Correlation between the structural features of the *ortho*-quinone monooxime complexes and the charge distribution within the ligands. Part X

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Abstract

o-Quinone monooximes (**I**) are tautomeric forms of *o*-nitrosophenols (**II**). In their d metal complexes, where the ligands are deprotonated, this implies a mesomeric equilibrium between the two limiting forms **I** and **II**. Since **II** is aromatic, but **I** is not, this equilibrium can be monitored by means of suitable aromaticity indices. This principle is applied to the known crystal structures of *o*-quinone monooximes and their complexes, and it is observed that the complexation to d metals implies a shift towards the limiting form **II**. These results are confirmed by principal component analysis (PCA) performed on the ligand bond distances. The complexation geometry is analyzed as well by PCA, showing that the position of the d metal ion is very sensible to the mesomeric equilibrium between **I** and **II**. A chemical interpretation of this dependence is proposed. The marked dependence of the actual charge distribution within the *o*-quinone monooxime ligands on small distortions in the complexation geometry explains the high variability which is found in the charge distributions among these ligands.

Introduction

Interest in metal complexes of unsaturated chelating ligands arose because of their unusual chemical and physical properties. Particular attention has been devoted to *o*-quinoid ligands, as for instance *o*-quinones [1], 1,2-diaminobenzene derivatives [2] and dithiolenes [3]. Increasing attention is also being devoted to complexes of *o*-quinone monooximes [4], mainly because of their applications in organic synthesis [5].**

Neutral *o*-quinone monooximes are known to be tautomeric forms of *o*-nitrosophenols. Since they coordinate metal ions as monoanions, through the oxime (nitroso) nitrogen atom and the carbonyl (phenol) oxygen atom, their complexes can be represented by the mesomeric equilibrium (see Scheme 1) between the *o*-quinone monooximato (**I**) and the *o*-nitrosophenoxide (**II**) forms. The possibility that the chelation to a d metal ion influences this equilibrium has been suggested by McPartlin [6] and has been extensively studied [7] by means of a statistical analysis of the crystallographic data which allowed it to be supposed that the complexation to d metal ions implies a shift towards the limiting form **II** in the mesomeric equilibrium between **I** and **II**.

I II

Scheme 1.

In order to verify the previously reported results [7], in the present paper we describe different strategies to study the charge distribution within *o*-quinone monooxime ligands through crystallographic data; moreover, the structural features of the metal center are related to those of the ligands.

Experimental

As most of the crystallographic information on the complexes of the *o*-quinone monooximes deals with

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**The ligands examined in the present paper are generally termed '*o*-quinone monooximes' independently of their actual charge distribution.

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their benzo derivatives, we limited our attention to the *o*-benzoquinone monooximes ligands. We considered the molecular structures of twenty-one *o*-benzoquinone monooxime ligands taken from ten complexes [6, 8–13]; the ligands coordinated to the same metal center but crystallographically independent were considered independent; all the metal centers are copper(II) ions with the exception of one which is a nickel(II) ion. For comparison purposes, the three known crystal structures of *o*-benzoquinone monooxime ligands not bonded to d metal ions were also taken into account [14–16].

From Scheme 1 it can be observed that while **II** is a benzenoid compounds, thus aromatic, **I** is not. It is therefore reasonable to correlate the charge distribution within a ligand with its aromaticity. The most popular ways of evaluating the aromaticity of a ring on the basis of structural data are the aromaticity parameters HOMAS [17] and I6 [18]. These aromaticity parameters, calculated for all the twenty-four *o*-quinone monooximes here examined, are reported in Table 1. The relative weight of **II**, P_{II}, can be evaluated as

$$P_{II}(\text{HOMAS}) = 100\ (\text{HOMAS} - \text{HOMAS}_I)/(\text{HOMAS}_{II} - \text{HOMAS}_I) \quad (1)$$

$$P_{II}(\text{I6}) = 100\ (\text{I6} - \text{I6}_I)/(\text{I6}_{II} - \text{I6}_I) \quad (2)$$

where the subscripts I and II refer to the pure limiting form **I** and **II**. Since the latter ones are of course crystallographically unknown, their structural parameters were evaluated on the basis of the data published in ref. 19, as already reported [7]. The P_{II} values for all the twenty-four *o*-quinone monooximes here examined are presented in Table 1.

