X-Ray Photoelectron Spectra of Manganese(III), Iron(III), Nickel(II), Copper(II) and Zinc(II) Schiff Base Complexes

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We measured X-ray photoelectron spectra of manganese(III), iron(III), nickel(II), copper(II) and zinc(II) Schiff base complexes with a variety of coordination structure. Relation between the magnetic susceptibility and satellite peaks was examined.

1. Introduction

The 2p XPS spectra on the first row transition metal oxides or complexes with paramagnetism have frequently been found to have some satellite peaks in the higher energy regions above each main peak (See Fig. 1). The relation between the intensity of the 2p satellite and the magnitude of the magnetic moment has been previously investigated for a variety of transition metals complexes, such as Cu(II), Co(II), Ni(II), and Zn(II) complexes by Frost *et al.* [1,2], Borod'ko *et al.* [3], Fujiwara, Ikeda, Kawai *et al.* [4-9].

According to the study of Ghijsen *et al.* [10], it has been clarified that satellite peaks reflect the valence-electron configuration of the ground state, and that the main peaks reflect a charge transfer state.

In the present work we investigate the dependence between the magnetic moment and the 2p satellite intensity of the XPS spectra for the class of Schiff base complexes. We try to consider the effect of various factors, such as structure symmetry, covalency and basic electronic configuration of the central metal atom, chemical structure of the binding radical, by analysing a large variety of Ni(II), Cu(II), Zn(II), and Mn(III), Fe(III) complexes.

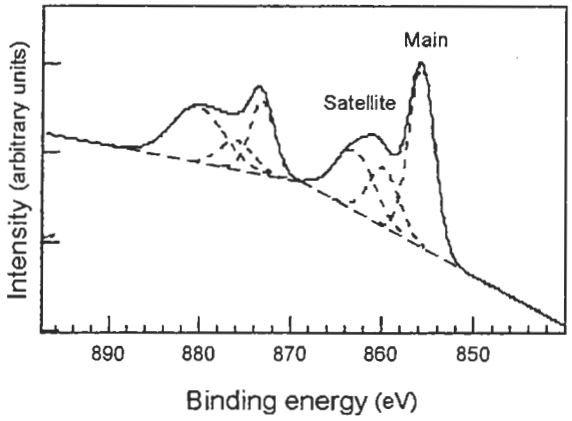
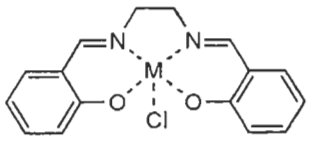


Fig. 1 Schematic illustration for peak separation between main and satellite peaks and background

2. Experimental

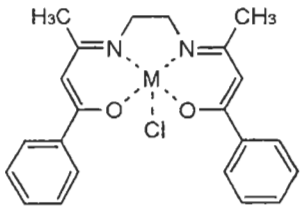
The XPS spectra were measured on a Rigaku XPS-7000 spectrometer. Mg Kα (1253.6 eV) X-ray line was used as the excitation source (the applied power was typically 10 kV and 30 mA). The abscissa of the chart was the binding energy and the ordinate was the intensity of photoelectrons in counts/0.5sec. The step size was 0.1 eV (except for zinc(II) complexes: 0.05 eV) with a dwelling time of 0.5 sec. The sample complexes were ground to fine powder form, dusted onto a double-backed adhesive tape with electronic conduction, and set inside the measuring chamber automatically. The measurements were run at room temperature under a vacuum below 10^{-6} Pa. The pass energy of the spherical electron energy analyzer was 15 eV. The blank carbon tape was measured and then the C1s electron line was 286.0 eV. To compensate for any sample charging effects, the calibration of the spectra was done using the C 1s electron line from the carbons present in the samples. The spectra for the complexes possessed two peaks due to the carbons directly connected to oxygen atoms such as carbonyl. The binding energy of the latter was lower than that of the former, and was taken to be 284.6 eV. The resolution of overlapping peaks in measured transition metal 2p spectra was carried out by non-linear least squares procedures [11] to give the six calculated Gaussian peaks in order to evaluate the area ratio ($I = A_{sat}/A_{main}$) of transition metal $2p_{3/2}$ satellite peaks to their main peaks (Refer to Fig.1). The magnetic susceptibility was measured at room temperature by Gouy method.

The names of complexes and their abbreviations are tabulated in Table 1. The chemical structures and abbreviations of manganese(III), iron(III), nickel(II), copper(II) and zinc(II) Schiff base complexes are shown as follows:

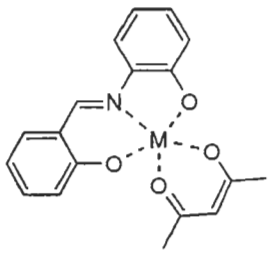


M(salen)Cl

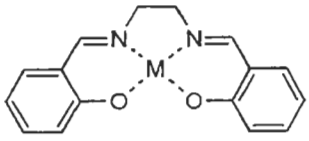
M = Mn(III), Fe(III)



M(BE)Cl

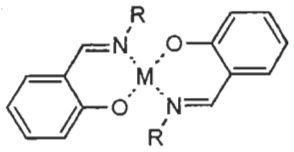


M(*N*-PhO-sal)(acac)



M(salen)

M = Ni(II), Cu(II), Zn(II)



M(*N*-R sal)$_2$

R = n-Pro : —CH_2—CH_2—CH_3 iso-Pro : —CH(—CH_3)—CH_3

n-Bu : —CH_2—CH_2—CH_2—CH_3 iso-Bu : —CH_2—CH(—CH_3)—CH_3

sec-Bu : —CH(—CH_3)—CH_2—CH_3 tert-Bu : —C(—CH_3)(—CH_3)—CH_3

Table 1 The names and abbreviations of manganese(III), iron(III), nickel(II), copper(II) and zinc(II) Schiff base complexes.

