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FIRST COMPARATIVE STUDY OF THE STRUCTURE OF A 1,2-QUINONE MONOOXIME, ITS HYDROCHLORIDE SALT AND MAIN-GROUP METAL COMPLEX

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Abstract—The synthesis of 5-ethylamino-4-methyl-1,2-benzoquinone-2-oxime (5-EtaqoH), its hydrochloride salt (5-EtaqoH$_2^+$Cl$^-$·H$_2$O) and potassium complex K(5-Etaqo)(5-EtaqoH)·2H$_2$O are described. The X-ray crystal structure of all three compounds are also reported. The neutral 5-EtaqoH was found to show largely quinone oxime rather than nitrosophenol character. The hydrochloride salt had essentially a 2,5-oxime imino structure with the acidic proton attached to the quinonoid carbonyl oxygen. The potassium atom in the complex K(5-Etaqo)(5-EtaqoH)·2H$_2$O is coordinated to one neutral and one ionic ligand via the oxime nitrogens and the quinonoid carbonyl oxygen forming a five-membered chelate ring. The metal is therefore coordinated to seven donor atoms and is in a distorted pentagonal bipyramidal environment.

1,2-Quinone monooximes (2-nitrosophenols; **1**) have been known for some time.[1] These chelating agents form stable, highly coloured complexes with a wide range of metal ions. To date, most studies of quinone monooxime complexes have focused on the transition metal complexes.[2] In contrast, only a few reports on the main-group metal complexes have been published.[3] Because of their propensity to selectively precipitate certain metal ions, 1,2-quinone monooximes have found some use in metal extraction and analysis.[4] However, the strength of the metal–ligand bonds in some of the complexes, especially those of second- and third-row transition metals, and the resultant difficulty of ligand recycling by acidolysis, limits the use of 1,2-quinone monooxime ligands for continuous metal extraction processes.[5] With the exception of the nitroso-R-salts, the 1,2-quinone monooximes investigated for extraction purposes contain either halogen, alkyl or aryl substituents,[6] thereby precluding any major induced effects on metal–ligand bonding through changes in the electronic character or reaction of the substituent.

The introduction of an amino or mono-alkylamino group with its labile hydrogen and basic character into the quinone monooxime ring presents the possibility of affecting the nature and strength of the metal–ligand bond in the complexes through resonance (Scheme 1). Additionally, such a group could lower the susceptibility of the quinone monooxime moiety to decomposition by acid and hence facilitate their use in continuous extraction process. Preliminary results obtained in these laboratories show that such compounds are stable in strong acids and afford the separation of certain

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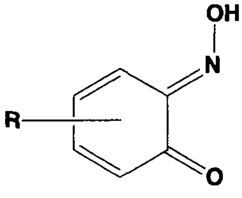
transition metal ions.[7] This finding has been tentatively attributed to the structure of the alkylamino-substituted 1,2-benzoquinone-2-oximes.



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As part of our continued interest in quinone monooxime chemistry, we describe in this paper the synthesis and structure of 5-ethylamino-4-methyl-1,2-benzoquinone-2-oxime, its reaction with hydrochloric acid and potassium salts. This report also presents the first comparative study of the structure of a 1,2-quinone monooxime, its hydrochloride salt and one of its main-group metal complexes.

EXPERIMENTAL

All reagents were of G.P.R. grade and no purification prior to use was performed. Elemental analyses were carried out using a Carlo Erba 1160 micro-analytical apparatus. IR spectra were recorded as KBr discs on a Broad FTS40 FTIR spectrophotometer. NMR spectra were recorded on a Bruker AM250 NMR spectrometer using deuterated methanol as the solvent and TMS as an internal standard.

Preparation of 5-ethylamino-4-methyl-1,2-benzoquinone-2-oxime [5-EtaqoH]

To a solution of 3-ethylamino-4-methylphenol (10.0 g, 66 mmol) in methanol (23 cm^3) was added concentrated hydrochloric acid (100 cm^3). The mixture was cooled to -10°C before sodium nitrite (4.5 g, 66 mmol) in water (25 cm^3) was added dropwise (0.5 h) with stirring. The mixture was stirred for a further 1 h. Filtration afforded a yellow solid which was washed with dilute hydrochloric acid (3 × 50 cm^3) and diethyl ether (3 × 50 cm^3). The resultant solid was dissolved in water : methanol (2 : 1, 100 cm^3) and saturated, aqueous sodium carbonate was added dropwise with stirring until a precipitate formed. The mixture was stirred for a further 0.5 h and filtered to afford an orange solid which was washed with water (5 × 25 cm^3) and dried *in vacuo* to give the product: 5-ethylamino-4-methyl-1,2-benzoquinone-2-oxime (8.5 g, 71%); m.p. 152–153°C. Found: C, 60.0; H, 6.7; N, 15.6; Calc. for $C_9H_{12}N_2O_2$: C, 60.0; H, 6.7; N, 15.6%. 5-EtaqoH was recrystallized from water : methanol (1 : 3).

