Studies on Metal Complexes of *ortho*-Quinone Mono-oximes. Part 6.[1] Redox Behaviour of Bis(4-chloro-1,2-benzoquinone 2-oximato)-copper(II) and -nickel(II); Synthesis and Characterization of Reduced Species containing a Paramagnetic Ligand

Carla Bisi Castellani,* Armando Buttafava, Oliviero Carugo, and Antonio Poggi
Dipartimento di Chimica Generale dell'Università di Pavia, via Taramelli 12, 27100 Pavia, Italy

Bis chelated complexes of Cu^{II} and Ni^{II} with 4-chloro-1,2-benzoquinone 2-oximate, $[M(cbqo)_2]$, have been reduced either electrochemically or chemically. The new species K[M(cbqo)(cbsqo)] (cbsqo = 4-chloro-1,2-benzosemiquinone 2-oximate), which contain a paramagnetic ligand, have been isolated and characterized. The mechanism of the chemical reduction, carried out by NCO^-–methanol, is discussed.

Copper(II) complexes of *o*-quinone mono-oximes have been thoroughly studied especially in view of their extensive reactivity towards organic substances.[2] The reaction mechanisms involve, as a preliminary step, the formation of acid–base adducts between the copper centre and the potentially basic reagent. In several cases a redox process is also involved, as shown by the copper(I)-containing residue recovered at the end of the reaction. In previous work[1,3] we studied the Lewis-acid behaviour of bis(4-chloro-1,2-benzoquinone 2-oximato)-copper(II), $[Cu(cbqo)_2]$ (**1a**) ⟷ (**1b**); we report now the redox properties of this complex and of its nickel(II) analogue.

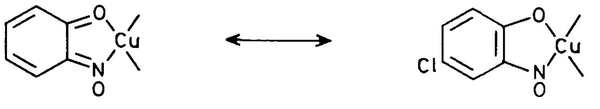
o-Quinone mono-oximes can be considered to be formally derived from *o*-benzoquinones; therefore it is possible to suppose that their metal complexes have a redox behaviour analogous to that of the corresponding *o*-quinone complexes.[4] These can be reduced either chemically or electrochemically to species containing semiquinonate radicals or catecholate; accordingly, it can be supposed that $[M(cbqo)_2]$ (and other *o*-mono-oximato complexes) undergo analogous reductions to give the anionic species $[M(cbqo)(cbsqo)]^-$ and possibly $[M(cbsqo)_2]^{2-}$ (cbsqo = 4-chloro-1,2-benzosemiquinone 2-oximate).

The present paper summarizes the results of an electrochemical study of $[Cu(cbqo)_2]$ and $[Ni(cbqo)_2]$ and describes the synthesis and the characterization of K[M(cbqo)(cbsqo)] (M = Cu^{II} or Ni^{II}), which were obtained by an unusual reduction with KOCN in methanol. Moreover, evidence is presented that in these species an unpaired electron is mainly localized on the ligands, as in the case of *o*-semiquinonato complexes.

Experimental

Voltammetry and controlled-potential electrolysis experiments were performed on a AMEL Electrochemolab system as previously described.[5] The u.v.–visible spectrophotometric measurements were made with a Cary 2300 spectrophotometer. I.r. spectra were obtained with a 1330 Perkin-Elmer spectrophotometer. Magnetic susceptibility data were obtained with a Faraday apparatus equipped with a Bruker electromagnet operating at 2.7 T and a R-100 Cahn microbalance. Diamagnetic corrections were introduced.[6] The e.s.r. measurements were performed with a Varian 1-109 spectrometer at *X*-band (9.5 GHz) frequency.

The solutions were transferred under nitrogen from the electrolysis cell to the e.s.r. tubes or to absorption cells by means of a simple siphon device.