Name of complex	Abbreviation
chloro(*N,N'*-ethylenebissalicylideneaminato)manganese(III)	Mn(salen)Cl
chloro[*N,N'*-ethylenebis(1-phenyl-3-imino-1-butanonato)]manganese(III)	Mn(BE)Cl
(*N*-hydroxyphenyl-salicylideneaminato)(acetylacetonato)manganese(III)	Mn(*N*-PhO-sal)(acac)
chloro(*N,N'*-ethylenebissalicylideneaminato)iron(III)	Fe(salen)Cl
chloro[*N,N'*-ethylenebis(1-phenyl-3-imino-1-butanonato)]iron(III)	Fe(BE)Cl
(*N*-hydroxyphenyl-salicylideneaminato)(acetylacetonato)iron(III)	Fe(*N*-PhO-sal)(acac)
(*N,N'*-ethylenebissalicylideneaminato)nickel(II)	Ni(salen)
bis(*N*-n-propylsalicylideneaminato)nickel(II)	Ni(*N*-n-Pro sal)$_2$
bis(*N*-iso-propylsalicylideneaminato)nickel(II)	Ni(*N*-iso-Pro sal)$_2$
bis(*N*-n-butylsalicylideneaminato)nickel(II)	Ni(*N*-n-Bu sal)$_2$
bis(*N*-iso-butylsalicylideneaminato)nickel(II)	Ni(*N*-iso-Bu sal)$_2$
bis(*N*-sec-butylsalicylideneaminato)nickel(II)	Ni(*N*-sec-Bu sal)$_2$
bis(*N*-tert-butylsalicylideneaminato)nickel(II)	Ni(*N*-tert-Bu sal)$_2$
(*N,N'*-ethylenebissalicylideneaminato)copper(II)	Cu(salen)
bis(*N*-n-propylsalicylideneaminato)copper(II)	Cu(*N*-n-Pro sal)$_2$
bis(*N*-iso-propylsalicylideneaminato)copper(II)	Cu(*N*-iso-Pro sal)$_2$
bis(*N*-n-butylsalicylideneaminato)copper(II)	Cu(*N*-n-Bu sal)$_2$
bis(*N*-iso-butylsalicylideneaminato)copper(II)	Cu(*N*-iso-Bu sal)$_2$
bis(*N*-sec-butylsalicylideneaminato)copper(II)	Cu(*N*-sec-Bu sal)$_2$
bis(*N*-tert-butylsalicylideneaminato)copper(II)	Cu(*N*-tert-Bu sal)$_2$
(*N,N'*-ethylenebissalicylideneaminato)zinc(II)	Zn(salen)
bis(*N*-n-propylsalicylideneaminato)zinc(II)	Zn(*N*-n-Pro sal)$_2$
bis(*N*-iso-propylsalicylideneaminato)zinc(II)	Zn(*N*-iso-Pro sal)$_2$
bis(*N*-n-butylsalicylideneaminato)zinc(II)	Zn(*N*-n-Bu sal)$_2$
bis(*N*-iso-butylsalicylideneaminato)zinc(II)	Zn(*N*-iso-Bu sal)$_2$
bis(*N*-sec-butylsalicylideneaminato)zinc(II)	Zn(*N*-sec-Bu sal)$_2$
bis(*N*-tert-butylsalicylideneaminato)zinc(II)	Zn(*N*-tert-Bu sal)$_2$.

3. Results and Discussion

The presence of the $K\alpha_{3,4}$ x-ray emission line in the standard Mg x-ray source causes a "satellite" structure on the lower binding energy side of the 2p XPS spectra. These peaks have a relative intensity of approximately 10 % of the peaks excited by principal $K\alpha_{1,2}$ lines [12], and appear about 10 eV lower on the binding energy side. On the other hand, some satellite peaks often exist on the higher binding energy side of the main peaks, and their properties and origin are the object of the present study.

The measured 2p XPS spectra for all the transition metals in various Schiff base complexes are shown in Figs. 2 - 6.

