

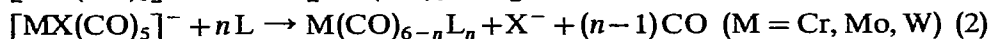
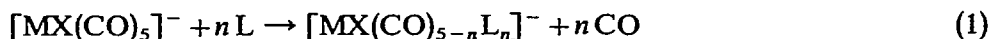
QUINONE COMPLEXES OF MOLYBDENUM AND TUNGSTEN

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In previous papers¹ from these laboratories it had been reported that halopentacarbonyl anions of Group VI transition elements react with nucleophiles in two different ways, as shown below.



A suggestion was made¹ that the π -acceptor properties of the ligand L were responsible for the different chemical behaviour.

Activated olefins, such as maleic anhydride and maleimide react¹ according to eqn. (1). It was anticipated that even stronger π -acceptors such as quinones would also react according to eqn. (1), yielding negatively charged complexes.

We have now found that *p*-benzoquinone substitutes all the carbon monoxide groups from the $[\text{MX}(\text{CO})_5]^-$ anions yielding new molybdenum and tungsten complexes of formula $[\text{MX}(\text{Quinone})_3]^-$.

The first quinone complex of a transition metal was reported some years ago by Sternberg, Markby and Wender² who prepared $\text{Fe}(\text{CO})_3(\text{Duroquinone})$ by irradiation of $\text{Fe}(\text{CO})_5$ in the presence of 2-butyne. Nickel complexes of substituted quinones were later described by Schrauzer and coworkers³⁻⁵. No quinone complexes of Group VI metals have been reported yet.

We also describe an uncharged *p*-benzoquinone compound of molybdenum of formula $\text{Mo}(\text{Quinone})_3$.

EXPERIMENTAL

All of the operations were carried out in an atmosphere of prepurified nitrogen.

Because of the sensitivity of the complexes, especially those of molybdenum, to moisture, carefully dried solvents were used throughout the preparations of the compounds. Tetrahydrofuran and 2,2'-dimethoxydiethyl ether (diglyme) were distilled over sodium and lithium aluminium hydride. *p*-Benzoquinone reagent grade (Fluka) was recrystallised three times from ethanol and sublimed before use.

Infrared spectra were measured with a Perkin-Elmer model 521 instrument equipped with grating. Except when indicated otherwise, nujol mulls of the compounds were used to measure the infrared spectra.

The NMR spectra were measured with a Varian DP60A instrument.

The magnetic susceptibilities were measured with a Gouy balance at different field strengths from 6,400 to 11,000 oersted.

TABLE I
ANALYTICAL DATA AND PROPERTIES OF *p*-BENZOQUINONE COMPLEXES^a OF MOLYBDENUM AND TUNGSTEN

Compound	No.	Colour	C(%)		H(%)		N(%)		Halogen(%)		Metal(%)		Yield (%)
			Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	
[NEt ₄][MoCl(C ₆ H ₄ O ₂) ₃]	(I)	black	53.30	53.16	5.50	5.45	2.39	2.32	6.05	5.91	16.37	16.10	96
[NEt ₄][MoBr(C ₆ H ₄ O ₂) ₃]	(II)	black	49.54	49.72	5.12	4.77	2.22	2.53	12.68	12.36	15.22	14.80	87
Li[MoCl(C ₆ H ₄ O ₂) ₃] 2 diglyme ^b	(III)	black	49.29	49.45	5.52	5.69			4.85	4.62	13.12	12.96	82
Li[MoBr(C ₆ H ₄ O ₂) ₃] 2 diglyme ^b	(IV)	black	46.47	46.05	5.20	5.29			10.30	9.34	12.37	13.64	88
Mo(C ₆ H ₄ O ₂) ₃	(V)	blueblack	51.45	51.65	2.88	3.18					22.83	22.25	95
[NEt ₄][WCl(C ₆ H ₄ O ₂) ₃]	(VI)	black	46.34	46.12	4.79	5.01	2.08	2.43	5.26	5.14	27.28	27.20	94
[NEt ₄][WBr(C ₆ H ₄ O ₂) ₃]	(VII)	black	43.47	43.29	4.49	4.73	1.95	2.03	11.12	10.85	25.59	25.51	89
[NEt ₄][W(C ₆ H ₄ O ₂) ₃]	(VIII)	deepbrown	40.81	41.98	4.21	4.68	1.83	1.97	16.58	16.12	24.02	23.26	95
Li[WCl(C ₆ H ₄ O ₂) ₃] 2 diglyme ^b	(IX)	black	44.00	44.22	4.92	4.89			4.33	4.00	22.45	22.20	93
Li[WBr(C ₆ H ₄ O ₂) ₃] 2 diglyme ^b	(X)	black	41.74	42.08	4.67	4.60			9.26	8.92	21.29	20.90	85