Reaction of 5-ethylamino-4-methyl-1,2-benzoquinone-2-oxime with hydrochloric acid [5-Etaqo $H_2^+Cl^- \cdot H_2O$]

To a solution of 5-EtaqoH (1.0 g, 5.5 mmol) in methanol : water (2 : 1, 50 cm^3) was added hydrochloric acid (4 M, 25 cm^3). The mixture was stirred and allowed to stand for 7 days. Yellow crystals of 5-ethylamino-4-methyl-1,2-benzoquinone-2-oxime chloridrate monohydrate were recovered by filtration (1.2 g, 90%); m.p. 250°C (decomp.) Found: C, 46.0; H, 6.5; N, 11.8. Calc. for $C_9H_{15}ClN_2O_3$: C, 46.1; H, 6.4; N, 11.9%.

Preparation of 5-ethylamino-4-methyl-1,2-benzoquinone-2-oxime(5-ethylamino-4-methyl-1,2-benzoquinone-2-oximato)potassium(I) dihydrate [K(5-Etaqo) (5-EtaqoH) · $2H_2O$]

To a solution of 5-Etaqo$H_2^+Cl^-$ (5.0 g, 23 mmol) in methanol : water (4 : 1, 100 cm^3) was added potassium carbonate (9.5 g, 69 mmol). The mixture was stirred (24 h) and then filtered to afford an orange solid. The latter was washed with water (3 × 25 cm^3), recrystallized from water : methanol and dried *in vacuo* to afford the product (5-ethylamino-4-methyl-1,2-benzoquinone-2-oxime(5-ethylamino-4-methyl-1,2-benzoquinone-2-oximato)potassium(I) dihydrate (4.5 g, 90%); m.p. 180–181°C. Found: C, 49.8; H, 6.0; K, 9.3; N, 12.7. Calc. for $C_{18}H_{27}KN_4O_6$: C, 49.7; H, 6.2; K, 9.1; N, 12.9%.

In another experiment, a solution of 5-EtaqoH (38.8 mmol) in water : methanol (1 : 4, 100 cm^3) was added portionwise to a solution of potassium hydroxide (19.4 mmol) in water (25 cm^3). The reaction mixture was heated at 65°C for 0.5 h and then filtered hot. Slow evaporation of the filtrate gave orange crystals of 5-ethylamino-4-methyl-1,2-benzoquinone-2-oxime(5-ethylamino-4-methyl-1,2-benzoquinone-2-oximato)potassium(I) dihydrate (97%).

Data collection and processing

Unit-cell parameters and intensity data were obtained on an Enraf–Nonius CAD-4 diffractometer. Calculations were performed with the SDP software[8] on a MicroVAX-3100 computer. Lp decay (only in the case of Etaqo$H_2^+Cl^- \cdot H_2O$) and empirical absorptions[9] were applied. Structure solutions were achieved by direct methods using MULTAN80.[10] Full-matrix least-squares refinement with anisotropic parameters for non-hydrogen atoms and isotropic parameters for the acidic hydrogen atoms were performed. The water hydrogen atoms in the complex were not found in the difference Fourier map and were disregarded. The other hydrogen atoms, geometrically positioned (at 0.95 Å from their neighbouring atom), were not refined but their thermal parameters were taken as being proportional (× 1.3) to those of their neighbouring non-hydrogen atoms. Secondary extinctions[11] were applied in all cases and atomic scattering factors were taken from *International Tables for X-ray Crystallography*.[12] All relevant experimental parameters for 5-EtaqoH, 5-EtaqoH$_2^+$Cl$^-$·H$_2$O and K(5-Etaqo)(5-EtaqoH)·2H$_2$O are listed in Table 1. Selected geometric parameters for all three molecules are given in Tables 2, 3 and 4, respectively.

RESULTS AND DISCUSSION

The reaction of 3-ethylamino-4-methylphenol with sodium nitrite in the presence of concentrated hydrochloric acid afforded the hydrochloride salt 5-EtaqoH$_2^+$Cl$^-$. The free base was released by the neutralization of the acid salt. Both compounds were highly coloured, stable materials which

Table 1. Crystal data, data collection and processing parameters for 5-ethylamino-4-methyl-1,2-benzoquinone-2-oxime (**a**), 5-ethylamino-4-methyl-1,2-benzoquinone-2-oxime chloridate monohydrate (**b**) and (5-ethylamino-4-methyl-1,2-benzoquinone-2-oxime)(5-ethylamino-4-methyl-1,2-benzoquinone-2-oximato)potassium(I) dihydrate (**c**)