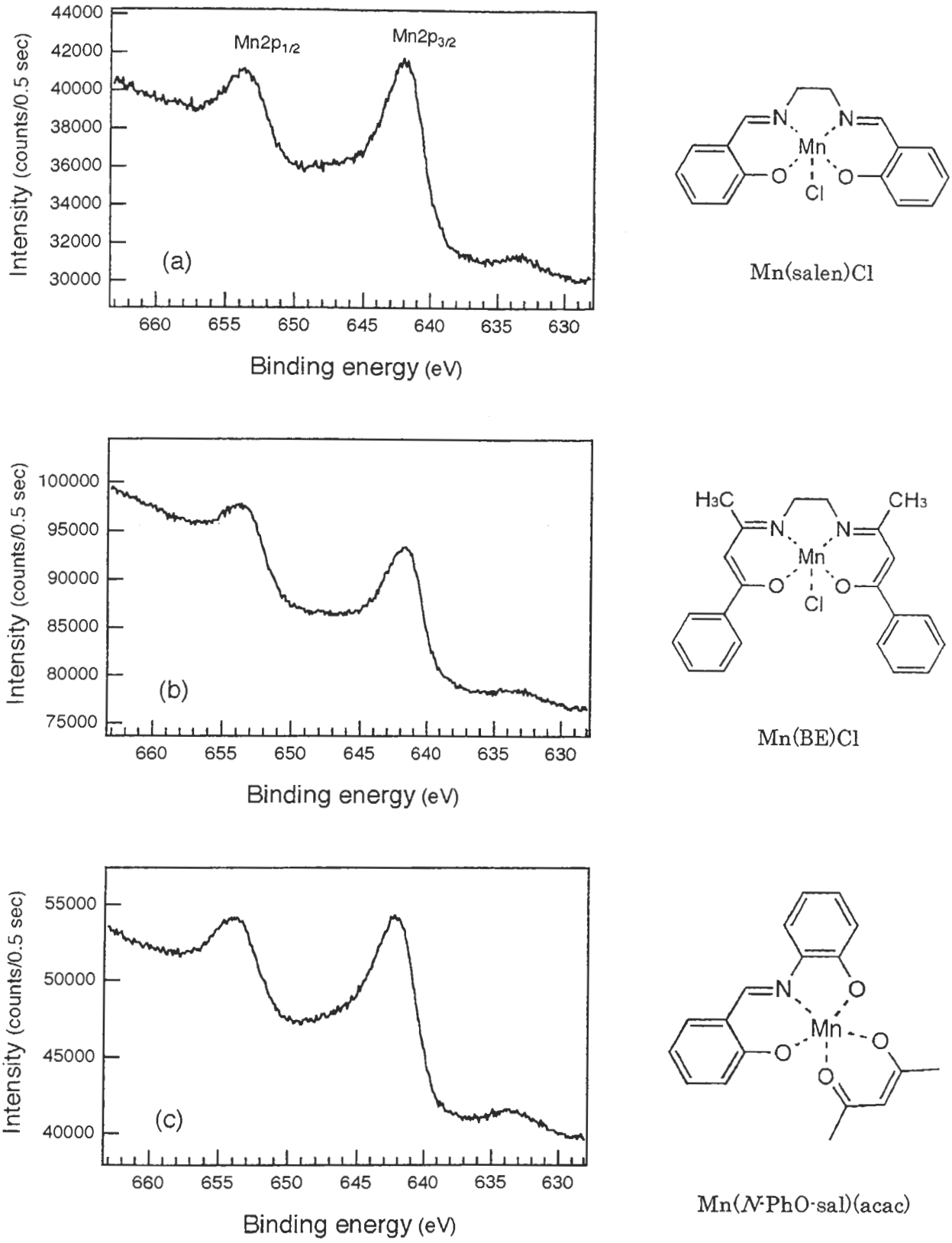
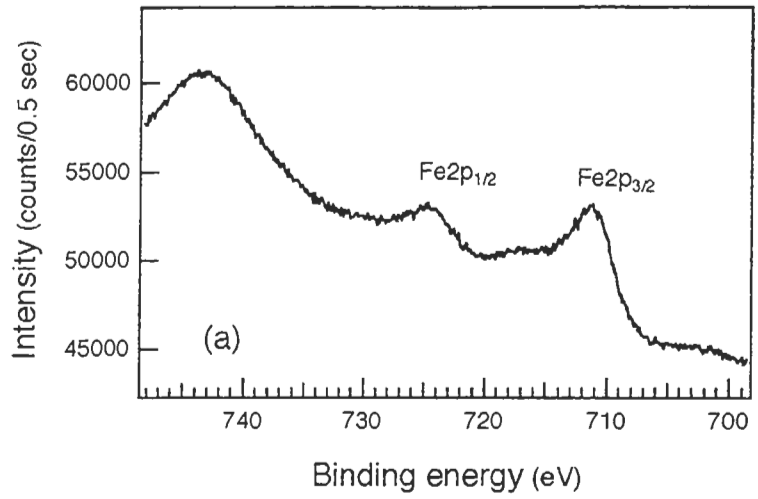
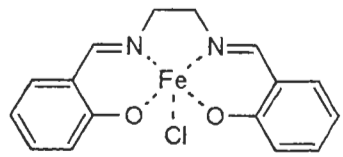
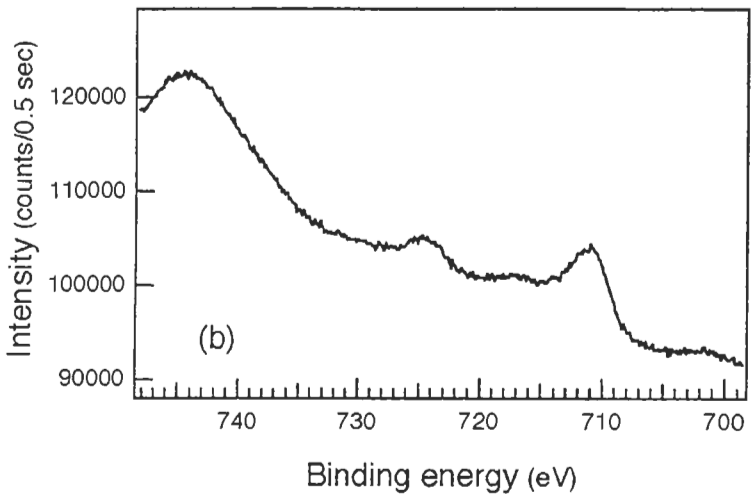


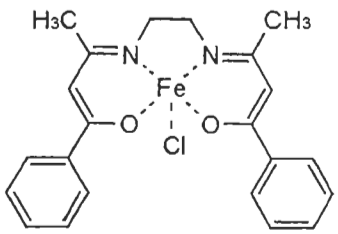
Fig. 2 Mn 2p XPS spectra and chemical structures for manganese(III) complexes.