^a The tetraethylammonium salts and tris(*p*-benzoquinone)molybdenum decompose above 160° about. Loss of diglyme from the lithium salts begins at about 100°.

^b Diglyme = CH₃O(CH₂)₂O(CH₂)₂OCH₃.

Microanalyses were by Dr. K. Eder, Ecole de Chimie, Geneva, Switzerland.

Preparation of the $[MX(\text{Quinone})_3]^-$ anions

(a) *Tetraethylammonium salts.* The preparation of compound (I) in Table 1 is described in detail, the experimental procedure being substantially the same for all the other compounds of the same type.

The tetraethylammonium salt $[\text{NEt}_4][\text{MoCl}(\text{CO})_5]$ (2.0 g; 4.98 mmoles) was dissolved in tetrahydrofuran (75 ml) and treated with *p*-benzoquinone (1.8 g; 16.6 mmoles) at room temperature under vigorous stirring. Gas evolution started immediately. After 15 h the blue-black precipitate of the quinone complex was filtered, washed with tetrahydrofuran and heptane several times and dried *in vacuo* (2.8 g; 96% yield). The compound is a black powder practically insoluble in common organic solvents and in liquid SO_2 .

The magnetic susceptibility of (I) was measured at 296° K at field strengths of 6,400, 9,600, 10,400 and 11,000 oersted. The magnetic susceptibility was practically field independent and the measured value averaged over the different fields was $\chi_M^{\text{corr}} = (381 \pm 4) \times 10^{-6}$ c.g.s.u.; $\mu_{\text{eff}} = 0.96$ B.M. per molybdenum.

Infrared bands at 1590 w, 1560 s, 1495 s-sh, 1480 s, 1200 vs, 1135 m, 1090 m, 1000 w, 968 w, 830 vs, 642 w, 610 w, 570 w and 530 w cm^{-1} .

When heated in a sublimation apparatus at 180–200° in high vacuum compound (I) decomposed. Hydroquinone sublimed and was recognised by melting point (172–173°, lit. 170°), admixed melting point and infrared spectrum.

The tetraethylammonium salts of molybdenum and tungsten show a remarkable resistance to air. Samples kept in an atmosphere of pure oxygen for several hours showed an infrared spectrum substantially identical with that of samples kept under nitrogen.

In their behaviour towards water, the molybdenum derivatives (I) and (II) are quite different from the tungsten derivatives (VI), (VII) and (VIII). The former dissolve readily in water to give a yellow solution, whereas the latter give black solids and halide ions. The black solids isolated from the treatment with water have infrared bands at 1595 and 1580 cm^{-1} characteristic of bonded *p*-benzoquinone. These results suggest that the molybdenum compounds are readily and completely decomposed by water. In the case of the tungsten compounds water displaces the coordinated halogen first and then the bonded quinone groups in a second slow step.

Magnetic susceptibility measurements on the tungsten tetraethylammonium salt (VI) gave the following results: $\chi_M^{\text{corr}} = (128 \pm 20) \times 10^{-6}$ c.g.s.u.; $\mu_{\text{eff}} = 0.55$ B.M. per tungsten. The infrared spectra of the other tetraethylammonium salts tabulated in Table 1 are reported below.

Compound (II): 1676 w, 1649 w, 1585 m-s, 1560 s, 1494 s, 1479 vs, 1210 vs, 1140 s, 1095 m, 1002 w, 972 w, 840 s, 805 m, 645 m, 570 w and 530 w cm^{-1} .

