

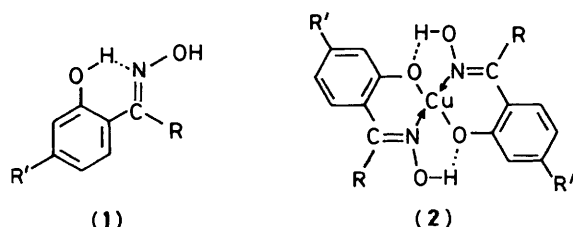
## Theoretical Studies on Organic Transition Metal Complexes. Part 4.<sup>1</sup> An Investigation of Electronic and Structural Effects in *o*-Hydroxyaryloximes

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The observed differences in selectivity between salicylaldoximes and 2-hydroxyacetophenone and 2-hydroxybenzophenone oximes as reagents for the extraction of copper from aqueous acids has been examined in terms of electronic and structural differences within the ligands. Geometry optimisation studies are reported on salicylaldoxime at the CNDO/2, MINDO/3, MNDO, AMI, STO-3G, STO-6G, and 3-21G levels and the results compared with the known crystallographic data. Geometries for the other oximes with unknown structures have been generated using the STO-3G method. The results obtained from the calculations suggest that steric factors are responsible for the different extraction behaviour.

There is renewed research interest in the structure and properties of bidentate chelates following the successful application of solvent extraction methods to the commercial recovery of copper from acidic leach solutions.<sup>2</sup> The efficacy of *o*-hydroxyaryloximes (1) in the extraction process to form bis(chelate)s (2) is well established, but the rate of extraction of copper from aqueous acid into a hydrocarbon solution of the chelate and the position of equilibrium is highly dependent on the nature and position of substituents in both the aromatic ring and side chain.<sup>3</sup> For example, 4-methylsalicylaldoxime (1a) is considerably more efficient in these respects (see Table 1) than 2-hydroxy-4-methylacetophenone oxime (1b) which in turn is more efficient than 2-hydroxy-4-methylbenzophenone oxime (1c). This behaviour is independent of the size of the alkyl group at the 4-position of the molecule and usually octyl or nonyl groups are present in commercial reagents<sup>2</sup> to facilitate the solubilisation of the copper complex in the hydrocarbon solvent and prevent its crystallisation during the extraction process.



a: R = H, R' = Me

b: R = R' = Me

c: R = Ph, R' = Me

d: R = C<sub>7</sub>H<sub>15</sub>, R' = Me

e: R = R' = H

f: R = Me, R' = H

g: R = Ph, R' = H

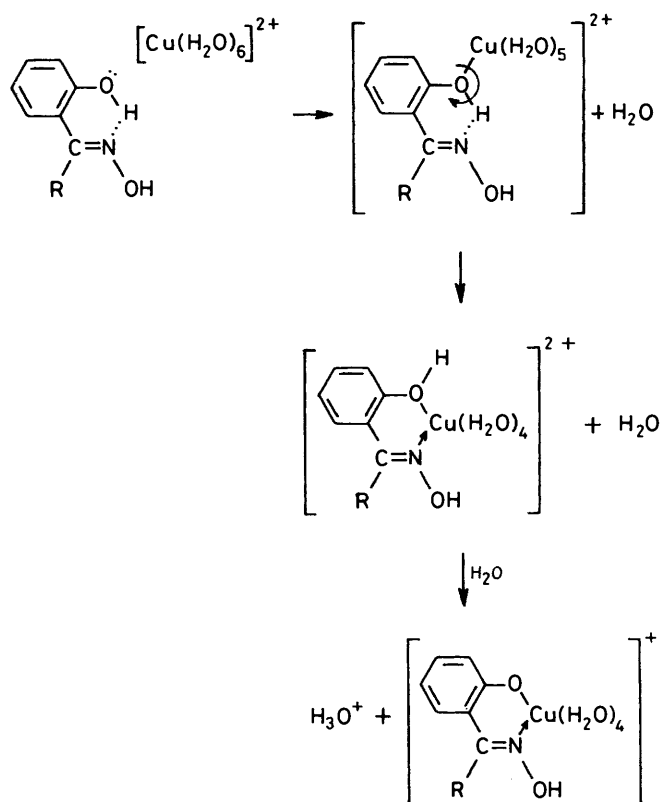
At low concentrations of oxime (<0.02M) the initial rate of the extraction reaction shows a second-order dependence on the oxime, which changes to a first-order dependence as the concentration increases to that found in the extraction process.<sup>2</sup>

