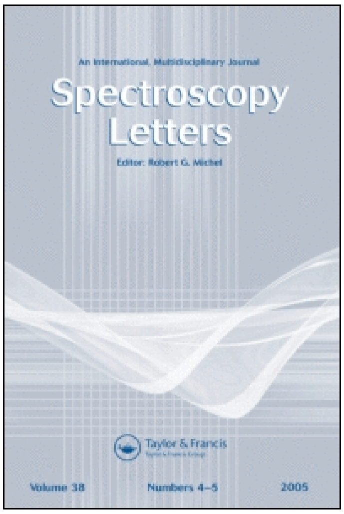

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Spectroscopy Study on Cobalt EDTA Complexes

Zhang Yugeng[a]
[a] Department of Applied Chemistry, University of Science and Technology of China, Hefei, Anhui, P.R. China

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SPECTROSCOPY STUDY ON COBALT EDTA COMPLEXES

Key words: double salt complex, PA spectrum, ligand field

Zhang Yugeng
Department of Applied Chemistry, University of Science
and Technology of China, Hefei, Anhui, 230026, P.R.China.

ABSTRACT

The photoacoustic spectra of $Co(H_2EDTA)\cdot 3H_2O$, $Ca[Co(EDTA)H_2O]\cdot 4H_2O$, $Sr[Co(HEDTA)H_2O]_2\cdot 4H_2O$, $Ba[Co(HEDTA)H_2O]_2\cdot 4H_2O$ complexes crystal are determined in the region of 300--800nm. In these spectra, the separations of absorption bands observed at 510nm and 650nm, the peak widths of 510nm band are variable in this series complexes. It is explained by the electron mutual effect, strength of ligand field and the symmetry of coordination group. The structure characters of these series complexes are also discussed.

INTRODUCTION

Ethylene diamine tetra acetic acid (EDTA) is used as a very important ligand of metal ions. The ease with which EDTA forms complexes, and an understanding of their natures, resulted in plenty of applications have been reviewed and reports are availabe on use of EDTA in industry[1], food-stuffs[2], pharmacy and medicine[3]. However, the literature reflects the major use in analysis[4]. The significant characteristics of complexes widely coordinated with many metal ions are very interesting. Especially, it coordinates with the first family transition metal ions, such as Co(II) ion, it is one of the essential trace elements of human body and has some important effect to circulatory system of human body. For example, EDTA is usually used as antidote to superfluity of Co(II) ion in human body. Some workers have determined series of crystal structures of M(II)-EDTA complexes (M= Cu,Ni,Co,Zn,Mn)[5,6] or M'M(II)-EDTA complexes[7,8]. However, electronic spectra of some complexes are also reported by us[9,10]. In this work, the spectral chemistry, structural chemistry and crystal field characters of M'Co-EDTA (M'= Ca,Sr,Ba) complexes are discussed.

EXPERIMENT

(I) Preparation of complexes

The purple crystal of $M[Co(HEDTA)(H_2O)]_2\cdot 4H_2O$ complexes were obtained by a reaction among $MCl_2\cdot 6H_2O$ (M= Sr,Ba), $CoSO_4\cdot 6H_2O$ and $Na_2(HEDTA)\cdot 2H_2O$ in the molar ratio 1:2:2 in aqueous solution at 70°C. Then, the solution mixture was evaporated slowly at room temperature and deep violet crystals were grown in two or three days.

The complex crystal of $Ca[Co(EDTA)]\cdot 5H_2O$ were prepared by the same reaction just with the $CaCl_2$ replacing of $BaCl_2\cdot 6H_2O$ and with molar ratio 1:1:1.And the crystal of $[Co(H_2EDTA)]\cdot 3H_2O$ complex was synthesized by the reaction between $CoSO_4\cdot 6H_2O$ and Na_2H_2EDTA aqueous solution in the same conditions. All the elemental analysis results and IR characters of these crystals were corresponding to their structural formula.

