Studies on Metal Complexes of *ortho*-Quinone Monooximes. Part 9.[1] Analysis of the Charge Distribution within the *o*-Quinone Monooxime Ligands through Crystallographic Data†

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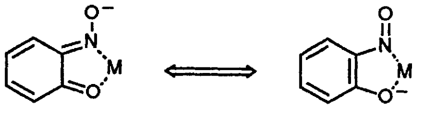
The known crystal structures of the *o*-benzoquinone monooxime complexes with d metals have been examined. In these compounds the ligands can, in principle, be present as *o*-benzoquinone monooximes **I** or *o*-nitrosophenols **II**. The available data indicate that the ligands are always intermediate between these limiting forms. Moreover, a comparison between the structures of the free ligands and those of their d-metal complexes shows that complexation to a d-metal influences the mesomeric equilibrium between forms **I** and **II**, causing a shift towards **II**. This feature is discussed in terms of the interaction of the ligands with the d orbitals of the metal.

Complexes of *o*-quinone monooximes‡ with d-metal ions have been known for a long time,[2] but they were systematically studied only in the last two decades.[3] While analytical applications were found at first,[4] more recently *o*-quinone monooxime complexes have been examined because of their implications in organic synthesis.[5] During all these studies, many crystal structures, in which the d-metal ions are chelated by the deprotonated *o*-quinone monooximes by means of the quinone carbonyl oxygen and the oxime nitrogen atoms (see Scheme 1), were determined.[1,6–15] However, few studies have been done to determine the charge distribution within the *o*-quinone monooxime complexes with d-metal ions, although this problem can be important in order to understand better the properties of these compounds.

As most works on the *o*-quinone monooxime complexes have been performed on their benzo derivatives, in the present paper we focus our attention on the *o*-benzoquinone monooxime complexes. The charge distribution within these compounds can be influenced mainly because of the fact that *o*-benzoquinone monooximes are tautomeric forms of *o*-nitrosophenols. In the case of their complexes with d-metal ions, this can be represented with the mesomeric equilibrium between the *o*-benzoquinone monooximato limiting form I and the o-nitrosophenoxide II (see Scheme 1).

It is possible that the chelation to a d-metal ion influences this equilibrium, with respect to the free ligands or to their salts with non-d-metal cations. From the literature it appears only that the 4-methyl-1,2-benzoquinone 2-oximato molecules (mbqo) contained in the complex [Cu(mbqo)$_2$]·py (py = pyridine) are 'consistent with a considerable contribution from the nitrosophenol structure', *i.e.* they have intermediate structures between the forms I and II.[11] In the present paper, all the known crystal structures of the *o*-benzoquinone monooxime complexes with d metals are examined, in order to understand the relative importance of the forms I and II in determining the charge distribution within these compounds.



I II

Scheme 1

Discussion

Since the actual charge and charge distribution in *o*-quinone monooxime ligands can be intermediate between the forms I and II, the bond distance d^j for each of the nine bonds j of the ligand can be expressed as in equation (1) where w_i are the weights and

$$(w_I d_I^j + w_{II} d_{II}^j)/[\sigma(d_I^j)^2 + \sigma(d_{II}^j)^2 + \sigma(d^j)^2] = d^j/[\sigma(d_I^j)^2 + \sigma(d_{II}^j)^2 + \sigma(d^j)^2] \quad (1)$$

d_i^j are the 'true' bond distances for the jth bond for the forms i = I and II, and where the variances of d_I^j, d_{II}^j and d^j, that is $\sigma(d_I^j)^2$, $\sigma(d_{II}^j)^2$ and $\sigma(d^j)^2$, account for the variability in the precision of the data (the sum of the variances is the variance of the sum). Therefore, knowing the nine experimental bond lengths d^j of a given crystal structure, the two weights w_i can be calculated by solving the nine equations (1) by the least-squares method. In order to perform this calculation it is necessary to provide the values of the 'true' bond distances d_I^j and d_{II}^j. Since no structural data can be used to overcome this problem, the values of the 'true' bond lengths d_i^j have been evaluated on the basis of the data reported in ref. 16. Thus, the bond distances corresponding to a pure *o*-benzoquinone monooxime III and a pure *o*-nitrosophenol IV are reported in Fig. 1.

