $\{[(HO)M(CO)_3]_4 . 4\ OPR_3\}$, in which the metal atoms have an oxidation state of +1. This formulation is not consistent with the fact that the potassium salts, $K_3[M_2(CO)_6(OH)_3]$, in which the metal atoms exibit an oxidation state of zero, can give with hydrochloric acid and $OPPh_3$ the compound (III) without evolving hydrogen (see Table I). The nuclear magnetic resonance spectra of compounds (III) (Figure 2) in addition to the signals of alkyl and aryl groups of the tertiary phosphine oxides and signals at τ 1-4 ppm, which we assign to the μ_3-OH protons show other signals at τ 12-14 ppm which must be attributed to hydrogen bonded to the metal (Table III). Therefore the compounds (III) are considered as hydrides and since the ratio between the integrated areas of OH and MH protons signals is 1:1, they are formulated as tertiary phosphine oxide adducts of tetrakis(μ_3-hydroxotricarbonylhydridometal) $\{[(HO)M(CO)_3H]_4 . 4\ OPPh_3\}$

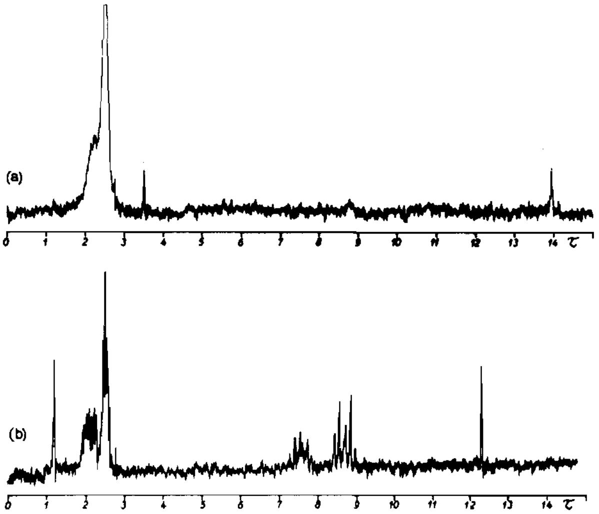


Figure 2. Proton magnetic resonance spectra of:
a) $\{[(HO)Mo(CO)_3H]_4 . 4\ OPPh_3\}$;
b) $\{[(HO)W(CO)_3H]_4 . 4\ OPPh_2Et\}$.

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(7) V. Albano, G. Ciani, M. Manassero, and M. Sansoni, results to be published.

Table III. Nuclear magnetic resonance data for compounds(II) and (III)

Compounds	solvents	τ–OH	τ–H_2O	τ–MH	τ—other protons signals ·		
					H–phenyl	CH_2–ethyl	CH_3–ethyl
(II) $\{[(HO)Mo(CO)_3H]_4 . 4H_2O\}$	(a)	3.73	6.30	13.70			
$\{[(HO)W(CO)_3H]_4 . 4H_2O\}$	(a)	2.31	6.68	12.28			
(III) $\{[(HO)Mo(CO)_3H]_4 . 4\ OPPh_3\}$	(b)	3.52	—	13.95	1.8-2.8		
$\{[(HO)W(CO)_3H]_4 . 4\ OPPh_2Et\}$	(b)	1.20	—	12.34	1.8-2.8	7.5	8.7

The spectra have been recorded at 35°C using TMS as internal reference; (a) in $(CD_3)_2CO$; (b) in $CDCl_3$.

Table IV. Infrared data for compounds (II) and (III) in the range 4000-600 cm^{-1}

Compounds	νH_2O	νOH (*)	νCO	δH_2O	δMOH	νPO	ρH_2O
(II) $\{[(HO)Mo(CO)_3H]_4 . 4H_2O\}$	3600(m) 3400(sh)	2950(w) 2920(m) 2850(w)	2030(sh) 2008(vs) 1920(vs) 1880(sh) 1855(s)	1620(m)	1050(w,br)		775(m) 715(m)
$\{[(HO)W(CO)_3H]_4 . 4H_2O\}$	3600(m) 3350(m)	2950(w) 2920(m) 2845(w)	2150(vw) 2000(vs) 1920(vs) 1880(s) 1845(s)	1620(m)	1110(w,br)		810(s) 715(m)
(III) $\{[(HO)Mo(CO)_3H]_4 . 4\ OPPh_3\}$		2960(m) 2930(m) 2860(sh)	1995(vs) 1910(vs) 1895(sh)			1185(s)	
$\{[(HO)W(CO)_3H]_4 . 4\ OPPh_3\}$		2920(w) 2850(w) 2730(m)	2110(m) 1995(vs) 1905(vs) 1865(s)			1180(s)	
$\{[(HO)W(CO)_3H]_4 . 4\ OPPh_2Et\}$		2920(w) 2850(w) 2730(m)	2120(m) 1990(vs) 1890(vs) 1855(s)			1165(s)	