From the data reported in Table 1 it appears that ligands 11–14 have unreasonably low values of the P_{II}(HOMAS) and P_{II}(I6) parameters. This could arise from a bias in selecting the structural features of the pure limiting forms **I** and **II**, or on the experimental structural parameters of the ligands 11–14. The second hypothesis seems preferable since the structures of the limiting forms **I** and **II** are reasonable in all the other examined cases (83%) and because of the already described strong packing effects present in the structures of the complexes carrying the ligands 11–14 [7, 8].

TABLE 1. Parameters describing the charge distribution within the *o*-quinone monooxime ligands

No.	Ligand[a]		HOMAS[b]	I6[b]	P_{II}(HOMAS)[c]	P_{II}(I6)[c]	w_{II}[d]	PC 1[e]	Reference
1	$Cu(Clqo)_2(MeOH)$	(ligand 1)	0.655	71.09	76.2	49.6	57.0	2.355	9
2		(ligand 2)	0.547	66.31	68.7	40.8	55.0	2.386	9
3	$[\{Cu(Clqo)_2\}_3]\cdot 2KI$	(ligand 1)	0.644	71.33	75.5	50.0	50.0	2.400	10
4		(ligand 2)	0.307	55.48	51.9	21.1	50.0	2.394	10
5		(ligand 3)	0.283	57.62	50.2	25.0	73.0	2.291	10
6		(ligand 4)	0.112	54.41	38.1	19.1	98.0	2.280	10
7	$K[Cu(Clqo)_2(NCO)]\cdot KOCN$	(ligand 1)	0.382	57.04	57.1	23.9	50.0	2.442	11
8		(ligand 2)	0.305	54.94	51.7	20.1	52.0	2.453	11
9	$Cu(Clqo)_2(MeIm)$	(ligand 1)	0.641	67.58	75.3	43.2	58.0	2.273	8
10		(ligand 2)	0.598	67.27	72.2	42.6	53.0	2.385	8
11	$Cu(Clqo)_2(MeIm)_2$	(ligand 1)	−0.799	24.96	−25.8	−34.6	68.0		8
12		(ligand 2)	−3.015	−26.62	−181.2	−128.6	2.0		8
13	$Cu(Clqo)_2(Im)_2$	(ligand 1)	−1.178	23.40	−52.3	−37.4	14.0		8
14		(ligand 2)	−2.173	2.67	−122.1	−75.2	74.0		8
15	$Cu(Clqo)_2(bipy)$	(ligand 1)	0.624	68.32	74.1	44.5	47.0	2.378	12
16		(ligand 2)	0.562	66.68	69.7	41.5	40.0	2.429	12
17		(ligand 3)	0.415	66.17	59.4	40.6	49.0	2.427	12
18		(ligand 4)	0.673	70.32	77.5	48.2	58.0	2.316	12
19	$K[Ni(Clqo)_3]\cdot Me_2CO$	(ligand 1)	0.557	69.50	69.4	46.7	41.0	2.440	13
20	$Cu(Meqo)_2(py)$	(ligand 2)	0.629	74.20	74.4	55.2	58.0	2.367	6
21		(ligand 2)	0.635	73.77	74.8	54.5	51.0	2.399	6
22	Hceqo		−0.051	52.93	26.7	16.4	20.0	2.623	15
23	Hpbqo		0.140	56.16	40.1	22.3	28.0	2.580	16
24	$K(Clqo)\cdot 0.5H_2O$		−0.003	49.66	30.1	10.5	33.0	2.482	14

[a]Clqo = 4-chloro-1,2-benzoquinone 2-oximato, Meqo = 4-methyl-1,2-benzoquinone 2-oximato, Hceqo = α-5-(2-chloroethoxy)-1,2-benzoquinone 2-oxime, Hpbqo = β-5-propoxy-1,2-benzoquinone 2-oxime, MeIm = 1-methylimidazole. [b]Aromaticity parameters defined in refs. 17 and 18. [c]Relative weights of the limiting form **II** as defined in eqns. (1) and (2). [d]Relative weight of the limiting form **II** as defined in ref. 7. [e]Scores of the PC describing the greatest variance among the ligands' bond lengths.