We focused our attention on the 21 molecular structures of *o*-quinone monooxime ligands bonded to d metals published so far.[1,6–11] The ligands bonded to the same metal cation were considered independent if they were crystallographically independent. Moreover, the three known molecular structures of *o*-benzoquinone monooximes not bonded to d-metal ions

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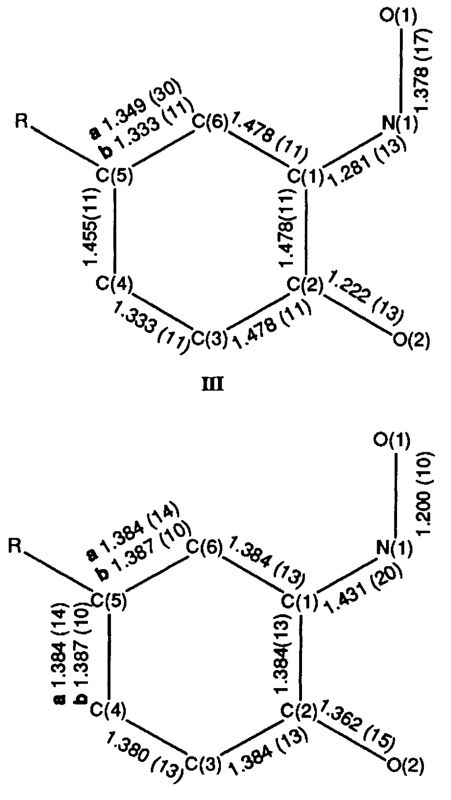
† *Supplementary data available* (No. SUP 56811, 8 pp.): experimental and calculated bond distances. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

‡ The term '*o*-quinone monooxime' indicates the ligands examined in the present paper independently of their actual charge distribution.



III

IV

Fig. 1 Bond lengths (Å) of the *o*-benzoquinone monooxime **III** and *o*-nitrosophenol **IV** model compounds, with the numbering scheme used in the present paper with estimated standard deviations (e.s.d.s) in parentheses (R = non-carbon substituent, **a**; carbon substituent, **b**). Values taken from ref. 16

Table 1 Values of w_{II} [equation (1)] and of the average of the agreement factors t ($\bar{t}$) over all the bond lengths [equation (2)] of the compounds studied; Hcebqo = α-5-(2′-chloroethoxy)-1,2-benzoquinone 2-oxime, Hpbqo = β-5-propoxy-1,2-benzoquinone 2-oxime

Compound		w_{II}*	$\bar{t}$	Ref.
$[Cu(cbqo)_2]\cdot MeOH$	(ligand 1)	0.57(7)	0.793	6
	(ligand 2)	0.55(7)	1.132	6
$[\{Cu(cbqo)_2\}_3]\cdot 2KI$	(ligand 1)	0.50(6)	0.798	7
	(ligand 2)	0.50(10)	1.016	7
	(ligand 3)	0.73(15)	1.141	7
	(ligand 4)	0.98(14)	1.044	7
$K[Cu(cbqo)_2(NCO)]\cdot KOCN$	(ligand 1)	0.50(8)	1.028	8
	(ligand 2)	0.52(9)	1.186	8
$[Cu(cbqo)_2]\cdot mim$	(ligand 1)	0.58(8)	1.049	1
	(ligand 2)	0.53(8)	1.085	1
$[Cu(cbqo)_2]\cdot 2mim$	(ligand 1)	0.68(22)	2.965	1
	(ligand 2)	0.02(42)	3.220	1
$[Cu(cbqo)_2]\cdot 2Him$	(ligand 1)	0.14(30)	3.848	1
	(ligand 2)	0.74(31)	4.125	1
$[Cu(cbqo)_2]\cdot bipy$	(ligand 1)	0.47(11)	1.458	9
	(ligand 2)	0.40(7)	0.835	9
	(ligand 3)	0.49(9)	1.011	9
	(ligand 4)	0.58(10)	1.463	9
$K[Ni(cbqo)_3]\cdot Me_2CO$	(ligand 1)	0.41(7)	0.658	11
$[Cu(mbqo)_2]\cdot py$	(ligand 1)	0.58(7)	0.685	10
	(ligand 2)	0.51(6)	0.635	10
Hcebqo		0.20(10)	1.283	13
Hpbqo		0.28(12)	1.199	14
$K(cbqo)\cdot 0.5H_2O$		0.33(8)	1.164	12

* E.s.d.s in parentheses.

were taken into account[12–14] in order to compare them with those of the ligands complexed to d metals. By solving the 24 systems of nine sets of equation (1) by least-squares methods, we obtained the weights w_{II} reported in Table 1 (the w_I values are normalized to $w_I + w_{II} = 1$). Experimental bond lengths of the molecules considered in this paper and those calculated on the basis of the obtained weights w_I and w_{II} are given in SUP 56811; the agreement factor t for each bond is also reported, defined as in equation (2) where d_{exptl} and d_{calc} are the experimental and

$$t = |d_{exptl} - d_{calc}|/(\sigma_{exptl}{}^2 + \sigma_{calc}{}^2)^{\frac{1}{2}} \qquad (2)$$

the calculated bond distances, and σ_{exptl} and σ_{calc} are their standard deviations. The agreement factor t monitors the difference between d_{exptl} and d_{calc}, which is statistically 'significant' only if $t > 2.576$, and 'possibly significant' only if $t > 1.960$.[17] Table 1 also gives the average agreement factor $\bar{t}$ for each ligand, calculated over the nine bond distances of the given ligand.