$OPPh_3$ ν_{PO} 1190 cm^{-1} (vs); $OPPh_2Et$ ν_{PO} 1170 cm^{-1} (vs). All spectra were obtained in nujol mull, (*) in fluorolube mull.

Table V. Infrared data for compounds (IV) and (V) in the range 4000-600 cm^{-1}

Compounds	νH_2O	νOH (*)	νCO	νNO	δH_2O	νPO	δMOH	ρH_2O
(IV) $\{[(HO)Mo(CO)_2(NO)]_4 . 4H_2O\}$	3500(s) 3320(vw)	2960(v,br) 2920(m) 2860(w)	2050(sh) 2030(vs) 1930(vs)	1670(vs)	1600(br)		1100(w,br)	795(m) 720(s)
$\{[(HO)W(CO)_2(NO)]_4 . 4H_2O\}$	3460(s) 3310(vw)	2950(v,br)	2010(vs) 1910(vs)	1680(vs)	1600(br)		1050(w,br)	810(w) 720(s)
(V) $\{[(HO)Mo(CO)_2(NO)]_4 . 4\ OPPh_3\}$		2950(sh) 2920(m) 2850(m)	2015(vs) 1915(vs)	1655(vs)		1185(s)		
$\{[(HO)W(CO)_2(NO)]_4 . 4\ OPPh_3\}$		2950(sh) 2925(m) 2850(m)	2070(m) 1996(vs) 1896(vs)	1645(vs)		1175(s)		

All spectra were obtained in nujol mull, (*) in fluorolube mull.

(M=Mo, W), $\{[(HO)W(CO)_3H]_4 . 4\ OPPh_2Et\}$. Moreover the NMR spectra of their nitrosyl derivatives, compounds (V), do not exhibit signals at $\tau > 10$ ppm and therefore they are triphenylphosphine oxide adducts of tetrakis(μ_3-hydroxodicarbonylnitrosylmetal) $\{[(HO)M(CO)_2(NO)]_4 . 4\ OPPh_3\}$. This is in agreement with the fact that in carbonyl hydrides the NO group usually displaces a CO and a hydridic hydrogen.

The infrared spectra of compounds (III) show bands in the regions 3000-2700 cm^{-1}, 2120-1855 cm^{-1} and 1185-1165 cm^{-1} attributed respectively to the OH, CO, and OP stretching modes (Table IV). The infrared spectra of the nitrosyl derivatives, compounds (V), apart from the features common to the compounds (III), show a strong band at about 1650 cm^{-1} assignable to the NO stretching mode (Table V). On this basis, the reactions of compounds (III) shown in Table I can be represented by the following equations:

$$\{[(HO)Mo(CO)_3H]_4 . 4\ OPPh_3\} + 8\ OPPh_3 \rightarrow \\ \rightarrow 4Mo(CO)_3(OPPh_3)_3 + 4H_2O$$

$$\{[(HO)M(CO)_3H]_4 . 4\ OPPh_3\} + 4NO \rightarrow \\ \rightarrow \{[(HO)M(CO)_2(NO)]_4 . 4\ OPPh_3\} + 4CO + 2H_2$$

