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A Density Functional Study of Some Physical Properties of Carnosine (N-b-alanyl-L-histidine)

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Equilibrium geometries, harmonic vibrational frequencies, electronic transition energies, and NMR chemical shifts are calculated for different structures of carnosine (N-b-alanyl-L-histidine) as a further step in the physical characterization of that molecule. The calculations are performed using the generalized gradient approximation to the density functional theory. Solvent effects are implicitly accounted. Although total energy results indicate that zwitterionic species are more stable than neutral ones, the comparison of calculated properties with experimental geometric parameters and chemical shifts seems to favor the neutral species. The calculated electronic transition energies and harmonic vibrational frequencies suggest that both the electronic and vibrational spectra could be used to determine the nature of the carnosine species under study.

Mean Amplitudes of Vibration of the Halogen Molecules

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Dedicated to Professor Achim Müller on the occasion of his 65th birthday

Mean amplitudes of vibration of the halogen molecules F₂, Cl₂, Br₂ and I₂ have been calculated from known spectroscopic data in the temperature range between 0 and 1000 K. The results are briefly discussed, and some comparisons with the results of the related diatomic interhalogen molecules, as well as with experimental values obtained by electron diffraction experiments, are made.

Characterization of a Cu(II) Complex of Sulfadimethoxine

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The molecular structure of $[\text{Cu}(\text{sulfadimet})_2]\cdot\text{SO}(\text{CH}_3)_2$ (sulfadimet=sulfadimethoxine=4-p-aminobenzenesulfonamido-2,6dimethoxypyrimidine) was determined by single X-ray diffractometry. It crystallizes in the monoclinic space group P21/c with Z=4. The Cu(II) cation is in a distorted CuN5 square pyramidal coordination, involving four sulfadimethoxine molecules, one of them acting as a bidentate ligand. The infrared spectrum is briefly discussed on the basis of the structural peculiarities of the complex.

Voltammetric and Spectroscopic Study of Chromium(III)/Picolinate Complexes

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Zeitschrift für Anorganische und allgemeine Chemie 629, 1085-1090 (2003)

The electrochemical properties and the stability of the Cr(III) complexes $[\text{Cr}(\text{pic})_3]\cdot\text{H}_2\text{O}$ and $[\text{Cr}(\text{pic})_2(\text{OH})]_2\cdot 5\text{H}_2\text{O}$ (Hpic=pyridine-2-carboxylic acid=picolinic acid) were investigated in DMF solutions by cyclic voltammetry, and complemented by electronic spectroscopy. The electrochemical results indicate that both compounds undergo a one-electron reversible reduction process. The mononuclear species has a more accessible reduction potential than the binuclear one. In this last case, the observed one-electron process can be ascribed to a considerable stabilization of the mixed valence Cr(III)/Cr(II) species. Both complexes were also characterized by infrared and Raman spectroscopy.

Vibrational Properties of Bismutine, BiH₃

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Structural and vibrational-spectroscopic data for BiH₃ have recently been reported for the first time. On the basis of these data the force constants, mean amplitudes of vibration and thermodynamic functions have been calculated. Some comparisons with the structurally related SbH₃ molecule are made.

Vibrational and Magnetic Properties of a Cu/Mg Glutamate Complex

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The recently reported mixed metal glutamate of complex stoichiometry $[\text{CuMg}(\text{L-glu})_2(\text{H}_2\text{O})_3] \cdot 2\text{H}_2\text{O}$ was obtained as microcrystalline powder from aqueous solution. Its structure was confirmed by X-ray diffractometry. The infrared spectrum of the complex was recorded and briefly discussed in relation to its structural characteristics. Its magnetic behavior was investigated by magnetic susceptibility measurements in the temperature range between 2 and 300 K, complemented with ESR (Q- and X-band) spectra. These measurements confirmed a certain magnetic interaction between the Cu(II) centers present in the polymeric structure of the compound. The study was complemented with a series of dissolution tests, which confirmed the potential usefulness of this complex for metal supplementation in human and veterinary medicine.

Vibrational Spectra of the Layered Compound $[(\text{VO}_2)_2(4,4'\text{-bipy})_{0.5}(4,4'\text{-Hbipy})(\text{PO}_4)] \cdot \text{H}_2\text{O}$

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The infrared and Raman spectra of the title complex were recorded and assignments for the VO_2^+ , PO_4^{3-} and V-O and V-N skeletal vibrations are proposed. The results are of interest in relation to the vibrational-spectroscopic properties of the active site of vanadium haloperoxidases.