The mechanism of the chelation reaction has not been elucidated but the possibility that it proceeds *via* simple ionisation of the phenolic hydrogen and subsequent co-ordination of the phenolate anion with copper(II) ion can be discounted in view of the high acidity of the aqueous phase.<sup>2,3</sup> A suggested alternative mechanism for the formation of the mono-complex involves the co-ordination of the *sp*<sup>3</sup>-hybridised phenolic oxygen to the hexaco-ordinated copper cation followed by an intramolecular inversion and displacement of water as shown in the Scheme.

**Table 1.** Relative extraction rates for aqueous copper(II) using *o*-hydroxyaryloximes<sup>a</sup>

Oxime	R	Extraction rate <sup>b</sup>	Distribution coefficient <sup>c</sup>
(1a)	H	59.2	19.5
(1b)	Me	11.1	2.3
(1c)	Ph	5.50	2.4
(1d)	C <sub>7</sub> H <sub>15</sub>	1.0	2.4

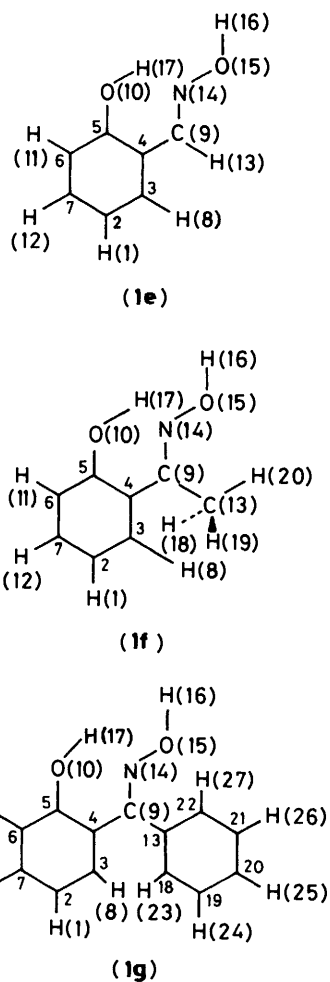
<sup>a</sup> Organic phase: 0.020M oxime in toluene; aqueous phase: 0.020M<sup>-</sup> Cu(ClO<sub>4</sub>)<sub>2</sub> in HClO<sub>4</sub> at pH 0.9 (from reference 3). <sup>b</sup> Initial extraction rate relative to oxime (1d). <sup>c</sup> Equilibrium constant ( $\times 10^2$ ) = [Cu<sub>org</sub>]/[Cu<sub>aq</sub>].



Scheme.

