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Structural, spectroscopic and magnetic properties of thiocyanate complexes of Mn(II), Ni(II) and Cu(II) with the 1-methylimidazole ligand

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ABSTRACT

New $[M(SCN)_2(L)_4]$ complexes, where M = Mn(II), Ni(II), Cu(II) and L = 1-methylimidazole have been synthesized. The electronic structures of the complexes were calculated using the DFT method, and the descriptions of frontier molecular orbitals and the relocation of the electron density of the compounds were determined. The crystal field splitting, Racah repulsion and nephelauxetic parameters were determined from the electronic spectra of the complexes. The magnetic properties revealed almost ideal paramagnetism for all the complexes under study, evidenced by values close to zero for both the Curie–Weiss temperature and the imaginary part of the ac magnetic susceptibility.

1. Introduction

The imidazole derivative ligands play an important role in the coordination chemistry of various transition metals [1]. The imidazole ring is present in many biological systems, metallo-proteins and anticancer drugs [2–4]. Ruthenium-imidazole and its derivatives have been proven to have antitumor and immunosuppressive activity [5–8]. Various 3*d* transition metal complexes with imidazole and its derivatives (for example 1-methylimidazole) have been studied as electrochemical hybridization indicators or electroactive markers of DNA [9–11]. The stability and relatively strong bonding to metals and the possibility of adjusting the electronic and steric properties by introducing sterically demanding substituents at the *N* atom are important advantages of the imidazole type ligands, especially in catalytic processes [12]. In general, studies of these complexes are concentrated around applications, and less attention is applied to the examination of their electronic structures and spectroscopic and magnetic properties. The study of the electronic structures of such complexes is valuable as a means to predict their properties.

On the other hand, many transition metal complexes containing ambidentate ligands have been synthesized, and their structures, physical properties and linkage isomerization reactions of ambidentate units have been investigated. Thiocyanate-containing metal complexes are considered to be the most investigated systems because of their diverse structures, applications in magnetic materials and luminescence properties. The SCN^- ion possesses a polarizable π system; the electron is dislocated and it may act as a mediator for magnetic interactions between paramagnetic transition metal centers. The geometry and coordination mode of NCS^- in 3*d* metal complexes is strongly influenced by the electronic and steric effects around the central ion [13–19].

Here we present the synthesis, crystal, molecular structures, spectroscopic characterization and magnetic properties of isothiocyanate manganese(II), nickel(II) and copper(II) complexes with the 1-methylimidazole ligand. Moreover, in order to better understand the electronic structures in the complexes and to explain the related experimental observations, density functional theory (DFT) calculations have also been carried out and the absorption-spectral properties in solution of the complexes were further studied by applying time-dependent DFT (TDDFT) calculations. Additionally, the chemistry of first-row transition elements is much less developed than that of second- and third-row transition metals for strongly donating ligands. However, once the molecular symmetry of the complex is known, LF theory can be fully utilized and the $10Dq$ and repulsion parameters (B, C) can be easily determined. As well, specification of the nephelauxetic parameter allows for a description of the metal–ligand bonding, with regard to its nature.

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2. Experimental

2.1. Synthesis

All reagents used for the synthesis of the complexes are commercially available and were used without further purification. The complexes were synthesized in the reactions between $MnCl_2{\cdot}4H_2O$, $NiCl_2{\cdot}6H_2O$, $CuCl_2{\cdot}2H_2O$, NH_4SCN and stoichiometric amounts of 1-methylimidazole in methanolic solution (50 cm^3). The mixtures of the compounds were refluxed for about 1 h. After this time, the volume of the solvent was reduced to about 20 cm^3 and the filtered solution was cooled and left for slow evaporation.