	(**a**)	(**b**)	(**c**)
Formula	$C_9H_{12}N_2O_2$	$C_9H_{15}ClN_2O_3$	$C_{18}H_{27}KN_4O_6$
F wt	180.21	234.68	434.54
Crystal system	Monoclinic	Triclinic	Orthorombic
Space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$Pbca$ (No. 61)
a (Å)	4.086(1)	7.458(1)	12.492(2)
b (Å)	17.098(1)	8.171(1)	8.241(1)
c (Å)	12.792(1)	10.010(1)	40.335(4)
α (°)	90	102.47(1)	90
β (°)	95.01(1)	104.35(1)	90
γ (°)	90	94.97(1)	90
V (Å^3)	890.3	577.5	4152.1
D_{calc} (g cm^{-3})	1.344	1.349	1.390
Z	4	2	8
Radiation	Cu-K_α (λ = 1.54184 Å), graphite monochromated		
μ (cm^{-1})	7.56	29.12	26.19
T (K)	293(2)	293(2)	293(2)
$R = \Sigma\|\|F_o\|-\|F_c\|\|/\Sigma\|F_o$	0.047	0.057	0.060
$R_w = [\Sigma w(\|F_o\|-\|F_c\|^2/\Sigma\|F_o\|^2]^{1/2}$	0.042	0.055	0.046
Weighting scheme	$w = \sigma(F_o)^{-2}$	$w = \sigma(F_o)^{-2}$	$w = F_o/P$ for $F_o < P$ $w = P/F_o$ for $F_o \geqslant P$ $P = (1/3)F_{o,\max}$
Crystal size (mm)	0.35 × 0.30 × 0.30	0.35 × 0.30 × 0.25	0.15 × 0.10 × 0.08
θ range for cell determination (°)	30–40	35–45	30–45
Scan type	ω–2θ	ω–2θ	ω–2θ
Scan speed (° min^{-1})	2.2	2.2	2.2
Scan width (°)	0.8+0.14 tan θ	0.8+0.14 tan θ	0.7+0.14 tan θ
Aperture (mm)	2.2+0.5 tan θ	2.2+0.5 tan θ	1.9+0.5 tan θ
Reflections measured	$hk\pm l$	$h\pm k\pm l$	hkl
	$0 < h < 4$	$0 < h < 9$	$0 < h < 15$
	$0 < k < 20$	$-9 < k < 9$	$0 < k < 10$
	$-15 < l < 15$	$-12 < l < 12$	$0 < l < 49$
Maximum decay (%)	−0.3	−6.9	−1.3
Transmission range (%)	93.6–99.9	86.5–99.9	88.9–99.9
Unique reflections	1744	2068	4189
Observed reflections [$I > 2\sigma(I)$]	1312	1871	1526
Refined parameters	167	157	275
(Shift/e.s.d.)$_{max}$	0.01	0.01	0.01
Final ΔF map (e Å^{-3})	−0.09/+0.11	−0.12/+0.12	−0.11/+0.14

Table 2. Bond distances (Å) for 5-ethylamino-4-methyl-1,2-benzoquinone-2-oxime

O(1)—N(1)	1.367(3)	C(5)—C(6)	1.335(3)
O(2)—C(2)	1.281(3)	C(5)—C(10)	1.503(3)
N(1)—C(1)	1.304(3)	C(8)—C(9)	1.496(3)
N(7)—C(4)	1.337(3)	C(2)—C(3)	1.381(3)
N(7)—C(8)	1.469(3)	C(3)—C(4)	1.394(3)
C(1)—C(2)	1.476(3)	C(4)—C(5)	1.467(3)
C(1)—C(6)	1.444(3)		

O(1)—N(1)—C(1)	116.3(2)	N(7)—C(8)—C(9)	111.4(2)
C(4)—N(7)—C(8)	122.8(1)	N(7)—C(4)—C(3)	121.2(1)
N(1)—C(1)—C(2)	125.9(2)	N(7)—C(4)—C(5)	118.3(2)
N(1)—C(1)—C(6)	115.7(2)	C(3)—C(4)—C(5)	120.4(2)
C(2)—C(1)—C(6)	118.4(2)	C(4)—C(5)—C(6)	118.5(2)
O(2)—C(2)—C(1)	118.5(2)	C(4)—C(5)—C(10)	120.0(2)
O(2)—C(2)—C(3)	123.6(2)	C(6)—C(5)—C(10)	121.6(2)
C(1)—C(2)—C(3)	117.9(1)	C(1)—C(6)—C(5)	122.7(2)
C(2)—C(3)—C(4)	122.0(2)		

showed variable solubility in such solvents as acetone, methanol and diethyl ether. The hydrochloride salt was also soluble in water.

The reaction of the free 1,2-quinone monooxime with potassium hydroxide (2 : 1) or the hydrochloride salt with potassium carbonate gave the same complex, K(5-Etaqo)(5-EtaqoH)·$2H_2O$. This orange complex was stable in air at room temperature and was soluble in such solvents as methanol, pyridine and dimethyl sulphoxide.

Spectroscopic characterization of the compounds

The IR spectra of both the hydrochloride salt and the free base contained two bands between 1610 and 1635 cm^{-1}, which are characteristic of the

Table 3. Bond distances (Å) and angles (°) for 5-ethylamino-4-methyl-1,2-benzoquinone-2-oxime hydrochloride monohydrate

O(1)—N(1)	1.363(4)	C(2)—C(3)	1.356(4)
O(2)—C(2)	1.326(3)	C(3)—C(4)	1.425(4)
N(1)—C(1)	1.302(4)	C(4)—C(5)	1.461(5)
N(7)—C(4)	1.310(4)	C(5)—C(6)	1.339(4)
N(7)—C(8)	1.468(5)	C(5)—C(10)	1.508(4)
C(1)—C(2)	1.458(5)	C(8)—C(9)	1.480(6)
C(1)—C(6)	1.450(3)		

