

Charge Distribution in Complexes Derived from *o*-Benzoquinones

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In studies of the preparation and properties of complexes derived from substituted *o*-benzoquinones, the assignment of the oxidation state of the metal and of the ligand are clearly interrelated problems. The ligand may be in the *o*-quinone (Q), *o*-semiquinone (SQ⁻), or catecholate (CAT²⁻) form, and hence the metal–ligand interaction in a complex containing a metal of variable oxidation state may be written as (Q)Mⁿ⁺, (SQ⁻)M⁽ⁿ⁺¹⁾, or (CAT)M⁽ⁿ⁺²⁾⁺. Since stoichiometry alone can do nothing to resolve this problem, a variety of spectroscopic and spectral arguments have been used to establish the detailed structure. In a recent publication,¹ changes in the ¹³C NMR chemical shifts in the benzenoid ring, the $\nu(\text{C}-\text{O})$ vibrational frequency, the $r(\text{C}-\text{O})$ bond length, and electron paramagnetic resonance (EPR) spectra were all identified as being useful in this respect.

In generalized terms, the C–O bond lengths are ca. 1.21 Å for *o*-quinones, 1.29 Å for *o*-semiquinones, and 1.35 Å for catecholates. A detailed discussion of such values has been presented by Carugo, Castellani, Djinovic, and Rizzi,² who have analyzed the published X-ray crystallographic data for 75 compounds, using not only $r(\text{C}-\text{O})$ but also the C–C bond distances in the C₆ ring, since an *o*-quinone for example clearly differs from the corresponding catecholate in this respect.^{3,4} The main conclusion from this analysis is that, of the 146 ligands considered, there is no doubt about the assignment as Q, SQ⁻, or CAT²⁻ in 135 of the cases.

Satisfying as this appears, there remain the 11 molecules for which the assignment is in doubt, and we draw attention here to the compound originally described by us as In(dbbsq⁻)Br₂(pic)₂ (**1**) (dbbsq⁻ = 3,5-di-*tert*-butyl-1,2-benzosemiquinonate anion; pic = 4-methylpyridine).⁵ According to the analysis of Carugo *et al.*,² the crystallographic results do not support this structure, and they conclude that the ligand is intermediate between the semiquinonate and benzoquinone limiting forms, implying significant electron transfer to the InBr₂(pic)₂ residue. We suggest that this conclusion is unwarranted, since the following evidence supports our original structure.

(i) The EPR spectrum of **1** in benzene, and of In(dbbsq⁻)Br₂ in CH₂Cl₂/picoline at –60 °C, consists only of the signal of one species and is that of a typical free radical with $g = 2.0039$ and coupling constants of $A_{\text{H}4} = 3.53$ and 3.20 G, respectively, which can be compared to $A_{\text{H}4} = 3.50$ G in free dbbsq⁻.⁶ In our opinion, this of itself constitutes sufficient evidence on which to reject a model in which the charge on the ligand is presumed to be reduced to approximately –1/2, since such a charge distribution would give rise to a value of $A_{\text{H}4}$ in the range 1.5–1.8 G, in keeping with 50% occupancy of the HOMO orbital. It might be argued that charge redistribution could occur through the σ -framework of the ligand, or from filled π -orbitals, but again this would produce significant changes in both $A_{\text{H}4}$ and $A_{\text{H}6}$ relative to the values found for the free ligand, and such effects are clearly not observed.

Table I

compd	Fermi contact term for M (MHz)	coupling const A_{M} (G)	fractional spin density on M	ref
GaL ₃	12 210	9	2×10^{-3}	8
InLBr ₂ (pic) ₂	20 180	6	1×10^{-3}	5
SnLCl ₂ I	43 980	8.5	5×10^{-4}	9
CdL ₂	13 650	7	1×10^{-3}	10
PbL ₂	81 510	50	2×10^{-3}	11
TlL	183 800	45	7×10^{-4}	11
TeL ₂	55 590	36	2×10^{-3}	12

(ii) There is no evidence of electron density on the γ -picoline ligand or on the bromide.

(iii) The EPR spectra of **1**, and of analogous species, show that although coupling to indium (¹¹⁵In; $I = 9/2$) is observed, the spin density at the indium atom is about 0.1% of that on the dbbsq⁻ ligand. This is in keeping with results for other related ML_n (L = dbbsq⁻) complexes, for which the spin densities, Fermi contact terms,⁷ and typical hyperfine coupling constants are found in Table I. It is clear that the spin density on indium in **1** does not deviate from the general pattern for this group of SQ compounds. Furthermore, any transfer of spin density from dbbsq⁻ to indium would change A_{In} drastically; for a 1% spin density in an indium s-orbital, A_{In} is calculated to be in the order of 70 G.

Thus, the direct and detailed information available from EPR spectroscopy requires the rejection of the conclusion reached by Carugo *et al.*² in this particular case, since there is no evidence for electron transfer from the *o*-semiquinone ligand in **1**. We suggest that this throws their whole statistical analysis into question and point to the following matters which underline some of the uncertainties involved:

(i) In any discussion of bond distances in a metal complex, the experimentally derived $r(\text{C}-\text{C})$ and $r(\text{C}-\text{O})$ values are necessarily among the least reliable, since much of the significance of the final R -value depends on the correct siting of the heavy atoms. It is therefore necessary to exercise caution in analyzing differences in (e.g.) $r(\text{C}-\text{O})$ when these differences are in the order of the experimental error in this parameter.

(ii) There is an implicit assumption in the analysis that the bond distances involved are a linear function of ligand charge in the Q, SQ⁻, and CAT²⁻ series, and this is as yet unproven.

(iii) The use of the crystal structure of catechol³ as one of the reference points in the analysis introduces some uncertainty, since this substance is extensively hydrogen-bonded in the solid state, which could bring about some change in $r(\text{C}-\text{O})$ relative to the idealized free molecule.

(iv) There may be significant differences between complexes of transition metal elements and those of main group metals. In the latter case, the energy level differences between different oxidation states are generally such as to mitigate against ill-defined oxidation states of the sort implied by "partial electron transfer" from a semiquinonate ligand.

Given the importance of the correct formulation of this class of compounds, it seems more prudent to use all the available experimental information than to rely exclusively on only one parameter.

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