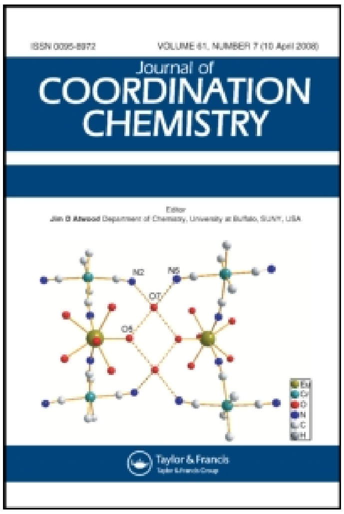

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Electronic structure and bonding in chrysenequinone complexes. synthesis and characterization of m(co)$_3$ (chrysenequinone), m = ru and os

Ramadan M. Ramadan[a]
[a] Chemistry Department, Faculty of Science, Ain Shams University Cairo, Egypt

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ELECTRONIC STRUCTURE AND BONDING IN CHRYSENEQUINONE COMPLEXES. SYNTHESIS AND CHARACTERIZATION OF M(CO)3 (CHRYSENEQUINONE), M = Ru AND Os

RAMADAN M. RAMADAN,

Chemistry Department, Faculty of Science, Ain Shams University Cairo, Egypt

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From the reaction of $M_3(CO)_{12}$ (M = Ru or Os) with chrysenequinone, trigonal bipyramidal complexes $[M(CO)_3(ChryQ)]$ were isolated. Vibrational spectra of the two complexes display three CO stretching frequencies in the terminal metal carbonyl region and strong v(CO) frequency at 1665 cm^{-1} due to the quinone. Investigation of the complexes by electronic, ^1H and ^{13}C NMR spectroscopy confirmed the proposed structure. Cyclic voltammograms of chrysenequinone show two *quasi*-reversible redox reactions due to a tautomeric change to semiquinone and catecholate derivatives. Cyclic voltammograms of the ruthenim complex show irreversible behaviour, presumably to oxidation of the metal.

Keywords: Chrysenequinone; metal carbonyl; iron; redox; benzoquinone

INTRODUCTION

The coordination properties of bidentate ligands which form unsaturated five-membered chelate rings with metal ions have long been studied.[1] Interest in these systems arises in part from the electrochemical properties observed for such complexes. The vast majority of the ligands used contain nitrogen or sulfur as donors. Chemical and structural properties of related oxygen donor ligands such as quinone and quinoid molecules were also investigated.[2] The importance of quinone complexes is related to the use of *o*-benzoquinones in oxidative addition reactions to basic metals,[3] as well as the analogy of these ligands to 1,2-dithiolene systems.[4] Furthermore, quinones and their coordination compounds have been found to play a significant role in biology.[5] Quinone complexes may be formed by the addition of the ligands to a complex containing the desired metal in a low oxidation state. Oxidative addition reactions have been also used to synthesis catecholate adducts of Group VIII metals. Direct reaction of quinones with metal carbonyls are also used for preparation of binary quinone complexes.[2]

Bis(quinone) complexes of ruthenium and osmium, $ML_2(Q)_2$, prepared from Ru(II), Ru(III), Os(II) and Os(III) salts, have been extensively studied with coligands that include N-donors, PPh_3 and CO. These complexes are related to the members of the Fe(N-N) (SQ)-(Cat) series, (SQ = semiquinone and Cat = catecholate), with the difference that the larger metals may show a tendency towards electronic structures with high oxidation state metal ions and quinone ligands that are more catecholate-like.[6] Characterization of the *bis*(bipyridine) (quinone)- as well as the *tris*-(quinone) ruthenium and osmium complexes shows that both metal quinone delocalization and delocalization between quinone ligands contributes to the electronic structure.[7–9]