O(1)—N(1)—C(1)	112.1(2)	N(7)—C(4)—C(3)	121.2(3)
C(4)—N(7)—C(8)	127.5(3)	N(7)—C(4)—C(5)	118.2(3)
N(1)—C(1)—C(2)	116.3(3)	C(3)—C(4)—C(5)	120.6(3)
N(1)—C(1)—C(6)	125.3(3)	C(4)—C(5)—C(6)	118.7(3)
C(2)—C(1)—C(6)	118.4(3)	C(4)—C(5)—C(10)	120.2(3)
O(2)—C(2)—C(1)	115.6(2)	C(6)—C(5)—C(10)	121.1(3)
O(2)—C(2)—C(3)	124.3(3)	C(1)—C(6)—C(5)	121.9(3)
C(1)—C(2)—C(3)	120.0(2)	N(7)—C(8)—C(9)	111.8(3)
C(2)—C(3)—C(4)	120.4(3)		

Table 4. Bond distances (Å) and angles (°) for 5-ethylamino-4-methyl-1,2-benzoquinone-2-oxime(5-ethylamino-4-methyl-1,2-benzoquinone-2-oximato)potassium(I) dihydrate

K—O(W1)	2.939(7)	C(1)—C(2)	1.48(1)
K—O(2)	2.848(5)	C(1)—C(6)	1.438(9)
K—O(2)	2.702(5)	C(2)—C(3)	1.405(9)
K—O(12)	3.082(5)	C(3)—C(4)	1.357(9)
K—O(12)	2.783(5)	C(4)—C(5)	1.48(1)
K—N(1)	2.901(6)	C(5)—C(6)	1.341(9)
K—N(11)	3.022(6)	C(5)—C(10)	1.51(1)
O(1)—N(1)	1.381(8)	C(6)—C(9)	1.53(1)
O(2)—C(2)	1.256(8)	C(11)—C(12)	1.47(1)
O(11)—N(11)	1.324(8)	C(11)—C(16)	1.43(1)
O(12)—C(12)	1.255(8)	C(12)—C(13)	1.420(8)
N(1)—C(1)	1.308(8)	C(13)—C(14)	1.382(9)
N(7)—C(4)	1.351(8)	C(14)—C(15)	1.455(9)
N(7)—C(8)	1.45(1)	C(15)—C(16)	1.348(9)
N(11)—C(11)	1.340(8)	C(15)—C(20)	1.499(9)
N(17)—C(14)	1.357(8)	C(18)—C(19)	1.516(9)
N(17)—C(18)	1.464(8)		
O(W1)—K—O(2)	102.5(2)	N(1)—C(1)—C(2)	114.9(6)
O(W1)—K—O(2)	84.6(2)	N(1)—C(1)—C(6)	125.3(6)
O(W1)—K—O(12)	83.2(2)	C(2)—C(1)—C(6)	119.8(6)
O(W1)—K—O(12)	99.9(2)	O(2)—C(2)—C(1)	120.2(6)
O(W1)—K—N(1)	151.2(2)	O(2)—C(2)—C(3)	124.3(6)
O(W1)—K—N(11)	135.9(2)	C(1)—C(2)—C(3)	115.6(6)
O(2)—K—O(2)	97.3(1)	C(2)—C(3)—C(4)	124.0(7)
O(2)—K—O(12)	174.2(2)	N(7)—C(4)—C(3)	123.8(6)
O(2)—K—O(12)	87.51	N(7)—C(4)—C(5)	116.1(6)
O(2)—K—N(1)	55.2(2)	C(3)—C(4)—C(5)	120.1(6)
O(2)—K—N(11)	121.8(2)	C(4)—C(5)—C(6)	118.7(6)
O(2)—K—O(12)	84.4(1)	C(4)—C(5)—C(10)	120.0(6)
O(2)—K—O(12)	172.5(2)	C(6)—C(5)—C(10)	121.8(8)
O(2)—K—N(1)	81.1(2)	O(1)—C(6)—C(5)	121.9(6)
O(2)—K—N(11)	90.9(2)	N(7)—C(8)—C(9)	110.0(6)
O(12)—K—O(12)	90.3(1)	N(11)—C(11)—C(12)	116.5(6)
O(12)—K—N(1)	119.8(2)	N(11)—C(11)—C(16)	124.1(7)
O(12)—K—N(11)	52.7(2)	C(12)—C(11)—C(16)	119.4(6)
O(12)—K—N(1)	97.1(2)	O(12)—C(12)—C(11)	120.4(6)
O(12)—K—N(11)	81.7(2)	O(12)—C(12)—C(13)	123.7(6)
N(1)—K—N(11)	69.5(2)	C(11)—C(12)—C(13)	115.9(6)
O(1)—N(1)—C(1)	113.7(5)	C(12)—C(13)—C(14)	122.0(6)
C(4)—N(7)—C(8)	122.0(6)	N(17)—C(14)—C(13)	121.8(6)
C(11)—N(11)—C(11)	115.2(6)	N(17)—C(14)—C(15)	116.9(6)
C(14)—N(17)—C(18)	123.0(5)	C(13)—C(14)—C(15)	121.3(6)
C(14)—C(15)—C(16)	117.7(6)	C(11)—C(16)—C(15)	122.8(6)
C(14)—C(15)—C(20)	120.2(6)	N(17)—C(18)—C(19)	111.2(6)
C(16)—C(15)—C(20)	122.1(6)		

quinonoid carbonyl stretch of 1,2-quinone monoximes.[13] The analogous band in the potassium complex occurred at lower frequency (1600–1610 cm^{-1}), reflecting the involvement of the carbonyl group in metal–ligand bond formation.

