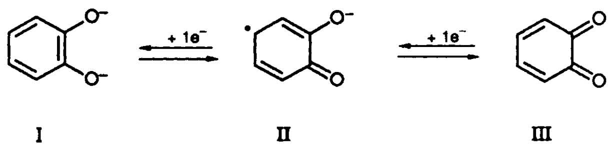
Ligands derived from *o*-Benzoquinone: Statistical Correlation between Oxidation State and Structural Features†

Oliviero Carugo,[*,a] **Carla Bisi Castellani,**[a] **Kristina Djinović**[b] **and Menico Rizzi**[c]
[a] *Dipartimento di Chimica Generale, Università di Pavia, via Taramelli 12, I-27100 Pavia, Italy*
[b] *Vto Kemija in Kem. Tehnologia, Univerza v Ljubljani, Murnikova 6, 61001 Ljubljana, Slovenia*
[c] *Dipartimento di Genetica e Microbiologia, Università di Pavia, via Abbiategrasso 207, I-27100 Pavia, Italy*

The known crystal structures of co-ordination compounds containing *o*-benzoquinone, tetrachloro-*o*-benzoquinone and 3,5-di-*tert*-butyl-*o*-benzoquinone derivatives in the form of catecholates **I**, semiquinonates **II** or benzoquinones **III** have been examined. Since forms **I**–**III** differ both in oxidation state and structural features, a simple method is proposed to correlate the oxidation states of these ligands with their structural parameters, thus allowing the determination of the oxidation state on the basis of crystallographic data. By this procedure it is possible to confirm that the *o*-benzoquinone complexes in most cases assume charge-localized electronic structures, and the same conclusion is reached by factor analysis. The results are compared with literature oxidation-state assignments, and the periodic trend in the charge distribution across a transition series is discussed for homoleptic complexes.

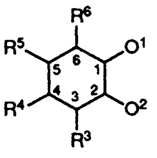
Transition-metal complexes with *o*-quinone-type ligands have intriguing redox properties, mainly because of the number of formal oxidation states that these ligands can assume.[1–3] Among the more studied of such ligands are the *o*-benzoquinone derivatives. Scheme 1 shows the various forms they can present: catecholates **I**, semiquinonates **II** and benzoquinones **III** which are related by one-electron redox steps.‡ Generally, quinone complexes assume charge-localized electronic structures, which is quite a unique property not shared with other unsaturated chelating ligands such as dithiolenes[2] or 1,2-diaminobenzene[4] which form complexes with delocalized ground states. A few cases are known where complexed quinones present electronic structures that are intermediate between the catecholato and semiquinonato limiting forms.[5,6] In these cases, the presence of charge-transfer transitions in the near-infrared region generally suggests that population of the low-lying excited-states contributes to the observed electronic structure. The marked preference for charge-localized ground states is emphasized by the case of some complexes where quinones having different oxidation states are bonded to the same metal ion.[7,8]

Since the best way to assign an oxidation state to a quinone is to determine its crystal structure accurately,[1,9] in the last ten years the crystallographic information on quinones has grown impressively. Attention is generally focused on the C–O lengths which are around 1.23 Å for benzoquinones, 1.29 Å for semiquinonates and 1.35 Å for catecholates.[1,5] However, the diagnostic value of the C–O lengths can be lowered because of the different types of co-ordination (chelation, bridging, asymmetric bridging) and the different stereochemical features of the metal centre (for example Jahn–Teller distortions). Therefore, more articulated diagnostic criteria should be used; for example, the alternance of short and long bonds within the hexaatomic ring, which is shown by benzoquinones but not by catecholates which are aromatic molecules.



