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EPR Spectroscopic Investigation of Mn^{+2} Acesulfam Metal Complex, $[Mn(acs)_2(H2O)_4]$

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Abstract

In this study, the structure of Mn^{+2} doped $[Mn(acs)_2(H2O)_4]$ acesulfame metal complex was investigated by EPR spectroscopy. Transition metal ion complexes have important applications in both science and technology. Some of these complexes are formed using paramagnetic metal ions Mn^{+2}, VO^{+2}, Cu^{+2}, Fe^{+3}, Cr^{+3} and therefore are analyzed with EPR spectroscopy to provide structural information. The synthetic sweetener acesulfame is widely used in food and medicine and has widely used in cosmetics. The reason for widespread use depends basically on that acesulfame is easily digested and is not deposited in the body. In addition, acesulfame used as ligands in transition metal complexes show thermochromic and solvatochromic properties. In this study, mixed ligand complex $Mn(acs)_2(H2O)_4$ was produced and crystallized and examined with EPR spectroscopy. Structure of the complex and behaviors at different temperatures were discussed.

Keywords: EPR, acesulfame, metal complex, thermochromism, solvatochromism.

Mn^{+2} katkılı $[Mn(acs)_2(H20)_4]$ Asesülfam Metal Kompleksinin EPR Spektroskopisi İle İncelenmesi

Öz

Bu çalışmada Mn^{+2} katkılı $[Mn(acs)_2(H2O)_4]$ asesülfam metal kompleksinin yapısı EPR spektroskopisi ile incelenmiştir. Geçiş metali iyon kompleksleri hem bilim hem de teknolojide önemli uygulamalara sahiptir. Bu komplekslerin bazıları, paramanyetik metal iyonları Mn^{+2}, VO^{+2}, Cu^{+2}, Fe^{+3}, Cr^{+3} kullanılarak oluşturulur ve yapısal bilgi sağlamak için EPR spektroskopisi ile analiz edilir. Sentetik tatlandırıcı asesülfam, gıda, tıp ve kozmetikte yaygın şekilde kullanılır. Yaygın kullanımın nedeni temel olarak asesülfamın kolayca sindirilmesine ve vücutta birikmemesine bağlıdır. Ek olarak, geçiş metali komplekslerinde ligandlar olarak kullanılan asesülfam, termokromik ve solvatokromik özellikler gösterir. Bu çalışmada, karışık ligandkompleksi $Mn(acs)_2(H2O)_4$ üretilmiş ve kristalleştirilmiştir. Daha sonra EPR spektroskopisi ile incelenmiştir. Kompleksin yapısı ve farklı sıcaklıklardaki davranışları tartışılmıştır.

Anahtar Kelimeler: EPR, asesülfam, metal kompleks, termokromizm, solvatokromizm.

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Introduction

Electron Paramagnetic Resonance (EPR) spectroscopy is capable of giving valuable information about the type and structure of paramagnetic species in host materials in liquid, bulk, powder and especially single crystal forms. Since in concentrated samples the magnetic dipole due to unpaired spins interact with each other and broadens the spectral transition lines, the paramagnetic species must be very dilute and can rarely be detectable by other spectroscopic techniques. Complexes of paramagnetic transition metals Cu^{+2}, Mn^{+2}, Fe^{+3}, Cr^{+3} and V^{+4} is one of the important subject of EPR spectroscopy. Structural information, molecular orbital parameters and dynamic behaviors can be obtained from EPR spectroscopic studies. The synthetic and non-caloric sweetener acesulfame is commercially found as acesulfame potassium salt and is used mainly as food additive, chemical reagent in drugs and cosmetics. The surveys on cancer risk reached the result that acesulfame sweetener has almost no cancer risk with the ratio of 90%. Acesulfame potassium salt, ($C_4H_5SO_4NK$), is a compound chemically known as oxathiazinone dioxide, and systematically named as 6-methyl-1,2,3-oxathiazin-4(3H)-one2,2-dioxide. Acesulfame has chemical similarities with other synthetic sweeteners like saccharine [1].