The ^{1}H NMR spectra of 5-EtaqoH and 5-EtaqoH$_2^+$Cl$^-$ confirmed the compounds as being ring- and not N-nitrosated. The *ortho*-H–H coupling in these spectra provided further evidence of quinone monooxime character.[14] The observed J_{ortho} of 8.51 Hz was considerably greater than that of the corresponding phenol (7.04 Hz).

The mass spectra of both the hydrochloride salt and the free base contained prominent molecular

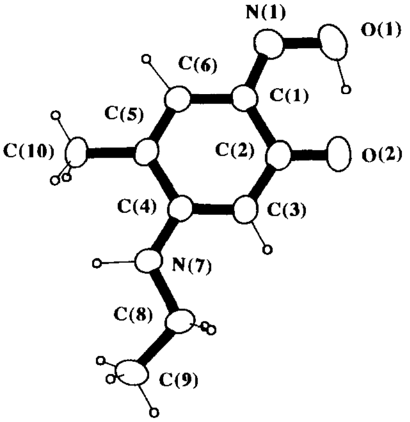


Fig. 1. View of the 5-ethylamino-4-methyl-1,2-benzoquinone-2-oxime with atomic numbering scheme.

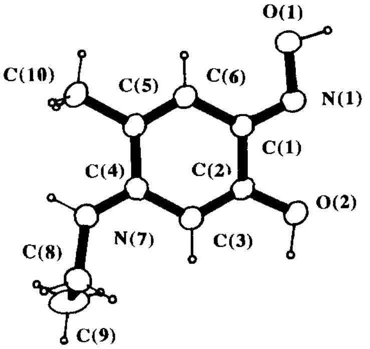


Fig. 2. View of the protonated 5-ethylamino-4-methyl-1,2-benzoquinone-2-oxime.

ions as well as ions assignable to the loss of such fragments as NO, OH˙, NOH and CO, all of which have previously been associated with quinone monooxime compounds.[15] The structures of all three compounds were confirmed by X-ray crystallographic studies.

X-ray crystal structure of 5-EtaqoH *and* 5-Etaqo $H_2^+Cl^- \cdot H_2O$

Perspective views of both molecules with relevant atomic numbering are presented in Figs 1 and 2. In contrast to the 5-pentylamino[16] and 5-hexylamino analogues,[17] the oxime OH group in 5-ethylamino-4-methyl-1,2-benzoquinone-2-oxime was found to be *syn* (*cis*) to the quinonoid carbonyl group. Thus, the molecule contained an intramolecular hydrogen bond between the quinoid carbonyl oxygen and the oximic hydrogen [O(1)—H(O1) = 0.99(3), H(O1)—O(2) 1.56(3) Å, O(1)—H(O1)—O(2) = 156(3)°, O(1)···O(2) = 2.489(3) Å; Fig. 3]. The bond distances in this molecule are quite similar to those found in both the 5-pentylamino and 5-hexylamino analogues. Thus, the bonds C(2)—C(3) [1.381(3) Å], C(3)—C(4) [1.394(3) Å], C(2)—O(2) [1.281(3) Å] and C(4)—N(7) [1.337(3) Å] compare well with those found in the 5-hexylamino [1.398(5), 1.397(4), 1.281(4) and 1.330(4) Å] and 5-pentylamino [1.40(2), 1.40(2), 1.25(2) and 1.35(2)] derivatives. This marked similarity with the two previously described structures suggests that, like the 5-pentylamino and 5-hexylamino analogues, this molecule also has some 2,5-oxime imino character. The crystal packing in this molecule is relatively simple. The molecules are arranged in strands through weak hydrogen bonds [N(7)—H(N(7) = 1.04(3), HN(7)—$O(2^i)$ = 2.21(3) Å, N(7)—HN(7)—$O(2^i)$ = 149(2)°, N(7)···$O(2^i)$ = 3.141(2) Å; symmetry code (i) = $x-1/2$, $1/2-y$, $z-1/2$; Fig. 3]. The inter-strand interactions are weak van der Waals interactions. Besides the hydrogen bond, no other intermolecular contacts involving non-hydrogen atoms < 3 Å are observed.

