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Chemical effects on the K_β/K_α X-ray intensity ratios of Mn, Ni and Cu complexes

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Abstract. Chemical effects on the K_β/K_α X-ray intensity ratios for some Mn, Ni, and Cu complexes of a new schiff-base with salen N_2H_2 type were investigated. The samples were excited by 59.543 keV γ-rays from a ^{241}Am annular radioactive source. K X-rays emitted by samples were counted by a Si(Li) detector with resolution 157 eV at 5.9 keV. We observed the chemical effect on the K_β/K_α X-ray intensity ratios for Mn, Ni and Cu complexes. The experimental results showed that the K_β/K_α X-ray intensity ratios for compounds with complexes are generally larger than those with salt form. The experimental values have been compared with the other experimental and the theoretically calculated values of pure elements. The results are in very good agreement with the others.

PACS. 32.30.Rj X-ray spectra – 32.70.Fw Absolute and relative intensities

1 Introduction

The schiff-base reaction formed by the condensation of amine with an aldehyde is known as one of the oldest reactions in chemistry [1]. Schiff-base ligands coordinate to a metal through the amine nitrogen and another group, usually oxygen, situated on the original aldehyde [2–10]. The salen ligand was obtained from combination of a diamine with two equivalent of salicylaldehyde [11]. The ligands possess two covalent and two coordinate covalent sites situated in a planar array. This makes the ligands ideal for the equatorial coordination of transition metals, leaving the two axial sites open for ancillary ligands. They are very much like porphyrins in this regard, but unlike porphyrins, the salen ligands are easy to prepare and inexpensive [12]. The first reviews in this area published in 1966 appeared as a demonstration of evidence for the tremendous amount of transition-metal chemistry that has been conducted [13]. By incorporating additional groups around the phenol portion of ligands such as ^{t}Bu, OR ($R = CH_3$ etc.), and X (Cl, Br, I), the ligands can be made highly soluble in aryl and alkyl solvents. This form of the ligand has been used to great effect in Mn derivates for olefin epoxidations [14]. In the same way, incorporation of hydrophilic groups may also lead to ligands that are soluble in water and alcohols. The malleability inherent to the salen ligands has led to their extensive use in transition-metal chemistry, particularly in modeling enzymes and in catalysis [14]. More recent applications include use as metal containing liquid-crystalline polymers [15], as non-radioactive models for Tc [16], as antiviral agents [17], and in asymmetric catalysis [18]. The structural formulae of the salen ligand and complexes used in this paper were illustrated in Figure 1.

The physical state and chemical combination of elements affect the characteristic X-rays. It is well-known experimentally and theoretically that K_β/K_α X-ray intensity ratios in $3d$ elements depend on the chemical environment and the excitation mode [19–30]. In earlier studies, the influence of chemical effects has shown differences in the K_β to K_α X-ray intensity ratios up to nearly 10%. Such chemical effects can be caused either by a varying $3d$ electron population or by the admixture of $3p$ states from the ligand atoms to the $3d$ states of the metal or both. In fact, anything that alters the $3d$ wave function can alter the ratio, such as a change in the $3d$ electron population and the number of ligand atoms. The change of the $3d$ electron population of the transition metal atom in the chemical compound modifies $3p$ orbitals of the atom stronger than $2p$ orbitals, which must be followed by a change of the K_β/K_α X-ray intensity ratios of the metal atoms in the compound. Due to the importance of the K_β/K_α intensity ratios for elemental analysis and many other subjects, many investigations have been done in the past. Tamaki et al. [31,32] reported a general increase of the K_β/K_α intensity ratios with increasing formal oxidation number and a large spread of the intensity ratios for different compounds at a fixed oxidation number. Mukoyama et al. [33] who investigated the elements Mn and Cr showed that