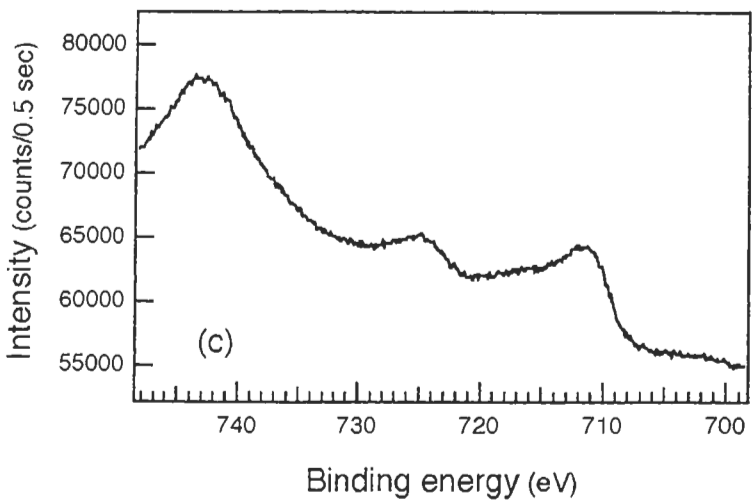


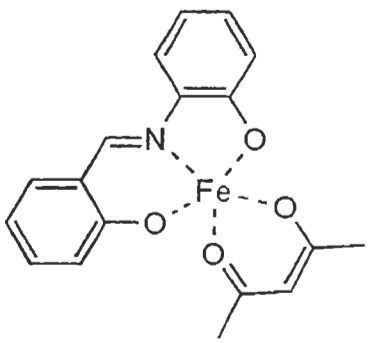
Fe(salen)Cl





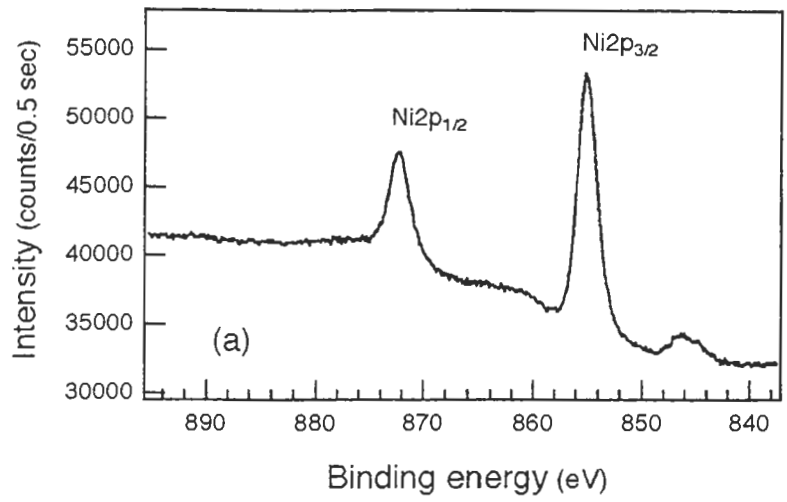
Fe(BE)Cl

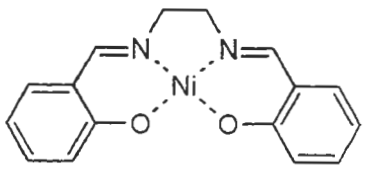




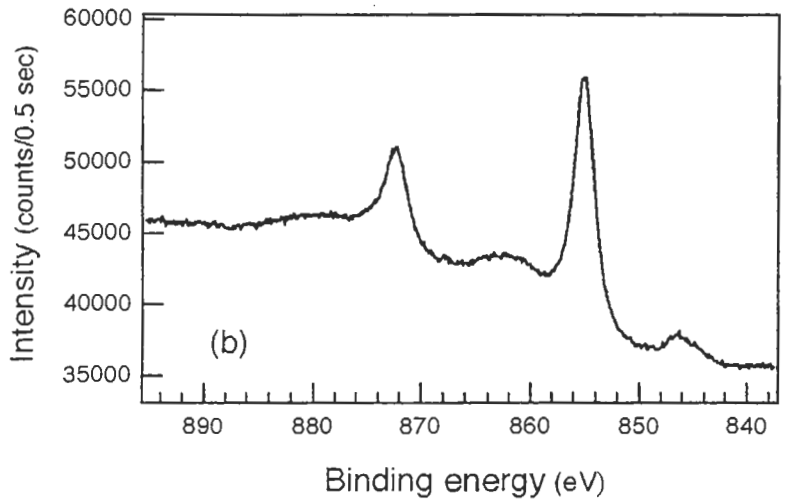
Fe(*N*-PhO-sal)(acac)

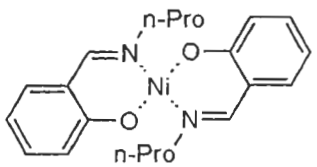
Fig. 3 Fe 2p XPS spectra and chemical structures for iron(III) complexes.