I II III

Scheme 1



L

L1; $R^3 = R^4 = R^5 = R^6 = H$
L2; $R^3 = R^5 = Bu^t$, $R^4 = R^6 = H$
L3; $R^3 = R^4 = R^5 = R^6 = Cl$

Scheme 2

In the present study, we have correlated the oxidation state of a given ligand with all of its eight bond distances, with the aim of obtaining a less qualitative way to interpret the crystallographic information. Other structural features such as bond angles or torsion angles were disregarded since it is reasonable to suppose that they do not change significantly on going from a benzoquinone to a semiquinonate and to a catecholate. In this way, we obtained the dependences of the structural features on the oxidation states, thus allowing a quantitative 'crystallographic monitoring' of the degree of reduction/oxidation within the series catecholate, semiquinonate, benzoquinone.

Methods

Crystal structures of 75 compounds containing one of the three quinone ligands in Scheme 2, which are by far the most studied,§ were considered. By examining separately the crystallographically independent ligands we obtained a set of 146 quinones, bonded to the following atoms: Si (10 cases), P (9), Ti (8), V (12), Cr (7), Mn (7), Fe (12), Co (13), Ni(2), Cu (6), Ge (11),

---

† *Supplementary data available* (No. SUP 56866, 27 pp.): experimental and calculated bond distances. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

‡ In the present work, we indicate 'quinones', or more briefly 'L', those ligands having one of the formulae in Scheme 1.

§ The literature search was performed on the Cambridge Structural Database, version 3.10 (see ref. 10).

Table 1 Eigenvectors of and percentage variance described by the eight principal components

Bond	p.c. 1	p.c. 2	p.c. 3	p.c. 4	p.c. 5	p.c. 6	p.c. 7	p.c. 8
C(1)–O(1)	0.4872	−0.4017	0.3096	0.4564	0.5010	0.1272	0.1619	0.0612
C(2)–O(2)	0.4706	0.0519	0.3358	−0.0861	−0.6504	0.4006	−0.0850	0.2546
C(1)–C(2)	−0.4024	−0.3210	0.6515	0.0043	−0.2434	−0.0965	0.1617	−0.4646
C(2)–C(3)	−0.3160	0.3969	0.2174	0.7092	−0.1219	−0.1669	−0.1115	0.3706
C(3)–C(4)	0.1799	0.3409	0.2709	−0.3131	0.0865	−0.4349	0.6466	0.2557
C(4)–C(5)	−0.3648	0.0160	−0.1700	0.0737	0.0248	0.6743	0.6014	0.1234
C(5)–C(6)	0.2359	−0.1905	−0.4592	0.3987	−0.4763	−0.3041	0.3847	−0.2663
C(1)–C(6)	−0.2414	−0.6501	−0.0810	−0.1373	−0.1301	−0.2232	−0.0137	0.6532
Percentage variance	56.4	13.1	10.2	7.2	5.0	3.4	2.9	1.9

Table 2 Percentage of cases in which $t < 1.960$, $1.960 < t < 2.576$ and $t > 2.576$ [see equation (4)] for the bonds of the compounds studied

Bond	Percentage of cases with		
	$t < 1.960$	$1.960 < t < 2.576$	$t < 2.576$
C(1)–O(1)	62.4	7.5	30.1
C(2)–O(2)	61.7	13.0	25.3
C(1)–C(2)	77.4	13.0	13.7
C(2)–C(3)	85.6	8.2	6.2
C(3)–C(4)	88.4	6.8	4.8
C(4)–C(5)	81.5	8.9	9.6
C(5)–C(6)	92.5	3.4	4.1
C(1)–C(6)	88.4	5.5	6.1

As (3), Mo (9), Tc (3), Ru (8), Rh (2), Pd (1), In (1), Sn (5), Sb (4), W(2), Re (7) and Os (4). A list of the compounds, with their sources, and a list of the bond distances with their estimated standard deviations are deposited as SUP 56866.