Compound (VI): 1600 w-sh, 1579 m, 1498 s-sh, 1480 vs, 1210 vs, 1145 w, 1090 w, 1000 w, 882 m-sh, 845 vs, 810 m, 755 vw, 642 vw and 575 vw cm^{-1} .

Compound (VII): 1595 w-sh, 1580 m, 1495 s-sh, 1480 vs, 1200 vs, 1145 w, 1090 w, 1000 w, 850 vs, 810 m, 640 w, 580 w and 525 cm^{-1} .

Compound (VIII): 1600 w-sh, 1585 m, 1495 s-sh, 1485 vs, 1205 vs, 1095 w, 1030 w, 1005 w, 860 vs, 810 m, 660 w and 585 m cm^{-1} .

(b) *Lithium salts.* The preparation of compound (III) in Table 1 is described in detail, the experimental procedure being substantially the same for all the other compounds of the same type.

The lithium salt $\text{Li}[\text{MoCl}(\text{CO})_5] \cdot 2$ diglyme (1.65 g; 3.02 mmoles) was dissolved in diglyme (100 ml) and treated with *p*-benzoquinone (2.5 g; 23.1 mmoles) at room temperature under vigorous stirring. Carbon monoxide was evolved and after 2 h the reaction was practically complete. The black precipitate was filtered and washed abundantly with diglyme and heptane. The reaction product was finally dried *in vacuo* (1.8 g; 81.6% yield).

In a control experiment 0.56 g (0.947 mmoles; corresponding to 4.74 mmoles of CO) of $\text{Li}[\text{MoBr}(\text{CO})_5] \cdot 2$ diglyme (calcd. CO 23.69%; found 23.43%) was treated with *p*-benzoquinone (0.50 g; 4.62 mmoles) in 50 ml diglyme at 29.1°. The reaction was carried out in a gasvolumetric apparatus of the type described previously⁶ under an atmosphere of carbon monoxide. In about 4 h 4.56 mmoles of CO were evolved corresponding to 96.2% of the expected amount.

The lithium salts (III) and (IV) are black powders. Their solubility in dry acetone and dimethyl sulphoxide is very small. They are also insoluble in all the other common organic solvents. The compounds are very sensitive to moisture, becoming deliquescent in a few seconds without change of colour. By treatment with water, a deep blue solution is readily obtained. This is, however, the result of an attack by water on the complex. When the lithium salt (III) was treated with D_2O a peak at 192 c/s downfield from the methyl protons of diglyme was observed. The ring protons of hydroquinone give a peak at 192 c/s downfield from the same reference.

By treatment of the lithium salts of tungsten (IX) and (X) with water a completely different behaviour was observed. Practically quantitative elimination of lithium halide occurred and a black precipitate was left behind. This was filtered, dried *in vacuo* and found by infrared spectrum to contain bonded *p*-benzoquinone (bands at 1595 and 1580 cm^{-1}).

In the infrared spectra the following bands were observed.

Compound (III): 1865 w, 1635 w, 1610 m, 1590 m, 1575 m, 1505 s, 1495 s-sh, 1348 s, 1260 m, 1235 s, 1212 s, 1105 m, 1075 m, 1012 m, 968 m, 945 m, 868 m, 842 s, 810 w, 760 s, 660 w-m, 565 w, 520 m and 470 w cm^{-1} .

Compound (IV): 1850 w, 1585 m, 1570 m-s, 1508 m, 1490 s-sh, 1345 s, 1260 m, 1200 vs, 1140 m, 1100 m, 1070 s, 1010 m, 942 w, 868 m, 825 vs, 795 s, 755 m, 638 w, 565 m and 515 w cm^{-1} .

Compound (IX): 1595 w-sh, 1580 m, 1515 w, 1495 s-sh, 1480 vs, 1405 w, 1325 m, 1260 w, 1200 vs-br, 1142 m, 1108 m, 1080 m, 1070 m, 1020 w, 980 w, 965 w, 860 vs, 830 s, 810 m-s, 650 w, 580 w, 568 w, 508 w and 475 w cm^{-1} .