**Table 2.** Calculated *versus* experimental geometries for salicylaldoxime using various methods

Bond lengths (Å)	Bond angle (°)	Crystal structure <sup>4</sup>	CINMIN <sup>6</sup>	MINDO/3 <sup>7</sup>	MNDO <sup>8</sup>	AM1 <sup>9</sup>	STO-3G <sup>10</sup>	STO-6G <sup>10</sup>	3-21G <sup>10</sup>
C(4)–C(9)		1.4593	1.4421	1.5000	1.4875	1.4675	1.4899	1.4870	1.4633
C(5)–O(10)		1.3587	1.3651	1.3257	1.3571	1.3710	1.3829	1.3774	1.3577
C(9)–H(13)		1.0864	1.1196	1.1276	1.1010	1.1131	1.0906	1.0871	1.0748
C(9)–N(14)		1.2702	1.3054	1.2691	1.3117	1.3054	1.2893	1.2896	1.2623
N(14)–O(15)		1.4051	1.2775	1.3666	1.3025	1.3160	1.4097	1.4076	1.4437
O(15)–H(16)		0.8651	1.0355	0.9584	0.9593	0.9782	0.9946	0.9918	0.9666
O(10)–H(17)		0.8879	1.0508	0.9485	0.9446	0.9678	0.9895	0.9875	0.9738
O(10)–N(14)		2.6258	2.5285	2.9684	2.9365	2.9027	2.6951	2.6581	2.6722
N(14)–H(17)		1.8338	1.5620	2.3155	2.2427	2.1129	1.8077	1.7633	1.8659
C(3)–C(4)–C(9)	120.191	120.733	114.238	113.825	115.06	118.129	118.441	118.301	
C(4)–C(5)–O(10)	121.292	121.456	128.324	126.807	126.11	123.589	123.028	122.808	
C(4)–C(9)–H(13)	117.217	118.754	111.576	115.259	114.47	117.304	117.598	117.242	
C(4)–C(9)–N(14)	121.900	122.550	122.980	122.533	124.35	121.716	121.295	122.974	
C(9)–N(14)–O(15)	112.880	115.493	116.130	116.517	115.29	111.213	111.414	110.618	
N(14)–O(15)–H(16)	99.466	106.929	106.935	107.922	104.59	101.605	101.486	104.031	
C(5)–O(10)–H(17)	107.791	105.917	118.369	116.306	110.19	105.611	105.320	112.669	
Total energy (a.u.)			–103.5736	–66.3076	–67.7699	–67.5708	–467.2614	–471.8112	–470.6247
Dipole moment (D)			1.784	0.2511	0.8543	0.995	1.3255	1.3767	1.4119
CPU time (min)			16.85	5.21	4.18	4.34	436.51	1 492.77	2 185.50

**Figure.** Labelling convention for molecules (1a), (1b), and (1c)

A similar scheme can be drawn for the formation of the bis-complex although this will be stabilised additionally by hydrogen bonding as shown in (2).

The theoretical studies reported here have been carried out in an attempt to explain the observed differences between the three oximes and to provide a model which would be useful for the design of other ligands for selected metals by using a combination of molecular orbital calculations and molecular graphics for display purposes. If it is assumed that the transition state for mono-chelation occurs early along the reaction coordinate, a picture of charge distribution coupled with the calculated geometry of the respective oxime should correlate with the observed extraction kinetics, though clearly the equilibrium position of each requires calculations on the respective copper chelates. Because geometry optimisation of large transition metal complexes is not feasible at the present time the studies reported here have been directed at an investigation of the structural and electronic properties of the ligands themselves.

## Results and Discussion

The crystal structures of both salicylaldoxime<sup>4</sup> and its bis(chelate) with copper<sup>5</sup> are known, but no data are available on the corresponding oximes (1f) and (1g). Geometry optimisation calculations were performed on the latter molecules, therefore, in order to generate structures for a comparison of electronic and steric features with the known oxime (1e). Initially, however, the structure of salicylaldoxime was optimised using a number of semiempirical and *ab initio* molecular orbital methods and compared with the crystal structure to provide a reliable method for the oximes with unknown structures. The 4-alkyl group present in the commercial extractants was assumed to be unimportant in these studies because of its distance from the site of chelation. Because large CPU times were anticipated for full geometry optimisation studies, salicylaldoxime was assumed to be constructed from a fixed regular hexagon with C–C and C–H bond lengths of 1.40 and 1.08 Å respectively. The substituents were attached initially to the ring using standard bond lengths and angles which were then allowed to vary during the optimisation procedure though the torsional angles were constrained. The results of these calculations using the labelling convention shown in the Figure are given in Table 2.

