9,10-Phenanthrenequinone Binary Complexes of Iron, Cobalt, and Nickel

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9,10-Phenanthrenequinone complexes of iron, cobalt, and nickel of formula M(quon)$_n$ (n = 2 for Co and Ni, n = 3 for Fe) have been prepared by the direct thermal reactions of the corresponding metal carbonyls with the quinone. These are the first binary phenanthrenequinone complexes of transition metals to be reported. In these complexes, which contain a new type of highly delocalised unsaturated system, the quinone moiety is believed to be co-ordinated to the metal through the oxygen atoms, as suggested by the i.r. spectra.

9,10-PHENANTHRENEQUINONE is known [1] to form complexes of formula MX_2,quon (M = Mn, Co, Zn, Cd, Ni, and Hg) and MX_3,quon (M = In and Fe) with metal chlorides. In these compounds the *o*-quinone moiety can be assumed to be linked to the metal by metal–oxygen bonds with a predominant σ-donor character. On the other hand, it is possible to conceive a series of uncharged binary complexes of 9,10-phenanthrenequinone of formula $[M(quon)_n]^0$, in which the bond to the metal may be described in terms of σ-donation to the metal and π-back-donation from filled *d* orbitals of the metal to anti-bonding orbitals of the highly delocalised organic system.

The bonding would then be similar to that existing in uncharged transition metal complexes of dithia-*o*-quinones,[2] 1,2-di-iminocyclohexa-3,5-diene,[3] 1,10-phenanthroline,[4] and 2,2′-bipyridyl.[4]

Earlier attempts [5] to prepare uncharged *o*-quinone complexes of nickel and iron by reacting the corresponding metal carbonyls with tetrachloro-*o*-benzoquinone (nickel and iron) and with 3,5-di-t-butyl-*o*-benzoquinone (nickel) were only partially successful, since the products were regarded not to be sufficiently pure and they were not completely characterised. It has also been reported [6] that attempts to prepare complexes of *o*-quinones similar to those obtained [6] by thermal reactions of $Ni(CO)_4$ with *p*-benzoquinone had failed.

We wish to report in this paper that the highly delocalised system of 9,10-phenanthrenequinone has been used to prepare the corresponding complexes of iron, nickel, and cobalt in high yields and in a pure state.

RESULTS AND DISCUSSION

Reactions with 9,10-*Phenanthrenequinone.*—We have found that enneacarbonyldi-iron, pentacarbonyliron, octacarbonyldicobalt, and tetracarbonylnickel react thermally with 9,10-phenanthrenequinone giving green-black solids containing the *o*-quinone as ligand.

The reactions were carried out either in dimethylformamide (DMF) or in tetrahydrofuran (THF). The phenanthrenequinone complexes of cobalt and nickel usually crystallise out with solvent. In the case of cobalt, solids of analytical composition $Co(quon)_2(DMF)$ and $Co(quon)_2(THF)$ were isolated. The co-ordinated oxygen donor solvents could be eliminated by heating *in vacuo* to *ca.* 140°. Presumably six-co-ordinate cobalt was obtained by recrystallising the above complexes from pyridine, which resulted in the isolation of $Co(quon)_2py_2$.

Similar results were obtained in the case of nickel. The reaction in dimethylformamide yielded a compound of analytical composition $Ni(quon)_2(DMF)_2$ which had a band at 1650 cm^{-1} attributed to the co-ordinated amido-group. The pyridine complex $Ni(quon)_2py_2$ of presumably six-co-ordinate nickel was isolated by recrystallising the tetrahydrofuran adduct from pyridine.

These reactions might be regarded either as carbon monoxide substitution reactions by the quinone or as oxidative additions of 9,10-phenanthrenequinone to zerovalent iron, cobalt, and nickel. It is interesting to note that oxidative additions of 9,10-phenanthrenequinone [7] and tetrachloro-*o*-quinone [8,9] to tertiary phosphine complexes of platinum(0), iridium(I), and rhodium(I) have been described.

The iron, cobalt, and nickel complexes are little soluble in solvents such as toluene and tetrahydrofuran, but they can be recrystallised from these solvents and have an elevated thermal stability. They are not particularly sensitive to air and moisture and can be handled in air (especially those of iron and nickel) for some minutes without appreciable decomposition, as judged from the i.r. spectrum. The solutions of the quinone complexes are, however, sensitive to air: decompositions take place within a few minutes with formation of 9,10-phenanthrenequinone. The latter was also the product of the thermal decomposition of the complexes above 140° thus showing that no irreversible alteration of the quinone had taken place in the course of reactions.

