Les molécules forment des colonnes le long des axes ternaires (Fig. 2). La liaison hydrogène qui s'établit entre N(2) et N(2^{ii}) unit deux molécules consécutives d'une même colonne. Deux autres distances interatomiques intermoléculaires sont inférieures à 3,700 Å. Il s'agit de N(2)---C(2^{ii}) [3,469 (8) Å] et de C(2)---C(2^{iii}) [3,532 (9) Å] [(iii): $\frac{1}{3}+y, -\frac{1}{3}+x, \frac{2}{3}-z$].

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Potassium 4-Chloro-1,2-benzoquinone 2-Oximate Hemihydrate, $K(Clqo).\frac{1}{2}H_2O$

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Abstract. $2K^+.2C_6H_3ClNO_2^-.H_2O$, $M_r = 409{\cdot}4$, monoclinic, $C2/c$, $a = 31{\cdot}098\,(9)$, $b = 3{\cdot}897\,(1)$, $c = 12{\cdot}995\,(3)$ Å, $\beta = 102{\cdot}29\,(4)°$, $V = 1538{\cdot}8\,(7)$ Å^3, $Z = 4$, $D_x = 1{\cdot}77$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 9{\cdot}77$ cm^{-1}, $F(000) = 824$, $T = 296$ K, final $R = 3{\cdot}3\%$ for 772 unique reflections. Each Clqo molecule shares its two O donor atoms with different K ions, thus behaving as a bidentate but not a chelated ligand. The K ion is in a distorted octahedral coordination, being surrounded by five Clqo ligands and one water molecule.

Introduction. It is well established that 2-nitrosophenols are tautomeric with *o*-quinone monooximes (Van Oijen & Romers, 1966) and that in the chelated compounds, formed by replacing the proton with a metal ion, the oximic form largely predominates. All the structural work on *o*-quinone monooximato complexes of *d*-transition metals (McPartlin, 1973; Saarinen & Korvenranta, 1975*a*,*b*; Bisi Castellani, Gatti & Millini, 1984; Bisi Castellani, Carugo & Coda, 1987, 1988) demonstrates that the chelated ring is pentaatomic and the metal is N-bonded to the oximic group (Fig. 1).

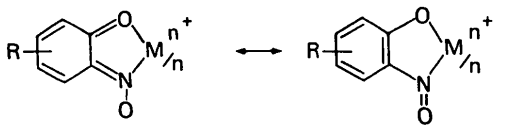

Fig. 1. *o*-Quinone monooximato complexes of *d*-transition metals.

However, this is not the only possibility; for instance, in the dioxouranium(VI) complex, the ligand is bonded to the metal through both O and N atoms of the oximic group, thus forming a triatomic chelate ring (Graziani, Casellato, Vigato, Tamburrini & Vidali, 1983). No structures of typical hard-metal (*e.g.* alkali metals) derivatives are reported. In the course of our studies on copper(II) complexes of *o*-benzoquinone monooximes, we obtained the potassium salt of 4-chloro-1,2-benzoquinone 2-oxime in a well crystallized form; thus its X-ray crystal structure determination was carried out in order to establish which is, in this case, the bonding site of the NO group, and whether the *o*-quinone monooximato moiety behaves as a chelating or unchelating ligand.

Experimental. The title compound was obtained by refluxing in methanol a suspension of bis(4-chloro-

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1,2-benzoquinone 2-oximato)copper(II) [referred to as $Cu(Clqo)_2$] with an excess of KCN, and adding benzene to the resulting solution. Orange needles were formed on standing for a few days.

A crystal with very different dimensions (1·30 × 0·29 × 0·024 mm) was mounted on a computer-controlled Philips PW 1100 four-circle diffractometer (graphite-monochromatized radiation). Cell parameters and standard deviations by least-squares analysis of measured θ angles of 25 strong reflections within the range 5–18°; the refinement was carried out with a Philips routine (*LAT*) that measures accurate profiles on both the positive and the negative range of θ. 1438 reflections measured by ω–2θ scan mode. Three standard reflections measured every 2 h (800, 020, 004) revealed a slight linear decrease in intensity (8%), and a linear correction was applied accordingly. θ range: 2–20°, $(\sin\theta)/\lambda \leq 0{\cdot}4813$ Å^{-1}, $\pm h$, $\pm k$, $+l$ set with maximum absolute values 28, 3, 12, respectively. $R_{\rm int} = 4{\cdot}2\%$ from merging symmetry-equivalent reflections; merged independent reflections: 720. Lp correction and analytical absorption correction for the sphere of the same volume (radius = 0·01 cm) as the crystal, plus North, Phillips & Mathews (1968) empirical correction by azimuthal scan of six reflections ($\chi \simeq 90°$): $73\bar{2}$, $42\bar{1}$, $31\bar{1}$ and centrosymmetric ones. Minimum and maximum absorption corrections applied to intensities, on a relative scale: 1·00–1·18. Space group $C2/c$ derived from the systematic absences and intensity statistics.