Spectroscopic and electrochemical studies of metal quinone complexes have been useful to elucidate the structures and chemical behaviour of these species. Such methods facilitate investigation of these complexes in their biological environments.[2,5] Our interest in characterization of electronic structure and bonding type of chrysenequinone with metal carbonyls[10–12] has prompted us to investigate the reactions of chrysenequinone with the cluster compounds $M_3(CO)_{12}$, M = Ru and Os. Different structural features were expected for these complexes relative to those previously reported due to differences in oxidation states as well as metal radius

EXPERIMENTAL

Materials

The dodecacarbonyls $M_3(CO)_{12}$, M = Ru and Os, were purchased from Aldrich Chemical Co. 1,2-Chrysenequinone (ChryQ) was prepared as described in the literature.[10]

Complex Syntheses

$Ru(CO)_3(ChryQ)$

$Ru_3(CO)_{12}$ (0.1 g, 0.16 mmol) and chrysenequinone (0.09 g, 0.35 mmol) were mixed together in a sealed tube containing about 20 cm^3 of benzene. The mixture was degassed with one freeze-thaw cycle and then heated at 80 °C for 2 h. The reaction mixture was cooled and then transferred to a Schlenk flask and the solvent removed on a vacuum line. The residue was washed several times with 60–80 petroleum ether and then recrystallized from benzene to give a dark brown compound, which was left to dry *in vacuo* for ~ 3 h. The complex (yield 59%) was found to be air stable. *Anal.* Calc. (found) for $C_{21}H_{10}O_5Ru$(%): C, 56.9 (56.2); H, 2.3 (2.6). The molecular ion was observed for the complex at *m/z* 444 (P^+) in the mass spectrum.

Os(CO)$_3$(ChryQ)

The complex was prepared by using the same procedure used for the synthesis of $Ru(CO)_3$(ChryQ) but the reaction period was 38 h. The complex was recrystallized from dioxan. The resulting brown crystals were dried on a vacuum line (yield 51%). Elemental analysis and mass spectrometry showed that the complex crystallized with a dioxan molecule. *Anal.* Calc. (found) for $C_{25}H_{14}O_7Os$(%): C, 48.7 (48.2); H, 2.3 (2.6). The molecular ion was observed for the complex at *m/z* 590 (P-CO) $^+$.

Physical Measurements

IR measurements were carried out on a Unicam - Mattson 1000 FT-IR spectrometer with samples prepared in KBr pellets. Electronic spectra were measured on a Perkin-Elmer Lambda 4B spectrophotometer with 10.0 mm quartz cells. Samples of concentrations *ca* 1×10^{-6} M in CH_2Cl_2 or DMSO, were measured against the solvent in the reference cell. ^1H and ^{13}C NMR measurements were performed on a Bruker AC 200 MHz NMR spectrometer. Samples were dissolved in $CDCl_3$ with tetramethylsilane (TMS) as internal reference. Cyclic voltammetry measurements were carried out using a three-electrode cell connected to an EG and G 362 scanning potentiostat linked to an XY recorder. A platinum disc was used as working electrode and a platinum wire as counter electrode. The reference electrode was silver-silver chloride. Sample solutions (10.0 cm^3) *ca* 1×10^{-4} M in CH_2Cl_2 with 0.1 M $NaNO_3$ as supporting electrolyte were used for the measurements. A potential range from +2000 to −2000 mV with scan rates of 10, 50, 100 and 200 mV s^{-1} was used to detect potential peaks.

RESULTS AND DISCUSSION

Reactions of the cluster compounds $M_3(CO)_{12}$, M = Ru or Os, with chrysenequinone gave $M(CO)_3$(ChryQ) complexes. IR spectra of the two complexes (Table I) showed three CO stretching frequencies in the metal carbonyl

TABLE I Characteristic IR and NMR data for chrysenequinone and its ruthenium and osmium complexes

Compound	*IR (cm^{-1})*[a]		*NMR*
	ν (CO)	*ν (C=C)*	*(ppm)*[b]
ChryQ	1683 (s)	1614 (s)	7.48 (m), 7.72 (m), 8.09 (m), 9.36 (d)
$Ru(CO)_3(ChryQ)$	2055 (s) 1993 (vs) 1927 (m) 1665 (s)	1600 (s)	7.54 (m), 7.78 (m), 8.13 (m), 9.42 (d)
$Os\ (CO)_3\ (ChryQ)$	2120 (s) 2024 (vs) 1950 (s) 1665 (s)	1596 (s)	3.71 (s)[c], 7.54 (m), 7.77 (m), 8.13 (m), 9.40 (d)