Characterization of the water adducts of tetrakis(μ_3-hydroxotricarbonylhydridometal) and of tetrakis(μ_3-hydroxodicarbonylnitrosylmetal) (M = Mo, W) Compounds (II) and (IV) of Table I. For these compounds, at present, there is no direct X-ray evidence. The nuclear magnetic resonance spectra of compounds (II) (Fgiure 3) show signals due to OH and MH protons whose chemical shifts are similar to those found in the spectra of their corresponding adducts with tertiary phosphine oxides, compounds (III) $\{[(HO)M(CO)_3H]_4 . 4\ OPR_3\}$ (Figure 2), and other signals at τ 6-7 ppm due to the H_2O protons (Table III). Moreover, their IR spectra show bands in the region 3600-3300 cm^{-1}, at 1620 cm^{-1}, and in the region 810-715 cm^{-1} due to the stretching, bending and rocking modes of water molecules.[8] Such bands are absent in the spectra of the corresponding phosphine oxide adducts, compounds (III). By comparison of the IR spectra of compounds (II) and (III) (Table IV) it can be seen that the average values of their carbonyl stretching bands are practically the same. The relative intensity of the NMR signals due to the MH and OH groups, and the similarities between their infrared spectra, strongly support the fact that the ratio between the number of metal atoms and the hydride hydrogen atoms in compounds (II) and (III) are the same. Therefore, it is reasonable to formulate the compounds (II) as water adducts of tetrakis(μ_3-hydroxotricarbonylhydridometal): $\{[(HO)M(CO)_3H]_4 . 4\ H_2O\}$. The NMR spectra of their nitrosyl derivatives, compounds (IV), do not exhibit high field signals due to MH protons and their IR spectra show bands due to the stretching and bending modes of water molecules, which disappear in their triphenylphosphine oxide adducts, compounds (V) (Table V). Compounds (IV) can therefore be formulated as water adducts of tetrakis(μ_3-hydroxodicarbonylnitrosylmetal): $\{[(HO)M(CO)_2(NO)]_4 . 4\ H_2O\}$ (M = Mo, W).

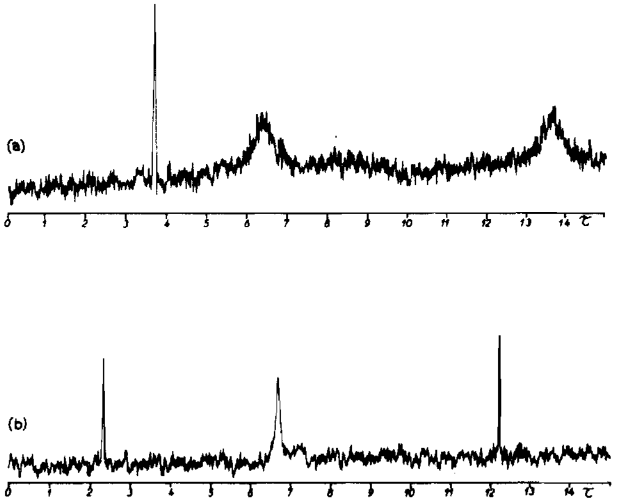

Figure 3. Proton magnetic resonance spectra of:
a) $\{[(HO)Mo(CO)_3H]_4 . 4H_2O\}$;
b) $\{[(HO)W(CO)_3H]_4 . 4H_2O\}$.

The metal-hydrogen bond. Compounds (II), $\{[(HO)M(CO)_3H]_4 . 4\ H_2O\}$, are acidic in aqueous solution, a property which is common to various carbonyl hydrides. Hieber determined the first dissociation constant of the molybdenum compound, giving a value of 1.4×10^{-3}.[1] These hydrides are extremely unstable, air sensitive, solid compounds; however a greater stability is achieved in their phosphine oxide adducts, $\{[(HO)M(CO)_3H]_4 . 4\ OPR_3\}$.

The compounds (II) are obtained by protonation of the anions, $[M_2(CO)_6(OH)_3]^{3-}$, with hydrochloric acid, and compounds (III) by allowing an ethanolic solution of compound (II) to react with tertiary phosphine oxides. These reactions are represented by the following equations:

$$2K_3[M_2(CO_6(OH)_3] + 6HCl + 2H_2O \rightarrow \\ \rightarrow \{[(HO)M(CO)_3H]_4 . 4H_2O\} + 6KCl$$

$$\{[(HO)M(CO)_3H]_4 . 4H_2O\} + 4\ OPR_3 \rightarrow \\ \rightarrow \{[(HO)M(CO)_3H]_4 . 4\ OPR_3\} + 4H_2O$$

The metal-hydrogen bond formation implies the attack by a proton on an electron pair of the metal atom, which acts as a base. As a consequence less back-donation from the metal atom to the three CO groups attached to it must be expected in the compounds (II) and (III) than in $M(CO)_3(\sigma{-}L_3)$ complexes. The average ν_{CO} values of the molybdenum hydrides and other molybdenum carbonyl derivatives reported in Table VI are in agreement with these considerations. Unfortunately, it was impossible to see the IR bands due to the MH stretching and bending modes, even by investigation of the deuterated compounds. In these hydrides each metal atom is seven-coordinate. From the crystallographic study of the compound $\{[(HO)W(CO)_3]_4 . 4\ OPPh_2Et\}$[7] seven-coordination appears to be a triangle-square system with the three oxygen atoms of the bridging OH groups on one side and the three CO groups including the hydrogen atom on the other side.

