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A series of d^n transition metal coordination complexes: Structures and comparative study of surface electron behaviors (n = 9, 8, 7, 6, 5)

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ABSTRACT

Ten transition metal coordination complexes $[Cu_2(phen)(p\text{-}tpha)(\mu\text{-}O)]_n$ **1**, $[Cu(m\text{-}tpha)(imH)_2]_n$ **2**, $[Ni(5\text{-}Haipa)_2(H_2O)_2]_n$ **3**, $[Ni(phen)_2(H_2O)_2]\cdot btc\cdot[Ni(H_2O)_6]_{0.5}\cdot 9H_2O$ **4**, $[Co(2,5\text{-}pdc)(H_2O)_2]_n\cdot nH_2O$ **5**, $[Co_2(2,5\text{-}pdc)_2(H_2O)_6]_n\cdot 2nH_2O$ **6**, $[Fe(2,5\text{-}Hpdc)_2(H_2O)_2]\cdot H_2O$ **7**, $[Co(C_6H_4NO_2)_3]\cdot H_2O$ **8**, $[Fe_2(\mu_2\text{-}btec)(\mu_2\text{-}H_2btec)(bipy)_2(H_2O)_2]_n$ **9**, $[Mn(phen)(2,5\text{-}pdc)(H_2O)_2]\cdot H_2O$ **10** (H_4btec = 1,2,4,5-benzenetetracarboxylic acid, phen = 1,10-phenanthroline, 2,5-H_2pdc = 2,5-pyridine-dicarboxylic acid, p-tpha = p-phthalic acid, m-tpha = m-phthalic acid, bipy = 2,2′-bipyridine, 5-H_2aipa = 5-aminoisophthalic acid, imH = imidazole, H_3btc = 1,3,5-benzenetricarboxylic acid) were synthesized through hydrothermal method. They were characterized by UV–Vis absorption spectra, single-crystal X-ray diffraction and surface photovoltage spectra (SPS). Structural analysis indicated that the complexes **1**, **2**, **3**, **5**, **6** and **9** were linked into infinite structures bridged by organic acid ligands. The other four complexes were molecular complexes and further connected to 2D or 3D structures by the hydrogen bonds. The SPS of complexes **1**–**10** indicate that there are positive response bands in the range of 300–800 nm showing different levels of photo-electric conversion properties. The intensity, position, shape and the number of the response bands in SPS are obviously different since the structure, species, valence, d^n electrons configuration and coordinated environment of the center metals are different. There are good relationships between SPS and UV–Vis spectra.

1. Introduction

The design and synthesis of coordination polymers and supramolecules with transition metal have caused much attention in the past few years [1–3]. The aims of the research of this field are the discovery and synthesis of new complexes and materials with practical function and application value [4–12], in which the following two aspects of the research are key points: (i) forecast the style and structure of the product; (ii) study the properties of the complexes and the relationships between the properties and structures. At this respect, the bridging ligands play important roles because they can influence the structural assemblies of final product. Aromatic polycarboxylic acid ligands have been proved to be good building blocks for the construction of coordination complexes with multidimensional structures [13–15]. The aromatic polycarboxylate ligands containing two or more carboxyl groups can form the complexes with diverse structures due to their various bridging modes and strong coordination tendency with transition metals. In the recent years, a large number of coordination complexes with aromatic polycarboxylate ligands have been reported, such as the complexes containing 1,4-benzenedicarboxylate acid [16,17], 1,3,5-benzenetricarboxylate acid [18,19] and 1,2,4,5-benzenetetracarboxylate acid [20,21]. As building blocks, the heterocyclic carboxylic acids (pyridine-, pyrazole-, and imidazole-carboxylic acids) have been used in the construction of coordination polymers. In particular, pyridine dicarboxylic acids have been proved to be versatile ligands by various coordination modes resulting in novel transition metal complexes with 3D structures [22–24]. Compared with other pyridine dicarboxylic acids, 2,5-H_2pdc seems to coordinate to metal easily with infinite structure, because two carboxyl groups with an angle of 180° may lead to more stable framework [25,26]. All of which indicate that different carboxylic acid can make a certain degree of predictability of the structures of complexes.

In fact, there are osculating relationships between the properties of transition metal complexes and changes of electron behaviors. For example, the transitions of electrons between different components are correlated with the catalytic function; the changes of the electron arrangement can change the magnetic properties. In addition, the change of electron behaviors under the light-induced not only lead to the change of light absorption and emission properties, but also lead to the change of the electricity or voltage on

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the solid surface, which is photo-electric conversion. Therefore, the deep research on the surface electron behaviors of complexes under light-induced has a good significance for the exploiture and application of transition metal complexes. Surface photovoltage spectra (SPS) technology, as a sensitive tool, has been used to detect the charge transitions of the functional semiconductor [27–29]. SPS not only relates to the electron transition process caused by light absorption, but also reflects the properties of separation and transition of photogenerated charges directly, so it is significant to study the electron behaviors of the solid surface and interface [30–35].

At present, SPS has been applied to functional materials, semiconductor, materials of catalyst and solar power conversion, and a lot of significant results have been reported. In the recent years, our group selected the SPS technology to study the surface electron behaviors and photo-electric conversion property of coordination polymers and supramolecular complexes containing Ni, Mn and other transition metal, and some preliminary results have been achieved [36–41]. But the study of a series of d^n transition metal coordination complexes is the first report. In this paper, 10 complexes were divided into five groups according to the different d^n electron configuration for comparative analysis and discussion. SPS and UV–Vis absorption spectra were associated to study the surface electron behaviors under light-induced and photo-electric properties of the complexes, which may provide an important foundation and reference for the deep research in this area.