(**1a**) (**1b**)

Synthesis of Potassium (4-*Chloro*-1,2-*benzoquinone* 2-*oximato*)(4-*chloro*-1,2-*benzosemiquinone* 2-*oximato*)*cuprate*(II) *and of Potassium* (4-*Chloro*-1,2-*benzoquinone* 2-*oximato*)(4-*chloro*-1,2-*benzosemiquinone* 2-*oximato*)*nickelate*(II), K[M(cbqo)(cbsqo)] (M = Cu *or* Ni).—A suspension of $[M(cbqo)_2]$ (1 mmol), prepared as described,[7] and KOCN (10 mmol) in methanol (60 cm^3) was refluxed for 1 h, cooled to room temperature, and filtered. The solid residue was thoroughly washed with methanol and successively with water, in order to remove any KOCN present. By carrying out the reaction under a stream of nitrogen it was shown that carbon dioxide and ammonia were reaction by-products [the first one was collected in a $Ba(OH)_2$ trap, the second in a trap of diluted H_2SO_4 and identified with the Nessler reagent].

K[Cu(cbqo)(cbsqo)]: dark blue microcrystals, m.p. 180—185 °C (decomp.) (Found: C, 34.4; H, 1.4; Cu, 15.3; K, 8.8; N, 6.7. $C_{12}H_6Cl_2CuKN_2O_4$ requires C, 34.7; H, 1.4; Cu, 15.3; K, 9.4; N, 6.7%); $\nu_{max.}$ 1 517m, 1 419w, 1 350s, 1 318s, 1 302vs, 1 278s, 1 212vs, 1 162s, 1 150s, 1 050w, 928m, 858w, 840vw, and 814s cm^{-1} (Nujol). $K[Ni(cbqo)(cbsqo)]\cdot H_2O$: black microcrystals, m.p. 198—203 °C (decomp.) (Found: C, 33.9; H, 1.6; K, 9.1; N, 6.6; Ni, 13.1. $C_{12}H_8Cl_2KN_2NiO_5$ requires C, 33.6; H, 1.8; K, 9.1; N, 6.5; Ni, 13.7%); $\nu_{max.}$ 1 545m, 1 417w, 1 410w, 1 343s, 1 310m, 1 283m, 1 217m, 1 153vs, 1 055w, 930m, 841m, and 807s cm^{-1} (Nujol).

Results and Discussion

Electrochemical Reduction of $[Cu(cbqo)_2]$.—Cyclic voltammetric studies on $[Cu(cbqo)_2]$ in MeCN show two quasi-reversible one-electron reduction processes at −0.366 and −1.117 V *vs.* $[Fe(\eta\text{-}C_5H_5)_2]^+$–$[Fe(\eta\text{-}C_5H_5)_2]$. Controlled-potential electrolysis of a MeCN solution of $[Cu(cbqo)_2]$ (performed at a potential slightly lower than that of the first peak; about −0.5 V *vs.* ferrocenium–ferrocene) yielded an air-sensitive blue solution, which was characterized by u.v.–visible and e.s.r. spectroscopy and found identical to a solution of the product of the chemical reduction (see below). The experiment indicated the consumption of 1 mol of electrons per mol of complex. On continuing the electrolysis at a potential lower than that of the second peak, a multi-electron process took place, yielding an air-stable dark orange solution which could not be re-oxidized to the starting material. This indicates that the product of the second reduction step is stable only within the time-scale of the cyclic voltammetry experiment.

Chemical Reduction of [Cu(cbqo)$_2$].—Our first attempts to achieve the chemical reduction of [Cu(cbqo)$_2$] by conventional reducing agents (Na, NaBH$_4$, Na$_2$SO$_3$, CH$_2$O, or KI) were unsuccessful. The reaction with KI in methanol generated an anionic trinuclear complex 3Cu(cbqo)$_2$·2KI, in which the copper centres are linked by iodide bridges.[3b] Following this result, the research was extended to the Lewis acid–base interaction between [Cu(cbqo)$_2$] and the other halides and pseudohalides; during these studies a reaction with KOCN in methanol was carried out, and a microcrystalline compound was obtained whose analytical data were surprisingly consistent with the stoicheiometrically equivalent formulae K[Cu^{I}(cbqo)$_2$] or K[Cu^{II}(cbqo)(cbsqo)].* The dark blue compound is air stable as a solid, but in solution is sensitive to air and oxidizing agents (hydrogen peroxide, iodine, Ag$^+$, *etc.*); on oxidation its colour changes from blue to violet. The blue species, on the basis of u.v.–visible spectra and electrochemical measurements, is identical with the species obtained previously by controlled-potential reduction. This indicated that the system NCO$^-$–methanol behaves as a reductant towards [Cu(cbqo)$_2$], and it appeared worthwhile investigating the reaction mechanism.

