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Studies on Copper(II) Complexes of *o*-Quinone Monooximes. 7.* Cyanato Adducts of Bis(4-chloro-1,2-benzoquinone 2-oximato)copper(II), $Cu(Clqo)_2$

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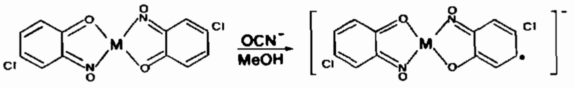
Abstract

Two novel adducts of $Cu(Clqo)_2$ (Clqo = 4-chloro-1,2-benzoquinone 2-oximato), *i.e.* $K[Cu(Clqo)_2(NCO)]$ (1) and $(Bu_4N)_2[Cu(Clqo)_2(NCO)]OCN$ (2) have been isolated and characterized by vibrational and electronic spectra. In both compounds the copper(II) atom is pentacoordinated; in fact the X-ray crystal structure determination of complex 2 showed that only one of the two cyanato groups is N-bonded of the Cu^{II} center, while the other one is non-coordinated.

Introduction

In a recent work [1], we isolated and characterized the first examples of semiquinone monooximato complexes, by reacting in methanol the copper(II) or nickel(II) bischelates of 4-chloro-1,2-benzoquinone 2-oximate, [$M(Clqo)_2$; $M = Cu^{II}$, Ni^{II}], with an excess of cyanate ion (Scheme 1).



Scheme 1.

Preliminary investigations on the reaction mechanism showed that the actual reductant is the methoxide anion, which is formed by acid–base interaction between MeOH and OCN^-. This interaction occurs only in the presence of $M(Clqo)_2$, which is known to behave as a Lewis acid, forming adducts with potentially basic reagents [2–5]. It is thus conceivable that the methanol and the cyanato adducts are intermediates or by-products in the reduction process.

The methanol adduct was actually isolated and characterized by its X-ray crystal structure determination [3]. Now we have also isolated the following cyanato adducts: potassium [bis(4-chloro-1,2-benzoquinone 2-oximato)isocyanatocuprate(II)], $K[Cu(Clqo)_2(NCO)]$ (1); and bis(tetrabutylammonium) [bis(4-chloro-1,2-benzoquinone 2-oximato) isocyanatocuprate(II)]cyanate, $(Bu_4N)_2[Cu(Clqo)_2(NCO)]OCN$ (2). These novel adducts were characterized by vibrational and electronic spectra. Moreover, for complex 2, it was also possible to carry out the X-ray crystal structure determination.

Experimental

IR and electronic spectra were recorded, and $Cu(Clqo)_2$ synthesized, as previously reported [4, 5].

Synthesis

Complex **1** was prepared by refluxing a mixture of $Cu(Clqo)_2$ (1 mmol) and KOCN (10 mmol) in MeCN (100 cm^3) for 1 h. The product was obtained as a red powder on slow evaporation of the resulting solution, at room temperature. Melting point (m.p.) 163–165 °C. *Anal.* Calc. for $C_{13}H_6Cl_2CuKN_3O_5$:

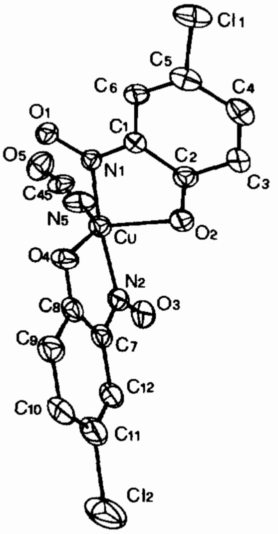


Fig. 1. An ORTEP view of $[Cu(Clqo)_2(NCO)]^-$.

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[*] For Part 6, see ref. 1.