Acesulfame has also chemical and physical importance due to its capability of forming ligands in various forms with transition metal complexes, and some mixed ligand complexes exhibit chromic properties which is a reversible color change of some special compounds under some external physical or chemical effects like solvent, temperature, pressure and light, and some acesulfame complexes exhibits solvatochromic property, [2, 3].

EPR spectroscopy is a very sensitive to spectroscopic technique to investigate paramagnetic species in substances with liquid, solid, powder, single crystal and glassy phases; [4-10].

In this paper, EPR spectroscopic investigation of complex of Mn^{+2} ion formed with acesulfame and aqua ligands $Mn(acs)_2(H_2O)_4$ to determine the structure and behavior under different temperatures.

Materials and Methods

Sample Preparation

$[Mn(acs)_2(H_2O)_4]$ was synthesized as follows: 0.02 mol$Mn(ClO_4)_2.6H_2O$ was dissolved at 70 ^oC in 100 ml 1:1 ethanol-water mixture, and then 0.04 molacesulfame potassium salt dissolved in 25 ml of 1:1 alcohol-water solution was added to the mixture. The resultant solution was stirred at 70 ºC in a water bath until all solvent was evaporated. The substance again was dissolved in alcohol-acetone mixture to precipitate the residual $KClO_4$ and the solution was left for slow evaporation for purification by crystallization. The microcrystals were selected and were dissolved again in 2-dichloroethane and left for slow evaporation to obtain larger single crystals. The single microcrystals of $Mn(acs)_2(H_2O)_4$ grown at suitable sizes in the solution were chosen to study by EPR spectroscopy. A single crystal of suitable size and the powder obtained by grinding microcrystals were used to obtain powder EPR spectra and estimations were made on both single and powder spectra.

EPR spectrometer

The X-band EPR spectra were recorded using a Varian E-109 Line Century Series spectrometer equipped with a Varian E-231 TE-102 rectangular cavity. The microwave frequency and power were kept at 9.52 GHz and 2 mW respectively. The spectra of single crystals were taken by mounting the crystals on tip of quartz rod of goniometer graded in one degree and powder samples were recorded by using quartz sample tube. The spectrometer frequency was corrected using DPPH (dihenylpicrylhydrazyl,g=2.0036) reference sample.

Results and Discussion

In this study, $[Mn(acs)_2(H_2O)_4]$ sample was not diluted in another host lattice and therefore both single crystal and powder spectra gave single broad envelope due to Mn^{2+}- Mn^{+2} dipolar interaction. EPR spectrum is shown in Figure 1a. Rotation of single crystals in magnetic field gave the same broad envelope, same as powder spectrum; therefore further investigations were made with powder sample.

The room temperature EPR spectrum covers an envelope approximately 500 Gauss, which is accepted as wide range. The Mn^{2+} centered spectrum is explained with the Hamiltonian

$$H = H_Z + H_{hf} + H_{ZFS} \tag{1}$$

where H_Z is Zeeman interaction term, H_{hf} is hyperfine interaction term and H_{ZFS} is zero-field splitting (ZFS) term. The explicit expressions of corresponding terms are given by as

$$H_Z = \mu_B B \cdot g \cdot S \tag{2}$$

$$H_h = A_X S_X I_X + A_Y S_Y I_Y + A_Z S_Z I_Z \tag{3}$$

$$H_{ZFS} = D[S_{Z^2} - S(S+1)/3] + E[S_{X^2} - S_{Y^2}]$$

$$+(a/6)\left[S_{X^2}+S_{y^2}+S_{Z^2}-S(S+1)(3S^2+3S-1)/5\right] \quad (4)$$

In the equations *D*, *E* and *a* are axial, rhombic and cubic components of ZFS, respectively. The other parameters are usual parameters of EPR spectroscopy.

The electron spin of Mn^{+2} ion is S = 5/2 and nuclear spin is I = 5/2. This spin system, without superhyperfine splitting due to nonzero nuclear spins of atoms at ligand positions, should give five groups of six lines, summing up to 30 transition lines. The five groups emerge from spin-spin dipolar interaction of 5 electrons occupying 3d orbital of Mn^{+2} ion and six lines in each group emerge from hyperfine interaction with nuclear spin of 5/2.