Principal component analyses[11] were performed with the software package STATGRAPHICS.[12] The input data matrix (D) consisted of a 146 × 8 matrix (eight bond lengths measured for 146 ligands). The row data were not scaled and standardized since their magnitude and range are very similar. The eigenvectors of the eight principal components are reported in Table 1, together with the percentage variance they describe. The factor matrix (F) was obtained by multiplying the eigenvector and eigenvalue matrices. Eventually, the principal components scores were obtained from DF. The correlation, covariance and factor matrix obtained from the input data matrix are available as SUP 56866.

The oxidation state of a given ligand was correlated to its bond distances by means of the function Δ, defined as in equations (1) and (2) where d_i is the experimental ith bond

$$\Delta_i = -2(d_i - d_{\mathrm{III}i})/(d_{\mathrm{I}i} - d_{\mathrm{III}i}) \qquad (1)$$

$$\Delta = (\Sigma w_i \Delta_i)/(\Sigma w_i) \qquad (2)$$

length, and $d_{\mathrm{I}i}$ and $d_{\mathrm{III}i}$ are the ith bond lengths of the pure forms **I** (catecholate) and **III** (benzoquinone) in Scheme 1. The eight Δ_i values of the given ligand were averaged by means of the semiweighted mathematical model previously described;[4,13] the published values of the estimated standard deviations of the bond distances were multiplied by a factor of 1.5 according to refs. 13 and 14. The Δ value calculated in this way can be conceived as the oxidation number of a given quinone. Equation (1) shows that while a neutral ligand isostructural with **III** has a Δ value of 0.0, a dianionic ligand isostructural with **I** has a Δ value of −2.0. The values of $d_{\mathrm{I}i}$ and $d_{\mathrm{III}i}$ [see equation (1)] were taken as the experimental bond lengths of the uncomplexed 1,2-dihydroxybenzene[15] and *o*-benzoquinone[16] [C_{2v} symmetry was imposed, by averaging the distances C(1)–O(1) and C(2)–O(2), C(2)–C(3) and C(1)–C(6), and C(3)–C(4) and C(5)–C(6)]. In this way we disregarded the effects of the substituents on the bond lengths within the hexaatomic ring of the ligands (see Scheme 2), but it is reasonable to suppose that they are not statistically significant.[17]

The consistency between the oxidation states evaluated with the Δ values and the structural features of the quinones considered here was verified by comparing the experimental bond distances with those calculated from equation (3). The

$$d_{\mathrm{calc},i} = d_{\mathrm{III}i} - [\Delta(d_{\mathrm{I}i} - d_{\mathrm{III}i})/2] \qquad (3)$$

agreement between the experimental and the calculated bond distances was evaluated from equation (4) where $d_{\mathrm{exptl},i}$ and

$$t = |d_{\mathrm{exptl},i} - d_{\mathrm{calc},i}|/\sigma(d_{\mathrm{exptl},i}) \qquad (4)$$

$d_{\mathrm{calc},i}$ are the experimental and calculated bond lengths and $\sigma(d_{\mathrm{exptl},i})$ the experimental standard deviation for the ith bond distance. The meaning of equation (4) is as follows:[18] the difference between $d_{\mathrm{exptl},i}$ and $d_{\mathrm{calc},i}$ is 'not significant' if $t < 1.960$, 'possibly significant' if $1.960 < t < 2.576$, and 'significant' if $t > 2.576$. In order to stress the comparison between calculated and experimental bond lengths, equation (3) was considered without the standard deviations of its addenda [in this way the calculated bond lengths are considered as if they were the theoretical ones, with the consequence that the significance test of equation (4) is reinforced[18]]. Table 2 reports, for each of the eight bonds of a quinone, the percentage of cases with $t < 1.960$, that with $1.960 < t < 2.576$, and that with $t > 2.576$. It appears that for the majority of the cases $t < 1.960$; the agreement between $d_{\mathrm{calc},i}$ and $d_{\mathrm{exptl},i}$ is less pronounced for the C–O than for the C–C bonds, presumably because the former are more markedly affected by the co-ordination and the environment than are the latter. Nevertheless, the agreement between the structural and redox changes can be considered satisfactory. A list of the Δ and $d_{\mathrm{calc},i}$ values is deposited as SUP 56866.