From the reactions of iron carbonyls with quinone in molar ratios 1 : 3, solids of composition $Fe(quon)_3$ were actually isolated. The latter, however, were shown by the i.r. spectra to contain unco-ordinated, possibly clathrated, 9,10-phenanthrenequinone having a strong C–O stretching vibration at 1675 cm^{-1}. Solids of composition $Fe(quon)_3$ and without i.r. bands at 1675

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cm^{-1} were isolated by boiling the impure product (containing an excess of 9,10-phenanthrenequinone) in tetrahydrofuran for several hours. The resulting solid gave excellent analytical results (see Table, including direct oxygen analysis) for the required stoicheiometry.

It is interesting to note that the product resulting from the oxidation of *NN'*-ethylenebis(salicylideneiminato)-iron(II), by 9,10-phenanthrenequinone does not contain the band of free quinone at 1675 cm^{-1}.

	Analytical data/%									
	Found				Calc.					
Compound	C	H	N	Metal	C	H	N	Metal	Infrared 1800—1300 cm^{-1} [a]	Δν cm^{-1} [b]
Fe(quon)$_3$	73·5	3·55	14·45 [c]	8·3	74·15	3·55	14·1 [c]	8·2	1590ms, 1570m, 1480ms, *1460*vs, 1425s, 1360s	215
Fe(quon)$_2$(py)$_2$	72·6	4·65	4·8	n.d.	72·4	4·15	4·45	8·85		
Fe(quon)$_2$(bipy)	72·8	4·6	4·15	n.d.	72·6	3·85	4·45	8·9		
Fe(saen)(quon) [d]	67·85	4·15	5·35	n.d.	67·95	4·2	5·3	10·55		
Co(quon)$_2$	70·6	3·6		12·5	70·75	3·4		12·4	1600m, 1580m, 1560ms, 1520s, 1490s, *1460*vs, 1420s	215
Co(quon)$_2$(py)$_2$	71·35	4·15	4·4	n.d.	72·05	4·15	4·4	9·3		
Ni(quon)$_2$	70·85	3·55		12·5	70·8	3·4		12·35	1600m, 1580m, 1560s, 1520s, 1490s(sh), *1460*vs, 1420s	215
Ni(quon)$_2$(py)$_2$	71·8	4·3	4·6	n.d.	72·05	4·15	4·4	9·25		
[TiCl$_4$(quon)]	42·45	2·15	35·9 [e]	12·25	42·25	2·05	35·65 [e]	12·05	1610m, *1575*vs(br), 1450s, 1360s	100
9,10-Phenanthrenequinone,quon									1675vs(C=O), 1590ms, 1475mw, 1450m, 1410w, 1370w	0

[a] In poly(chlorofluoroethylene) mulls. Bands attributed to the stretching vibration of co-ordinated quinone are in italics. These bands are probably partially coupled with C–C stretching vibrations. [b] With respect to the C–O stretching vibration of the free quinone at 1675 cm^{-1}. [c] Oxygen analysis. [d] Fe(saen) = *NN'*-ethylene-bis(salicylideneiminato)iron. [e] Chloride analysis.

That the metal in these compounds is co-ordinated to quinone through the oxygen atoms is strongly suggested by the fact that the C–O stretching vibration at 1675 cm^{-1} in the free quinone is shifted considerably upon complex formation. For example, in the iron complexes, the highest wavenumber band which, on the basis of the intensity (see Table), can be attributed to a C–O stretching vibration, is observed at 1460 cm^{-1}. This is a much higher shift than that observed[1] in halogeno-complexes of transition metals with 9,10-phenanthrenequinone (*ca.* 50 cm^{-1}). A shift such as that observed corresponds to what one should expect for co-ordination of iron to the reduced quinone ligand.

In order to confirm this hypothesis we have also prepared the titanium(IV) derivative, TiCl$_4$(quon). Previous attempts[1] to characterise this compound and to measure its i.r. spectrum had failed. In this compound, for which no electron transfer from the metal to the quinone is in question, a strong i.r. band is observed at 1575 cm^{-1}, corresponding to a shift of 100 cm^{-1} to lower wavenumbers for the C–O groups of the co-ordinated quinone.

Similar reasonings apply to the cobalt and nickel complexes (see Table), which have their strongest band in the 1800—1300 cm^{-1} region at 1460 cm^{-1}, the latter being therefore attributed to the C–O stretching vibration of co-ordinated phenanthrenequinone. No molecular weights could be measured because of the low solubility in hydrocarbon solvents.