In contrast to 5-ethylamino-4-methyl-1,2-benzoquinone-2-oxime, the oxime OH group of the hydrochloride salt was *anti* (*trans*) to the quinonoid carbonyl group. Comparison of the bond length of the CO group in the structure of 5-ethylamino-4-

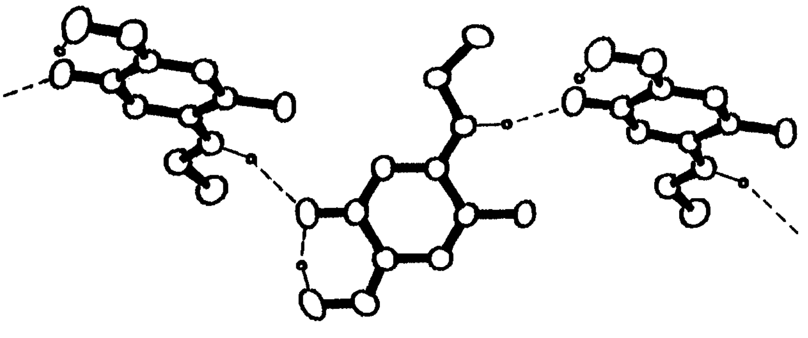


Fig. 3. Hydrogen bonding scheme in the crystals of 5-ethylamino-4-methyl-1,2-benzoquinone-2-oxime.

methyl-1,2-benzoquinone-2-oxime hydrochloride monohydrate to those reported for compounds of confirmed quinone monooxime structure[18–22] show that C(2)—O(2) [1.326(1) Å] is longer than the average CO bond length for compounds of this type. Significantly, this bond is longer than the corresponding bond in the free bases 5-ethylamino-4-methyl-, 5-pentylamino- and 5-hexylamino-1,2-benzoquinone-2-oximes [1.281(1), 1.25(2) and 1.281(1) Å, respectively]. This increased bond length is consistent with more single-bond character and confirms the CO group as bearing one of the acidic hydrogens. The C(1)—N(1) bond length [1.302(4) Å] is within the range observed for oximic C—N bonds. The C(4)—N(7) bond [1.310(4) Å] is considerably shorter than the typical C_{sp^2}—NRH bond and thus shows that the latter has much double bond character.[23]

On the basis of these results, the molecule is best represented by structure **b** (Scheme 2). Further supporting evidence for this conclusion is provided by consideration of the C—C bond distances in the hexa-atomic ring. A pattern of four long and two short bonds is observed. The short bonds were C(2)—C(3) [1.356(4) Å] and C(5)—C(6) [1.339(4) Å], confirming the 2,5-oxime imino structure of the molecule.

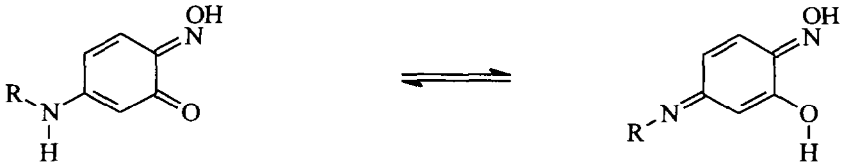
The molecule packing arrangements of the crystal are shown in Fig. 4. Extensive hydrogen bonding is observed in this crystal. The three acidic protons of each molecule are hydrogen bonded, two with two different chloride anions and the other with a water molecule [O(2)—HO(2) = 0.98(5), HO(2)—O(3) = 1.59(5) Å, O(2)—HO(2)—O3 = 166(3)°, O(2)···O(3) = 2.555(4), O(1)—HO(1) = 0.96(4), HO(1)—Cl = 2.01(4) Å, O(1)—HO(1)—Cl = 164(4)°, O(1)···Cl = 2.949(2), N(7)—HN(7) = 0.91(4), HN(7)—Cl^{i} = 2.45(4) Å, N(7)—HN(7)—Cl^{i} = 145(4)°, N(7)···Cl^{i} = 3.246(3) Å; symmetry code: (i) = x, $y-1$, $z+1$]. The water molecule forms hydrogen bonds with a chloride anion and an adjacent oximic nitrogen atom [O(3)—HO(3)A = 0.94(4), HO(3)A—N(1^{i}) = 2.08(4) Å, O(3)—HO(3)A—N(1^{i}) = 176(4)°, O(3)···N(1^{i}) = 3.018(3), O(3)—HO(3)B = 1.00(4), HO(3)B—Cl^{ii} = 2.13(4) Å, O(3)—HO(3)B—Cl^{ii} = 157(5)°, O(3)···Cl^{ii} = 3.072(2) Å; symmetry codes: (i) = $1-x, 2-y, 2-z$, (ii) = $x, y, z+1$]. The chloride ion is thus surrounded by three hydrogen atoms. Stacking interactions between the hexa-atomic rings are also present as shown in Fig. 5.

X-ray crystal structure of K(5-Etaqo)(5EtaqoH)·2H_2O

A perspective view of the molecule with the relevant atomic numbering scheme is shown in Fig. 6. The potassium cation is seven-coordinated in a distorted pentagonal-bipyramidal stereochemistry. This type of coordination is not unusual for potassium and has been observed previously.[24] The equatorial positions are occupied by one water molecule O(W1) and two quinone monooxime ligands, which chelate the metal through the carbonyl oxygen atoms O(2) and O(12) and the oxime nitrogen atoms N(1) and N(11). The axial positions are occupied by the two carbonyl oxygens of two other monooximic ligands O(2^{i}) and O(12^{ii}) [(i) = $3/2-x$, $1.2+x$, (ii) = $3/2-x$, $y-1/2$, z].