Results and Discussion

Compounds containing quinone derivatives generally have charge-localized electronic structures, with no ambiguity of ligand charge. This is confirmed by our principal component analysis of the bond distances of the quinones considered. Fig. 1 shows a scatter plot of the two principal component (p.c.) scores describing the greatest variance of the original sample (p.c. 1 represents 56.4% of the variance, p.c. 2 13.1%). Analogous plots are obtained by considering the dependence of the p.c. 3–5 scores on the p.c. 1 scores (p.c. 3–5 represent 10.2, 7.2 and 5.0% of the variance respectively). It appears that the 146 quinones considered are grouped into two quite well separated clusters, one including the ligands regarded in the literature as semiquinones and the other one including the ligands regarded as catechols. Some points, located in the region intermediate between these two clusters, refer to ligands which are considered

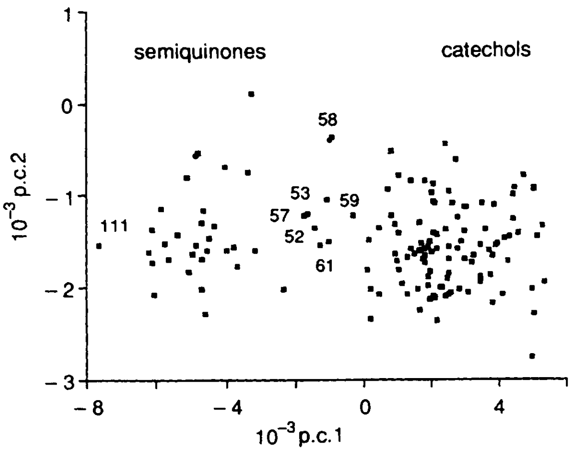


Fig. 1 Results of the principal component analysis: component 2 *versus* component 1

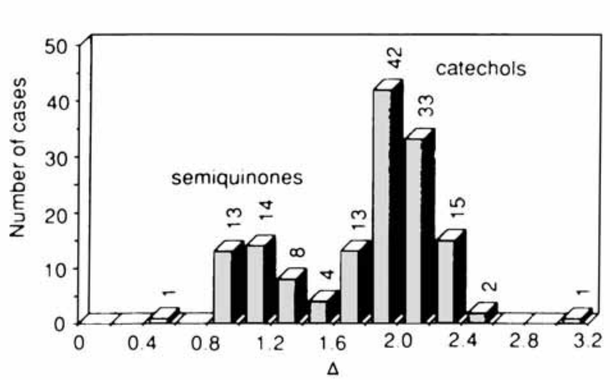


Fig. 2 Frequency of occurrence of Δ values [see equations (1) and (2)] for intervals of 0.2

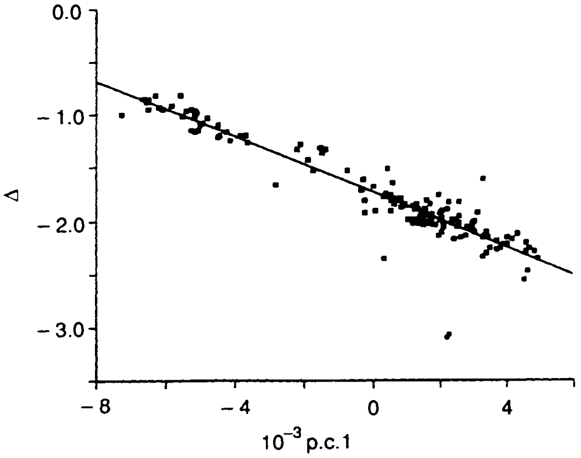


Fig. 3 Dependence of the Δ values on the principal component 1 scores [least-squares fitting weighted with $\sigma(\Delta)^{-2}$]: $y = -1.7286 - 0.131x$ where $R = 0.95$