During the reaction, carbon dioxide and ammonia are evolved, which however do not form on refluxing KOCN in methanol in the absence of [Cu(cbqo)$_2$]. In order to investigate the role of the medium, the reaction was carried out either in protic (methanol, ethanol, propan-2-ol, and water), or in aprotic solvents (ethylene glycol, dimethyl ether, acetonitrile, tetrahydrofuran, acetone, and dimethyl sulphoxide). The reaction does not occur in aprotic media. Among the protic solvents, methanol is the most effective followed by ethanol; no reaction takes place in propan-2-ol or in water. This behaviour can be explained by the fact that the reaction medium not only has to be protic but also must be a good solvent for both reagents; KOCN is quite insoluble in propan-2-ol, and [Cu(cbqo)$_2$] is insoluble in water.

On the basis of these results, the reaction can be rationalized as follows. In the presence of KOCN and methanol, the copper complex (**1**) forms isocyanato† and methanol adducts.[3b] The crystal structure of [Cu(cbqo)$_2$]·MeOH, recently determined by us,[1] shows that there is a Lewis acid–base interaction between the copper(II) centre and methanol [Cu–O 2.274(4) Å]; therefore the Brönsted acidity of methanol is enhanced. Thus, owing to the adduct formation, methanol can be deprotonated by cyanate, giving cyanic (or isocyanic) acid and methoxide ion. The latter is probably the real reducing agent for [Cu(cbqo)$_2$]. This hypothesis was verified by direct reaction between [Cu(cbqo)$_2$] and potassium methoxide in various solvents (methanol, acetonitrile, and acetone) under dry conditions: the species K[Cu(cbqo)(cbsqo)] was obtained, although not in a pure form, and it was unambiguously identified by its i.r. and u.v.–visible spectra.

This mechanism is also consistent with the presence of CO$_2$ and NH$_3$ among the reaction products. They may be originated from the decomposition of cyanic (or isocyanic) acid, probably through methylcarbamate as an intermediate.[8] This view is supported by the fact that refluxing methylcarbamate in dry methanol in the presence of a Lewis acid, *e.g.* [Cu(cbqo)$_2$] or CuCl$_2$, under nitrogen yields CO$_2$ and NH$_3$.

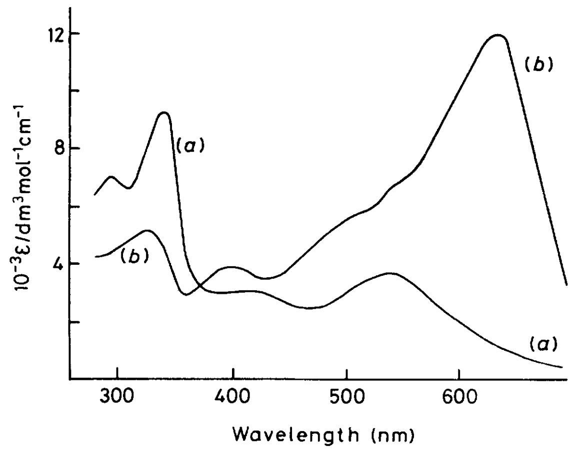


Figure 1. Absorption spectra of [Cu(cbqo)$_2$] (*a*) and [Cu(cbqo)(cbsqo)]$^-$ (*b*) in acetonitrile