2. Experimental

All chemicals and reagents were AR without further purification. Single-crystal X–ray diffraction data were collected with the Bruker Smart APEX II X-diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 293 (2) K. UV–Vis absorption spectra were recorded with a JASCO V-570 UV–Vis/NIR spectrophotometer in the 200–2500 nm. SPS were recorded with a home-built surface photovoltage spectrophotometer. The electron paramagnetic resonance (EPR) spectra of **7**–**10** were determined on a Bruker A-200 spectrometer (Modulation Frequency = 100 kHz, Spectroscopy Frequency = 9.40 GHz). All tests were carried out under room temperature and pressure.

The syntheses, crystal data and structure refinements were listed in Supplementary materials (Sections 1 and 2).

3. Results and discussions

3.1. Structure descriptions of complexes

3.1.1. Structure description of [Cu$_2$(phen)(p-tpha)(μ-O)]$_n$ 1

There are two crystallographic independent Cu(II) ions, one phen, one p-tpha group, and one μ-O in the asymmetry unit of **1** (Fig. 1). The Cu1 ion is four-coordinated with O_4 donor, two of which are from different p-tpha groups and the other two O atoms belong to μ-O atoms. The Cu2 ion is five-coordinated with an N_2O_3 donor, in which two N atoms are from phen ligand and two O atoms are from different p-tpha groups, while the other O atom is μ-O. As bridging ligand, p-tpha groups have two coordinated modes in **1**: (i) both of two carboxyl groups adopt bidentate mode bridging Cu1 and Cu2; (ii) two carboxyl groups adopt monodentate mode coordinating to Cu2 (Fig. S1).

The **1** was linked to 1D ladderlike chain by p-tpha groups with monodentate and bidentate fashions along the *c*-axis (Fig. S1). The adjacent 1D chains were also linked along the *b*-axis (Fig. S2) to form 2D layer in the *bc* plane (Fig. 2).

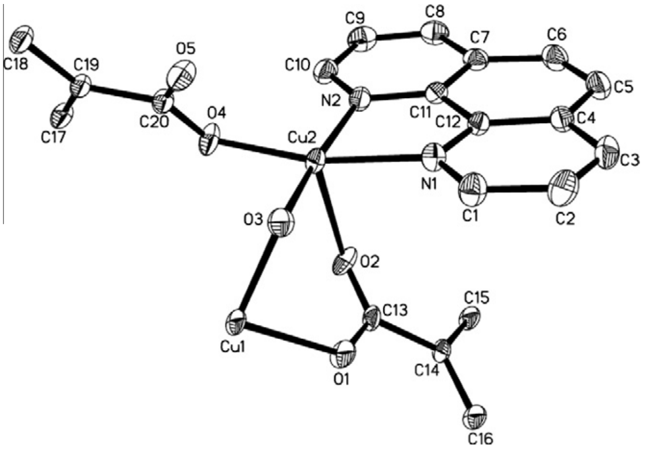

Fig. 1. The asymmetry unit of **1**.

3.1.2. Structure description of [Cu(m-tpha)(imH)$_2$]$_n$ 2

There are one Cu(II) ion, one m-tpha group, and two imH molecules in the asymmetry unit of **2** (Fig. 3). The Cu(II) ion is four-coordinated with an N_2O_2 donor, in which O atoms are from different m-tpha groups and N atoms are from different imH ligands, so the symmetry of Cu(II) ion can be described as a distorted quadrilateral plane. In the crystal, the adjacent Cu ions were linked to 1D chain by the m-tpha group along the *c*-axis (Fig. 4). The 2D layer was formed by the hydrogen bonds that formed by uncoordinated carboxylic O atoms of m-tpha groups and the C–H groups of imH molecules (C11–H···O4, 0.2862 nm) (Fig. S3).

3.1.3. Structure description of [Ni(5-Haipa)$_2$(H$_2$O)$_2$]$_n$ 3

Structure analysis indicate that the **3** is a 2D structure with the building unit of [Ni(5-Haipa)$_2$(H$_2$O)$_2$] (Fig. 5). The Ni(II) ion is six-coordinated with the NiN_2O_4 mode, in which two N and two O atoms are from different Haipa$^-$ groups and the other O atoms are from the coordinated waters. So its geometry is a distorted octahedron, in which four O atoms constructed the equator plane and two N atoms occupied the apical positions.

In the crystal, the adjacent Ni ions were linked by the Haipa$^-$ groups along the *b*-axis and *c*-axis to form 2D layer in the *bc* plane (Fig. 6).

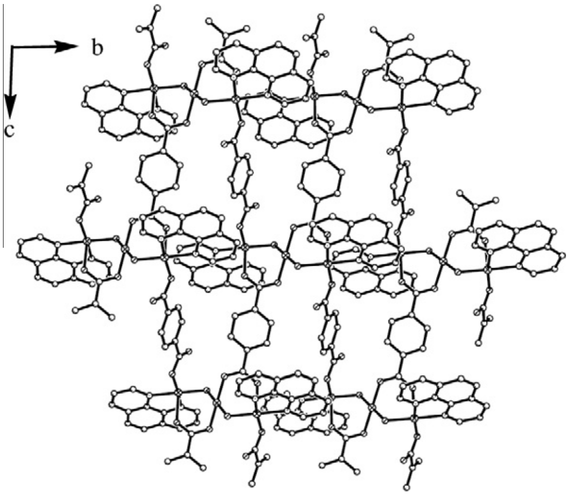

Fig. 2. The 2D structure of **1** in the *bc* plane.