A different approach to study the charge distribution within the *o*-quinone monooxime ligands is to perform a principal component analysis (PCA) [20] on the bond distances of the ligands. A 20×9 input data matrix was considered (20 *o*-quinone monooxime ligands; 9 intra-ligand bond lengths). Only the bond distances within each ligand were considered because the bond angles in ranging between **I** and **II** are assumed to be nearly constant. PCAs were performed with the software package STATGRAPHIC [21], by scaling and standardizing the data. Ligands 11–14 were disregarded in PCA since they were found markedly different from all the other ligands, both bonded and non-bonded to d metal ions, according to the above reported results. Table 2 reports the eigenvectors of the 3 principal components (PC), together with the variance percent they describe. The other PCs are not taken into consideration since they individually represent very small fractions (less than 5%) of the total variance. The values of the PC scores describing the greatest variance of the original sample are reported in Table 1.

In order to correlate the stereochemical fcaturcs of the chelated metal center with the charge distribution within the *o*-quinone monooxime ligand, a PCA was performed considering an input data matrix consisting of a 17×16 matrix (17 ligands complexed to a d metal ion M; 9 intra-ligand bond lengths plus the M–N1 and M–O2 bond lengths plus the M–N1–O1, M–N1–C1, M–O2–C2 and O2–M–N1 bond angles and plus the displacement of the M cation from the plane of the ligand). As above, ligands 11–14 were not considered. Table 3 reports the eigenvectors of the two PCs describing the greatest variance of the original sample, together with the variance they represent. The other PCs individually describe small fractions (less than 8%) of the total variance and are thus neglected.

TABLE 2. Eigenvectors of and percentage variance described by the three PCs describing the greatest variance among the ligands' bond lengths

Bond	PC 1	PC 2	PC 3
N1–O1	0.454	−0.083	−0.177
C1–N1	−0.492	0.084	−0.122
C2–O2	−0.211	−0.162	−0.617
C1–C2	0.471	0.097	−0.107
C2–C3	−0.004	−0.611	0.306
C3–C4	0.199	0.106	0.493
C4–C5	0.348	−0.040	−0.474
C5–C6	−0.176	−0.637	−0.034
C1–C6	0.304	−0.399	0.003
Percentage variance	39.2	19.4	14.6

TABLE 3. Eigenvectors of and percentage variance described by the two PCs describing the greatest variance among the parameters describing the geometry of the fragments reported in Scheme 1

Parameter	PC 1	PC 2
Bonds		
N1–O1	0.215	−0.207
C1–N1	−0.162	0.517
C2–O2	−0.354	0.081
C1–C2	0.310	−0.309
C2–C3	0.000	−0.136
C3–C4	0.089	0.011
C4–C5	0.155	0.000
C5–C6	−0.062	−0.139
C1–C6	0.150	−0.093
M–N1	0.126	0.239
M–O2	0.363	0.205
Angles		
M–N1–O1	−0.356	0.175
M–N1–C1	0.380	0.050
M–O2–C2	−0.293	−0.371
O2–M–N1	−0.378	−0.219
Distance M–ligand plane	0.001	0.473
Percentage variance	49.5	20.2

Discussion

The HOMAS and I6 values reported in Table 1 show that the *o*-quinone monooxime ligands bonded to d metal ions tend (with the exception of ligands 11–14 which will be neglected therein after) to have higher aromaticity parameters, i.e. they are more aromatic, than the free ligands. While the latter ones have HOMAS (I6) values ranging between −0.051 (49.66) and 0.140 (56.16) with mean value of 0.029 (59.92), the ligands bonded to d metals have HOMAS (I6) values ranging between 0.112 (54.41) and 0.673 (74.20) with mean value of 0.504 (65.41). The higher aromaticity of the *o*-quinone monooxime ligands bonded to d metal ions indicates a shift towards the limiting form **II** in the mesomeric equilibrium between **I** and **II**, with respect to the free ligands, thus confirming the previously reported hypothesis [7]. The frequency distributions of the HOMAS and I6 values are reported in Fig. 1. It appears that the ligands bonded to d metals tend to be grouped on the right-hand-side of the histograms, while the free ligands are rather grouped on the left-hand-side. A sort of a bimodal distribution also appears among the ligands bonded to d metals, but it does not seem to allow us to discriminate two classes of *o*-quinone monooximes.