in the literature as having electronic structures intermediate between the catecholato and semiquinonato limiting forms: ligands 52 and 53 of the complex *cis*-$[RuL^2{}_3]$,[5] 57–59 of *trans*-$[OsL^2{}_3]$[5] and 61 of $[Ru(bipy)_2L^2]^+$ (bipy = 2,2′-bipyridyl).[6] For the chemical meaning of the p.c.s it is necessary to refer to the eigenvectors in Table 1. From these data it appears that p.c. 1, which is predominantly responsible for the separation of semiquinones and catechols into two clusters (see Fig. 1), corresponds to the effects expected for the redox couple semiquinone–catechol: while the bonds C(1)–O(1), C(2)–O(2), C(3)–C(4) and C(5)–C(6) lengthen, C(1)–C(2), C(2)–C(3), C(4)–C(5) and C(1)–C(6) shorten (and *vice versa*). The eigenvectors of the other p.c.s do not seem to indicate any chemically interpretable trend; it can just be noted that in p.c.s 2 and 4 the bonds C(1)–O(1) and C(2)–O(2) have eigenvectors of opposite sign, which could suggest that the asymmetry in bonding to the metals is important.

In order to have a quantitative approach to the problem of the charge distribution within compounds containing quinone derivatives, we assumed the Δ parameter [see equations (1) and (2)] as being representative of the oxidation state of any given quinone. Fig. 2 reports the frequency of occurrence of Δ values for intervals of 0.2. A bimodal distribution appears, with maxima around −1 (the oxidation state of a semiquinonate ligand) and −2 (the oxidation state of a catecholate ligand), in accord with the results of the principal component analysis reported above. Nevertheless, some cases have Δ values intermediate between −1 and −2, and a very few cases have Δ values far from those. It is worthwhile noting that the Δ values are quite highly correlated with the p.c. 1 scores (see Fig. 3); this suggests that the chemical meaning assigned above to p.c. 1 is correct, *i.e.* that the maximum variance on the bond-length data set is actually dependent on the oxidation states of the ligands. Moreover, it is worth noting that the correlation coefficients for the linear dependence of the C(1)–O(1) or C(2)–O(2) bond lengths on p.c. 1 (0.88 and 0.85) are lower than those in Fig. 3. This suggests that the diagnostic value of the C–O lengths in assigning oxidation states to the ligands[1,5] is actually lower than that of the Δ function. It can be stressed that although the p.c. 1 scores and the Δ values can be considered as alternatives, it is advantageous to use the Δ function (instead of p.c. 1) since while all the p.c. 1 values have to be recalculated '*ab initio*' once a new crystal structure of a quinone derivative is determined, the Δ values previously calculated are not affected by those of new crystal structures.

The oxidation-state assignments found in the literature can be considered equal to those based on the Δ values if the absolute difference between Δ and the literature assigned oxidation state is lower than 1.960 times the standard deviation of Δ.[18] We found that in 135 out of the 146 cases considered the oxidation-state assignment found in the literature agreed with that based on the Δ values. The other 11 cases will be discussed briefly.

Ligands 75 and 76, contained in the complex $[Co\{MeC(CH_2PPh_2)_3\}L^2]^+$ (which crystallizes as the tetrafluoroborate with two molecules in the asymmetric unit), were described as catecholates chelated to a cobalt(III) cation.[19] We calculated Δ values of −1.36(27) and −1.31(30) for them, which implies that it would be better to consider them as semiquinonates bonded to a cobalt(II) ion. This hypothesis is more consistent than the previous one with the synthetic route followed in ref. 18, but disagrees with some spectroscopic evidence. However, it should be noted that it was impossible to refine the structures of ligands 75 and 76 to such a point that a detailed discussion on their structural features could be made (the estimated standard deviations for the bond lengths range between 0.01 and 0.03 Å); moreover, it is worth noting that spectroscopy can sometimes be ambiguous when determining the charge distribution within quinone complexes.[9]