Characterization of the Reduced Species.—The i.r. spectrum of K[Cu(cbqo)(cbsqo)] has been compared with those of Hcbqo (prepared as described in ref. 9), K(cbqo) {prepared by reaction between [Cu(cbqo)$_2$] and KCN as described in ref. 3*b*}, [Cu(cbqo)$_2$], and other *o*-quinone mono-oximates.[10] The most significant features are: (*i*) the absence of a carbonyl stretching mode, which in the other spectra is found in the range 1 622—1 600 cm^{-1}; (*ii*) the presence of a strong band at 1 275 cm^{-1}, absent in all the other spectra. This band compares well with bands at similar wavelengths present in the spectra of metal complexes of catecholate ligands, which have been assigned to the C–O (phenolic) stretching;[11] therefore it seems possible that the C–O stretching mode has been shifted from 1 600 to 1 275 cm^{-1} due to reduction of the carbonyl group. The C=N and N–O stretching frequencies, which in the [Cu(cbqo)$_2$] spectrum appear at 1 525 and 940 cm^{-1} respectively, are not shifted to a significant extent after reduction to [Cu(cbqo)(cbsqo)]$^-$ (1 517 and 930 cm^{-1} respectively).

The u.v.–visible spectra of acetonitrile solutions of [Cu(cbqo)$_2$], before (*a*) and after electrochemical reduction (*b*), are shown in Figure 1. Spectrum (*b*) is identical to that of the species obtained by chemical reduction. It is characterized by three absorption bands in the visible region: two of them [$\lambda_{max.}$ 408 (ε 3 520) and 500 nm (4 890 dm^3 mol^{-1} cm^{-1})] compare well with the absorption bands in (*a*) in the same region [$\lambda_{max.}$ 415 (ε 3 221) and 536 nm (3 945 dm^3 mol^{-1} cm^{-1})]. The last one, which appears at 620 nm and is absent for unreduced [Cu(cbqo)$_2$], is too intense (ε 12 300 dm^3 mol^{-1} cm^{-1}) to be a *d–d* transition. In view of the i.r. data discussed above, it is better interpreted as a low-energy charge-transfer band from the reduced ligand to the copper(II) centre or as a ligand-to-ligand charge transfer from the reduced ligand to the non-reduced one.[12] This band gradually disappears as the blue species is oxidized by air. However the spectrum of the oxidized species does not coincide with that of [Cu(cbqo)$_2$] indicating that different oxidation products are also formed. The acetonitrile solution of the blue species obtained by electrochemical reduction is e.s.r. inactive both at 77 K and at room temperature, if kept under a nitrogen atmosphere; however it is air sensitive and on oxidation gives an e.s.r. spectrum typical of Cu^{II}. Magnetic measurements at room temperature, carried out on the solid obtained by chemical

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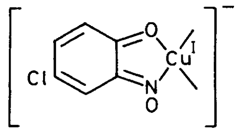
* From now the reduced species will be referred to as [M(cbqo)(cbsqo)]$^-$.

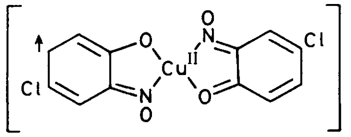
† The tetrabutylammonium isocyanate adduct of [Cu(cbqo)$_2$] has been isolated by us. Its synthesis and crystal structure will be reported elsewhere.

reduction, gave a value of $\mu_{eff.} = 1.33$. The e.s.r. behaviour could be explained by the reduction of the copper centre to diamagnetic Cu^{I}, as in structure (2). However the magnetic

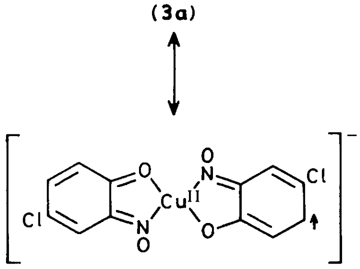


(2)

moment and the i.r. spectral data point to an antiferromagnetic coupling between a copper(II) centre and the reduced paramagnetic ligand [(**3a**) ⟷ (**3b**)]. An analogous behaviour has been found for all the complexes of Cu^{II} with one semiquinonate ligand so far described.[13,14] The absence of the carbonyl stretching band indicates that the unpaired electron is equally delocalized on both ligands. Comparison with the corresponding nickel(II) complex further supports this interpretation.