Compound (X): 1595 w-sh, 1575 s, 1495 sh, 1480 vs, 1350 m, 1200 vs-br, 1130 s, 1108 m, 1090 m, 1080 m, 1015 w, 1004 w, 855 vs, 810 m-s, 660 w, 645 w, 580 w and 520 cm^{-1} .

Preparation of tris(p-benzoquinone)molybdenum

Hexacarbonylmolybdenum (0.7 g; 2.65 mmoles) was treated with *p*-benzoquinone (1.2 g; 11.01 mmoles) in 60 ml toluene at reflux temperature. After about 3 h the gas evolution ceased. The solid formed during the reaction was filtered, washed abundantly with toluene and petroleum ether and dried *in vacuo* (1.06 g; 95.2% yield).

Tris(*p*-benzoquinone)molybdenum is a blue-black powder insoluble in common organic solvents. It deliquesces in moist air but is stable to dry oxygen in the solid state, as shown by the invariance of the infrared spectrum on a sample maintained in an atmosphere of pure dry oxygen at room temperature for about two days.

Infrared spectrum (nujol and halocarbon mulls): 1650 w, 1590 sh, 1565 s, 1495 s-sh, 1480 vs, 1220 vs-br, 1140 w, 1090 w, 1000 vw, 960 w, 845 s, 800 w, 640 w and 580 w cm^{-1} .

Magnetic susceptibility measurements gave the following results: $\chi_M^{\text{corr}} = -(74 \pm 7) \times 10^{-6}$ c.g.s.u.

By pyrolysis of the compound at 180–200° hydroquinone and quinhydrone were obtained and identified by melting point and infrared spectra.

RESULTS AND DISCUSSION

p-Benzoquinone reacts smoothly with halopentacarbonylmetal anions of molybdenum and tungsten to give complete elimination of carbon monoxide and formation of the $[\text{MX}(\text{Quinone})_3]^-$ anions as tetraethylammonium and lithium salts. From approximate measurements of the carbon monoxide evolved with time, the reactivity of the $[\text{MX}(\text{CO})_5]^-$ anions decreases from the chloro to the iodo derivative. The same order of reactivity was found for the reactions of halogeno carbonyls of manganese⁷ and rhenium⁸ with various ligands.

The replacement of all the carbon monoxide groups from a metal carbonyl is rather unusual but hardly surprising for ligands of the type of quinones. The availability of low-lying antibonding orbitals makes quinone a probably better π -acceptor than carbon monoxide. The net result will be the weakening of the metal-carbon (to carbon monoxide) bonds in the intermediate $[\text{MX}(\text{CO})_{5-2n}(\text{Quinone})_n]^-$, thus facilitating further substitution by quinone. The isolation of the previously reported¹ $[\text{MX}(\text{CO})_2(\text{Olefin})_3]^-$ from the reactions of $[\text{MX}(\text{CO})_5]^-$ with maleic anhydride and maleimide suggests that the latter ligands should be regarded as π -acceptors of intermediate strength between carbon monoxide and *p*-benzoquinone.

The preparation of the lithium salts $\text{Li}[\text{MX}(\text{Quinone})_3] \cdot 2$ diglyme ($\text{M} = \text{Mo}, \text{W}$; $\text{X} = \text{Cl}, \text{Br}$) was necessary in order to exclude the possibility that the tetraethylammonium derivatives were mixtures of $\text{M}(\text{Quinone})_3$ and NEt_4X . This possibility had to be taken into consideration in view of the insolubility of both $\text{Mo}(\text{Quinone})_3$ (*vide infra*) and NEt_4X in the reaction medium. Contrary to tetraethylammonium halides, lithium halides are moderately soluble in diglyme. Thus, the isolation of the lithium salts (III), (IV), (IX) and (X) makes us sure that the products obtained from the $[\text{MX}(\text{CO})_5]^-$ anions contain a direct metal-halogen bond.

Particularly interesting is the question concerning the bonding and the structure of the quinone complexes. Unfortunately, their insolubility prevented measuring NMR spectra.

The infrared spectra are of importance. All the anionic compounds have very similar and rather simple infrared spectra, provided the vibrations due to the tetraethylammonium cation or to diglyme are subtracted. For band assignment, the spectrum of the uncharged compound $\text{Mo}(\text{Quinone})_3$ is also taken into consideration. The main vibrations characteristic of the bonded quinone are then recognised as being those at 1600–1565 m (a doublet), 1480–1485 vs, 1200–1220 vs and 840–845 vs cm^{-1} .