Structural and Spectroscopic Characterization of Two New Cd(II) Complexes: Bis(thiosaccharinato)bis(imidazole)cadmium(II) and Tris(thiosaccharinato)aquacadmium(II)

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Dedicated to Prof. Achim Müller on the occasion of his 65th birthday

The crystal structures of $[\text{Cd}(\text{tsac})_2(\text{im})_2]$ (1) (tsac=anion of thiosaccharine; im=imidazole) and of $(\text{Him})[\text{Cd}(\text{tsac})_3(\text{H}_2\text{O})]$ (2) (Him=imidazolium cation) have been determined at 120 K by single crystal X-ray diffractometry. Complex 1 crystallizes in the monoclinic space group $P2_1/n$ with $Z=4$ whereas compound 2 is triclinic, space group $P(-1)$ and $Z=2$. In both compounds, Cd(II) is in a distorted tetrahedral environment. In the neutral complex 1 the metal is coordinated to the S-atom of the two thiosaccharinato ligands and to the N-atom of the imidazole molecules. In the anionic complex 2, Cd(II) is coordinated to three thiosaccharinato S-atoms and to the O-atom of the water molecule. The FTIR spectra of both compounds were also recorded and briefly discussed.

IR-Spectroscopic Characterization of $A_2BB'O_6$ Perovskites

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Vibrational Spectroscopy 32, 167-174 (2003)

A large series of ternary oxides of composition $A_2BB'O_6$ and belonging to the perovskite structural type have been prepared and their structures confirmed by X-ray powder diffractometry. Most of these materials present deviations and distortions regarding the ideal perovskite structure. The infrared spectra of all the materials were recorded and briefly discussed in relation to their structural peculiarities and by comparison with those of related oxides. The usefulness of these compounds as substrates for the deposition of high T_c superconducting films is commented.

Structural and Spectroscopic Characterization of Two New Thallium(I)/Thiosaccharinate Complexes

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Zeitschrift für Anorganische und allgemeine Chemie 629, 1975-1979 (2003).

The crystal structures of $[Tl(tsac)]$ (1) and $[Tl(tsac)(ophen)]$ (2) (tsac=anion of thiosaccharin; ophen=1,10 phenanthroline) have been determined at 116 K by single crystal X-ray diffractometry. Complex 1 crystallizes in the monoclinic space group $P2_1/a$ with $Z=4$ and complex 2 in the monoclinic space group $C2/c$ with $Z=8$. In both complexes Tl(I) is coordinated to a thiosaccharinate anion through its sulphur and nitrogen atoms. A distorted eight fold coordination sphere around the cation in complex 1 is completed with two other longer Tl-S bonds and four Tl...O contacts with five symmetry related neighbouring thiosaccharinate anions. A phenanthroline molecule acting as a bidentate ligand through its nitrogen atoms completes a four-fold coordination around the metal atom in complex 2. The infrared spectra of both complexes were also recorded and their most important features discussed on the basis of its structural peculiarities.

Model Studies Related to Vanadium Biochemistry: Recent Advances and Perspectives

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Journal of the Brazilian Chemical Society 14, 878-888 (2003).

Increasing evidence on the needs of the higher forms of life for vanadium has been accumulated during recent years. Model studies have become a very important tool to attain a better understanding of different aspects of the biochemistry of this bioelement. In this account we present the results of our own studies, as well as those of other research groups, on models related to different aspects of its metabolism and detoxification and to vanadium dependent haloperoxidases. Additional information about the interaction of the biologically relevant oxovanadium(IV) cation with important bioligands such as nucleotides, carbohydrates, phosphates and related systems are also presented.

Mean Amplitudes of Vibration of Some Octahedral MF₆⁻ Anions

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The mean amplitudes of vibration of the hexafluoroanions of the groups 5 and 15 of the Periodic System have been calculated from known spectroscopic data between 0 and 1000 K. Bond peculiarities of these compounds, are discussed and some comparisons with related species are made.

Cu(II) Complexation with His-Gly and His-Ala. X-Ray Structure of [Cu(his-gly)₂·(H₂O)₂].6H₂O

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Two novel Cu(II)-dipeptide complexes containing L-histidil-L-glycine and L-histidil-L-alanine as ligands were prepared and characterised by infrared and electronic spectroscopies. EPR measurements were also made in solution and in the solid state. Cyclic voltametric studies were carried out on aqueous solutions. The crystalline structure of [Cu(L-histidil-L-glycine)₂(H₂O)₂].6H₂O was determined by X-ray diffractometry. It crystallises in the space group C2. The Cu(II) is in a tetragonally distorted octahedral coordination, where the basal plane is occupied by N-atoms belonging to the histidine portion. Two molecules of water occupy the apical positions.