Many of the bond lengths and angles calculated by the

**Table 3.** Calculated geometries of *o*-hydroxyaryloximes using the STO-3G method

Bond distances (Å)	(1e)	(1f)	(1g)
C(4)–C(9)	1.4899	1.5094	1.5091
C(5)–O(10)	1.3829	1.3801	1.3795
C(9)–H(13)	1.0906		
C(9)–C(13)		1.5302	1.5211
C(9)–N(14)	1.2893	1.2941	1.2945
N(14)–O(15)	1.4097	1.4092	1.4094
O(15)–H(16)	0.9946	0.9939	0.9946
O(10)–H(17)	0.9895	0.9905	0.9904
C(13)–H(18)		1.0862	
C(13)–H(19)		1.0836	
C(13)–H(20)		1.0862	
O(10)–N(14)	2.6951	2.6114	2.6142
N(14)–H(17)	1.8077	1.7205	1.7231
<b>Bond angles (°)</b>			
C(3)–C(4)–C(9)	118.129	118.847	119.235
C(4)–C(5)–O(10)	123.589	124.358	124.317
C(4)–C(9)–H(13)	117.304		
C(4)–C(9)–C(13)		119.625	120.3744
C(4)–C(9)–N(14)	121.716	117.583	118.374
C(9)–N(14)–O(15)	111.213	113.502	112.114
N(14)–O(15)–H(16)	101.605	101.207	101.414
C(5)–O(10)–H(17)	105.611	105.118	105.357
C(9)–C(13)–H(18)		110.388	
C(9)–C(13)–H(19)		109.764	
C(9)–C(13)–H(20)		110.388	
<b>Torsion angles (°)</b>			
C(4)–C(9)–C(13)–H(18)		59.979	
C(4)–C(9)–C(13)–H(19)		180.000	
C(4)–C(9)–C(13)–H(20)		300.021	
C(4)–C(9)–C(13)–C(18)		89.988	

MINDO/3<sup>7</sup> or MNDO<sup>8</sup> methods are inaccurate and reflect the known inability of either method to reproduce hydrogen bonding interactions.<sup>11,12</sup> Indeed, both methods increase the bond angles at the phenolic oxygen and move atoms H(17) and N(14) which were initially hydrogen-bonded in the input structure to non-bonding distances. Surprisingly, a similar result is obtained with the more recent AM1 method which is claimed to overcome these deficiencies.<sup>13</sup> In contrast, the results obtained with the CINMIN<sup>6</sup> program are remarkably accurate in view of the approximations of the CNDO/2 method with the exception of the interatomic distance between O(15)–N(14) and H(17)–N(15) which are underestimated relative to the crystallographic data. The STO-3G results are generally superior to the semiempirical calculations but the C(4)–C(9) and C(5)–O(10) bonds are overestimated. A slightly better correlation is obtained at the STO-6G level with the overall molecular energy at a lower value than that calculated at the 3-21G level. The latter method produces an excellent correlation with the experimental data except for the N(14)–O(15) bond which is substantially overestimated.

On balance, the STO-3G method gives a good correlation in a reasonable CPU time and this method was selected for the geometry optimisation of the oximes (1f and g), therefore, in preference to the other *ab initio* methods which would be expected to have much longer CPU times in view of their increased size. The calculations were carried out as before with fixed geometries for the aromatic rings including the phenyl group in (1g), and allowing the bond lengths and angles of the substituents along with the torsional angles of the methyl and phenyl groups to vary. The labelling convention shown in the Figure was used for each molecule, and the results are given in Tables 3 and 4.

An analysis of the total atomic charges both at the phenolic oxygen O(10) and nitrogen atoms N(14) shows an increase along the series (1f) > (1g) > (1e) (Table 4) which is

**Table 4.** Calculated atomic charges for *o*-hydroxyaryloximes using *ab initio* methods

Atom label	Total atomic charges				
	(1e) (3-21G)	(1e) (STO-6G)	(1e) (STO-3G)	(1f) (STO-3G)	(1g) (STO-3G)
H(1)	+0.2404	+0.0614	+0.0612	+0.0592	+0.0609
C(2)	–0.2532	–0.0801	–0.0796	–0.0813	–0.0921
C(3)	–0.2010	–0.0478	–0.0472	–0.0515	–0.0039
C(4)	–0.2494	–0.0441	–0.0438	–0.0474	–0.0564
C(5)	+0.4496	+0.1417	+0.1358	+0.1346	+0.1370
C(6)	–0.2426	–0.0882	–0.0854	–0.0866	–0.0898
C(7)	–0.2195	–0.0470	–0.0476	–0.0489	–0.0465
H(8)	+0.2499	+0.0672	+0.0664	+0.0667	+0.0398
C(9)	+0.2766	+0.0507	+0.0473	+0.1236	+0.1149
O(10)	–0.7831	–0.3230	–0.3055	–0.3154	–0.3141
H(11)	+0.2651	+0.0743	+0.0729	+0.0715	+0.0711
H(12)	+0.2515	+0.0688	+0.0683	+0.0666	+0.0679
H(13)/C(13)	+0.2778	+0.0842	+0.0818	–0.1974	+0.0045
N(14)	–0.3955	–0.1786	–0.1730	–0.1897	–0.1854
O(15)	–0.5206	–0.2158	–0.2060	–0.2109	–0.2062
H(16)	+0.4140	+0.2200	+0.2096	+0.2092	+0.2075
H(17)	+0.4398	+0.2562	+0.2449	+0.2518	+0.2520
H(18)/C(18)				+0.0769	–0.0591
H(19)/C(19)				+0.0769	–0.0597
H(20)/C(20)				+0.0920	–0.0607
C(21)					–0.0597
C(22)					–0.0591
H(23)					+0.0684
H(24)					+0.0670
H(25)					+0.0662
H(26)					+0.0670
H(27)					+0.0684