Analogous conclusions can be derived by considering the P_{II}(HOMAS), P_{II}(I6) and w_{II} values reported in Table 1. While the free ligands have P_{II}(HOMAS)

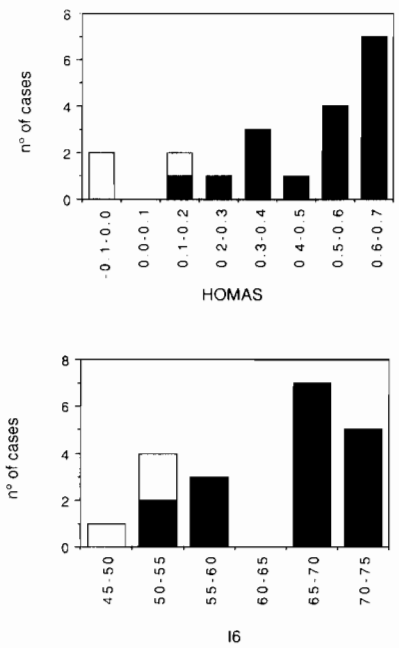

Fig. 1. Frequency distribution of the HOMAS and I6 values for the *o*-quinone monooxime ligands bonded (■) and non-bonded (□) to d metal ions.

[P_{II}(I6); w_{II}] values ranging between 26.7 and 40.1 [10.5 and 22.3; 20.0 and 33.0] with mean value of 32.3 [16.4; 27.0], the ligands bonded to d metals have P_{II}(HOMAS) [P_{II}(I6); w_{II}] values ranging between 38.1 and 77.5 [19.1 and 55.2; 40.0 and 98.0] with mean value of 65.7 [39.2; 55.3]. These data show a certain inconsistency between the P_{II}(HOMAS), P_{II}(I6) and w_{II} values. The absolute values of the differences between the P_{II}(HOMAS) and the P_{II}(I6) (w_{II}) values range between 10.3 and 33.2 (0.3 and 59.9) with mean value of 24.9 (18.2); the deviations between the P_{II}(I6) and w_{II} values range between 0.0 and 78.9 with mean value of 16.3; the correlation coefficient between P_{II}(HOMAS) and P_{II}(I6) is 0.93 and those between P_{II}(HOMAS) and w_{II} and between P_{II}(I6) and w_{II} are only 0.20 and 0.12, respectively. However, this apparent inconsistency is unlikely to indicate a bias within the three different approaches in determining the mesomeric equilibrium between **I** and **II**. In fact, while the w_{II} values are obtained by considering all the nine bond distances within each ligand [7], the P_{II}(HOMAS) and P_{II}(I6) ones depend only on the evaluation of the aromaticity of the hexa-atomic ring C1–C6. Moreover, it has been pointed out that the HOMAS and I6 aromaticity parameters are not linearly but parabolically dependent [17]; actually, a parabolic relationship can be found between the values of P_{II}(I6) and P_{II}(HOMAS) reported in Table 1.

The above discussed results support the previously reported hypothesis that the complexation of *o*-quinone monooxime ligands to d metal ions causes a shift towards the limiting form **II** in the mesomeric equilibrium between **I** and **II**. A completely independent way to verify this interpretation is to perform a PCA over the ligand bond lengths. The eigenvectors of the PC describing the greatest variance of the original sample of bond distances (PC 1) indicate that the main stereochemical variability within the *o*-quinone monooxime ligand is related to the mesomeric equilibrium between **I** and **II**. In fact, from the values reported in Table 2 it can be seen that the PC 1 eigenvectors of N1–O, C1–C2, C4–C5 and C1–C6 and those of C1–N1, C2–O2 and C5–C6 have opposite sign; the values of the PC 1 eigenvectors of C2–C3 and C3–C4, which do not follow the expected trend, are small and they probably account for some additional variance due, for example, to asymmetric chelation of the metal by the ligand or to the influence of the other ligands coordinated to the same metal center. The eigenvectors of PC 2 and PC 3 do not find a sound chemical interpretation. In the first case, for example, the opposite sign of the eigenvectors of the C1–N1 and C2–O2 bonds could suggest the importance of the asymmetric chelation of the metal by the ligand. In the second one, the fact that the eigenvectors of the C1–N1, C2–O2 and N1–O1 bonds have the same sign could suggest that interactions with other ligands bonded to the same metal center or packing effects play quite a relevant role in distorting the geometry of the *o*-quinone monooximes. Figure 2 reports the scatter plots of the PC 2 and PC 3 scores versus the PC 1 ones. The points are not grouped into well separated clusters; the free ligands are discriminated from the complexed ones mainly by the PC 1 scores, while the complexed ligands are well spread over all the three PCs. Any attempt to perform PCAs only on the *o*-quinone monooxime ligands bonded to d metals, in order to give a chemical meaning of the variance not related to the mesomeric equilibrium between **I** and **II** was unsuccessful.