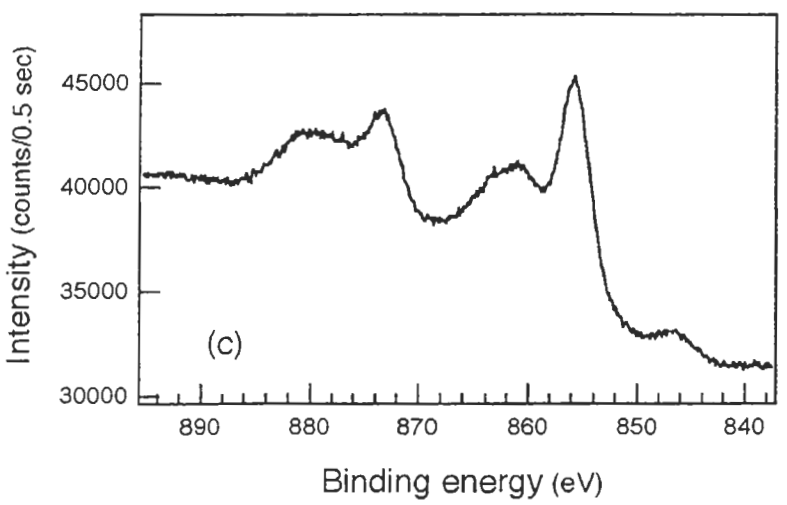


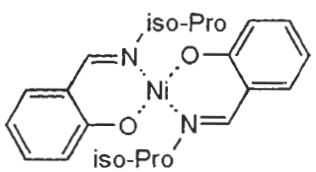
Ni(salen)





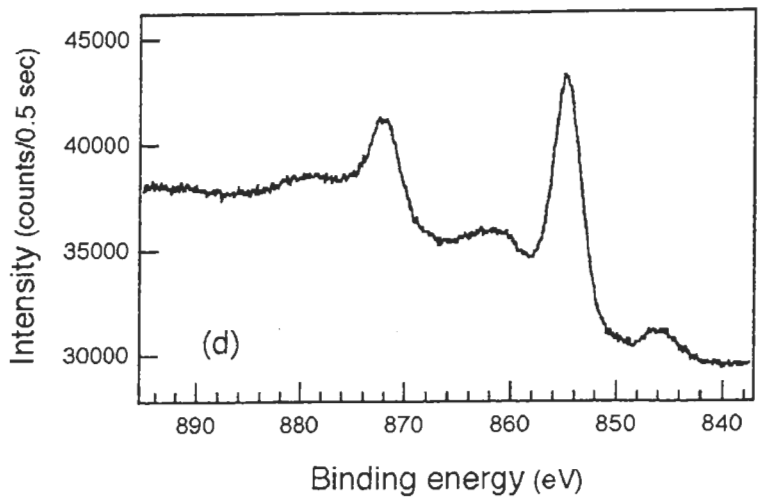
Ni(*N*-n-Pro sal)$_2$

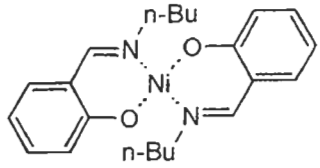




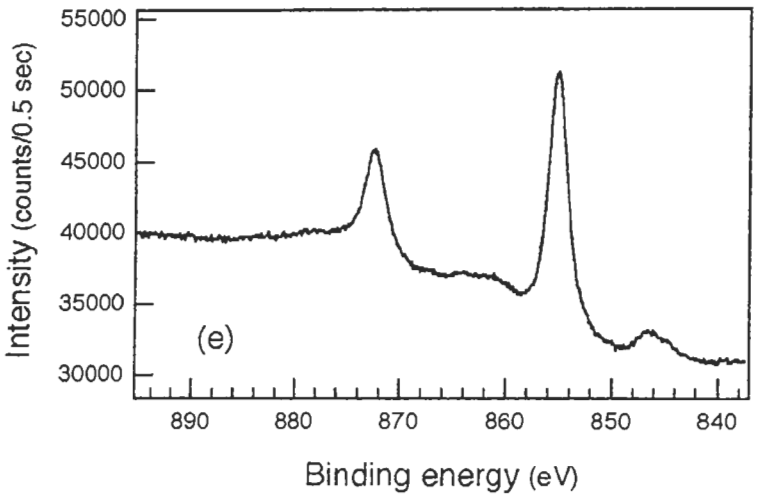
Ni(*N*-iso-Pro sal)$_2$

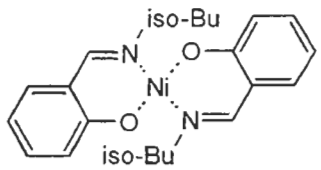
Fig. 4 Ni 2p XPS spectra and chemical structures for nickel(II) complexes (continued).