(II) Characterization

The photoacoustic spectra recorded in the region of 300--800nm at room temperature. The excitation source was a 500W xenon lamp. The light source was modulated by a variable speed mechanical chopper at a frequency of 12Hz. The acoustic signal was detected with the sample placed in a locally built photoacoustic cell fitted with an ERM 10 electret microphone. The output signal was normalized for changes in lamp intensity using a carbon-black reference.

RESULTS AND DISCUSSION

Fig. 1 is the PA spectra of MCo-EDTA complexes in the region of 300--800nm. In this series PA spectra, we find that there exist a common transition absorptions of ^{4}T1gy(^{4}F)--^{4}T1g(^{4}P) observed at about 510nm and a transition absorptions of ^{4}T1gy(^{4}F) --^{4}A2g lying at the region of 600--700nm of all these complexes. But, the PA spectra of different complexes have a apparent difference. According to Fig.1, we find the separations between absorption bands of ^{4}T1gy(^{4}F)--^{4}T1g(^{4}P) and ^{4}T1gy(^{4}F)--^{4}A2g transitions have a evident tendency: d<a<b<c, see Table 1. On the other hand, the peak width of ^{4}T1g(^{4}P) (indicates the split strength of ^{4}T1g(^{4}P) spectrum term) in Fig.1 are in such a order: a<b<c<d.

In ligand field theory, we have suggested a wave function scaling radial theory of non-free ions used to discuss the electronic structures of transition metal complexes[11]. And a Program package used for the calculation of Ligand Field Theory (PLFT) has also been finished. The d-d transition energy levels of complexes may be calculated by PLFT with their crystal structure data. The calculated results of complexes in this work are presented in Table 1 and the calculated values are in good agreement with the experimental fitting ones.

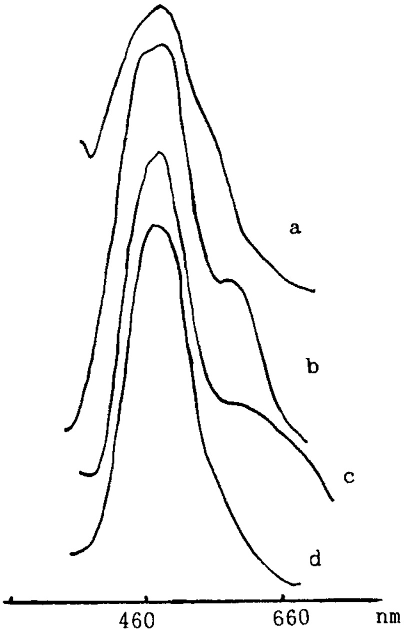

FIG.1 The PA spectra of MCo-EDTA complexes.
a, $Ca[Co(EDTA)H_2O]\cdot 4H_2O$; b, $Sr[Co(HEDTA)H_2O]_2\cdot 4H_2O$;
c, $Ba[Co(HEDTA)H_2O]_2\cdot 4H_2O$; d, $Co(H_2EDTA)\cdot 3H_2O$.

TABLE 1.
The Energy Levels of MCo-EDTA Complexes (cm^{-1}).

energy levels	complexes						
	Ba/Co		Sr/Co		Ca/Co		Co-
	cal.	obv.	cal.	obv.	cal.	obv.	obv.
$^{4}T_{1gy}(^{4}F)$	0.	0.	0.	0.	0.	0.	0.
$^{4}A_{2g}(^{4}F)$	13913.	14142.	15762.	16544.	15220.	16800.	17200.
$^{4}T_{1gz}(^{4}P)$	18100.	17494.	19250.	19173.	19460.	19210.	19180.
$^{4}T_{1gy}(^{4}P)$	18940.	19329.	20448.	20335.	20410.	20320.	20220.
$^{4}T_{1gx}(^{4}P)$	21760.	21284.	23197.	21498.	21320.	22720.	21300.

