Aromaticity and Quasi-Aromaticity in Polycyclic Aromatic Derivatives of Ortho-Hydroxybenzaldehyde Acting as Ligands in Co(III) Complexes

Abstract
The interrelation between local aromaticity and metal-ligand bonding was investigated by means of high level quantum chemical calculations. Several model systems containing derivatives of polycyclic aromatic heterocycles acting as chelate ligands in complexes of cobalt (III) were chosen for the analysis. The ADF software package based on Density Functional Theory (DFT) was used for calculations. The energy decomposition was performed according to the concept of Kohn-Sham Molecular Orbital theory.

Introduction
In our previous studies we have described in details the interplay between aromaticity and the other π-electron effects acting in derivatives of polycyclic aromatic hydrocarbons (PAH) in which the motif of resonance-assisted hydrogen bond (RAHB) was present (1, 2). We have shown that the position of the extra ring formed by substituents interacting through the hydrogen bond (HB) influences both the strength of the HB and the local aromaticity of the PAH skeleton. This relation was explained by means of the concept of Clar’s aromatic sextet (3). According to the results obtained, the communication between the quasiring and two PAH skeletons proceeds through p-electronic effects. Since we have shown that the aromaticity indices can be used not only for benzenoid rings, but also for quasi-aromatic rings (4), in these studies we use a set of such indices in order to estimate the degree of π-electron delocalization within individual rings in given PAH acting as ligand in cobalt (III) complexes. The example of the molecular systems investigated in this work is shown in Fig. 1.

Methodology
All calculations were based on DFT (5, 6, 7, 8) and performed with the use of ADF package (9). B88 functional (10, 11) was applied in combination with a large uncontracted set of Slater-type orbitals (STOs) containing diffuse functions, that is, the valence-split triple-ζ basis set augmented with two sets of polarization functions (TZ2P in ADF). Scalar relativistic effects for all atoms were accounted for by means of zeroth-order regular approximation (ZORA) (12). Equilibrium geometries were fully optimized using analytical gradient techniques. All structures were verified to be energy minima through a vibrational analysis.

Results and conclusions
Complexes of Co(III) containing polycyclic aromatic hydrocarbons as ligands coordinating the metal centre were considered as model systems (see Fig. 1). Different ligands were investigated, such that the full possibility of polycyclic topology – from one to three benzene rings – has been taken into account. The special attention was paid on the relation between the quasi-aromatic character of the extra-ring, formed due to metal centre complexation, and local aromaticity of individual benzene rings in polycyclic hydrocarbons.

Fig. 1. – Example molecular structure investigated in this work. Atoms are designed with the following colours: Co – metallic blue, P – yellow, O – red, C – black, H – white.

carbon moiety. Additionally, a bonding analysis was performed for the TM-L bond, and the results of bonding energy decomposition were compared with results of the analysis of local aromaticity.

It appears from our investigations that there is a direct relation between the topology of the polycyclic ligand and the distribution of the local aromaticity. These results are in agreement with results of our earlier studies on H-bonded analogues of systems considered in this project. (1,2) It occurs however, that in metal complexes the location of the quasi-aromatic ring influences the rest of polycyclic moiety much more effectively than it took place in H-bonded systems. This may be explained by the fact, that in the case of transition metals the d-type orbitals of the metal are also available in cyclic delocalization within the quasi-ring, and thus the quasi-ring may play the role of typical aromatic ring, interacting with the rest of the system in more effective way.

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References

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