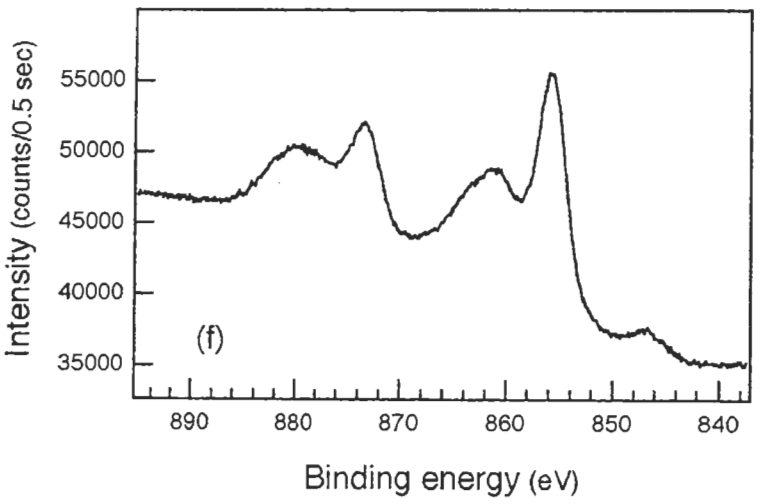


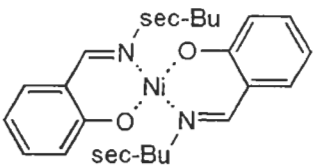
Ni(*N*-n-Bu sal)$_2$





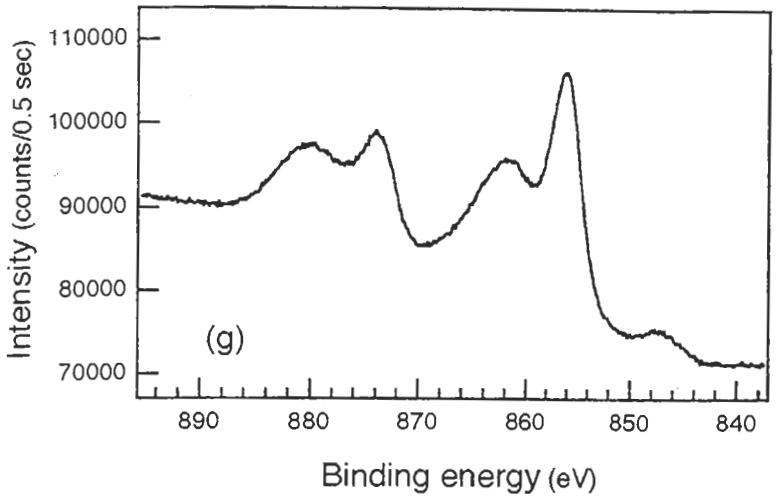
Ni(*N*-iso-Bu sal)$_2$

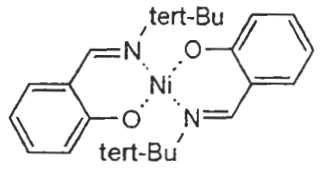




Ni(*N*-sec-Bu sal)$_2$

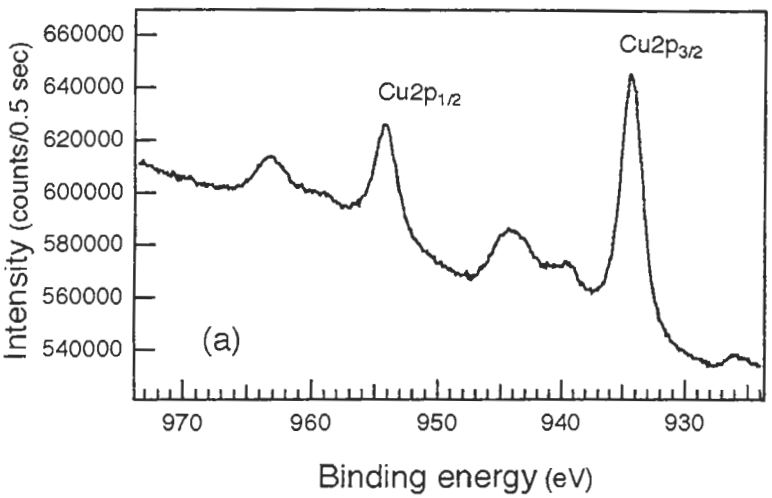
Fig. 4 Ni 2p XPS spectra and chemical structures for nickel(II) complexes (continued).

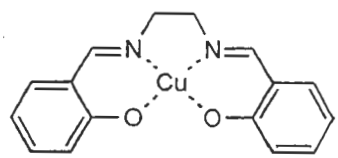




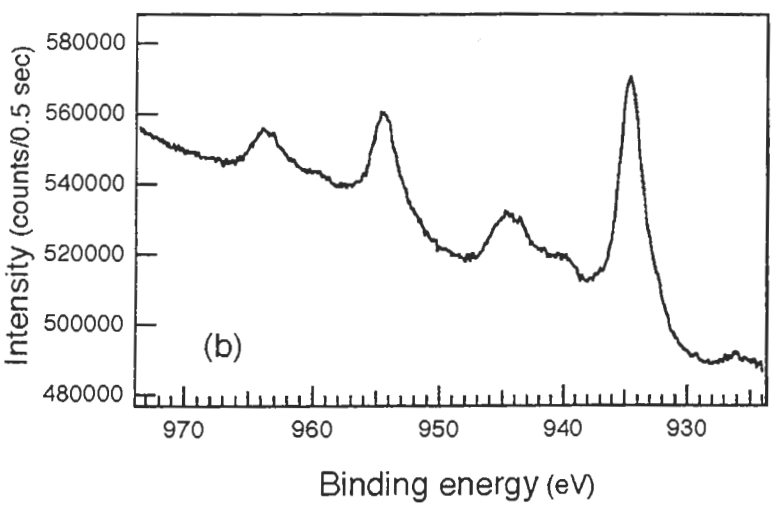
Ni(*N*-tert-Bu sal)$_2$

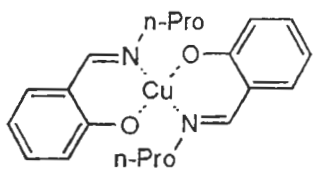
Fig. 4 Ni 2p XPS spectra and chemical structures for nickel(II) complexes.