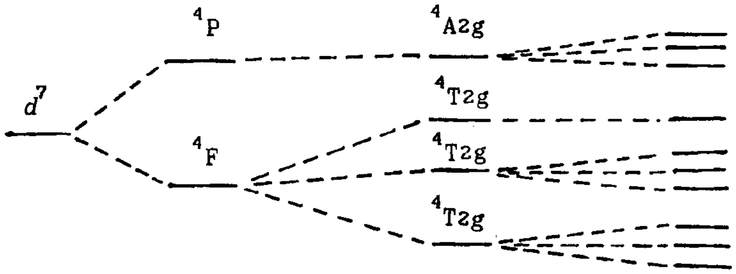

FIG.2 Energy levels of d^7 configuration (only tetra-state).

We know that all the macroscopic properties of matters are decided by its microscopic structures. In the weak ligand field theory, the *d* electron configuration will produce series spectrum terms for the electron mutual effect, and the spectrum terms will be split to series branch spectrum terms for the ligand field effect. In the lower symmetry crystal field, the spectrum terms will have a forward splits. As to Co^{2+} ion, d^7 configuration has such a energy levels split figure, see Fig.2. The first step split is decided by electron mutual effect of central ion, and then the second split step is decided by the strength of ligand field, the third split step is controlled by the symmetry of ligand field.

In ethylene diamine tetra acetic acid complex system, the EDTA molecule can present six donor atoms and forming five chelating rings with the central ion: one ethylene diamine ring (E-ring), two glycinic rings (R-ring) and another two glycinic rings (G-ring)[12]. And the structure properties of EDTA complexes are mostly decided by these chelating rings. Certainly, if the EDTA group can only present five donor atoms, there only four chelating rings exist in coordination structure. According to the crystal structural data we find: in $Co(H_2EDTA)\cdot 3H_2O$ complex[6], six donor atoms are presented by H_2EDTA^{2-} group forming five chelating rings, in Ba/Co-EDTA[13] or Sr/Co-EDTA[14] complexes, $HEDTA^{3-}$ presents five donor atoms and form four chelating rings, in Ca/Co-EDTA complex[15], $(EDTA)^{4-}$ also presents five donor atoms, but in this complex, a weak Co-O(EDTA) bond is existed, its bond length is 2.743A. So, in this MCo-EDTA complex system, the complex $Ca[Co(EDTA)H_2O]\cdot4H_2O$ is existed as a structural transfer state during the changes of these coordination groups. As to a coordination group, one more chelating ring will bring a small freedom of space puckered and strained. And it will make the coordination group to form a low symmetry, large split energy levels system. In this system, the split of spectrum term $^4T_{1g}(^4P)$ in crystal field will be large. On the other hand, the existed of salt metal ions are also the reason to form lower symmetry of coordination group. However, different metal ion certainly have different effect. Ba^{2+} has a large ion radius (1.35A) and the distance between Ba^{2+} to central ion are also large, and the distortion of coordination structure is also small in this system. So, the split strength of spectrum term $^4T_{1g}(^4P)$ in crystal field of this series will have this order: Ba/Co-EDTA < Sr/Co-EDTA < Co-EDTA < Ca/Co-EDTA. As to $Co(H_2EDTA)\cdot3H_2O$ complex, it has puckered and strained chelating rings, but without any effect of salt metal ions. So, its split strength of spectrum term $^4T_{1g}(^4P)$ is small than that of Ca/Co-EDTA and large than that of Sr/Co-EDTA complex. And this is corresponding to the experimental PA spectra, see Fig.1.

In this series complexes, the strength of ligand field is also variable for the existed of salt metal ions. In complex $Co(H_2EDTA)\cdot3H_2O$, central ion Co(II) forms a seven coordination bonds system. In Ca/Co complex, the seventh coordination bond is very weak. And in Sr/Co, Ba/Co complexes, they are six coordination bond system. So the strength of ligand field is increased in this order: Co < Ca/Co < Sr/Co < Ba/Co. It indicates that the second step split strength of Fig.2 will increased in such a order. On the other hand, there exists some weak mutual effect between salt metal ion and central ion, it makes the electron mutual effect term to be strong. Just for this two kind of effects, the transition energies between $^4T_{1g}(^4F)$--$^4A_{2g}$ increase in above order. And it is verified in PA spectra by the separations between the 510nm band ($^4T_{1g}(^4P)$) and band at about 660nm ($^4A_{2g}(^4F)$).

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