(3a)



(3b)

Redox Behaviour of [Ni(cbqo)$_2$].—The species K[Ni(cbqo)(cbsqo)]·H$_2$O has been isolated as a microcrystalline powder from the above reaction with KOCN in methanol. The compound is air stable as a solid, but in solution is extremely air sensitive. Its i.r. spectrum is characterized by the lack of the carbonyl stretching mode that for [Ni(cbqo)$_2$] is found at 1 600 cm^{-1}.

Voltammetric studies on [Ni(cbqo)$_2$] in MeCN showed a quasi-reversible one-electron oxidation process at +0.640 V *vs.* ferrocenium–ferrocene, which can probably be assigned to a nickel(II)–nickel(III) oxidation, and a quasi-reversible one-electron reduction process at −1.12 V. Controlled-potential electrolysis, performed at a potential slightly lower than that of the reduction peak, indicated the consumption of 1 mol of electrons per mol of complex.

The u.v.–visible spectrum of the electrochemically reduced species is characterized by a quite symmetrical absorption band with $\lambda_{max.}$ 480 nm (ε 9 330 dm^3 mol^{-1} cm^{-1}). The same electronic spectrum is shown by K[Ni(cbqo)(cbsqo)]·H$_2$O. The spectrum of the unreduced parent compound in the same region shows a broad band with $\lambda_{max.}$ 495 nm (ε 4 070 dm^3 mol^{-1} cm^{-1}) and shoulders at 515 and 565 nm (ε 3 890 and 2 041 dm^3 mol^{-1} cm^{-1}) (Figure 2). The e.s.r. spectrum of K[Ni(cbqo)(cbsqo)]·H$_2$O in a methanol glass consists of a single isotropic line at g = 2.006 [peak-to-peak line width 24 G (2.4 × 10^{-3} T)] and indicates the formation of a nickel(II)-stabilized ligand radical species. The same e.s.r. behaviour has been found for an acetonitrile glass of the species obtained by electrochemical reduction. These data indicate that the proposed formulation [(**3a**) ⟷ (**3b**)] is also appropriate for the complex obtained by the reduction of [Ni(cbqo)$_2$].

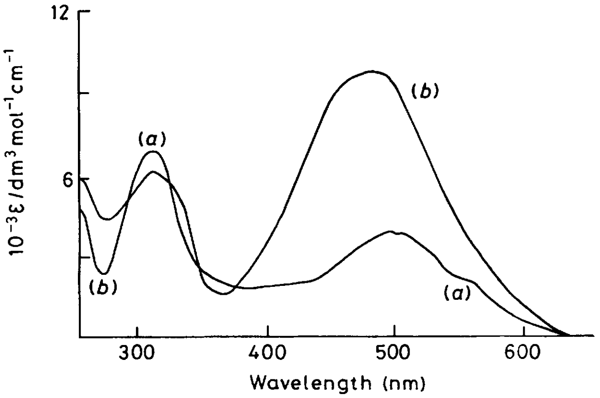


Figure 2. Absorption spectra of [Ni(cbqo)$_2$] (*a*) and [Ni(cbqo)(cbsqo)]$^-$ (*b*) in acetonitrile

Conclusions

We can conclude that the neutral complexes [M(cbqo)$_2$] (M = Cu^{II} or Ni^{II}) undergo electrochemical or chemical reduction to give the anionic species [M(cbqo)(cbsqo)]$^-$ in which the electron is mainly localized on the ligands. Thus the described complexes are examples of a new class of compounds containing a paramagnetic ligand and compare with metal derivatives of *o*-semiquinones.

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