The ligand 23 contained in the complex $[Co(\eta^5\text{-}C_5Me_5)L^1]$ was described as a fully reduced catecholate.[20] On the basis of our results [Δ = −1.76(7)] it appears that the electronic structure of this ligand has a significant semiquinonato character. This could be explained as a consequence of a partial electron transfer from the quinone ligand to the η^5-pentamethylcyclopentadienyl ligand, which is in fact significantly distorted from its theoretical C_{5v} symmetry.

Ligands 101 and 103 contained in the complex $[TcL^2{}_3]$ together with ligand 102 were considered as fully reduced catecholates chelated to a technetium(VI) ion.[21] On the basis of our results [Δ = −1.62(14), −1.62(17) and −1.74(10) for ligands 101, 102 and 103 respectively] it would be better to consider this complex as a technetium(V) ion chelated by three equivalent ligands bearing five negative charges. Both ligands

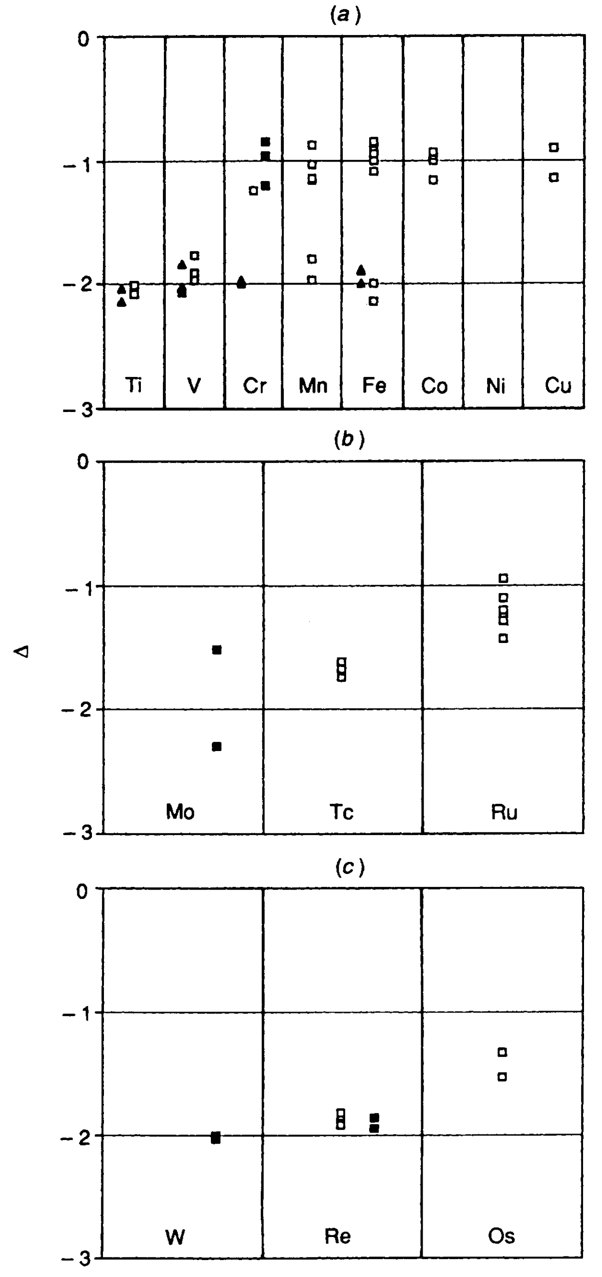


Fig. 4 Dependence of the Δ values for homoleptic complexes of the first (*a*), second (*b*) and third (*c*) transition series on the metal atomic number (▲ refers to tetrachlorobenzoquinones, □ to benzoquinones and ■ to 3,5-di-*tert*-butylbenzoquinones)

101 and 103 have a Δ value significantly different from −2, and the average of the Δ values of ligands 101–103 is −1.69(7). In addition, it is worth noting that an oxidation state of v is much more common than vi for this metal.