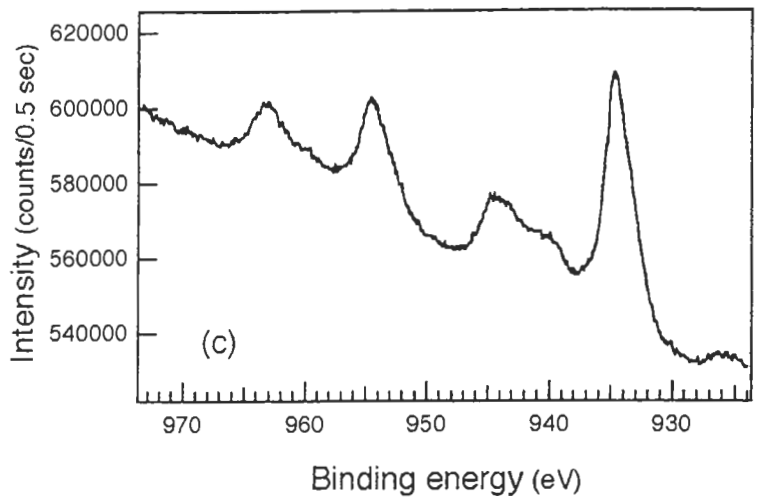
Cu(salen)

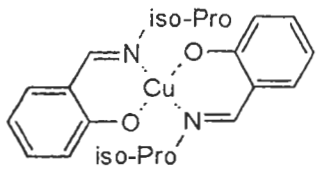




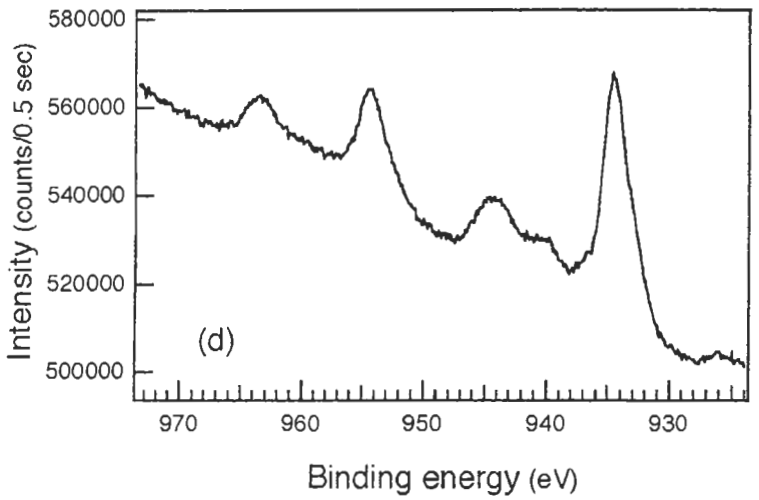
Cu(*N*-n-Pro sal)$_2$

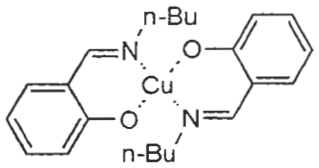
Fig. 5 Cu 2p XPS spectra and chemical structures for copper(II) complexes (continued).



