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Para- and *Meta*-Substituted Benzeneseleninic Acids Interactions with Cr(III), Mn(II), Fe(II), Fe(III), Sn(II) and Ag(I)

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Working on the study of the chemical reactivity and linkage isomers of the coordination compounds of the *para*- and *meta*-substituted benzeneseleninic acids as ligands, we report the interaction of Cr(III), Mn(II), Fe(II), Fe(III), Sn(II) and Ag(I) with $XC_6H_4SeO_2^-$ (X = H, *p*-Cl, *m*-Cl, *p*-Br, *m*-Br, *p*-Me).

The seleninato ion is well known for its capability to coordinate to a metal ion as unidentate or bidentate ligand either *inter*- or *intra*-molecularly through the two oxygen and the selenium atoms. I.r. spectroscopy provides a convenient means of distinguishing between the different possibilities. All these possible types of binding have been reported in previous papers [1], and the chemical reactivity of some of the obtained complexes, of the type $[M(H_2O)_2(XC_6H_4SeO_2)_2]$ (M = Co, Ni, Zn), towards N-donor ligands has been described in other works [2–4].

In the present work we have obtained complexes of general formula $Cr(L)_3$, $Mn(H_2O)_2(L)_2$, $Fe(H_2O)_2(L)_2$, $Fe(L)_3$, $Sn(L)_2$ and Ag(L); the compounds are microcrystalline or powder-like and with the exception of the tin derivatives, whose limited solubility prohibits conductance measurements, all are non-conducting in nitromethane, indicating the covalent nature of the compounds.

Infrared spectra. The bands due to the substituent X and all the bands assigned to fundamentals of the benzene ring appear in the complexes at the same wavenumbers as in the starting ligands.

In the Mn(II), Fe(II) and Ag(I) derivatives the bands due to the sym. and asym. ν(SeO) are shifted towards lower energies in comparison with the stretching values of the free anions. This fact and the small frequency differences between these modes point to a O,O′-seleninato coordination. Three SeO bands with the irreducible representations $A_2 + 2E$ are observed in the i.r. spectra of all the Cr(III) and Fe(III) trisderivatives, suggesting an octahedral configuration with D_3 symmetry.

The i.r. spectra of the tin(II) derivatives show a more complex profile, significantly different from those above discussed. The number of the bands, in the $\nu(SeO_2)$ region, is indicative of the non-equivalence in the manner in which the two areneseleninato ligands are coordinated. We could suggest that one group is O,O′-bonded intermolecularly to the tin atoms in linear chains, whereas the second group is seleninato-O bonded. Taking into account the lone pair of electrons, the tin atom has a ψ-tetrahedral environment.

The vibrational spectra of the Mn(II) and Fe(II) complexes show meaningful differences with the spectra of the other water-containing derivatives as regards the related-water bands; the spectra of these compounds show the absorptions characteristic of the coordinated water, and the complexes can be regarded as distorted octahedral.

In the far-i.r. region the ν(M–O) vibrational modes have been assigned and discussed. It is noteworthy that ν(Fe–O) in the iron(II) derivatives is at lower wavenumbers than in the corresponding iron(III) complexes, in very good agreement with the fact that, in a change of oxidation number, the metal–ligand vibration increases in frequency with an increase of the oxidation number.

Electronic spectra and magnetic moments. For the chromium(III) derivatives the calculated Dq and B′ parameters suggest the presence of CrO_6 chromophores, thus confirming the conclusions reached from the i.r. studies.

As for the manganese(II) derivatives the value of B, C and 10 Dq have been calculated by the method already reported, together with the energies of the bands arising from the transitions $^6A_1 \rightarrow {}^4T_{1g}(^4G)$, $\rightarrow {}^4T_{1g}(^4P)$, and $\rightarrow {}^4T_{1g}(^4F)$. In this way good agreement between calculated and observed energies has been found for all the states.

The iron(II) derivatives exhibit an absorption band clearly split into two components, which represents the transition $^5T_{2g} \rightarrow {}^5E_g$ for octahedral iron(II) complexes.

The room temperature magnetic moment values are in agreement with the literature data.

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