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TABLE I. Selected Bond Distances (Å) and Angles (°) for Complex 2

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Cu	O2	2.14(1)	N5	C45	1.09(2)
Cu	O4	2.03(1)	C1	C2	1.45(2)
Cu	N1	2.00(2)	C1	C6	1.41(2)
Cu	N2	2.00(2)	C2	C3	1.41(2)
Cu	N5	1.85(1)	C3	C4	1.38(2)
Cl1	C5	1.74(2)	C4	C5	1.43(2)
Cl2	C11	1.76(2)	C5	C6	1.30(2)
O1	N1	1.28(1)	C7	C8	1.46(2)
O2	C2	1.26(2)	C7	C12	1.42(2)
O3	N2	1.26(1)	C8	C9	1.40(2)
O4	C8	1.26(2)	C9	C10	1.37(2)
O5	C45	1.27(2)	C10	C11	1.43(2)
N1	C1	1.36(2)	C11	C12	1.30(2)
N2	C7	1.34(2)			

Atom 1	Atom 2	Atom 3	Angle
O2	Cu	O4	109.9(4)
O2	Cu	N1	79.5(4)
O2	Cu	N2	93.2(4)
O2	Cu	N5	115.3(6)
O4	Cu	N1	91.2(5)
O4	Cu	N2	80.8(4)
O4	Cu	N5	134.8(7)
N1	Cu	N2	166.6(5)
N1	Cu	N5	96.1(5)
N2	Cu	N5	97.1(5)

C, 34.11; H, 1.32; N, 9.18; K, 8.58; Cu, 13.88. Found: C, 33.64; H, 1.28; N, 9.12; K, 7.71; Cu, 13.54%.

Complex 2 was obtained by refluxing Cu(Clqo)$_2$ (1 mmol) and (Bu$_4$N)OCN (10 mmol) in methanol (40 cm^3) for 5 min only. Very thin dark red crystals were isolated on slow evaporation of the resulting solution. If the reaction is carried out for a longer time, the adduct cannot be isolated because of the reduction of Cu(Clqo)$_2$. m.p. 78–80 °C. *Anal.* Calc. for $C_{46}H_{78}Cl_2CuN_6O_6$: C, 58.43; H, 8.31; N, 8.89. Found: C, 57.84; H, 8.57; N, 8.89%.

The electronic absorption spectra (nujol mulls) of 1 and 2 are quite similar: λ_{max} 350, 450(sh), 465, 510(sh), 544 nm.

Crystal Structure

The crystal structure of complex 2 (Fig. 1) was determined with a CAD4 diffractometer (graphite monochromatized Cu Kα radiation, λ = 1.5418 Å), using a needle of dimensions 0.08 × 0.11 × 0.70 nm. Selected bond lengths and angles are reported in Table I.

The cell constants were determined from a least-squares refinement of the setting angles of 25 reflections automatically centered. Crystal data: space group $P2_1/n$; $a = 14.706(4)$; $b = 23.859(4)$; $c = 15.661(5)$ Å; $\beta = 96.79(2)°$; $V = 5456.6(1)$ Å^3; $Z = 4$; D(calc.) = 1.151 g cm^{-3}; $\mu = 18.3$ cm^{-1}; $F(000) = 507$. The $\pm h \pm k + l$ reflections were measured in the $2 \leqslant \theta \leqslant 70$ range, with the ω/θ scan mode, at room temperature. The intensities of 10 954 unique total data were corrected for Lp, absorption [6] and decay (maximum decay variation 10.4%). The structure was solved and refined with standard methods (Patterson, Fourier, least-squares full matrix), by using 3624 reflections with $I \geqslant 3\sigma(I)$. Calculations were carried out with the SDP Enraf-Nonius programs [7]. Scattering factors and anomalous dispersion components were taken from ref. 8. Because of the low number of reflections, only the [Cu(Clqo)$_2$(NCO)]$^-$ anion was anisotropically refined (number of reflections/number of variables = 3624/389). Moreover, the uncoordinated OCN$^-$ anion could not be easily located owing to the diffuse electron density distribution, which indicated a statistical occupancy disorder. In order to optimize the filling of this electron density, three independent positions were taken for OCN$^-$ (O6–C46–N6, O7–C47–N7 and O8–C48–N8) with occupancy factors of 0.4, 0.4 and 0.2 respectively) and not refined. As a consequence of the small size of the available crystals and of the severe disorder in the crystal structure itself, it was not possible to reach a final R factor less than 10.2% (R_w = 11.3%; unit weight).

Results and Discussion

A characteristic feature of the structure of complex 2 is the presence of two different cyanato groups, one of which is bonded to the copper(II) center through its nitrogen atom, while the other one is non-coordinated. The tetrabutylammonium cations show quite a regular T_d symmetry around their central nitrogen atom.