[a] M. medium; s, strong; vs very strong. [b] S. singlet; d, doublet; m multiplet. [c] Due to dioxan in the complex crystals.

region. From the pattern and the number of the CO bands (2*a′* +*a″*), the complexes have trigonal bipyramid structures with the chrysenequinone bound to two equatorial positions.[13] Both ruthenium and osmium complexes also showed a ν(CO) frequency at 1665 cm^{-1} due to the quinone group. This band shifted only 18 cm^{-1} to lower frequency from ν(CO) of chrysenequinone itself. Thus it is concluded that chrysenequinone is bound to the metal as a quinone. The shift is slightly smaller than those observed for other quinone complexes,[6] and may be attributed to the larger number of fused benzene rings in chrysenequinone. Changes in charge distribution often result in changes in the infrared spectra of quinone, semiquinone and catecholate complexes.[6] Chromium and molybdenum chrysenequinone and chrysenequinonemonoxime complexes show strong ν(CO) bands at 1418–1470 cm^{-1} due to semiquinone.[10–12] Also, the IR spectrum of $Fe(DBSQ)_3$, DBSQ = di-*tert*-butylsemiquinone, is typical of a semiquinone complex. On the other hand, vibrational spectra of the delocalized complexes $Ru(DBQ)_3$ and $Os(DBQ)_3$, DBQ = di-*tert*-butylbenzoquinone, are typical for quinone complexes and differ from charge-localized forms.[9] Furthermore, IR spectra of ruthenium and osmium complexes prepared with catechol and di-*tert*-butylcatechol ligands showed significant differences that may be related to differences in charge distribution.[14]

The ^1H NMR spectrum of chrysenequinone in $CDCl_3$ displayed three multiplets and a doublet due to phenolic protons. Both ruthenium and osmium chrysenequinone complexes showed identical proton NMR spectra with a slight shifts to lower field from that of chrysenequinone itself. This small shift is consistent with complex formation involving quinone-type bonding.

Tris(chrysenesemiquinone) chromium did not show NMR signals due to its paramagnetic properties.[10] On the other hand, the molybdenum chrysenesemiquinone complexes displayed NMR spectra with appropriate shifts of signals to lower field.[11] However, the shifts in the case of the molybdenum complexes were larger than those of the ruthenium and osmium complexes. This may be due to a change in the bonding of chrysenequinone from quinone to semiquinone with different metals.

In order to gain additional insight into the structure of the complexes, investigation of the ^{13}C NMR of the osmium derivative was undertaken. The ^{13}C resonance for terminally bonded carbonyl groups is shifted about 200 ppm to higher frequency from TMS. There is an increase in carbonyl carbon shielding as the atomic weight of the transition metal is increased.[15] The ^{13}C NMR spectrum of $Os(CO)_3$ (ChryQ) (10% ^{13}CO enriched), displayed two CO signals at 182.6 and 184.8 ppm (relative intensity 1:2) in the terminal metal carbonyl region as expected from the proposed structure. It also showed eighteen signals in the range 120–142 ppm due to the carbon atoms of the chrysenequinone ligand.

