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Note

Principal component analysis of the structures of the 1,2-diaminobenzene derivatives chelated to metal ions: correlation between structural parameters and redox behavior

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Abstract

1,2-Diaminobenzene dianion (**1**) can be oxidized to 1,2-benzosemiquinone diimine monoanion (**2**) and to 1,2-benzoquinone diimine (**3**). The known structural parameters of 28 ligands of formula **1**–**3** (the charge is disregarded) are analyzed by multivariate methods (principal component analysis). It is found that: (i) the greatest part of the variance is related to the oxidation state of the ligands; (ii) there are two reaction pathways from **1** to **3**, only one conserving the C_{2v} symmetry; (iii) the factor determining which path is followed depends on the hydrogen bonds between the NH functions and surrounding hydrogen acceptor molecules.

Key words: Metal complexes; Bidentate ligand complexes; Chelate complexes

Introduction

o-Quinoid ligands are among the most popular objects of mainstream inorganic chemistry because of their redox and magnetic properties and because of their metal assisted reactivity. In particular, recent studies have been concerned with *o*-quinones [1,2], *o*-quinone monooximes [3] and 1,2-diaminobenzene derivatives [4–6]. By analyzing the geometries of the latest ones, it has been found that most structures show delocalization, with ambiguous charge distribution between the ligands and the metal [5]: it is therefore generally impossible to interpret the structures of complexes containing 1,2-diaminobenzene derivatives* in terms of localized oxidation states corresponding to 1,2-diaminobenzene dianions (**1**), 1,2-benzosemiquinone diimine monoanions (**2**) or neutral 1,2-benzoquinone diimines (**3**). In order to fully correlate the redox behaviour of the 1,2-diaminobenzene derivatives with their structural parameters, a principal component analysis of the structures of these ligands is now reported.

Methods

All the 28 known crystal structures of crystallographic independent 1,2-diaminobenzene derivatives chelated to metal ions were located in the literature from 14 complexes [6]. The correlations between each pair of variables range (in absolute value) between 0.6609 (C1–N1 and C2–N2) and 0.0280 (C1–C6 and C3–C4), indicating that a maximum of 43.7% of the overall variance can be described by two variables only. This also justifies the application of multivariate statistical techniques. Principal component analyses [7] were performed on the eight intraligand bond distances, with the software package STATGRAPHICS [8]. Other structural parameters, like bond angles, dihedral angles, etc. were disregarded since they were found to be insensitive to the oxidation state changes ranging between **1**, **2** and **3**. Only ligand 5 [6b] has a C_{2v} symmetry crystallographically imposed. Therefore, atoms N1 and N2, C1 and C2, C6 and C3, and C5 and C4 were permuted, because of the intrinsic symmetry of the ligands, obtaining a set of 56 structures. The 56×8 data matrix **D** was analyzed without scaling and standardizing its elements, whose magnitude and range are very similar. Eigenanalysis of the covariance matrix of **D**, calculated by pre-multiplying **D** with its transposed matrix, yield eight couples of eigenvalues and eigenvectors, which are referred to as principal components (PC). The factor matrix **F** was obtained by multiplying the eigenvector and eigenvalue matrices, and the principal component scores, that is the coordinates of the 56 samples in the space spanned by the principal components, were obtained from $\mathbf{D}\cdot\mathbf{F}$. The eigenvectors of the first three principal components are reported in Table 1, together with the percentage variance they describe. The other five PCs were disregarded since they individually represent less than 7% of the overall variance.

Results and discussion

The eigenvector of the PC describing the greatest part of the original sample variance (see PC 1 in Table

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*In the present paper, the term '1,2-diaminobenzene derivatives' indicates any ligand of formula 1,2-$(HN)_2C_6H_4$, independent of its actual charge.

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TABLE 1 Eigenvectors of and percentage variance described by the first three principal components

Bond	PC 1	PC 2	PC 3
C1–N1	0.487	0.138	0.099
C2–N2	0.487	−0.138	0.099
C1–C2	−0.407	0.001	0.437
C2–C3	−0.256	0.564	−0.165
C3–C4	0.303	−0.404	0.266
C4–C5	−0.212	0.003	0.770
C5–C6	0.303	0.404	0.266
C1–C6	−0.256	−0.564	−0.165
Variance (%)	38.1	21.1	14.2

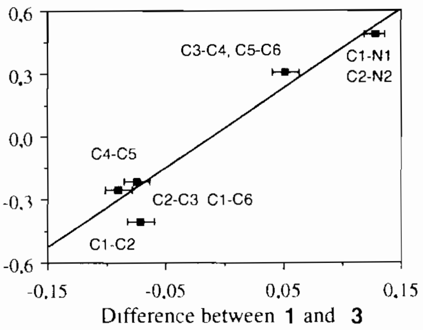

Fig. 1 Dependence of the PC 1 eigenvector elements on the corresponding differences between the bond distances of the standard structures of **1** and **3** reported in ref 5. On going from **3** to **1** the C1–N1 and C2–N2 bonds go from 1.279(8) to 1.407(3) Å (difference = 0.128(9) Å), the C1–C2 bond from 1.478(11) to 1.407(3) Å (difference = −0.071(11) Å), the C2–C3 and C1–C6 bonds from 1.478(11) to 1.388(3) Å (difference = −0.090(11) Å), the C3–C4 and C5–C6 bonds from 1.333(11) to 1.385(3) Å (difference = 0.052(11) Å), and the C4–C5 bond from 1.455(11) to 1.381(3) Å (difference = −0.074(11) Å).