The copper(II) center is surrounded by a N_3O_2 donor atom set. Its stereochemistry is intermediate between the trigonal bipyramid (TBP) and the square pyramid (SP). Most of the 1:1 adducts of Cu(Clqo)$_2$ so far described have been found in the SP geometry, with the two chelated Clqo ligands at the vertices of the square plane [2, 3]. In the present case, if we describe the coordination polyhedron as a square pyramid, we have to consider the quinonic O2 atom in the axial position, and the other four donor atoms at the vertices of the square base. In this way, we obtain a value of 0.112 for the Zemann R factor [9]. On the contrary, if we choose the TBP geometry, we have to consider the two oximic nitrogen atoms in the axial positions while two quinonic oxygen and the cyanato nitrogen atoms lie in the equatorial positions. So doing, the Zemann R factor takes the value of 0.074, which is lower than that calculated for the SP geometry. On this basis, the choice of TBP stereochemistry might be preferable; moreover, the fact that the Cu^{II} atom is not significantly out of the TBP equatorial plane defined by O2, O4, and N5, can support this view. Anyway, the two extreme stereochemistries (TBP and SP) are linked by a structural pathway involving ν_7 and ν_8 bending vibrations, as suggested in order to rationalize the plasticity effect in copper(II) complexes [10]. It is worth noting that the mean equatorial Cu–donor atom distance [2.01(1) Å] is not significantly longer than the mean axial Cu–donor atom distance [2.00(2) Å]. This feature is quite unusual for the TBP geometry in copper(II) complexes [11].

The two Clqo ligands form a dihedral angle of 71.2°, and the copper(II) center lies on both their planes. The bond lengths and angles within the $Cu(Clqo)_2$ moiety are quite similar to those reported for other copper(II) *o*-quinone monooximates [2, 3], except the Cu–O2 distance which is longer [2.14(1) Å instead of 1.98 Å]. This might agree with the hypothesis of an elongated SP stereochemistry with the quinonic O2 in the axial position, as discussed above.

It is interesting to point out that the Cu–N5 bond distance of 1.85(1) Å is markedly shorter than the Cu–N(oximic) bond distances of 2.00(2) Å. A similar value [1.87(1) Å] has been found in the dimeric $[Cu_2(tren)_2(NCO)_2]^{2+}$ cation (tren = 2,2′,2″-triaminetriethylamine) [12]. On the other hand, the N–C and C–O bond lengths of 1.09(2) and 1.27(2) Å appear to be respectively, shorter and longer than the usual values reported for coordinated cyanate groups [13] (1.12–1.15 Å and 1.18–1.24 Å for N–C and C–O bond distances respectively). However, any interpretation of these bond distances would be very speculative, because of the low accuracy of the present structure determination and the lack of strictly related compounds.

The IR spectrum of complex **2** shows two strong bands in the region of ν_{as}(NCO), assignable to the ionic OCN^- (2140 cm^{-1}) and to the coordinated NCO^- (2210 cm^{-1}) respectively [14]. The ν_{sym}(NCO) and the δ(NCO) bands are covered by other signals, except a weak band at 715 cm^{-1} attributable to the bending of the coordinated NCO^-. The IR spectrum of complex **1** shows two signals at 2185 and 710 cm^{-1}, assignable to the ν_{as}(NCO) and to the δ(NCO) respectively, while the ν_{sym}(NCO) is hidden by other signals. The bands typical of the Clqo ligand are found at the same frequencies in both complexes, indicating that probably the stereochemistry of the two compounds is similar. This hypothesis is further supported by the strict analogy between their electronic spectra in the solid state. The ν(C=O) and ν(C=N) stretching vibrations (1605 and 1530 cm^{-1}, respectively) are found at higher frequencies than in the parent $Cu(Clqo)_2$ (1590 and 1520 cm^{-1}, respectively). This feature might be caused by a decrease of the electron delocalization through the chelated rings, due to the non-planarity of the $Cu(Clqo)_2$ unit.

Supplementary Material

Observed and calculated structure factors, positional parameters for non-hydrogen atoms, calculated positional parameters for hydrogen atoms, anisotropic displacement parameters, and bond distances and angles are available from the authors on request.

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