From the data in Table 1 it appears that the *o*-quinone monooxime ligands present in the complexes $[Cu(cbqo)_2]\cdot 2mim$ and $[Cu(cbqo)_2]\cdot 2Him$ have $\bar{t}$ values higher than 2.576 (cbqo = 4-chloro-1,2-benzoquinone 2-oximate, mim = 1-methylimidazole and Him = imidazole). This means that their w_I and w_{II} values lead to calculated bond lengths [d_{calc} in equation (2)] which are significantly different from the experimental ones [d_{exptl} in equation (2)].[17] Therefore, an inconsistency appears between the experimental structural parameters of the *o*-quinone monooxime ligands of these two complexes and those of the model compounds **III** and **IV**. This may be due either to the model compounds, or to the experimental structural parameters of the *o*-quinone monooximes contained in the two copper complexes. The first hypothesis seems less probable than the second one, because the model compounds **III** and **IV** are consistent with all the other *o*-quinone monooximes considered in this paper, which have $\bar{t}$ values lower than 1.960. Moreover the *o*-quinone monooxime ligands of the complex $[Cu(cbqo)_2]\cdot 2Him$ are strongly hydrogen bonded (*via* the quinone oxygen atoms) to the NH of the imidazole ligands.[1] This interaction could imply a considerable structural deformation within these *o*-quinone monooxime ligands. In the complex $[Cu(cbqo)_2]\cdot 2mim$, containing the other two anomalous *o*-quinone monooxime ligands, the two mim ligands have replaced the two Him of $[Cu(cbqo)_2]\cdot$-2Him, thus preventing the formation of hydrogen bonds. However, the stereochemistry of the copper(II) chromophore is not changed drastically.[1] Therefore, it is possible that the *o*-quinone monooximes of $[Cu(cbqo)_2]\cdot 2mim$ are deformed because of strong non-bonding interactions as well. It might be reasonable to suppose that the *o*-quinone monooxime ligands of $[Cu(cbqo)_2]\cdot 2Him$ and $[Cu(cbqo)_2]\cdot 2mim$ are inconsistent with the model compounds **III** and **IV** for reasons pertaining to the crystal and molecular packing of these complexes. They are therefore disregarded in the following discussion.

Considering the data reported in Table 1 and SUP 56811, it is also possible to evaluate the agreement of the model compounds **III** and **IV** with the experimental structures taken into account in this paper. Thus Table 2 reports, for each of the nine bonds of the *o*-quinone monooximes, the minimum, maximum and mean t value, obtained from the ligands both bonded and non-bonded to d metals {with the exception of those contained in the complexes $[Cu(cbqo)_2]\cdot 2mim$ and $[Cu(cbqo)_2]\cdot 2Him$}. In Table 2 are also given the numbers of cases in which $t < 1.960$, those in which $1.960 < t < 2.576$ and those in which $t > 2.576$. From these data, although many bonds have maximum t values greater than 1.960 and/or 2.576, all of them have mean t values lower than 1.960. Moreover, the cases with $t < 1.960$ are more numerous than those with $t > 1.960$, and there are very few cases with $t > 2.576$. This means that in general the experimental bond distances are statistically equivalent to those calculated on the basis of the model compounds **III** and **IV**.[17] The agreement between **III** and **IV** and the experimental structures can therefore be considered satisfactory.

Table 2 Minimum (t_{min}), maximum (t_{max}) and mean (t_{mean}) values of the agreement factor t [equation (2)] and numbers of cases in which $t < 1.960$, $1.960 < t < 2.576$ and $t > 2.576$, for the bonds of the compounds studied

Bond	t_{min}	t_{max}	t_{mean}	$t < 1.960$	$1.960 < t < 2.576$	$t > 2.576$
N(1)–O(1)	0.632	3.536	1.932	9	9	2
C(1)–N(1)	0.000	1.789	0.521	20	0	0
C(2)–O(2)	0.203	3.480	1.588	14	4	2
C(1)–C(2)	0.000	3.161	1.103	17	1	2
C(2)–C(3)	0.000	2.132	0.733	19	1	0
C(3)–C(4)	0.086	2.561	0.686	19	1	0
C(4)–C(5)	0.126	2.183	0.776	18	2	0
C(5)–C(6)	0.000	2.475	0.866	18	2	0
C(6)–C(1)	0.000	3.120	1.049	18	0	2