The five-membered chelate ring formed by coordination of the ligand to the cation is not dissimilar from the situation found in transition-metal complexes[25] and the lithium complex of 1-nqoH.[26] This

Scheme 1.



a **b**

Scheme 2.

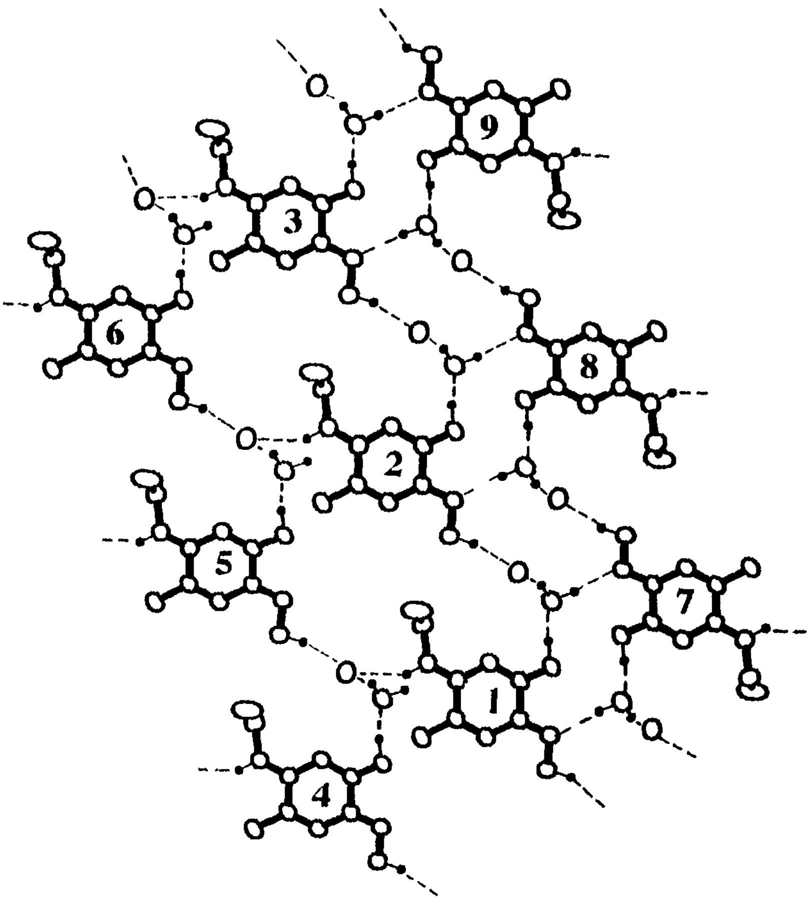


Fig. 4. Hydrogen bonding scheme in the crystals 5-ethylamino-4-methyl-1,2-benzoquinone-2-oxime chloridate monohydrate. Symmetry codes: $1 = x, y, z-1$; $2 = x, y, z$; $3 = x, y, z+1$; $4 = x, y-1, z-1$; $5 = x, y-1, z$; $6 = x, y-1, z+1$; $7 = 1-x, 2-y, 1-z$; $8 = 1-x, 2-y, 2-z$; $9 = 1-x, 2-y, 3-z$.

is, however, in contrast to the potassium complex of 4-chloro-1,2-benzoquinone-2-oxime in which the ligand is acting in bidentate but bridging mode. Thus, the potassium atom in the latter complex is bound to the oxime oxygen of one ligand and the quinonoid carbonyl oxygen of another.[27]

As for the lithium complex with 1-nqoH,[27] the oxime NO groups in the complex K(5-Etaqo)(5 EtaqoH)$\cdot$2H_2O are *cis* to each other and a short O(1)—O(11) bond appears [2.483(7) Å]. A possible position for the hydrogen atom HO(1) has been experimentally found, suggesting a very strong hydrogen bond [O(1)—HO(1) = 1.16(1), HO(1)—O(11) = 1.39(10) Å, O(1)—HO(1)—O(11) = 153(9)°]. Similar hydrogen bonds are quite common in oxime complexes.[28]

The two quinone monooxime ligands are statistically equivalent, apart from the oxime moiety which presents different N—O [1.381(8) and 1.324(8) Å] and C—N bond distances [1.308(8) and 1.340(8) Å]. This difference could arise from the protonation: the hydrogen atom HO(1) appears in fact to be nearer O(1) than O(11). However, both ligands show more 1,2-quinone monooxime character than the uncoordinated or protonated ligands. Thus, the C—O bonds [1.256(8) and 1.255(8) Å] are significantly shorter than in 5-EtaqoH [1.281(3) Å] and 5-Etaqo$H_2^+Cl^-$ [1.326(3) Å]. Within the hexaatomic ring the C(3)—C(4) and C(5)—(6) bonds are the shortest.

Besides the above description of the crystal, the overall packing is completed by a crystallization water molecule O(W2) hydrogen bonded to O(W1) [O(W1)$\cdots$O(W2) = 2.848(8) Å], to O(12) [O(W2)$\cdots$O(12) = 2.793(8) Å] and to O(11) [O(W2)$\cdots$O(11^i) = 2.844(8) Å; (i) = $3/2-x$, $1/2 = y, z$].

