

Advances in Synthesis, Structure and Structure-Activity Relationship of Lead Complexes Containing Nitrogen and Oxyheterocyclic Compounds

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Abstract: Metal carboxylate coordination compounds with polydentate ligands containing nitrogen and oxygen donors has been greatly developed in the past decade, especially for the coordination polymers with the transition metal. However, the coordination polymers of main group elements, especially for the Pb (II) of such compounds is scarcely reported. In this paper, the supramolecular action of complexes, the development status of lead compounds, luminescent complexes and their mechanism, the transformation of single crystal structure and the progress are reviewed.

1. Introduction

J. M. Lehn, a Nobel laureate in chemistry, defined supramolecular chemistry as "chemistry beyond the scope of molecules." It is a science that studies the complex and ordered molecular aggregates with specific functions formed by the interaction between molecules. Such molecular aggregates are referred to as supramolecule^[1]. Molecular recognition through the synergy of weak intermolecular interaction forces is a central concept in supramolecular chemistry. molecular recognition refers to the process of selective binding of subject (or receptor) to guest (or substrate) and producing a specific function. A molecule can be identified from the geometry and size of another molecule, as well as from chemical factors such as hydrogen bond formation, stacking interactions, and electrostatic forces. With the development and deepening of supramolecular chemistry research, intramolecular and intermolecular weak interactions, especially weak coordination and metalphilic interactions, have become one of the current research hotspots in inorganic chemistry, showing a trend of rapid development^[2]. These weak interactions are not only an effective bridge between coordination chemistry and supramolecular chemistry, but also a key issue involving the stability and construction of supramolecular systems, molecular recognition, and even the performance of supramolecular systems. Heterocyclic nitrogen-based chelating ligands, dicarboxylic acids and transition metal compounds have been thoroughly studied among the existing aggregates for the construction of ordered high-level molecules. However, there are few studies on the main group metal ions, especially the compounds formed by Pb²⁺ are rarely reported.

Pb²⁺ exhibits interesting behavior characteristics different from transition metal compounds due to its large ionic radius, rich coordination number and potential lone pair electron effect, which is of great research significance in the process of expanding the breadth and depth of coordination chemistry.

2. Lead (II) Complexes

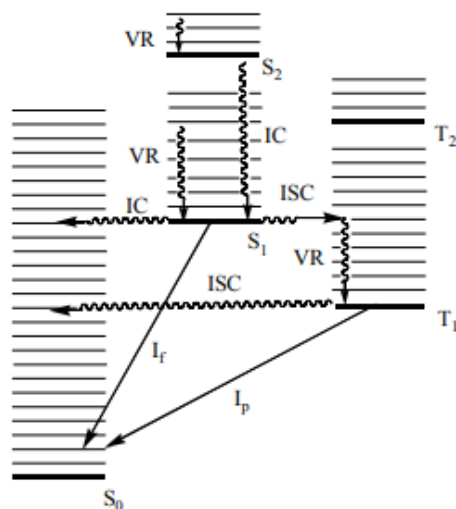
For all P-region elements, the coordination chemistry of divalent lead is unique in that it can take on different geometric coordination configurations and allow for certain distortions, which are rare in D-region and other elements. It has the dual function of combining hard and soft ligands, and these properties make divalent lead a very interesting metal ion. It often forms compounds that are not what you would expect. At THE SAME TIME, THE TOXIC nature AND environmental pollution of lead and its application in production have also increased people's interest in its research, so people are eager to find materials and ligands that can neutralize lead ions. Because there is no effective oral chelating drug specifically designed to treat lead poisoning. Although many studies in this field have been reported, the coordination chemistry of lead is still worth further exploration in many aspects [3]. In the study of lead complexes, a large number of compounds formed by various conventional ligands and lead have been reported. However, most of the studies on divalent lead mixed ligands containing nitrogen and oxygen are limited to a variety of macrocyclic ligands, and such studies on the mixed coordination of nitrogen-like heterocycles and carboxylic acids are extremely rare.

3. Luminescent Complex

Organic compounds characterized by the electronic structure of conjugated π and metal functional complexes with conjugated π as ligands exhibit special optical and electromagnetic properties [4]. For example, metal luminescence complexes are intermediate between organic matter and inorganic matter, which not only have the advantages of high fluorescence quantum efficiency of organic matter, but also have the characteristics of good stability of inorganic matter, so they are considered as the most promising type of luminescence materials. The luminescence phenomenon produced by absorbing a certain amount of light energy is called Photoluminescence (PL); And when the substance is under a certain electric field, excited by the corresponding electric energy can also produce luminescence, which is called Electroluminescence (EL). Because of the special molecular structure of metal complexes, on the one hand, the radiation transition probability of the molecules is greatly enhanced because of the rigid structure of the molecules. On the other hand, its molecular stability guarantees its application as functional materials [5].

3.1. Radiative Transitions of Molecules

A molecule absorbs light of a particular wavelength and reaches an excited state. Since the excited state is an unstable intermediate state, the excited substance must dissipate the excess energy through various ways to reach a certain stable state. The energy dissipation process of an excited molecule can be represented by a Jablonski diagram (Figure1).