The structure was solved by Patterson and Fourier methods. All non-H atoms refined anisotropically, on F, by full-matrix least-squares techniques. Function minimized: $w(\Delta F)$, $w = 1/\sigma_F$, 610 reflections used with $I > 2\sigma_I$. Atomic scattering factors with anomalous-dispersion coefficients from *International Tables for X-ray Crystallography* (1974). Secondary-extinction correction, following Zachariasen (1963); refined $g = 38\ (15) \times 10^{-6}$. All H atoms found in $\Delta\rho$ maps, not refined and placed in calculated positions except for H(O3); arbitrary isotropic temperature factors $B = 4$ Å^2. Least-squares program: *ORFLS*, by Busing, Martin & Levy (1963). $S = 1{\cdot}29$; $\Delta\rho$ peaks in final ΔF map in the range −0·43 to +0·69 e Å^{-3}. Final maximum $\Delta/\sigma = 0{\cdot}002$. Final F agreement factors for 610 unique reflections: $R = 3{\cdot}3$; $wR = 2{\cdot}5\%$.

Table 1. *Fractional atomic coordinates* (×10^5), *e.s.d.'s in parentheses, and equivalent isotropic thermal parameters*, B_{eq}

B_{eq} according to Hamilton (1959), in Å^2.

	x	y	z	B_{eq}
K	4562 (1)	7971 (4)	5851 (1)	3·09
C(1)	6183 (2)	3172 (13)	7873 (3)	2·20
C(2)	6035 (2)	4788 (14)	6824 (3)	1·30
C(3)	6328 (2)	5091 (14)	6112 (3)	1·90
C(4)	6734 (2)	3854 (14)	6401 (3)	2·11
C(5)	6890 (2)	2150 (16)	7392 (3)	2·71
C(6)	6627 (2)	1818 (14)	8080 (3)	2·67
N	5612 (1)	5832 (12)	6606 (3)	2·55
O(1)	5944 (1)	2966 (9)	8535 (2)	3·03
O(2)	5461 (1)	7181 (10)	5701 (2)	2·85
O(3*W*)	5000	1834 (15)	7500	3·53
Cl	7108 (1)	4211 (5)	5581 (1)	3·96

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

K—O(1$^{\rm iii}$)	2·728 (4)	K—O(2$^{\rm i}$)	2·836 (4)
K—O(1$^{\rm iv}$)	2·731 (4)	K—O(2$^{\rm ii}$)	2·753 (4)
K—O(2)	2·859 (3)	K—O(3*W*)	2·733 (3)
O(2)—N	1·283 (4)	O(1)—C(1)	1·254 (5)
N—C(2)	1·348 (5)	Cl—C(4)	1·742 (5)
O(1)—C(1)—C(2)	122·9 (4)	C(1)—C(2)—N	114·8 (4)
O(1)—C(1)—C(6)	122·1 (4)	N—C(2)—C(3)	124·3 (4)
C(2)—N—O(2)	117·9 (3)		

Key for symmetry transformations: (i) $1-x$, $1-y$, $1-z$; (ii) $1-x$, $2-y$, $1-z$; (iii) $1-x$, $1+y$, $1{\cdot}5-z$; (iv) $1-x$, y, $1{\cdot}5-z$.

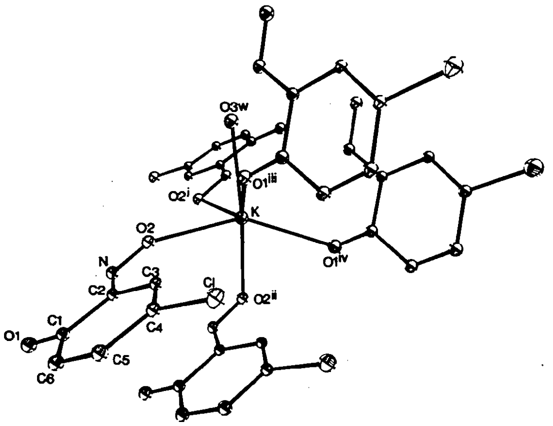

Fig. 2. *ORTEP* (Johnson, 1965) view of the potassium coordination, with 50% probability ellipsoids.