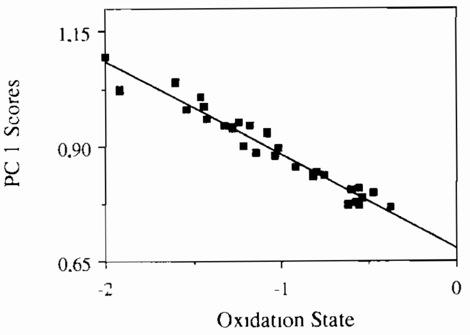

Fig 2 Dependence of the PC 1 scores on the oxidation states determined according to ref 5

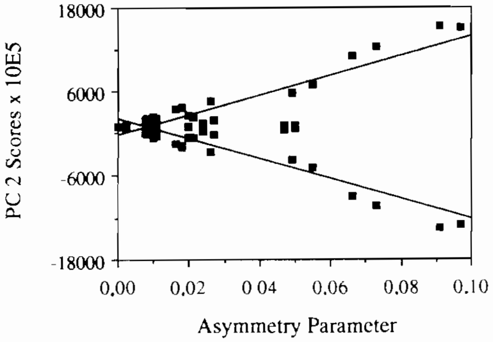

Fig 3 Dependence of the PC 2 scores on the asymmetry parameters of the ligands determined as $\{(1/3)[(d_{C1-N1}-d_{C2-N2})^2+(d_{C2-C3}-d_{C1-C6})^2+(d_{C3-C4}-d_{C5-C6})^2]\}^{1/2}$

1) is clearly related to the redox behavior of the 1,2-diaminobenzene derivatives: in fact, as expected on going from **1** to **3**, the C1–N1, C2–N2, C3–C4 and C5–C6 bonds shorten while the others lengthen (and vice versa). Moreover, the values of the elements of this eigenvector are proportional to the differences between the bond distances of the standard structures of **1** and **3** reported in ref. 5 (see Fig. 1; correlation coefficient = 0.97), and the PC 1 scores are well correlated with the oxidation state assignments reported in ref. 5 (see Fig. 2; correlation coefficient = 0.97). Therefore, the structural parameters of the 1,2-diaminobenzene derivatives *imprimis* depend on the oxidation state

The eigenvectors of the PCs describing the second and third greatest portions of the original sample variance (see PC 2 and PC 3 in Table 1) are not related to the redox reaction from **1** to **3**, and their chemical meanings are quite obscure. In the eigenvector of PC 2, the terms of the bonds C1–N1 and C2–N2, C2–C3 and C1–C6, and C3–C4 and C5–C6 have opposite sign, suggesting the unreasonable idea that while one half of the molecule is reduced from **3** to **1** the other half is oxidized from **1** to **3**; concerning PC 3, if the molecule is oxidized from **1** to **3** (the C1–N1, C2–N2, C3–C4 and C5–C6 bonds shorten while the C2–C3 and C1–C6 lengthen) the bonds C1–C2 and C4–C5 shorten, suggesting a 1,2-benzoquinone diimine **3** with two electronically independent diene moieties, C5=C6–C1=N1 and C4=C3–C2=N2. However, the PC 2 scores are quite well correlated with the asymmetry parameter defined as $\{(1/3)[(d_{C1-N1}-d_{C2-N2})^2+(d_{C2-C3}-d_{C1-C6})^2+(d_{C3-C4}-d_{C5-C6})^2]\}^{1/2}$, which measures the deviation from the ideal C_{2v} symmetry resulting from the loss of the two-fold axis (see Fig. 3; correlation coefficient = 0.88; the double trend is due to the permutations between N1 and N2, C1 and C2, C6 and C3, and C5 and C4 imposed to PCA). Similar results are obtained by considering the asymmetry parameters of Duax *et al.* [9] and Nardelli [10], although with lower correlation coefficients, probably because these asymmetry parameters work on the hexa-atomic ring only, while the PC 2 scores reflect also the variance of the C–N bonds.