Ligand 28 was described as a tetrachlorocatecholate[3] chelated to P^V, in a spirophosphorane also containing a phenyl and a catecholate (ligand 27) bonded to the P atom.[22] We found a Δ value significantly lower than −2 for ligand 28 [−2.21(7)], and even lower than that of ligand 27 [−1.92(19)]. This clearly indicates that both ligands 27 and 28 are catecholates; the charge on 28 is higher (in absolute value) than that on 27 owing to the higher electronegativity of ligand 28 (a tetrachloro-*o*-catechol is more electronegative than an *o*-catechol). The same observations can be applied to the cases of ligands 29 and 30, which have Δ values significantly lower than −2 [−2.29(13) and −2.17(8) respectively] and are more electronegative than the other ligands bonded to the phosphorus(v) centre (*o*-aminophenol and *N*-methyl-*o*-aminophenol).[23]

Ligand 111 was described as a semiquinonate chelated to an indium(III) ion in the complex $[InL^2Br_2(4Me\text{-}py)_2]$ (4Me-py = 4-methylpyridine).[24] For this ligand we found a Δ value of −0.57(15), significantly different from −1, indicating that it is intermediate between the semiquinonate and benzoquinone limiting forms. Therefore, there is a partial electron transfer from the quinone to the $InBr_2(4Me\text{-}py)_2$ moiety.

The complex *trans*-$[RuL^2{}_3]$, containing ligands 54–56, was considered to have an electronic structure intermediate between Ru^{VI}(catecholate)$_3$ and Ru^{III}(semiquinonate)$_3$ charge-localized limiting forms.[5] On the contrary, the Δ values [−0.95(27), −1.20(22) and −1.10(23)] suggest that these ligands can be considered as semiquinonates. However, it was impossible to obtain estimated standard deviations of lower than 0.02 Å on the bond lengths, which makes this structural determination of limited value.

The above discussion stresses that the use of the Δ values in assigning oxidation states to quinone ligands can give some less-qualitative estimate about the charge distribution in co-ordination compounds containing quinones. The utility of this procedure can be underlined by the following observations.

As pointed out above, it is well known that compounds containing quinone derivatives generally have charge-localized electronic structures. Of the 146 quinones considered in the present paper, only 12 have structures significantly different from the semiquinonato and the catecholato limiting forms. Ligands 51–53 in *cis*-$[RuL^2{}_3]$,[5] 57–59 in *trans*-$[OsL^2{}_3]$,[5] 61 in $[Ru(bipy)_2L^2]^+$,[6] 23 in $[Co(\eta^5\text{-}C_5Me_5)L^1]$[20] and 101–103 in $[TcL^2{}_3]$[21] can be considered as intermediate between catecholates and semiquinonates; ligand 111 in $[InL^2Br_2(4Me\text{-}py)_3]$[24] can be considered as intermediate between benzoquinone and semiquinonate. All the others are clearly semiquinonates or catecholates. Moreover, it is well known that *o*-benzoquinone is very easily reduced to semiquinonate or catecholate owing to complexation with d metals whose d orbitals are close in energy to those of the ligand, as none of the quinones considered here has a Δ value of 0.0 (that is the oxidation number of the *o*-benzoquinone), and only one ligand (111) has a significant (although partial) *o*-benzoquinone character.