*Complex **1**:* Yield 62%. Color: colorless. IR (KBr, cm^{-1}): 3113 ν_{ArH}; 2955 ν_{CH}; 2072 $\nu_{(CN\ from\ SCN)}$; 1618 ν_{CN}; $\nu_{C=C}$; 1533 wag_{CH_3}; 1416, 1288, 1231, 1103, 1083, 1026 (imidazole ring); 934 $\delta_{(imidazole;\ Mn–N(Im))}$; 843 $\nu_{(SC\ from\ SCN)}$; 753 $\delta_{(C–C\ in\ the\ plane)}$; 476 $\delta_{(NCS)}$. UV–Vis (methanol, nm (log ε, $M^{-1}\,cm^{-1}$)): 601.0 (0.99), 436.5 (1.14), 371.0 (1.74), 213.5 (4.78).

*Complex **2***: Yield 76%. Color: blue. IR (KBr, cm^{-1}): 3113 $\nu_{CH(Im)}$; 2917 ν_{CH_3}; 2093 $\nu_{(CN\ from\ SCN)}$; 1617 ν_{CN}; $\nu_{C=C}$; 1531 wag_{CH_3}; 1415, 1283, 1231, 1102, 1087, 1027, 939 (imidazole ring); 842 $\nu_{(SC\ from\ SCN)}$; 752 $\delta_{(C–C\ in\ the\ plane)}$; 474 $\delta_{(NCS)}$. UV–Vis (methanol, nm (log ε, $M^{-1}\,cm^{-1}$)): 988.5 (1.02), 749.0 (0.98), 637.0 (1.29), 360.0 (2.02), 211.5 (4.17).

*Complex **3***: Yield 69%. Color: green. IR (KBr, cm^{-1}): 3124 $\nu_{CH(Im)}$; 2920 ν_{CH_3}; 2097 $\nu_{(CN\ from\ SCN)}$; 1614 ν_{CN}; $\nu_{C=C}$; 1520 wag_{CH_3}; 1421, 1289, 1232, 1109, 1092, 1028, 952 (imidazole ring); 838 $\nu_{(SC\ from\ SCN)}$; 763 $\delta_{(C–C\ in\ the\ plane)}$; 481 $\delta_{(NCS)}$. UV–Vis (methanol, nm (log ε, $M^{-1}\,cm^{-1}$)): 680.0 (1.13), 472.0 (1.31), 388.5 (2.23), 213.5 (4.77).

2.2. Measurements

Infrared spectra were recorded on a Nicolet Magna 560 spectrophotometer in the spectral range 4000–400 cm^{-1} with the sample in the form of a KBr pellet. Electronic spectra were measured on a Lab Alliance UV–VIS 8500 spectrophotometer in the range 1100–180 nm in methanol solution. Luminescence measurement of complex **2** was made in methanolic solution on an F-2500 FL spectrophotometer at room temperature.

Dynamic (ac) magnetic susceptibility was measured with the aid of a Quantum Design System (MPMS XL) and recorded in the temperature range 2–300 K and at an internal oscillating magnetic field H_{ac} = 3.9 Oe with an internal frequency f = 300 Hz. The effective magnetic moment was calculated from the equation: $\mu_{eff} = 2.83\sqrt{C}$, where C is the Curie constant. Magnetization isotherms were measured at 4.3 K in the static (dc) magnetic field up to 70 kOe.