We take g=2.01. The hyperfine values of Mn^{+2} have values between 75×10^{-4} cm^{-1} and 95×10^{-4} cm^{-1}. *D* and *E* parameters, however, show relatively large variations depending on the structure and distortion of the complexes. In regular octahedral and tetrahedral structures, the value of *D* is about two or three times the hyperfine splitting, while *E* is smaller than or nearly equal to hyperfine values. When axial or rhombic distortions occur in the complex, the values of *D* and *E* increase up to 600×10^{-4} cm^{-1} and 300×10^{-4} cm^{-1} respectively. Therefore, the anisotropies and hence the shapes of the powder spectra depend largely on *D* and *E* parameters, [11, 12]. Cubic parameter was not determined because of its small value relative to other parameters.

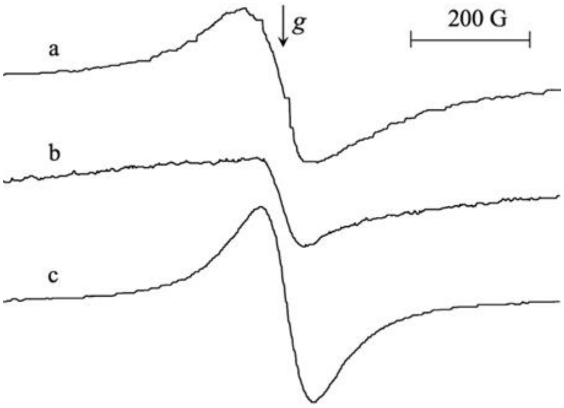

Figure 1. *EPR spectrum of [Mn(acs)$_2$(H$_2$O)$_4$] singlecrystal at (a) 30°C, (b) at 90°C and (c) at 120 °C*

The axial component of ZFS are relatively large indicating high distortion of the regular octahedral structure, where two acesulfame ligands occupy apex positions and four aqua molecules occupy equatorial positions as shown in Figure 2. When temperature is increased up to 90°C, the envelope broadens over wider range because of increasing axial *D* and equatorial *E* parameters.

When temperature is increased more up to 120°C, the symmetry of the complex shifts toward cubic symmetry and ZFS parameters get more isotropic because of increasing vibrations of bonds which reflects highly regular tetrahedral structure which is reflected by the narrower and more symmetric envelope, Figure 1c. A previous EPR study on similar complex [Zn(acs)$_2$(H$_2$O)$_4$] with trace amount Mn^{2+} impurity gives almost the same results determined by means of Mn^{+2} impurity spectra at different temperatures and DTA analysis; [13]. Since the spectra recovers original spectrum at room temperature, dependent changes of the complex are reversible in given range.

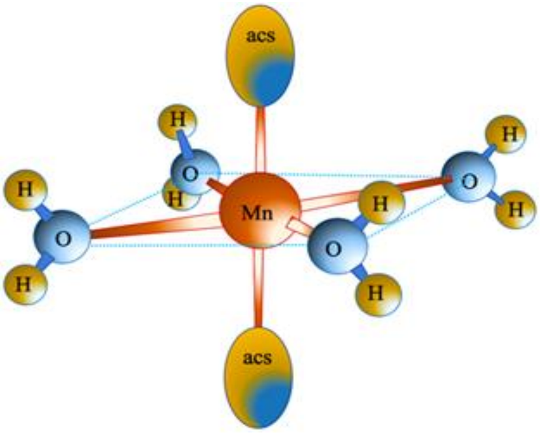

Figure 2. *Suggested [Mn(acs)$_2$(H$_2$O)$_4$] structure. Aqua ligands occupy equatorial plane and acesulfame ligands occupy apex positions.*

Conclusions

In this study, [Mn(acs)$_2$(H$_2$O)$_4$] complex was studied. In the complex [Mn (acs)$_2$(H$_2$O)$_4$], it was observed that the complex loses some of the ligands with temperature, and the width and amplitude of the envelope change. If [Mn(acs)$_2$(H$_2$O)$_4$] can be diluted in another diamagnetic mesh, its detailed structure can be examined.

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