It is interesting to consider by means of the Δ values the periodic trend in the charge distribution across a transition series. Since the charge distribution depends on the relative values of metal and quinone orbital energies, by increasing the metal orbital stability (that is by increasing the atomic number within each transition series) the oxidation number of the ligands would increase from −2 (catecholates) to −1 (semiquinonates). Fig. 4 shows for the three transition series the Δ values observed for homoleptic ML_n complexes, where there are no effects due to different ligands. As expected, for all the three series, an ascending trend appears on increasing the atomic number. Moreover while the ligand Δ values switch clearly from −2 to −1 in the first transition series [Fig. 4(*a*)], in the second and third transition series [Figs. 4(*b*) and 4(*c*)] the increase in Δ values is more diffuse, with sound cases of charge delocalization between the metal and the ligands, as can be expected for less-hard Lewis acids.

References

1 C. G. Pierpont and R. M. Buchanan, *Coord. Chem. Rev.*, 1981, **38**, 45.
2 J. A. McCleverty, *Prog. Inorg. Chem.*, 1968, **10**, 49.
3 M. J. O'Connor, *Prog. Inorg. Chem.*, 1971, **14**, 241.
4 O. Carugo, K. Djinovic, M. Rizzi and C. Bisi Castellani, *J. Chem. Soc., Dalton Trans.*, 1991, 1551.
5 S. Battacharya, S. R. Boone, G. A. Fox and C. G. Pierpont, *J. Am. Chem. Soc.*, 1990, **112**, 1088.
6 S. R. Boone and C. G. Pierpont, *Inorg. Chem.*, 1987, **26**, 1769.
7 S. R. Boone, G. H. Purser, H.-R. Chang, M. D. Lowery, D. N. Hendrickson and C. G. Pierpont, *J. Am. Chem. Soc.*, 1989, **111**, 2292.
8 R. M. Buchanan and C. G. Pierpont, *J. Am. Chem. Soc.*, 1980, **102**, 4951.

9 A. Dei and M. Wicholas, *Inorg. Chim. Acta*, 1989, **166**, 151.

10 F. H. Allen, S. Bellard, M. D. Brice, B. A. Cartwright, A. Doubleday, H. Higgs, T. Hummelink, B. G. Hummelink-Peters, O. Kennard, W. D. S. Motherwell, J. D. Rodgers and D. G. Watson, *Acta Crystallogr., Sect. B*, 1979, **35**, 2331.

11 T. P. Auf der Heyde, *J. Chem. Educ.*, 1990, **67**, 461 and refs. therein.

12 STAGRAPHICS, version 2.0, Statistical Graphics Corporation Inc., Laver Software, Rockville, Maryland, 1986.

13 R. Taylor and O. Kennard, *Acta Crystallogr., Sect. B*, 1983, **39**, 517.

14 R. Taylor and O. Kennard, *Acta Crystallogr., Sect. B*, 1983, **39**, 133.

15 W. Hunderlich and D. Mootz, *Acta Crystallogr., Sect. B*, 1971, **27**, 1684.

16 A. L. Macdonald and J. Trotter, *J. Chem. Soc., Perkin Trans. 2*, 1973, 476.

17 F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1987, S1.

18 D. W. J. Cruickshank and A. P. Robertson, *Acta Crystallogr.*, 1953, **6**, 698.

19 C. Bianchini, D. Masi, C. Mealli, G. Martini, F. Laschi and P. Zanello, *Inorg. Chem.*, 1987, **26**, 3683.

20 E. J. Miller, A. L. Rheingold and T. B. Brill, *J. Organomet. Chem.*, 1984, **273**, 377.

21 L. A. deLearie, R. C. Haltiwanger and C. G. Pierpont, *J. Am. Chem. Soc.*, 1989, **111**, 4324.

22 T. E. Clark, R. O. Day and R. R. Holmes, *Inorg. Chem.*, 1979, **18**, 1668.

23 T. E. Clark, R. O. Day and R. R. Holmes, *Inorg. Chem.*, 1979, **18**, 1653.

24 T. A. Annan, R. K. Chadha, P. Doan, D. H. McConville, B. R. McGarvey, A. Ozarowski and D. G. Tuck, *Inorg. Chem.*, 1990, **29**, 3936.

Received 24th July 1991; *Paper* 1/03803F