It is quite important to note that the systems M(quon)$_n$ may be regarded as a source of zerovalent transition metals in a reactive form. Attempts to carry out the preparation of zerovalent metal complexes by ligand exchange are now being made. Further characterisation of the complexes by magnetic susceptibility measurements is being undertaken.

EXPERIMENTAL

All the manipulations aimed at the isolation of the complexes described in this paper were carried out under an atmosphere of purified nitrogen. Commercial (Fluka, Buchs, Switzerland and Schuchardt, Munich, Germany) 9,10-phenanthrenequinone was purified before use by recrystallisation from tetrahydrofuran.

The i.r. spectra were measured with Perkin-Elmer 337 and 521 grating spectrophotometers. Mulls of the complexes were prepared under an atmosphere of purified nitrogen.

Solvents were purified by the standard procedures and kept in an atmosphere of dry purified nitrogen.

Preparation of Fe(quon)$_3$.—Freshly distilled pentacarbonyliron (7·7 g, 39·2 mmol) was dissolved in tetrahydrofuran (400 ml) and treated with the quinone (25 g; 120 mmol) at reflux temperature for 20 h. In the last part of the treatment (8 h) the reaction mixture was irradiated with u.v. light while refluxing. The quinone complex formed in the course of the reaction was filtered off. Since the crude product (11·5 g) was found (i.r. spectrum) to contain free phenanthrenequinone, it was suspended in tetrahydrofuran and heated at reflux temperature for 2 days in the presence of an excess of phenanthrenequinone. The black-green solid precipitated upon cooling was filtered and dried *in vacuo*. The *compound* so obtained did not show the band at 1675 cm^{-1} of free quinone. It is slightly sensitive to air but it is attacked within one hour by water even under nitrogen.

Substances with a lower content of 9,10-phenanthrenequinone per iron atom and with no band at 1675 cm^{-1}, were obtained by recrystallising the crude reaction product with tetrahydrofuran in the absence of an excess of quinone. The compound, Fe(quin)$_3$, was prepared by substantially similar procedures starting with Fe$_2$(CO)$_9$ in dimethylformamide at 110 °C.

Preparation of [Fe(quon)$_2$py$_2$].—The crude product (0·43 g) obtained from the reaction betwen Fe(CO)$_5$ and 9,10-phenanthrenequinone was dissolved in dry pyridine (50 ml) at room temperature and toluene was added to the filtered solution. The black-green precipitate was filtered and dried *in vacuo* at room temperature for several hours (0·150 g).

Preparation of [Fe(quon)$_2$(2,2′-bipyridyl)].—The crude product (1·13 g) from the reaction between Fe(CO)$_5$ and 9,10-phenanthrenequinone was treated with 2,2′-bipyridyl (0·4 g) at room temperature in tetrahydrofuran (50 ml) for two days. Finally, the reaction mixture was refluxed for *ca.* 30 min, cooled again to room temperature, and filtered. The deep blue crystalline precipitate was dried *in vacuo* (0·7 g).

Preparation of [Fe(*NN*′-ethylenebis(salicylideneiminato)-(quon)].— *NN*′-Ethylenebis(salicylideneiminato)iron(II) (0·44 g, 1·37 mmol) was suspended in tetrahydrofuran and treated with 9,10-phenanthrenequinone (0·3 g, 1·38 mmol) when the solution become dark violet in colour. The mixture was stirred at room temperature for a day and finally the dark violet crystals were filtered and dried *in vacuo* (0·53 g; 73% yield). Its i.r. spectrum showed no band at 1675 cm^{-1} typical of free 9,10-phenanthrenequinone. The compound is stable in the solid state to air for *ca.* 30 min: its solutions in tetrahydrofuran are, however, very rapidly decomposed with formation of 9,10-phenanthrenequinone.

Magnetic susceptibility measurements were carried out by the Gouy method; magnetic susceptibility $\chi_M = 99{\cdot}92 \times 10^{-6}$ (including the diamagnetic correction $= -256 \times 10^{-6}$) at 288 K, corresponding to a magnetic moment $\mu_{eff} = 4{\cdot}82$ B.M.*

Preparation of Co(quon)$_2$.—Octacarbonyldicobalt (2·07 g; 12·1 mmol) was dissolved in tetrahydrofuran (150 ml) and maintained in this solvent for *ca.* 30 min at 30—40°. The resulting solution was then filtered into a flask containing the quinone (5·036 g; 24·2 mmol). Gas evolution started upon contact with the quinone while the solution, maintained at *ca.* 30°, became green. After *ca.* 30 min the reaction mixture was heated at 60—65° for *ca.* 15 min and then left overnight at room temperature. The black-green microcrystalline solid precipitated in the course of the treatment was filtered off and dried *in vacuo* at 80 °C for *ca.* 2 h. The filtered solution, which did not show any important quantity of metal carbonyl derivatives, gave by concentration *in vacuo* some more of the quinone cobalt complex (total yield 77%). The compound which was analysed as such without further purification, was found to be sparingly soluble in tetrahydrofuran and acetone. It is attacked by air, although slowly, and by water, even under an inert atmosphere.