In the case of the molybdenum derivatives, the bands at $1600\text{--}1565$ and $1480\text{--}1485\text{ cm}^{-1}$ are rapidly affected by exposure to moist air and are substituted by a band at 1510 cm^{-1} , which suggests the conversion of bonded quinone to hydroquinone. The doublet at $1600\text{--}1565\text{ cm}^{-1}$ is clearly due to C–O stretching vibrations of the quinone groups. The C–O stretching vibration of uncomplexed *p*-benzoquinone consists of two bands at 1662 cm^{-1} and at 1674 cm^{-1} in CHCl_3 ⁹. This shift of about 90 cm^{-1} on complex formation is only slightly larger than that observed in maleic anhydride and maleimide complexes¹ ($\Delta\nu = 50\text{--}75\text{ cm}^{-1}$).

It seems reasonable to assign the $1480\text{--}1485\text{ cm}^{-1}$ band to the carbon–carbon stretching vibration of bonded quinone, to be compared with 1595 cm^{-1} for the corresponding vibration of uncomplexed *p*-benzoquinone¹⁰. A shift of about 100 cm^{-1} is quite common for carbon–carbon stretching frequencies of complexed olefins. Not very much is known, however, about the intensity of these vibrations. In the case of our quinone complexes we note that the band at $1480\text{--}1485\text{ cm}^{-1}$ is more intense than the band at $1600\text{--}1565\text{ cm}^{-1}$; we have therefore a situation which is exactly the reverse of that observed in uncomplexed *p*-benzoquinone. The infrared spectrum of $\text{Mo}(\text{Quinone})_3$ is shown in Fig. 1.

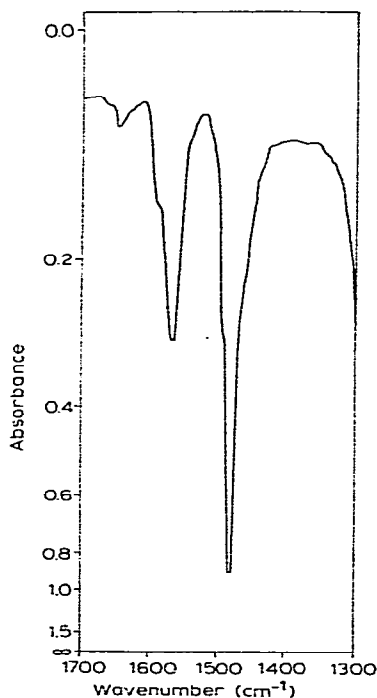
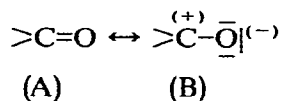


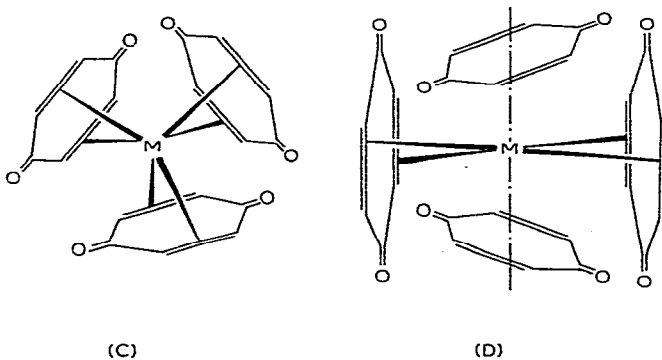
Fig. 1. Infrared spectrum of $\text{Mo}(\text{Quinone})_3$ (halocarbon mull).