A scatter plot of the PC 1 versus the PC 2 scores of the 56 crystal structures is reported in Fig 4. The

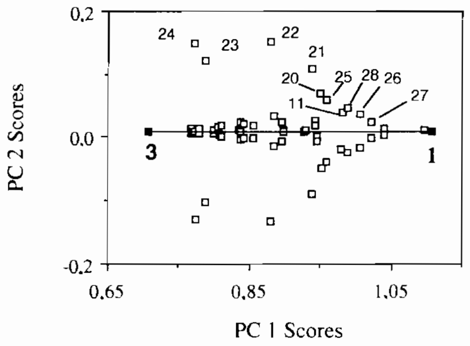

Fig 4. Scatter plot of the PC 1 vs. PC 2 scores

point distribution is symmetric with respect to the horizontal straight line at PC 2 score = 0.0, as a consequence of the permutations between N1 and N2, C1 and C2, C6 and C3, and C5 and C4 introduced in the input data matrix of PCA. No clustering is determined either by PC 1 or by PC 2, confirming that the complexes containing 1,2-diaminobenzene derivatives often show delocalization. However, it is evident that two well separated pathways linking the extreme points corresponding to **1** (1,2-diaminobenzene dianion) and **3** (1,2-benzoquinone diimine) exist. One of them is nearly parallel to the PC 1 scores axis, while the other, indicated by ligands 11 and 20–28, presents a strong dependence of the PC 2 scores on the PC 1 ones. Since PC 1 is markedly related to the oxidation state of the ligands and PC 2 depends on the loss of the two-fold symmetry from the ideal C_{2v} point group, it is reasonable to suppose that the oxidation of **1** to **3** can occur with a change in electron density 'more localized', reducing an assumed C_{2v} symmetry of the ligand, or 'delocalized' approximately keeping the C_{2v} symmetry along the entire redox pathway

The reasons for this double possibility cannot be argued from the results of PCA only. However, it can be observed that both the PC 1 and PC 2 eigenvectors can be easily related to two symmetry deformation coordinates, corresponding to irreducible representations within the C_{2v} point group [11]. The eight bond distances considered in the present paper may transform in a $5A_1+3B_1$ reducible representation. The A_1 irreducible ones are of the type $1/(2)^{1/2}$ $[d_{C1-N1}+d_{C2-N2}]$, etc., and correspond to the PC 1 eigenvector. The B_1 irreducible representations are of the type $1/(2)^{1/2}$ $[d_{C1-N1}-d_{C2-N2}]$, etc., and correspond to the PC 2 eigenvector. The reasons that determine which reaction coordinate is more energetically favorable have to be found in the environments of the ligands (thought as bonding to the metal ion, interactions with other ligands bonded to the same metal center, and packing effects), which have to be different for ligands 11 and 20–28 to one side, and for the rest on the other side. Concerning the bonding to the metal ion, no evidence appears that the chelation geometry can discriminate ligands 11 and 20–28 from the rest. The differences between the M–N1 and M–N2 bond lengths range between 0.000(9) Å (ligands 5, 13 and 27) and 0.050(13) Å (ligand 19), and their mean values for the two classes of ligands are not significantly different (0.018(21) Å for ligands 11 and 20–28; 0.015(12) Å for the rest); the deviations of the metal ion from the ligand plane range between 0.007(10) Å (ligand 14) and 0.294(13) Å (ligand 18), and their mean values for the two classes of ligands are not statistically different (0.071(12) Å for ligands 11 and 20–28; 0.073(10) Å for the rest). Also concerning the interactions between ligands bonded to the same metal center, no evident discrimination between the two classes of ligands appears. Both groups of ligands can present short interligand distances: for example ligands 20–22, which are in a homoleptic Re complex with trigonal prismatic geometry, have N···N interligand distances ranging between 2.65(3) and 2.73(3) Å, which compare well with the N···N interligand distances of ligands 14 and 15 (2.69(1) and 2.68(1) Å), which are in a homoleptic square planar Ni complex.

On the contrary, packing effects seem to present a trend discriminating the two groups of ligands. The main feature which can be monitored and which also discriminates the 1,2-diaminobenzene derivatives from the dithiolene and dioxolene quinoid compounds* is the possibility to interact with surrounding molecules via hydrogen bonding through the NH functions. In the data sample here examined, ligands 11 and 20–28 are those more involved in hydrogen bonding with surrounding molecules. Extreme cases are those of ligands 14 and 15 on one side, and 23–25 on the other: while the first two ligands are not involved at all in hydrogen bonding (the shortest N·· X contact, with X = C, is 3.48(1) Å), the latter three are asymmetrically hydrogen bonded (some of the NH groups are hydrogen bonded to ReO_4^- or acetone, with N···O distances ranging between 2.91(3) and 3.02(3) Å, C–N···O angles ranging between 100.6(1.0) and 128.6(1.2)°, and Re–N ··O angles ranging between 108.4(1.2) and 144.4(1.5)°). These hydrogen bonds are not strong [12], especially for the case of NH functions coordinated to metal ions, but it is interesting to observe that the distortion degree from C_{2v} symmetry, which is proportional to the PC 2 scores, is higher for oxidized ligands, than it is for those having low PC 1 scores. This is what can be expected if the distortion from C_{2v} symmetry is related to the hydrogen bonds due to the NH groups, since the acidity of these protons

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*It is worth noting that a PCA of the structural parameters of the *o*-benzoquinones did not show any clustering of the complexes, apart from that caused by the variability of the oxidation states (see ref. 2) presumably increases with the oxidation state of the ligand.

It has been demonstrated that the oxidation of **1** to **3** can occur through two pathways, which present different degrees of localized/delocalized electron density. The factor determining which path is followed depends on the environment, and, in particular, on the possibility of having hydrogen bonds between the NH functions and the surrounding hydrogen acceptor molecules.

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