**Table 5.** Selected structural data for the Cu<sup>II</sup> bis complexes (3) of the salicylaldoximes and salicylaldimines

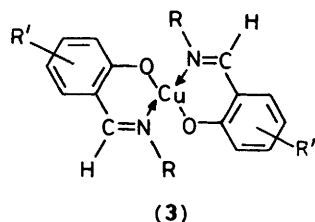
R	R'	N-O Distance (Å)	Cambridge reference <sup>a</sup>
H	H	2.7670	CUSAAI
Me	H	2.7778	MSACOP
Et	H	2.7870	CUESAL02
Cyclohexyl	H	2.7862	CHSALC01
Allyl	H	2.7606	ALSACU10
Ph	H	2.7715	PSALCU
HO	H	2.7625	SALCOP
HO	5-Cl	2.7762	CSALCU

<sup>a</sup> The names quoted are unique and taken from the Cambridge Structure Database System.<sup>14</sup>

inconsistent with the extraction behaviour observed and suggests that an early transition state model is unlikely.

However, the calculated geometries show that the angles C(3)–C(4)–C(9) and C(4)–C(9)–H(13) [or C(4)–C(9)–C(13)] increase along the series (1g) > (1f) > (1e) with the result that the interatomic distances between O(10)–N(14) and N(14)–H(17) are substantially reduced for oximes (1g) and (1f). The torsion angle of the phenyl ring present in (1g) increases from its starting point of 45° (selected to prevent clash between atoms H(8) and H(23)) to an orthogonal conformation relative to the general aryloxime ring plane.

An examination of the crystallographic data for the bis(salicylaldoximate-*O,N*)copper(II) complexes and the related complexes of the bis(salicylaldimines) (3) shows that the oxygen–



nitrogen distance seldom varies from the value of  $2.77 \pm 0.01$  Å irrespective of the substituent attached to nitrogen (Table 5).

This represents a substantial increase in the corresponding distance found in the salicylaldoxime (2.658 Å) which is able to increase without restriction during the formation of the copper chelate. However, it is clear from the calculations that both the methyl and phenyl groups present in oximes (1f) and (1g) experience a buttressing effect with respect to the ring hydrogen H(8) on the aryloxime ring resulting in a marked reduction in the O–N distance which can only increase to accommodate the copper atom by distortion of the bond and torsion angles of the

chelate ring. Furthermore, it seems probable that any rotation of the phenyl group about the C(9)–C(13) bond of the oxime (1g) will lead to a further decrease in this critical distance.

It is concluded that the observed extraction kinetics (and equilibrium constants) of the oximes are not related to the total atomic charge at the attacking phenolic oxygen, which is greatest for oxime (1f), but is a consequence of the strain energy which arises during the formation of the respective chelate.

### Calculations

All calculations were carried out on local IBM 3083 Series computers using the programs described in the text. Crystallographic co-ordinates for the ligands and complexes were obtained directly from the Cambridge database<sup>14</sup> (mounted on a local VAX 11/750 computer). A modified molecular graphics package<sup>15</sup> was used for observing and modifying the copper complexes and substituted derivatives. Data were generally submitted directly from DEC VT11 screen display to the IBM mainframe for calculations.

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