(If: fluorescence, I_p : phosphorescence, IC: internal conversion, ISC: interseries crossing, VR: vibrational relaxation)

Figure 1: Jablonski diagram involving fluorescence and phosphorescence processes

The release of energy in the form of radiated photons from the excited state back to the ground state is called a radiative transition. The radiation from the first excited singlet back to the ground state is called fluorescence (I_f). The radiation from the excited triplet state back to the ground state is called phosphorescence (I_p).

Under the premise of studying photoluminescence, it is hoped to enhance the radiative transition process, reduce the non-radiative transition process and other dissipation pathways, so as to improve the luminescence efficiency.

3.2. Luminescent Ligand

Metal complexes, as a molecular entity, usually absorb light by the photosensitive functional group of the ligand. If the lowest excited m^* electronic level of the metal ion is higher than the lowest excited singlet S_1 level of the ligand, the complex molecule may undergo a radiative transition from the S_1 level of the ligand back to the ground state (fluorescence, I_f), or from the excited triplet T_1 back to the ground state (phosphorescence, I_p). In this case, the metal ion is equivalent to an inert atom that forms chelating rings with different parts of the organic ligand. There are some differences in the optical activity of ligand molecules (ions) before and after the formation of complexes. Many ligand molecules do not emit light or emit light very weakly in the free state. After the formation of the complex, the original non-rigid ligand structure is transformed into a rigid structure, which greatly reduces the probability of non-radiative transition and significantly increases the probability of radiative transition. As a result, the original non-luminescent or weakly luminescent organic compounds are transformed into highly fluorescent complexes.

3.3. Luminescent Central Ion Complexes

If the m^* level of the metal ion in the complex is lower than the T_1 level of the complex, the transition from the excited state m^* to the ground state m ($m^* \rightarrow m$) of the metal ion may occur and the characteristic fluorescence of the metal will be emitted. The metal ions of such complexes are mostly rare earth ions. Since the f orbital of the secondary outer electron of the luminescent rare

earth ions is an unfilled orbital, m^* (f^* level off $\rightarrow f^*$ transition) is located below the T1 level of ligand, and there is no continuous energy level between m^* and m levels. Therefore, the metal ions of this kind of luminescent ligands will emit characteristic linear fluorescence. The most common luminescent rare earth ions are Eu^{3+} , Tb^{3+} , Sm^{3+} , Dy^{3+} , etc.

3.4. Complexes Based on Charge-Transfer Radiative Transitions

Two types of charge-transfer radiative transitions (CTS) may also exist in the complex: LMCT and MLCT. LMCT refers to the transition associated with the transfer of electrons from ligand to metal ions. It usually occurs when the ligand has a high energy lone pair electron or the metal has a low energy vacant orbital. However, MLCT represents the transition associated with electron transfer from metal to ligand, which generally occurs in ligands with low energy π^* vacant orbitals, especially aromatic ligands. It is worth noting that after the complex molecules are excited to the $^1\text{MLCT}$ state, the molecules often reach the $^3\text{MLCT}$ state very quickly (~ 300 fs) through the interline jump, the efficiency of which is very high, close to 100%. When the molecule reaches the $^3\text{MLCT}$ state, it can return to the ground state through non-radiation transition or radiation transition (phosphorescence) (Figure 2), but the lifetime is much shorter than ordinary phosphorescence, generally around 400 ns, because the strong spin-orbit coupling effect of heavy metal atoms enhances the originally blocked phosphorescence transition process [6].

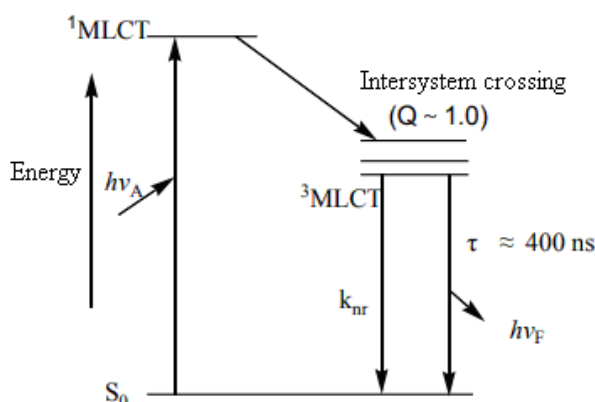


Figure 2: Deexcitation process of MLCT state

3.5. Luminescent Compounds with S_2 Ions

Various studies have been conducted on optical materials containing S_2 ions from different disciplines. From the viewpoint of functional materials, the study of compounds containing these ions are very meaningful, although the effect factors of luminescent properties of these compounds is not very clear, but because of inherent in S_2 ion $S_2 \leftrightarrow SP$ transition or related to S_2 ion charge transfer state will cause between them there is a wide range of fluorescence emission wavelength, It is called D level [7]. From a practical point of view, these compounds are only interesting because S_2 ions are used as effective catalysts in many applications, such as sun-tan lamps, X-ray phosphors, or flash lamps. In many compounds of divalent lead ($6S_2$), the lone pair electrons are not in a spherically symmetric orbital, thus distorting the symmetric environment (false Jahn-Teller effect). If the asymmetry in the excited state is reduced, a large Stokes shift will result [8]. In many lead compounds, the large Stokes shift can be attributed to the deviation of S_2 ion from its central position in the main lattice [9]. The absorption spectra of S_2 ions show that apart from the transitions of $^1S_0 \rightarrow ^3P_1$, $^1S_0 \rightarrow ^3P_2$ and $^1S_0 \rightarrow ^1P_1$, the other bands are not well identified and are considered as bands A, B, C and D, respectively. D with time is interpreted as "perturbed host transition" and can