Table VI.

Compound	Average ν_{CO} values in cm^{-1}	Ref.
$Mo(CO)_6$	1985	
$\{[(HO)Mo(CO)_3H]_4 . 4\ L\}$	1940	
cis-$Mo(CO)_3(OPPh_3)_3$	1860	14
cis-$Mo(CO)_3$dien	1828	15
$K_3[Mo_2(CO)_6(OH)_3] . 2H_2O$	1767	

L = H_2O, $OPPh_3$; dien = diethylentriamine
All spectra were obtained in najol mull.

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[8] K. Nakamoto: Infrared spectra of inorganic and coordination compounds - Wiley New York, London (1963) pag. 155.

Table VII. Elemental analyses and colours of compounds (III), (IV) and (V)

				Analyses			
Compounds	Colour	C%		H%		N%	
		found	reqd.	found	reqd.	found	reaqd.
(III) $\{[(HO)Mo(CO)_3H]_4 . 4\,OPPh_3\}$	yellow	52.85	52.94	3.56	3.57	—	—
$\{[(HO)W(CO)_3H]_4 . 4\,OPPh_3\}$	green-yellow	45.06	44.83	2.98	3.02	—	—
$\{[(HO)W(CO)_3H]_4 . 4\,OPPh_2Et\}$	green-yellow	39.20	39.53	3.35	3.29	—	—
(IV) $\{[(HO)Mo(CO)_2(NO)]_4 . 4H_2O\}$	orange-red	11.40	11.05	1.58	1.38	6.82	6.45
$\{[(HO)W(CO)_2(NO)]_4 . 4H_2O\}$	orange-red	8.06	7.86	1.14	0.98	4.73	4.59
(V) $\{[(HO)Mo(CO)_2(NO)]_4 . 4\,OPPh_3\}$	red	50.18	50.31	3.50	3.35	3.02	2.93
$\{[(HO)W(CO)_2(NO)]_4 . 4\,OPPh_3\}$	red	43.00	42.47	2.98	2.83	2.36	2.47

In Figure 1b, the hydrogen atoms bonded to the metals are not drawn but their position can be inferred because one of the OC—M—CO angles is considerably larger than the other two.

The bridging hydroxo groups and the hydrogen bonds. In the dimeric and tetrameric compounds, we have seen that the metal atoms are linked by double or triple bridging hydroxo groups respectively. Triple bridging OH groups are rather uncommon and have been previously characterized only in the compounds $[Cu_3(C_6H_5N_2O)_3OH]SO_4 . xH_2O$,[9] $Ni_6(CF_3COCHCOCH_3)_{10}(OH)_2(H_2O)_2$,[10] $Pb_4(OH)_4^{4+}$,[11] and $Ni_4(OH)_4^{4+}$,[12] (the last two only in solution). Both in double and triple bridging, the structural data indicate an approximate sp^3 hybridization of the atomic orbitals of the oxygen atoms. The hydrogens of the OH groups must be acidic, due to the relevant electron donation from the oxygen atoms to the metals. This condition favours the formation of strong hydrogen bonds with the H_2O and OPR_3 molecules. In fact the O - - - O hydrobond distance in the phosphine oxide adducts (compounds (III) and (V)) is in the range 2.45-2.50 Å,[5,7] remarkably lower than the value of Van der Waals contact (2.80 Å).

The stretching frequencies of the OH ligands have been found in the region 3000-2700 cm^{-1}. The ν_{O-H} values for the hydroxo groups bonded to transition metals are usually found in the range 3500-3300 cm^{-1}. The low values observed here may be considered as due both to the double or triple bridging of the hydroxo groups and to the presence of hydrogen bonds. The latter effect is certainly more important, as indicated by the very short O - - - O distances. Analogous considration explain the low τ values of the μ_3—OH protons τ 1.2-3.8) (Table III).