In the solid state spectra of all the compounds reported in this paper the C–O stretching vibration of the quinone is split into two distinct bands separated by about 30 cm^{-1} or a shoulder is present in addition to the main band at about 1565 cm^{-1} (see also Fig. 1). A similar splitting was also observed¹¹ in some duroquinone com-

plexes of nickel, cobalt, rhodium and iridium and tentatively assigned to a nonplanar conformation of the duroquinone groups in these complexes. On the other hand, *p*-benzoquinone itself shows two bands in the carbonyl stretching region, and still it is completely planar according to a X-ray investigation¹². The splitting of the carbonyl band in *p*-benzoquinone has not been clearly elucidated, although intramolecular vibrational effects have been invoked to explain the phenomenon⁹. In the case of complexed symmetrical quinones of the type of duroquinone and *p*-benzoquinone one of the just mentioned effects could also be operative. However an alternative explanation is that in ligands of this type also the C–O stretching symmetrical vibration becomes infrared active on symmetry grounds when one considers the whole complex molecule rather than the isolated ligand only. The lowering of the carbon–carbon stretching vibration of *p*-benzoquinone by more than 100 cm⁻¹ on complexation is a clear indication of direct bonding of the metal to the carbon–carbon double bond of the quinone. The simultaneous lowering of the C–O stretching vibration by about 90 cm⁻¹ can be explained in terms of the two resonance structures (A) and (B). Of these, (B) can largely contribute to the bonding as a consequence of stabilization of the carbonyl cation caused by π -back-donation from the metal to the ligand.



We believe that a true oxidation of the metal by the ligand does not occur in these complexes in contrast to what probably occurs in the similar complexes of nickel with *p*-benzoquinone⁴. Tris(*p*-benzoquinone)molybdenum is diamagnetic and reduced magnetic moments of 0.9 and 0.5 B.M. per metal atom were found for the tetraethylammonium salts (I) and (VI). These magnetic moments are well below the value for even one unpaired electron and are not believed to be significant in view of the sensitivity of the compounds to moisture and the consequent considerable experimental difficulties connected with the measurement. No unpaired spins are therefore present in these molecules. Although the assignment of oxidation states is always difficult in compounds of this type, we can conclude that a formulation as metal(III)·3 semibenzoquinone⁽⁻⁾ is to be excluded on the basis of the magnetic data. The alternative formulation as metal(VI)·3 quinone²⁻ which would be consistent with the magnetic data is in contradiction with the presence of a carbonyl stretching vibration which is shifted by 90 cm⁻¹ only with respect to uncomplexed *p*-benzoquinone.



For tris(*p*-benzoquinone)molybdenum the most reasonable structure seems that containing three quinone groups, considered as bidentate ligands, arranged octahedrally around the central metal atom. There are however two possible ways to do that as shown in (C) and (D). (C) would be a monomeric molecule whereas in (D) *p*-benzoquinone would be bonded to two different metal atoms, thus acting as a bridge to give a polymeric structure. Although a polymeric structure of type (D) could appear in better agreement with the failure of the compound to sublime and dissolve in organic solvents, we believe that a monomeric structure such as (C) cannot be excluded *a priori*. Very important crystal forces can in fact become operative in a compound of this type.

The structure of the lithium and tetraethylammonium salts must be substantially different because a halogen ligand is here present in addition to the three quinone groups. It appears reasonable to imagine that molybdenum and tungsten are seven-coordinate in these compounds with the quinone being regarded again as a bidentate ligand, the seventh coordination position being occupied by the halogen. Seven-coordinate molybdenum and tungsten complexes are known^{1,3}. It is also possible to visualize a polymeric structure for the $[\text{MX}(\text{Quinone})_3]^-$ anions, if one imagines the possibility for the quinone ligand to act as a bridge between two different metals, as for the previous case (D).

The electronic structures of the complexes described in this paper are probably very similar, as suggested by the similarity of the physical-chemical data, in particular the magnetic susceptibilities and the carbonyl stretching frequency in the infrared spectrum.

SUMMARY

The halopentacarbonyls anions of molybdenum and tungsten, $[\text{MX}(\text{CO})_5]^-$, react readily with *p*-benzoquinone yielding anionic complexes of formula $[\text{MX}(\text{Quinone})_3]^-$. These have been isolated as tetraethylammonium and lithium salts. Hexacarbonylmolybdenum reacts with *p*-benzoquinone in boiling toluene to give tris(*p*-benzoquinone)molybdenum, $\text{Mo}(\text{Quinone})_3$. All the complexes reported in this paper are substantially diamagnetic. Possible structures are discussed.

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