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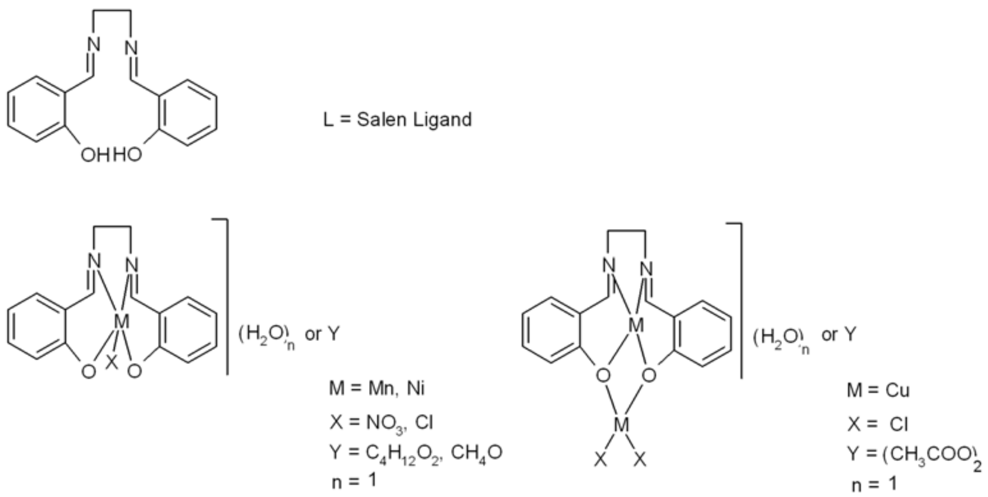

Fig. 1. The structural formulae of salen ligand and its complexes.

the K_β/K_α intensity ratio of compounds with tetrahedral symmetry is, in general, larger than that with octahedral symmetry. Brunner et al. [19] found deviations up to 5% for different compounds of Cr, Mn, Fe and Cu by precise PIXE measurements and explained the results of the change in screening of $3p$ electrons by a varying $3d$ valence charge and polarization effects. Chang et al. [23] observed that for strongly covalent V compounds, K_β/K_α intensity ratios are significantly high.

2 Experiment

The schiff base ligand (L = $C_{16}H_{14}N_2O_2$) was prepared by condensation of the aldehyde and the diamine in 2:1 molar ratio, and refluxing in absolute methanol for 5 h [34–36]. The complexes illustrated in Figure 1 Mn(L)(NO_3) [37], [Mn(L)]·H_2O [38], [Mn(L)Cl]·H_2O [39], [Ni(L)]·$C_4H_{12}O_2$ [40], Ni(L) [40], [Ni(L)]·CH_4O [40], [Cu(L)]·H_2O [41], Cu_2(L)Cl_2 [42], Cu(L)(CH_3COO)$_2$ [41] were prepared according to published procedures. Pure metal salts were obtained commercially by Aldrich. Purity of the materials was better than 99%. Powder samples were sieved for 400 mesh and prepared by supporting on Mylar film at 2–80×10^{-4} g cm^{-2} mass thickness. A Si(Li) solid state detector with a resolution of 157 eV at 5.9 keV and Nucleus II software with a pulse height analyzer were used to count the characteristic K X-rays emitted from the samples. The experimental set-up is shown in Figure 2.

The K_β/K_α intensity ratios values have been calculated by using the following equation

$$\frac{I(K_\beta)}{I(K_\alpha)} = \frac{N(K_\beta)}{N(K_\alpha)}\frac{\varepsilon(K_\alpha)}{\varepsilon(K_\beta)}\frac{\beta(K_\alpha)}{\beta(K_\beta)}, \tag{1}$$