This study has seen that there is a considerable

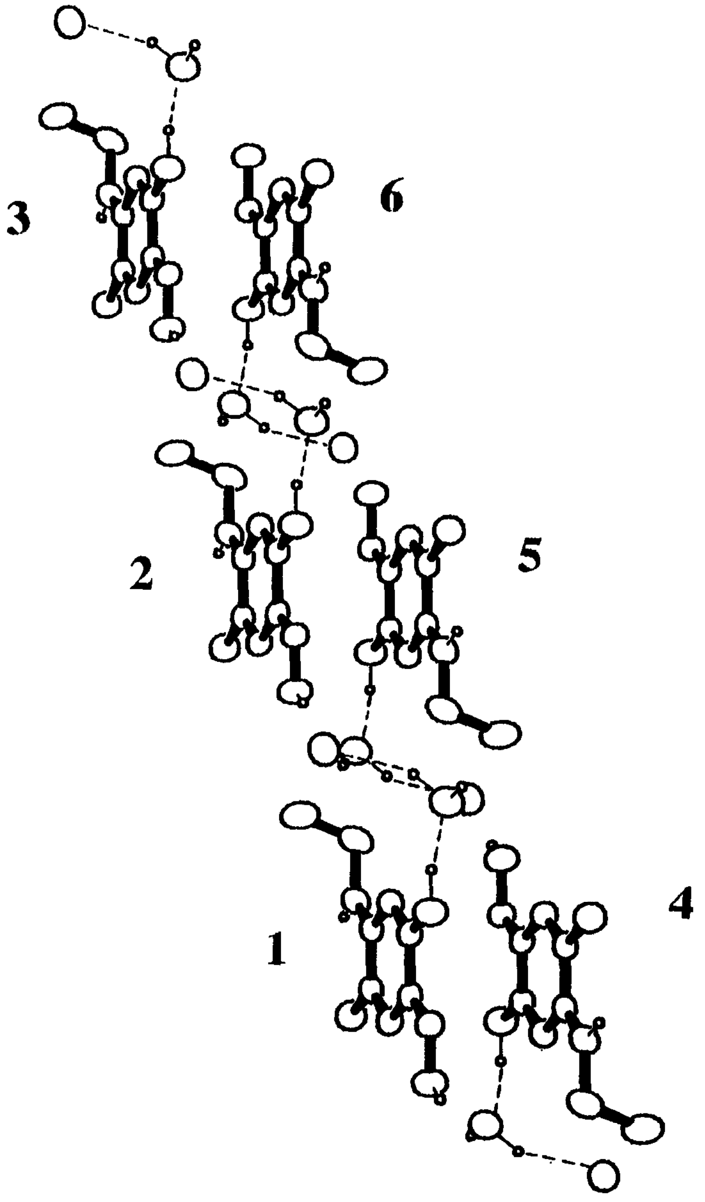


Fig. 5. Stacking interactions in the crystals of 5-ethylamino-4-methyl-1,2-benzoquinone-2-oxime chloridrate monohydrate. Symmetry codes: $1 = x, y, z-1$; $2 = x, y, z$; $3 = x, y, z+1$; $4 = 1-x, 1-y, 1-z$; $5 = 1-x, 1-y, 2-z$; $6 = 1-x, 1-y, 3-z$.

substituent effect on the structure of 1,2-quinone monooximes. Thus, the neutral 5-EtaqoH molecule shows 2,5-oxime imino character by virtue of the presence of the ethylamino group.

It is also interesting, although not unexpected, that at low pH the quinonoid carbonyl group becomes protonated in preference to the ethylamino group. Protonation of the former was shown to increase the 2,5-oxime imino character of the molecule. In contrast, deprotonation of the oxime group as occurs during complex formation increases the quinone oxime character of the molecule. Importantly, therefore, amino-substituted quinone monooximes show no nitrosophenol character even in the complexed form. The observed variation in the solid-state structure of 5-ethylamino-1,2-benzoquinone-2-oxime with degree of protonation has implications for the potential use of such compounds in extraction processes involving pH changes.

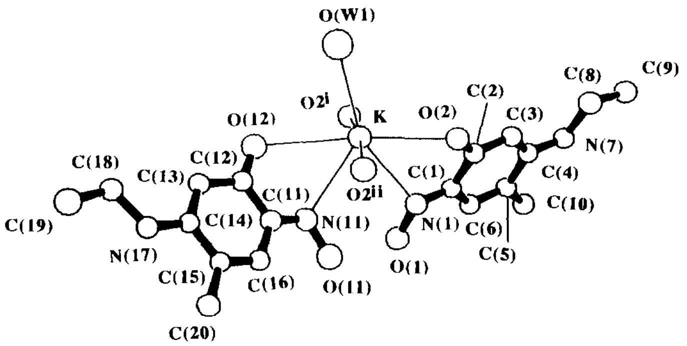


Fig. 6. View of 5-ethylamino-4-methyl-1,2-benzoquinone-2-oxime-(5-ethylamino-4-methyl-1,2-benzoquinone-2-oximato)potassium(I) dihydrate with atomic numbering.

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