Since either PC 1 (to a greater extent) or PC 2 or PC 3 (to a lower extent) are related to the mesomeric equilibrium between **I** and **II**, their scores can be considered as a measure of the position of the equilibrium. The PC 1 scores are in fact fairly highly correlated to the w_{II} values (correlation coefficient = 0.92; see Fig. 3(a)) and to a lower extent to the P_{II}(HOMAS) and P_{II}(I6) values (correlation coefficients = 0.54 and 0.68; see Fig. 3(b) and (c)). The discrepancy between the PC 1 scores and the P_{II}(HOMAS) and P_{II}(I6) values can be explained as above: while the PC 1 scores are obtained by considering the nine bond distances within each ligand, the P_{II}(HOMAS) and P_{II}(I6) values depend only on the bond distances within the hexa-atomic ring. Eventually, the results of the PCA strongly support the ones obtained

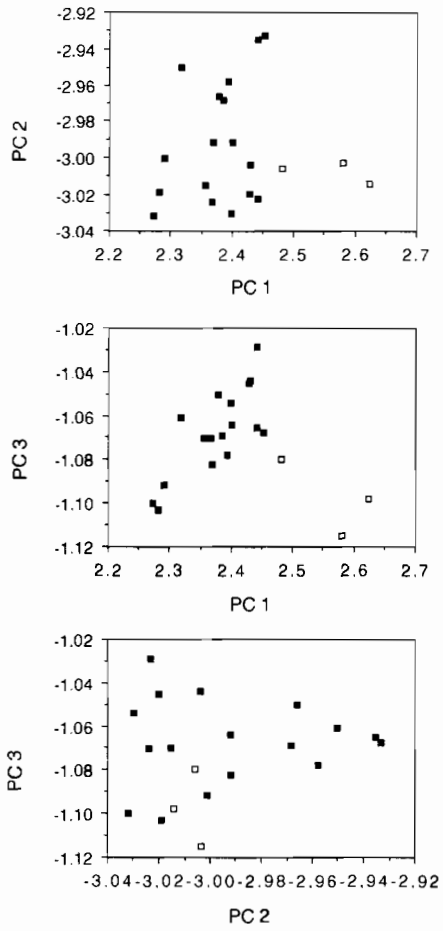

Fig. 2. Scatter plots relating the three PCs describing the greatest variance among the ligands' bond lengths: ligands bonded (■) and non-bonded (□) to d metal ions.

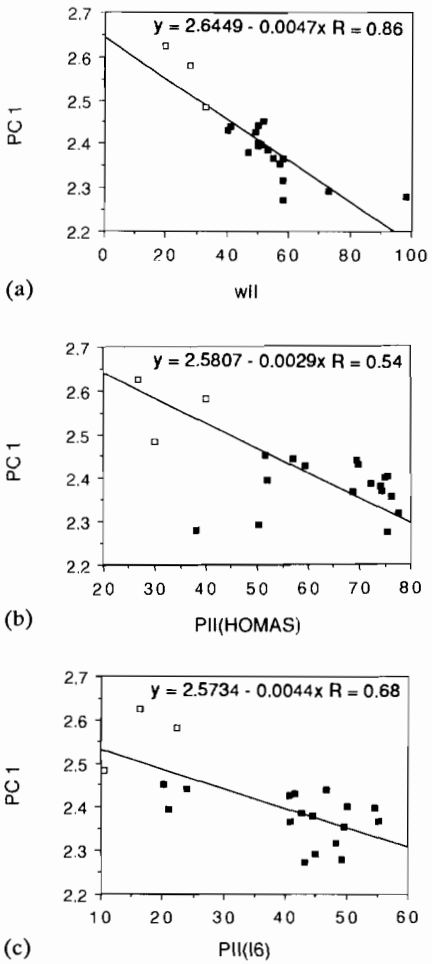

Fig. 3. Dependences of the PC describing the greatest variance among the ligands' bond lengths on the relative weights of the limiting form **II**: (a) w_{II} as defined in ref. 7, (b) P_{II}(HOMAS) as defined in eqn. (1), (c) P_{II}(I6) as defined in eqn. (2); ligands bonded (■) and non-bonded (□) to d metal ions.

by the simpler 'crystallographic monitoring' of the mesomeric equilibrium between **I** and **II** discussed above.