In the IR spectra of compound (II) and (IV), bands have been assigned to the M—O—H bending modes at 1150-1050 cm^{-1}, close to the value of 1100 cm^{-1} assigned by Nakamoto[13] to the same vibrations in the compound $K_4[(ox)_2Co(\mu\text{—}OH)_2Co(ox)_2]$. For compounds (III) and (V), due to the presence of the phosphine oxides, it has been impossible to see these bands. Finally, the ν_{P-O} values in the phosphine oxide adducts (III) and (V) are only slightly lower with respect to the free oxides due to the presence of the hydrogen bonds.

Experimental Section

All reactions have been carried out under nitrogen, solvents being saturated with nitrogen before use.

Starting materials: molybdenum and tungsten hexacarbonyls were Climax Molybdenum Co. products. Tertiary phosphine oxides have been prepared following the methods previously reported.[14]

The infrared spectra have been recorded with a Perkin-Elmer model 457 grating spectrophotometer and the nuclear magnetic resonance spectra with a Perkin-Elmer R-10 instrument operating at 35°C and 60 Mc.

Magnetic susceptibilities of the solids have been measured by the Gouy method.

Elemental analyses of the complexes are given in Table VII. Compounds (I) and (II) have been prepared following methods described by Hieber and co-workers.[1,2,3]

Preparation of compounds (III) $\{[(HO)M(CO)_3H]_4 . 4\,OPPh_3\}$ *(M=Mo, W).* To a solution prepared by dissolving triphenylphosphine oxide (1.7 g, 6 mmoles) in ethanol (15 ml) was added, at room temperature, a solution of $\{[(HO)M(CO)_3H]_4 . 4H_2O\}$ (1.5 mmoles) in ethanol (15 ml). Crystalline products, which separate immediately from the solution, were collected by filtration, washed with few milliliters of ethanol, and dried under vacuum. The compounds are soluble in chloroform, methylene chloride and acetone are partially soluble in ethanol and benzene and insoluble in n-pentane. They decompose readily in the air.

$\{[(HO)W(CO)_3H]_4 . 4\,OPPh_2Et\}$. To a warm solution prepared by dissolving diphenylethylphosphine oxide (1.61 g, 7 mmoles) in ethanol (15 ml) was added a solution of $\{[(HO)W(CO)_3H]_4 . 4H_2O\}$ (1.82 g, 1.5 mmoles) in ethanol (15 ml). The mixture was heated at 70-80°C for several minutes and then allowed to cool to room temperature. On evaporating of the solvent, green-yellow crystals were formed. These were collected by filtration, washed with n-pentane, and dried under vacuum. The compound is soluble in acetone, ethanol, chloroform and benzene but insoluble in n-pentane.

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[14] F. Canziani, F. Zingales, and U. Sartorelli, *Gazz. Chim. It.*, *94*, 841 (1964).

Preparation of compouns (IV) $\{[(HO)M(CO)_2(NO)]_4 . 4H_2O\}$ *(M=Mo, W).* Nitric oxide was bubbled through a solution of $\{[(HO)M(CO)_3H]_4 . 4H_2O\}$ (3 mmoles) in ethanol (30 ml), over a period of 10-12 hours at room temperature. The resulting red solutions were filtered and after removal of the solvent orange-red solids were obtained. The compounds are soluble in acetone, ethanol, chloroform and methylene chloride, slightly soluble in benzene, insoluble in n-pentane.

Preparation of compounds (V) $\{[(HO)M(CO)_2(NO)]_4 . 4\ OPPh_3\}$ *(M=Mo, W).* To a solution prepared by dissolving $\{[(HO)M(CO)_2(NO)]_4 . 4H_2O\}$ (1.5 mmoles) in ethanol (30 ml) was added at room temperature a solution of triphenylphosphine oxide (1.7 g, 6 mmoles) in ethanol (15 ml). After a few minutes red crystalline compounds separated off. These were collected by filtration, washed with ethanol, and dried under vacuum. These compounds can be also obtained if nitric oxide is bubbled through a solution of $\{[(HO)M(CO)_3]_4 . 4\ OPPh_3\}$ in ethanol over a period of 10-12 hours at room temperature. The complexes are soluble in acetone, chloroform and methylene chloride, slightly soluble in ethanol, insoluble in n-pentane.

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