where $N(K_\alpha)$ and $N(K_\beta)$ are the counts observed under peaks corresponding to K_α and K_β X-rays; $\varepsilon(K_\alpha)$ and $\varepsilon(K_\beta)$ are the efficiencies of the detector for the K_α and K_β series of X-rays, respectively. $\beta(K_\alpha)$ and $\beta(K_\beta)$ are the target self-absorption correction factors for both the incident and the emitted radiations. I_0 is the intensity of the incident radiation and G is a geometrical factor. In the present experimental set-up, the $I_0G\varepsilon$ values were determined in a separate experiment. The product $I_0G\varepsilon$, containing the terms related to the incident photon flux, geometrical factor and absolute efficiency of the X-ray detector, was determined by collecting the K_α and K_β X-ray spectra of samples of Ca, V, Co, Cu, Y, Mo, Cd, Te, Ba, Nd and Tb in the same geometry and calculated by using the following equation

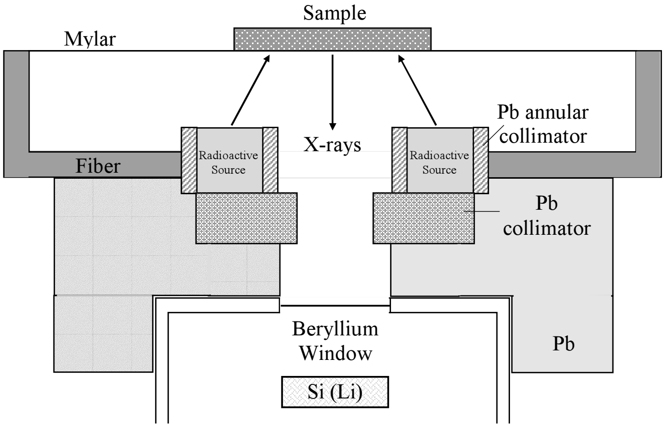

Fig. 2. The experimental set-up.

$$I_0G\varepsilon = \frac{N_{K_i}}{\sigma_{K_i}\beta_{K_i}t}, \tag{2}$$

where N_{K_i} is the number of K_α or K_β X-rays recorded at K_α or K_β peaks, and σ_{K_i} is the σ_{K_α} or σ_{K_β} fluorescence cross-section. The self-absorption correction factor has been calculated by using an expression obtained by assuming that the incidence angle of the fluorescence X-rays subtended at the detector was approximately 90°

$$\beta = \frac{1-\exp[-(\mu_{\text{inc}}/\cos\phi+\mu_{\text{emt}})t]}{(\mu_{\text{inc}}/\cos\phi+\mu_{\text{emt}})t} \tag{3}$$

Table 1. K_β/K_α X-ray intensity ratios of Mn, Ni and Cu complexes.

Element and compounds	$I(K_\beta)/I(K_\alpha)$	Oxidation state	Other experimental [45]	Theoretical [25]
$Mn(NO_3)_2{\cdot}4H_2O$	0.126±0.011	+2		
$Mn(L){\cdot}(NO_3)$ [37]	0.154±0.013	+2		
$MnCl_2{\cdot}4H_2O$	0.128±0.008	+2		
$[Mn(L)]{\cdot}H_2O$ [38]	0.158±0.014	+2		
$Mn(CH_3COO)_2{\cdot}4H_2O$	0.135±0.011	+2		
$[Mn(L)Cl]{\cdot}H_2O$ [39]	0.189±0.015	+3		
Mn	0.127±0.006	0	-	0.1342
$Ni(NO_3)_2{\cdot}6H_2O$	0.130±0.009	+2		
$[Ni(L)]{\cdot}C_4H_{12}O_2$ [40]	0.144±0.013	+2		
$NiCl_2{\cdot}6H_2O$	0.137±0.010	+2		
Ni(L) [40]	0.142±0.008	+2		
$Ni(CH_3COO)_2$	0.157±0.014	+2		
$[Ni(L)]{\cdot}H_2O$ [40]	0.116±0.006	+2		
Ni	0.141±0.012	0	0.1359	0.1361
$Cu(NO_3)_2{\cdot}3H_2O$	0.132±0.009	+2		
$[Cu(L)]{\cdot}H_2O$ [41]	0.146±0.012	+2		
$CuCl_2$	0.136±0.011	+2		
$Cu_2(L){\cdot}Cl_2$ [42]	0.141±0.013	+2		
$Cu(CH_3COO)_2{\cdot}H_2O$	0.110±0.007	+2		
$Cu(L)(CH_3COO)_2$ [41]	0.111±0.006	+2		
Cu	0.137±0.011	0	0.1373	0.1366