also be thought of as a charge-transfer transition. However, this interpretation does not mean that the transition has been fully understood [10]. Studies have shown that in many cases, the fluorescence of Pb^{2+} compounds tends to come from two types of excited states. The UV emission is attributed to the transition of ${}^3\text{P}_{0,1} \rightarrow {}^1\text{S}_0$ (transition A), while the emission in the visible region is considered to be a transition from a higher energy level, possibly a charge-transfer state (D) transition [11], as shown in Figure 3.

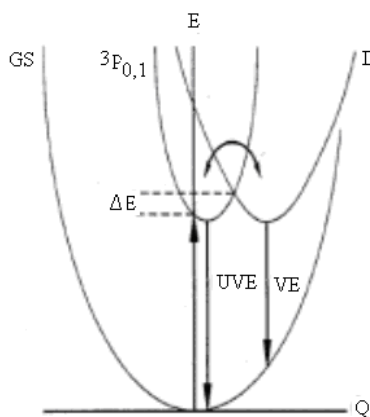


Figure 3: Ground state and two excited states of Pb^{2+} compound

4. Study on Solid Single Crystal Structure of Complex

Single crystal to single crystal structural conversion involves the cooperative behavior of atoms in the solid state. Classical studies have mainly understood the reactions in crystal topological chemistry through the study of different allotropes of styrene acids in the solid state by Schmidt et al. [12]. These previous works and a large number of subsequent studies on the photochemical excitation of dimerization [13], cyclization [14], polization [15] and racemic [16] have led to structural transformations, but relatively few studies on topological reactions caused by heat have been conducted [17].

5. Research Significance

With the development and development of supramolecular chemistry, intramolecular and intermolecular weak interactions, especially weak coordination and metalphilic interactions, have become one of the hot spots in inorganic chemistry, showing a trend of rapid development. These weak interactions are not only an effective bridge between coordination chemistry and supramolecular chemistry, but also a key issue involving the stability and construction of supramolecular systems, molecular recognition, and even the performance of supramolecular systems. It is a new level of physics and chemistry research, and is becoming one of the most advanced fields in the world, to explore the solid-state reactions of solid compounds under various strong or weak physicochemical conditions and the macroscopic properties and functional changes induced by the comprehensive interaction and synergistic effect between the corresponding molecules. Heterocyclic nitrogen-based chelating ligands, dicarboxylic acids and transmigration metal compounds have been studied in detail among the existing aggregates for structurally ordered molecules. However, there are few studies on the main group metal ions, especially the compounds formed by Pb^{2+} are rarely reported. Pb^{2+} exhibits interesting behavior characteristics different from transition metal compounds due to its large ionic radius, rich coordination number and potential lone pair electron effect, which is of great research significance in the process of expanding the breadth and depth of coordination chemistry. At the same time, elements in the heavy main group,

such as (T^{1+} , Sn^{2+} , Pb^{2+} , Sb^{3+} , Bi^{3+}), all have low-energy sp triplet states^[18]. At the same time, due to the presence of S_2 , the luminescence of the compounds is varied, which makes them in high energy physics, X-ray imaging device and low-voltage lamp have been widely used and gradually become a research hotspot.

6. Conclusions

In this paper, we systematically studied the triazolyl chelating ligands and lead dicarboxylate complexes, and preliminarily summarized the synergistic effects of supramolecular action and lone pair electron behavior on the coordination configuration of lead complexes. On the premise of summarizing other crystal structure transition rules, the aim of realizing the jump of lead compounds from hemispherical type to global type by finding suitable conditions is put forward. This article through to some compounds at room temperature and low temperature test, found that the structure of compounds at low temperature and does not take place obvious structure transformation, perhaps only through the behavior of physical cooling and not to reach such compounds hemisphere to global jump the required conditions, our next job is through combining the structure adjustment of content, It is hoped that other factors affecting the structure jump can be found from the structure of the compound. The luminescence properties of a large number of d10 and rare earth metal complexes have been well studied, but the luminescence of lead complexes, especially nitrogen-based chelating ligands and lead dicarboxylate complexes, is rarely studied. In this paper, the luminescence properties of these lead complexes were systematically studied, and the changes of the luminescence properties of these compounds in solution and solid were discussed, which provided a good idea for the future study of the luminescence of compounds containing S_2 electrons.

Acknowledgements

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