Discussion. Table 1 shows the atomic parameters.* The K ion is found (Fig. 2) in a distorted octahedral coordination, surrounded by five Clqo ligands and one water molecule. No N atom coordinates to the K ion, which is bonded to three Clqo ligands through the oximic O atom, and to the other two through the quinonic O atom. Each Clqo ligand shares its two O donor atoms with different K ions, thus behaving as a bidentate but not a chelating ligand. The metal–oxygen bond lengths (Table 2) are in agreement with the values expected for an ionic structure.

The N—O bond distance, 1·283 (4) Å, is significantly longer than those found in N-chelated compounds. In particular, the values in Å found for N—O in copper(II) complexes of *o*-quinone monooximes of known structure are the following: 1·23–1·27 (McPartlin, 1973; no

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and non-essential bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44437 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

e.s.d. reported); 1·257 (7) and 1·262 (11)–1·266 (11) (Saarinen & Korvenrantha, 1975*a*,*b*, respectively); 1·243 (7)–1·271 (6) (Bisi Castellani *et al.*, 1984); 1·18 (3)–1·26 (1) and 1·234 (6) (Bisi Castellani *et al.*, 1987, 1988, respectively). In fact, N coordination increases the double-bond character of the N—O bond, as is also shown by the N—O stretching frequencies found in the IR spectra (Baghlaf, Aly & Ganji, 1987).

A comparison of the bond lengths found in (*a*) $K(Clqo).\frac{1}{2}H_2O$, and in (*b*) the methanol adduct of $Cu(Clqo)_2$ (Bisi Castellani *et al.*, 1987) shows that the C—O and C—N bond distances are lengthened by chelation [(*a*): C—O, 1·254 (5); C—N, 1·348 (5) Å; (*b*): C—O, 1·278 (8); C—N, 1·358 (8) Å]. Such a difference in bond lengths is also observed between non-chelated (*anti*) and chelated (*syn*) *o*-quinone monooximes [*anti*-5-(2-chloroethoxy)-*o*-quinone 2-oxime (Van Oijen & Romers, 1966): C—O, 1·253 (7); C—N, 1·306 (7) Å; *syn*-5-*n*-propoxy-*o*-quinone 2-oxime (Romers, 1964): C—O, 1·270 (8); C—N, 1·319 (8) Å]. The other bond distances and angles within the organic ion compare well with the values reported for other *o*-quinone monooximes and their complexes.

The water molecule is hydrogen bonded to two N atoms through its two symmetry-equivalent H atoms: N···O(3*W*) = 2·888 (5) Å.

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Studies on Copper(II) Complexes of *o*-Quinone Monooximes. 5.* Bis(4-chloro-1,2-benzoquinone 2-oximato)(methanol)copper(II), $Cu(Clqo)_2.MeOH$

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Abstract. $[Cu(C_6H_3ClNO_2)_2(CH_4O)]$, $M_r = 408·7$, triclinic, $P\bar{1}$, $a = 12·389\,(9)$, $b = 11·730\,(9)$, $c = 5·462\,(3)$ Å, $\alpha = 87·21\,(5)$, $\beta = 78·48\,(4)$, $\gamma = 74·84\,(5)°$, $V = 750·7\,(9)$ Å^3, $Z = 2$, $D_x = 1·81$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0·71069$ Å, $\mu = 18·82$ cm^{-1}, $F(000) = 410$, $T = 296$ K, final $R = 3·3\%$ for 856 unique reflections. The copper(II) ion has distorted square-pyramidal coordination with the two bidentate ligands at the vertices of the square and the methanol O atom occupying the axial position.

Introduction. Copper(II) bis-chelated complexes of *o*-quinone monooximes are presently the focus of attention of many researchers because of their peculiar reactivity (McKillop & Sayer, 1976; Charalambous, Buckley & Brain, 1982; Charalambous, Kensett, Buckley, McPartlin, Mukerjee, Brain & Jenkins, 1983;

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* Parts 1, 2, 3 and 4 of this series: Bisi Castellani, Gatti & Millini (1984); Bisi Castellani & Millini (1984); Bisi Castellani, Carugo & Coda (1987); Bisi Castellani, Carugo, Tomba, Berbenni & Cinquetti (1987).

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