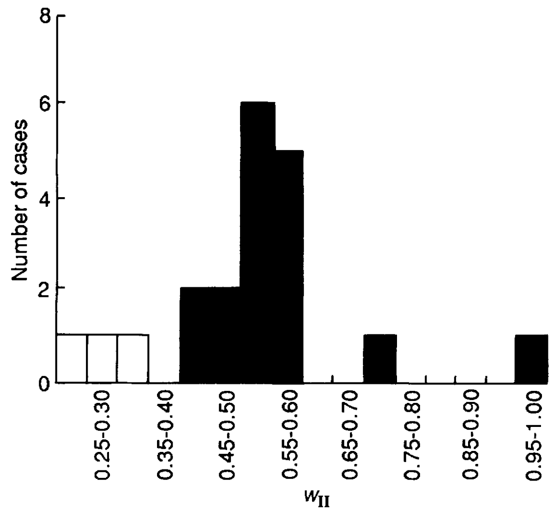
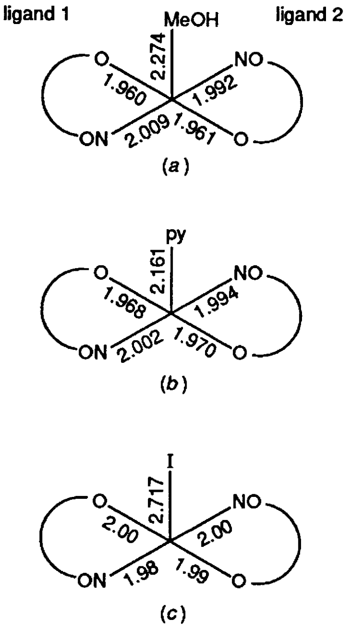


Fig. 2 Histograms showing the number of w_{II} values [equation (1)] for w_{II} spaces of 0.05 (■, ligands bonded to d metals; □, ligands not bonded to d metals)

The data reported in Table 1 show that the ligands not bonded to d metals have an average w_{II} value of 0.27, while those bonded to d metals have an average w_{II} of 0.55. This means that the complexation to d metals implies a shift towards the limiting form **II** in the mesomeric equilibrium between **I** and **II**. It is also evident, from the data presented in Table 1, that the w_{II} values of the ligands bonded to d metals are quite variable (w_{II} ranges between 0.40 and 0.98), although their distribution is unimodal with the maximum approximately corresponding to the average w_{II} value of 0.55 (see Fig. 2).

The available data do not seem to allow a detailed analysis of the factors determining the shift towards the limiting form **II** and the variability of the w_{II} values in the *o*-quinone monooxime ligands bonded to d metals. The fact that most of the crystal structures examined in the present paper are of copper(II) complexes implies a great variability in the stereochemistry around the metal centre. The plasticity of the copper(II) ion allows it to bind a variable number of ligands, and to assume a number of variably distorted stereochemistries.[18,19] Among the copper(II) complexes examined, [Cu(cbqo)$_2$]·bipy (bipy = 2,2′-bipyridine) and the central moiety of the trimeric [{Cu(cbqo)$_2$}$_3$]·2KI are six-co-ordinated and show a distorted-octahedral geometry, [Cu(cbqo)$_2$]·MeOH, [Cu(mbqo)$_2$]·py and the terminal moiety of [{Cu(cbqo)$_2$}$_3$]·2KI are five-co-ordinated and present a distorted square-pyramidal stereochemistry, [Cu(cbqo)$_2$]·mim and K[Cu(cbqo)$_2$(NCO)]·KOCN are five-co-ordinated and present a distorted trigonal-bipyramidal geometry. It is reasonable to suppose that the mesomerism between **I** and **II** can be influenced by the co-ordination number and the stereochemistry of the metal centre, and it is therefore not surprising that the geometry of the ligands is so variable.