It seems obvious that the shift towards the limiting form **II** of the *o*-quinone monooxime ligands complexed to d metal ions is due to the interaction with the d metal cation. However, the fact that most (9 out of 10) of the examined complexes contain a copper(II) metal center prevents a deep understanding of these reasons. In fact, the plasticity of the copper(II) ion, allowing it to bind a variable number of ligands and to assume a number of variably distorted stereochemistries [22], constrains the ligands to a number of different and not comparable situations. It was previously observed that the tetragonal distortion of the square pyramidal complexes (having the 'innocent' ligand in apical position) was maximum in correspondence with their mean w_{II} value [7], suggesting that the ligand metal orbital interaction is optimum for the ligands having a charge distribution corresponding to this mean w_{II} value. However, no sound reasons for that were found. A different approach to this problem is to analyze the geometry of the coordination of the *o*-quinone monooxime ligands to d metal ions. We performed a PCA over a data sample describing all the structural features relative to the fragments reported in Scheme 1. The resulting eigenvectors, reported in Table 3, indicate that both PC 1 and PC 2 are fairly strictly related to the mesomeric equilibrium between **I** and **II**. In fact the PC 1 and PC 2 eigenvectors corresponding to the nine bond distances within the organic ligand show a trend similar to that described above with regard to the PC 1 of the ligands. The other PCs representing smaller fractions of the variance of the original sample do not have a chemical meaning and are neglected since they probably reflect only irrelevant peculiarities owing to each single fragment examined. The eigenvectors corresponding to the chelated ring geometry are very different between PC 1 and PC 2. In the first case, if the ligand is transformed from **II** to **I** (i.e. for example N1–O1 and C1–C2 lengthen and C1–N1 and C2–O2 shorten) the metal ion goes away from the

ligand: the bonds M–N1 and M–O2 lengthen and, as a consequence, the angle O2–M–N1 tightens; moreover, the metal ion moves along the direction O2 − > N1: the angle M–O2–C2 tightens, the angle M–N1–C1 widens and, as a consequence, the angle M–N1–O1 tightens; the metal ion does not move from the ligand plane. The possible chemical explanation of this pattern is the following: in a nitrosophenoxide complex, where the ligand negative charge is mainly located on the O2 oxygen atom, the metal cation is closer to O2 than to N1; if the relative importance of the form **I** increases, the metal ion is displaced towards the O1 oxygen atom, which becomes more negatively charged and it goes away from the ligand because of the presence of N1, which is less attractive than the O2 oxygen atom of the limiting form **II**. In the case of the PC 2 eigenvectors, the metal ion mobility is completely different. The most important contribution to the variance is the movement of the metal ion away from the ligand plane and a minor contribution is a movement opposite to that previewed by PC 1: the more the ligand transforms from **II** to **I**, the more the chelated metal approaches the ligand (the eigenvectors of the coordinative bonds become negative and that of the O2–M–N1 angle becomes positive) and moves towards O2 along the direction N1 − > O2 (the eigenvectors of the angle M–N1–C1 becomes negative and that of the angle M–O2–C2 becomes positive). Figure 4 shows a scatter plot of the PC 1 and PC 2 scores; it can be observed that the points are well spread along both axes and are not clustered.

These results show that the shift towards limiting form **II** in the mesomeric equilibrium between **I** and **II** is accompanied by a quite well defined relative reorientation of the ligand and the metal; in general, the metal will move within the ligand plane and will be attracted by the more negative donor atom, but there is also a consistent probability to find cations displaced from the ligand plane which will respond to a lower extent to the local donor atom properties. The sensibility of the coordination geometry on the equilibrium between the limiting forms **I** and **II** suggests that the actual charge distribution within the *o*-quinone monooxime ligands is markedly affected not only by the complexation itself but also by small distortions in the coordination geometry which can arise from the overall structure of the complex. This explains why the *o*-quinone monooxime ligands are so spread along the distortion pathway from **I** to **II**, as can be seen from the high variability of the w_{II} and P_{II} values or from the lack of clustering within the scatter plots of the PCs.

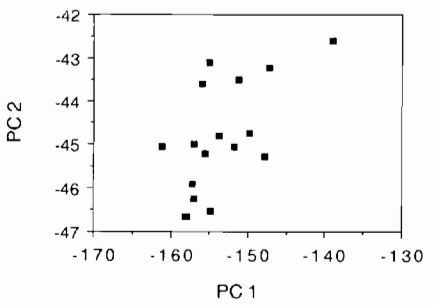

Fig. 4. Scatter plot relating the two PCs describing the greatest variance among the parameters describing the geometry of the fragments reported in Scheme 1.

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