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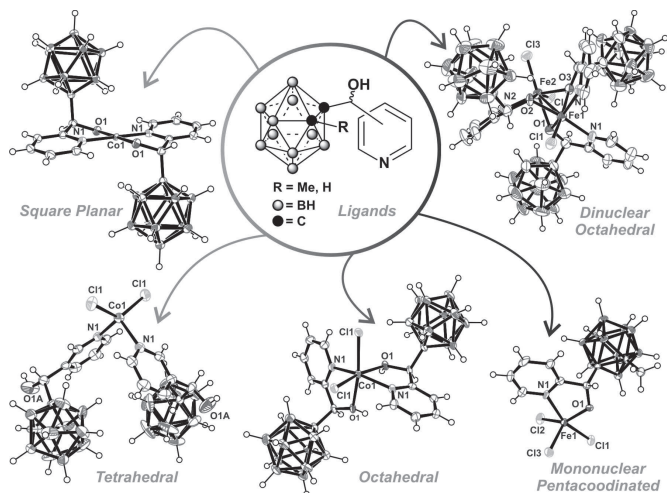
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Structure and properties of *o*-carboranylalcohols pyridines metal complexes

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The recently reported series of *ortho*-carboranymethylalcohols bearing pyridine substituents [1] opens a new door to the synthesis of very attractive carborane based transition metal complexes (Figure). The two different functionalities (OH and N) together with the chance to vary the nitrogen position along the aromatic ring, the metal, as well as the hydrophobic icosahedral heteroborane cluster, give place to compounds which exhibit different structural architectures and properties.

When an ethanolic or acetone solution of *ortho*-carboranymethylalcohol pyridine or quinolyne derivatives is mixed with a solution containing the desired metallic ion, the corresponding complex is obtained. For instance, for Co(II), the 3- and 4- pyridine and 4-quinoline derivatives give place to tetrahedral geometries whereas the 2-pyridine ones, due to the carboranylalcohol acting as a N, OH/O bidentate ligand, conducts to octahedral or square planar complexes (Figure). On the other hand, when Fe(III) and the 2-pyridine ligands are employed, different structures are obtained depending on the carborane substituents (R in the Figure). For R = H, a pentacoordinated mononuclear complex crystallized as a result of the reaction while for R = Me, an iron dinuclear compound with three oxo bridges is obtained (Figure). Magnetic measurements of the Co complexes are in agreement with their different structures and in the particular case of the octahedral complex, the negative sign of θ indicates antiferromagnetic interactions among the monomeric units and matches well with the number of OH...Cl hydrogen bonds found in the crystal structure.



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Crystallographic study of labile systems: Cobalt and lawsone complexes

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Bi-stable molecular systems presenting mixed valence (MV), spin crossover (SC) and valence tautomerism (VT) are associated with the development of new functional materials which can be used for applications in organic electric conductors, optoelectronic and molecular magnets [1]. The properties of these materials can be adjusted with little chemical changes or as a response to changes of external parameters such as pressure, temperature and illumination [2]. In VT compounds in particular, the electronic transfer is associated with the change in the electronic and spin properties of the metal [3]. The electronic transfer can be evidenced by the change in the metal-ligand bond length [4] or in some cases only in the bond lengths within the organic ligand. Typical examples of such systems are coordination compounds of Co and ligands like quinonas [4].

Few works investigating the electronic transfer in compounds formed by naphthoquinones and transition metal ion have been reported so far. The results concerning electron transfer in this compounds are discordant [5,6].

In this work we present synthesis and characterization of $[\text{Co}(\text{Law})_2(\text{Im})_2] \cdot \text{C}_6\text{H}_5\text{CH}_3$, $[\text{Co}(\text{Law})_2(\text{Phen})_2] \cdot (\text{C}_4\text{H}_8\text{O})_2$, $[\text{Co}(\text{Law})_2(2,2\text{-Dipy})]$ and $[\text{Co}(\text{Law})_2(2,2\text{-Dipy})] \cdot \text{C}_6\text{H}_5\text{CH}_3$, where Law stands for 2-hydroxy 1,4 naphthoquinone or Lawsone Crystals were isolated after evaporation or slow cooling of solvents and later characterized with elementary analysis, atomic absorption and IR spectroscopy. Single crystal X-ray diffraction experiments performed in the temperature range between 120 K and 150 K allowed the structural determination of compounds. The average bond lengths for Co-N (2,10(2) Å) and Co-O (2,10(6) Å) found in all investigated structures are typical of $\text{Co}^{\text{II-L}}$. The typical bond lengths for $\text{Co}^{\text{III-L}}$ in the systems that present electron transfer should be 0.1-0.15 Å shorter than $\text{Co}^{\text{II-L}}$ bond length [4]. Furthermore the C=O length value (1,22(1) Å) suggests a double bond in naphthoquinone [7]. Thus, in the investigated temperature range, the X-ray diffraction results did not show any evidence of charge transfer between Co- naphthoquinone.

The compound $[\text{Co}(\text{Law})_2(2,2\text{-Dipy})]$ formed both a unsolvated and a solvated structure with toluene. The solvated structure crystallizes in triclinic symmetry while the unsolvated crystal structure is orthorhombic. A number of weak intermolecular interactions like $\text{C}_{\text{ar}}\text{-H}\cdots\text{O}$ can explain the difference in the crystal packing.

Additional X-ray diffraction as well as spectroscopy studies at temperatures down to 10 K will be performed to investigate the presence of electron transfer in Co- naphthoquinone complexes.

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