If the solid reaction product was dried *in vacuo* without heating a product of analytical composition Co(quon)$_2$(THF) was obtained (Found: C, 69·9; H, 4·0; Co, 11·35. $C_{32}H_{24}CoO_5$ requires C, 70·2; H, 4·4; Co, 10·75%). The presence of tetrahydrofuran in this substance was ascertained by gas chromatography of the product of pyrolysis *in vacuo ca.* 140°.

Octacarbonyldicobalt was treated with 9,10-phenanthrenequinone in dimethylformamide at 20—60° for *ca.* 4 h. The precipitation of the quinone complex was then completed by addition of toluene at room temperature. After filtration and drying *in vacuo* for several hours the black-green solid analysed correctly for Co(quon)$_2$(DMF) (Found: C, 68·95; H, 4·5; Co, 10·25. $C_{31}H_{23}CoNO_5$ requires: C, 67·9; H, 4·25; Co, 10·75%).

Preparation of [Co(quon)$_2$py$_2$].—The cobalt complex (0·32 g) prepared as described above was treated with dry pyridine (15 ml). To the resulting filtered solution heptane was added and the black microcrystalline solid was collected by filtration, dried *in vacuo*, and analysed without further purification. The pyridine solution of the complex is very sensitive to oxidation by air; the pyridine adduct is oxidised by air even in the solid state, as shown by the appearance of the band of free 9,10-phenanthrenequinone at 1675 cm^{-1} after 10 min exposure.

Preparation of [Ni(quon)$_2$].—Tetracarbonylnickel (8·2 g, 48·0 mmol) was dissolved in tetrahydrofuran (100 ml) and treated with 9,10-phenanthrenequinone (22 g; 105·7 mmol) at room temperature for 2 h and at reflux temperature for 1 h. The resulting suspension was reduced to half its volume *in vacuo* and the precipitation of the complex was completed by addition of toluene (75 ml). The crude black-green compound which was obtained in 89% yield was recrystallised from boiling tetrahydrofuran and dried *in vacuo ca.* 80°.

If the final drying operation was carried out at room temperature a solid of the same colour having the analytical composition Ni(quon)$_2$(THF) was obtained (Found: C, 69·5; H, 4·3; Ni, 10·75. $C_{32}H_{24}NiO_5$ requires C, 70·25; H, 4·4; Ni, 10·75). Tetrahydrofuran liberated from this solid was identified by gas chromatography as 1 mol per mol of nickel. Tetracarbonylnickel was reacted with 9,10-phenanthrenequinone at room temperature in dimethylformamide at room temperature for 4 h. The black-green solid precipitated was collected by filtration, washed with toluene and dried *in vacuo* for several hours (65% yield). The solid so obtained analysed correctly for Ni(quon)$_2$(DMF)$_2$ and its i.r. spectrum had a band at 1650 cm^{-1} distinctly separated from that of free quinone at 1675 cm^{-1} (Found: C, 66·0; H, 4·8; Ni, 8·8. $C_{34}H_{30}N_2NiO_6$ requires C, 65·75; H, 4·9; Ni, 9·45%).

Preparation of [Ni(quon)$_2$py$_2$].—The nickel–quinone complex (3·2 g) prepared as described above was dissolved in warm dry pyridine (100 ml); the resulting solution was filtered when still warm and the compound was obtained by slow recrystallisation at room temperature (2·0 g).

Preparation of [TiCl$_4$(quon)].—Titanium tetrachloride (2·0 g; 9·6 mmol) was treated at room temperature with 9,10-phenanthrenequinone (1·9 g; 1·00 mmol) in dichloromethane (75 ml). The originally orange reaction mixture became rapidly black-green. After 90 min, the solvent was evaporated to half its volume and the solid precipitate was filtered off and dried *in vacuo* at room temperature (76% yield). The complex is very sensitive to humidity.

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