Scheme 2 Bond lengths in Å for (*a*) [Cu(cbqo)$_2$]·MeOH, (*b*) [Cu(mbqo)$_2$]·py and (*c*) the terminal moiety of [{Cu(cbqo)$_2$}$_3$]·2KI

Since the amount of data is not high enough to analyse each stereochemistry, we limited our analysis to the five-co-ordinated square-pyramidal complexes which are the more numerous. The two limiting regular geometries for five-co-ordinated complexes are the square pyramid (*SPY*) and the trigonal bipyramid (*TBPY*).[20] Although the latter is favoured on the basis of Kepert 'repulsive theory',[18,19] the *SPY* stereochemistry is more widely encountered among five-co-ordinated copper(II) complexes.[20] This can probably be explained by the 'repulsive theory' with a steric role for an asymmetrically filled d shell.[21] However, using a more conventional model, we can suppose that the extra stabilization of the copper(II) *SPY* complexes over the *TBPY* ones can depend on a particularly effective interaction between the d orbitals of the metal and the orbitals of the ligands that are at the square base vertices. Copper(II) *SPY* complexes always show a certain degree of tetragonal distortion (the apical co-ordinative bond is longer than the square-basal ones[20]) and it is presumed that the longer is the apical bond the bigger is the interaction between the copper(II) and the square-basal ligand orbitals.

Among the complexes examined in the present paper, three have a distorted *SPY* stereochemistry: [Cu(cbqo)$_2$]·MeOH, [Cu(mbqo)$_2$]·py and the terminal moiety of [{Cu(cbqo)$_2$}$_3$]·2KI. In all of them, the two *o*-quinone monooxime ligands are situated at the vertices of the square base, while the fifth ligand (MeOH, pyridine or iodide) occupies the apical position (see Scheme 2). The tetragonal distortion of these complexes (corrected for the different covalent radii of the donor atoms, taken as 0.70, 0.66 and 1.33 Å for oxygen, nitrogen and

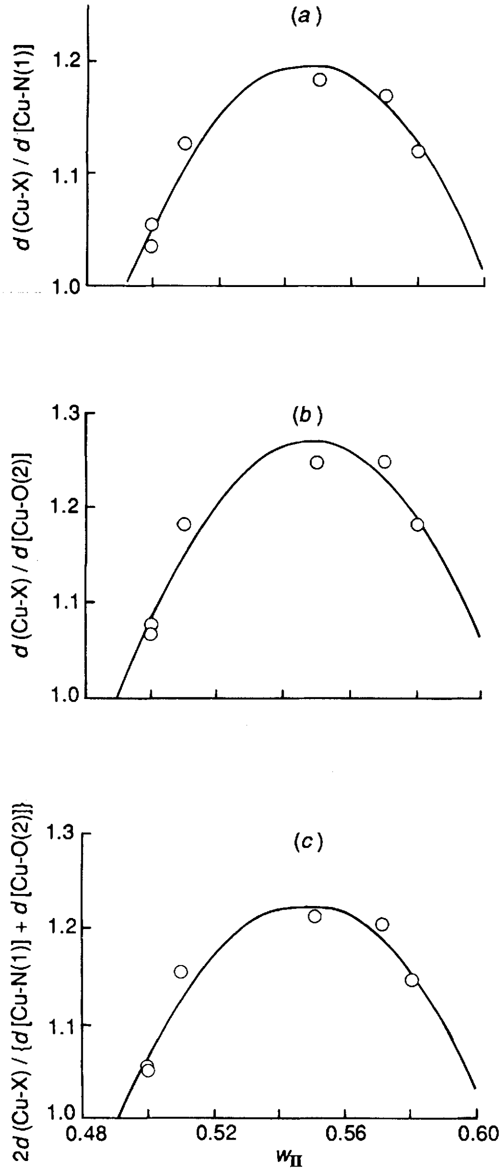


Fig. 3 Dependence on w_{II} [equation (1)] of the tetragonal distortion of the *SPY* complexes examined {d(Cu–X) = apical co-ordinative bond length; d[Cu–N(1)] and d[Cu–O(2)] = square-basal co-ordinative bond lengths; see Scheme 2}

iodide[22]) shows a unimodal dependence on their w_{II} values (see Fig. 3). In Fig. 3(*a*) the parabolic fitting curve reaches a maximum at $w_{II} = 0.546$, in Fig. 3(*b*) at $w_{II} = 0.548$ and in Fig. 3(*c*) at $w_{II} = 0.547$; the average of the three maxima is 0.547, very similar to the average w_{II} value of the ligands belonging to *SPY* complexes (0.54). This analogy between the average w_{II} value and that corresponding to the maximum elongation of the apical co-ordinative bond with respect to the basal ones (and thus corresponding to the maximum interaction between the metal d orbitals and those of the square-basal ligands) indicates that the charge distribution within the *o*-quinone monooximes located in the square base of the *SPY* complexes considered here is actually determined by the requirements of the d orbitals of the metal. It is also worthwhile noting that such a charge distribution, midway between the limiting forms **I** and **II**, is the one which best delocalizes the negative charge within the donor groups of the ligand.

Acknowledgements

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