2.3. Calculations

The density functional theory (DFT) calculations were carried out using the GAUSSIAN09 program [20]. The DFT/B3LYP [21] method was used for the geometry optimization and electronic structure determination. The calculations were performed using the polarization functions for all atoms: 6-311^{++} – manganese, nickel and copper, 6-31g^{++} – sulfur, carbon, nitrogen and 6-31g – hydrogen. The electronic transitions were calculated by the TD-DFT method [22] with use of the B3LYP functional, and 90 electronic transitions were calculated for each complex. The PCM (Polarizable Continuum Model) solvent model was used in the Gaussian calculations with methanol as the solvent. Natural bond orbital (NBO) calculations were performed with the NBO code [23] included in GAUSSIAN09. Natural bond orbitals are orbitals localized on one or two atomic centers that describe molecular bonding in a manner similar to a Lewis electron pair structure, and they correspond to an orthonormal set of localized orbitals of maximum occupancy. NBO analysis provides the contribution of atomic orbitals (s, p, d) to the NBO σ and π hybrid orbitals for bonded atom pairs. In this scheme, three NBO hybrid orbitals are defined, bonding orbital (BD), lone pair (LP) and core (CR), which were analyzed on the atoms directly bonded to or presenting some kind of interaction with the central ion. The contribution of a group to a molecular orbital was calculated using Mulliken population analysis. GAUSSSUM 2.2 [24] was used to calculate group contributions to the molecular orbitals and to prepare the partial density of states (DOS) and overlap population density of states (OPDOS) spectra. The DOS and OPDOS spectra were created by convoluting the molecular orbital information with Gaussian curves of unit height and a FWHM (Full Width at Half Maximum) of 0.3 eV.

2.4. Crystal structures determination and refinement

Crystals of $Mn(SCN)_2(ImCH)_4$ (**1**), $Ni(SCN)_2(ImCH)_4$ (**2**) and $Cu(SCN)_2(ImCH)_4$ (**3**) were mounted in turn on a Xcalibur, Atlas, Gemini ultra Oxford Diffraction automatic diffractometer equipped with a CCD detector, and used for data collection. X-ray intensity data were collected with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at a temperature of 295.0(2) K, with the ω scan mode. Ewald sphere reflections were collected up to 2θ = 50.10°. The unit cell parameters were determined from least-squares refinement of 1763, 5860 and 3417 strongest reflections for complexes **1**, **2** and **3**, respectively. During the data reduction, the decay correction coefficient was taken into account. Lorentz, polarization, and numerical absorption corrections were applied. The structures were solved by direct methods. All the non-hydrogen atoms were refined anisotropically using the full-matrix, least-squares technique on F^2. All the hydrogen atoms were found from difference Fourier synthesis after four cycles of anisotropic refinement, and refined as "riding" on the adjacent atom with individual isotropic temperature factors equal to 1.2 times the value of the equivalent temperature factor of the parent atom, with geometry idealization after each cycle. The OLEX2 [25] and SHELXS, SHELXL [26] programs were used for all calculations. Atomic scattering factors used were those incorporated in the computer programs.

3. Results and discussion

In the simple reactions between chloride salts of manganese(II), nickel(II) and copper(II) with ammonium thiocyanate and 1-methylimidazole in methanolic solutions, complexes with the formula $M(SCN)_2(L)_4$ have been prepared. Infrared spectra of the complexes present characteristic bands due to ligands vibrations. The stretching modes of the aromatic imidazole C–H bonds display maxima at 3113 cm^{-1} for **1** and **2**, and 3124 cm^{-1} for complex **3**. The methyl groups of the ImCH ligands are indicated by bands with maxima near 2955, 2917 and 2920 cm^{-1}, respectively, for complexes **1**, **2** and **3**. The $\nu_{C=N}$ and $\nu_{C=C}$ band of the imidazole ring appears close to 1618 cm^{-1}, which is different from the free ligand (1540 cm^{-1}) and indicates rather strong coordination of the ligand by the imidazole nitrogen atom in the complexes. The ν_{CN}, ν_{CS} and δ_{NCS} frequencies of the isothiocyanato ligands present maxima at 2072 (**1**), 2093 (**2**), 2097 (**3**) cm^{-1}, 843, 842, 838 cm^{-1}, and 476, 474, 481 cm^{-1}, respectively, and these values are in good agreement with end-on NCS^- coordination. The coordination modes of the thiocyanate ligands in the studied complexes are indeterminable from the IR spectral data of these compounds. For N-bonded complexes, generally the C–N stretching band is in a lower region around 2050 cm^{-1}, compared to 2100 cm^{-1} for S-bonded complexes. However, the frequencies of the bands are sensitive to other factors, like coexisting ligands, and the structure of the compounds