$L = C_{16}H_{14}N_2O_2$

where μ_{inc} and μ_{emt} are the mass attenuation coefficients (cm^2g^{-1}) of the incident photons and emitted characteristic X-rays, respectively [43]; and t ($\text{g}\,\text{cm}^{-2}$) is the measured mass-thickness of the sample. The angles of incident photons with respect to the surface of the samples ϕ were equal to 45° in the present set-up.

3 Results and discussion

The measured values of the K_β/K_α intensity ratios for Mn, Ni and Cu complexes of a new schiff-base with salen N_2H_2 type are presented in Table 1. The overall error in the present measurement is estimated to be 4–10%. This error is attributed to the uncertainties in different parameters used to deduce K_β/K_α values; namely, the area evaluation under the K_α and K_β X-ray peak ($\leq 3\%$), absorption correction factor ratio ($\leq 2\%$), detector efficiency ($\leq 2\%$) and determination of target thickness ($\leq 3\%$) and other systematic errors ($\leq 2\%$).

In Table 1, we observed chemical effects on the K_β/K_α X-ray intensity ratios. Chemical bonding type (ionic, metallic, and covalent) affects the K_β/K_α intensity ratios. The individual characteristics of the structure of molecules, complexes and crystals (polarity, valency, and electronegativity of atoms, co-ordination number, ionicities of covalent bond, etc.) also affect the K_β/K_α intensity ratios. A change in chemical bond leads to a change in its valance electron density. The effect of the electronegativity, the nature of the ligands and the distribution of ligands around the central emitting atoms are some of the factors which may cause this variation [44].

The changes of the K_β/K_α X-ray intensity ratios for Mn, Ni and Cu in the complexes can also be interpreted as due to changes in the electron population of the valance bands ($3d$ and $4s$). For the $3d$ transition metals, the change in the number of $3d$ electrons is the only important contribution for the change in the K_β/K_α intensity ratio and the effect of changing $4s$ and $4p$ electrons can practically be neglected. In fact, the change in the number of $3d$ electrons modifies $3p$ orbitals much more strongly than $2p$ orbitals, which must be followed by substantial modification of K_β transitions and almost no modification of K_α transitions. This leads to a change in the K_β/K_α X-ray intensity ratio [28]. In addition, the effect of $3d$ electron screening on $3p$ electrons leads to a change in the K_β/K_α X-ray intensity ratios [19,20].

Rebohle et al. [46] found deviations of only 1–5% for the K_β/K_α X-ray intensity ratios in the case of Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn for some compounds. For Ti and V, no significant dependence of chemical state on the K_β/K_α intensity ratio was observed, but the absolute K_α and K_β X-ray yields show a strong dependence on the chemical state of Ti and V. It was reported that K_β/K_α intensity ratios increase with increasing formal oxidation number of the elements for Cr, Mn, Co and Cu compounds [21,47] but except for $[Mn(L)Cl]{\cdot}H_2O$, we could not carry out any comparison between K_β/K_α intensity ratio and the formal oxidation number of the element in the complexes due to the nearly constant oxidation number.

The chemical effect on the K_β/K_α X-ray intensity ratios of Mn, Ni and Cu complexes have been studied experimentally. The present experimental results indicate that the K_β/K_α X-ray intensity ratios for compounds with complexes are, in general, larger than those with salt form. These results also indicate that K X-ray spectroscopy for the $3d$ element is very useful for studying the electronic structure of chemical compounds.

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