The electronic absorption spectrum of chrysenequinone in methylene chloride, Table II, consists of two bands. An intense band in the UV range (E_1, π - π^* transition) has two shoulders (E_2 and B; forbidden transitions). The broad visible band with very low intensity is attributed to the n- π^* transition. Electronic spectra of both ruthenium and osmium chrysenequinone complexes in CH_2Cl_2 are identical. They show a strong band in the UV region and a weak band in the visible range (Table II). The two shoulders due to forbidden transitions (E_2 and B) are not observed in the spectra. The strong UV band exerts a slight bathochromic shift with respect to the E_1 band of the ligand; the visible broad band is also shifted to the red relative to the ligand. These shifts are consistent with complex formation. In DMSO, the spectra of $Ru(CO)_3$(ChryQ) and $Os(CO)_3$(ChryQ) also show two bands. The strong UV band of the ruthenium complex has a shoulder at 315 nm (Table II). Strong UV bands display hypsochromic shifts with respect to those of the complexes in CH_2Cl_2. These shifts could be due to some sort of charge transfer between the solvent and the ruthenium or osmium compounds.[11] The ability of quinones and their metal derivatives to form charge transfer complexes with other substrates such as solvents is well established.[2,16] For example, $[Mo(O_2C_6Cl_4)_3]_2$ was found to crystallize with three molecules of benzene. These solvent molecules were found to be interstitially sandwiched between planes of chelating quinones of adjacent molecules.[2] Also, molybdenum chrysenesemiquinone and molybdenum chrysenesemiquinone monoxime complexes were found to co-crystallize with either solvent or ligand molecules.[11,12] On dissolving these complexes in donor

TABLE II Electronic spectral data for chrysenequinone and its ruthenium and osmium complexes

Compound	*λ (nm)*
ChryQ	CH_2Cl_2: 230, 280[a], 312[a], 394[b]
$Ru(CO)_3(ChryQ)$	CH_2Cl_2: 233, 400[b]
	DMSO: 269, 315[a], 390[b]
$Os\ (CO)_3(ChryQ)$	CH_2Cl_2: 233, 400[b]
	DMSO: 269, 397[b]

[a] Shoulder. [b] Broad.

s olvents such as DMSO, the colour changes and new bands in the spectra due to charge transfer complex formation were found.[11,12] The osmium derivative reported in this study was found to crystallize with a molecule of dioxan.

Electrochemical studies of various neutral metal quinone and semiquinone complexes show that they can undergo reversible or *quasi*-reversible one-electron oxidations and reductions without a change in the formal oxidation state of the metal centre.[17] Depending on localized valence-bonding, it was suggested that this behaviour was related to changes in the composition of the ligand π^* levels.[17] The number of redox reactions in the cyclic voltammogram was found to depend upon several factors such as the nature of the ligand, the central metal and the solubility of the complexes.[2,10–12] Cyclic voltammogram of chrysenequinone in CH_2Cl_2 at a scan rate of 100 mV s^{-1} shows two *quasi*-reversible redox reactions. Anodic peak potentials (Ep_a) occur at + 1.018 and + 0.745 V, while cathodic peak potentials (Ep_c) are found at + 0.636 and – 0.073 V. The redox couple at + 0.83 (average of anodic and cathodic potential peaks) represents the first reduction of the neutral ligand from quinone to semiquinone (0/1–) with ΔEp 0.382 V. The second couple at +0.34 V corresponds to reduction to the catecholate species (1–/2–) with ΔEp 0.818 V.

Cyclic voltammograms of $Ru(CO)_3(ChryQ)$ in CH_2Cl_2 at a scan rate of 200 mV s^{-1} display only one cathodic peak ($Ep_c = -1.473$ V) with a well-defined current maximum and no anodic wave on the reverse scan. The peak was found to be sensitive to the scan rate. As the scan rate increased from 50 to 200 mVs^{-1} the cathodic peak increased significantly and shifted to more negative values. The peak could not be detected at a 10 mV s^{-1} scan rate. Cyclic voltammograms also show a weak anodic peak at +0.564 V with no coupled cathodic wave on the reverse side. This peak occurs at more negative values than the corresponding one of chrysenequinone. Such behaviour suggests that electron transfer from the complex is irreversible and a change in oxidation state of ruthenium from Ru^0 to Ru^I.[5] Since the +1 oxidation state in ruthenium complexes is usually unstable, decomposition may occur. The anodic peak may be attributed to the formation of a semi-quinone. This will also lead to formation of Ru^{I} species. Such a mechanism is known in a variety of other organometallic systems showing irreversible cyclic voltammetry behaviour.[18]

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