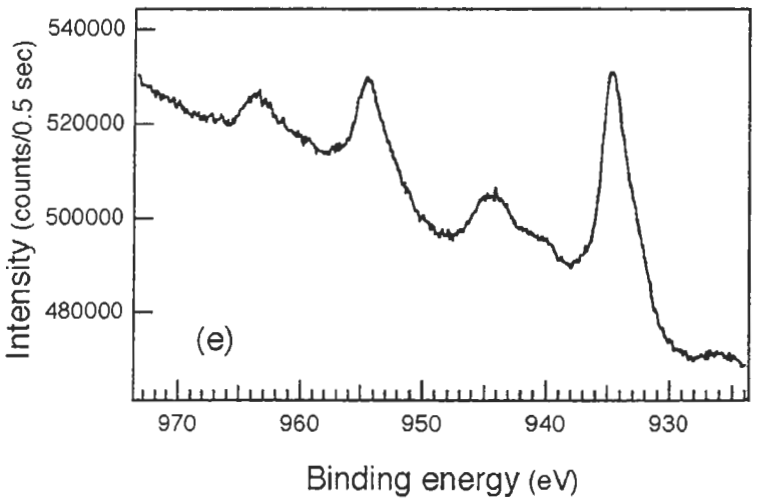


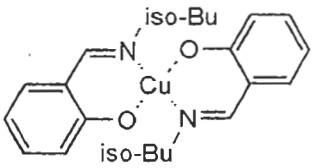
Cu(*N*-iso-Pro sal)$_2$





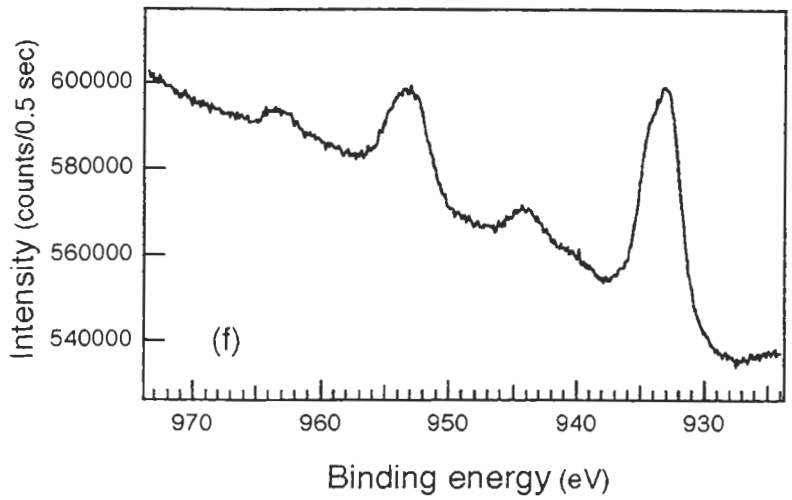
Cu(*N*-n-Bu sal)$_2$

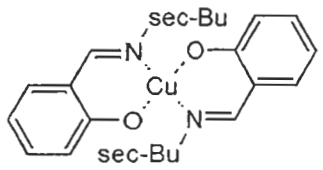




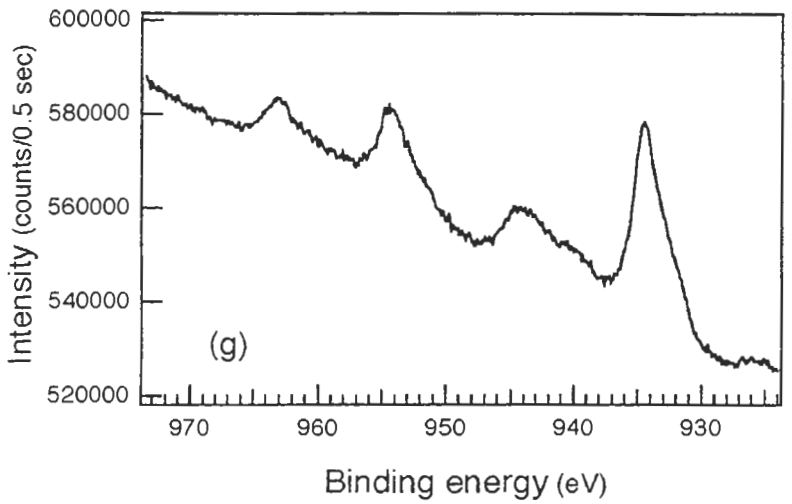
Cu(*N*-iso-Bu sal)$_2$

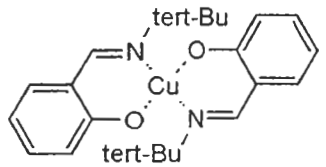
Fig. 5 Cu 2p XPS spectra and chemical structures for copper(II) complexes (continued).





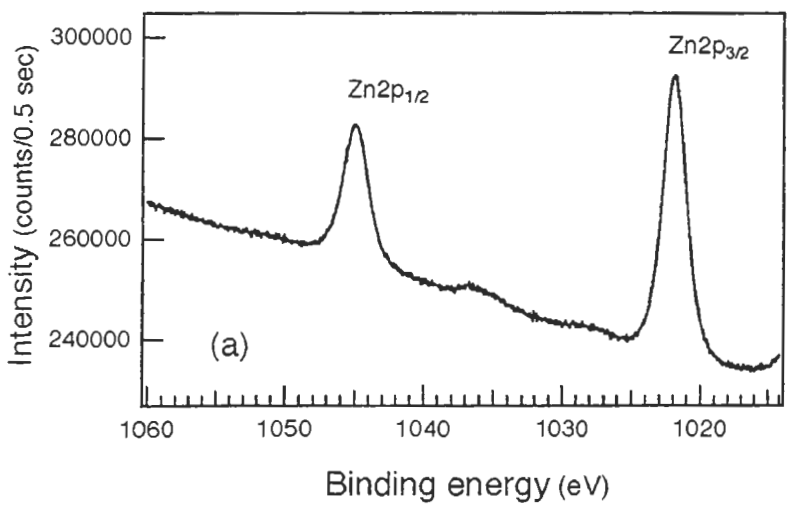
(19) Cu(*N*-sec-Bu sal)$_2$

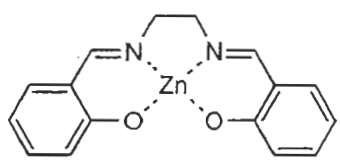




Cu(*N*-tert-Bu sal)$_2$

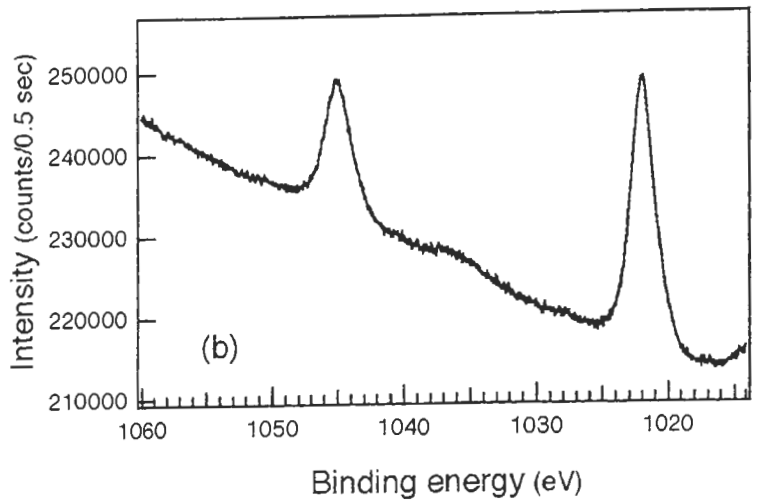
Fig. 5 Cu 2p XPS spectra and chemical structures for copper(II) complexes.

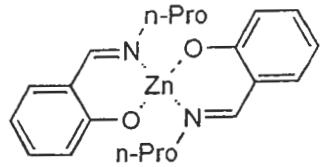




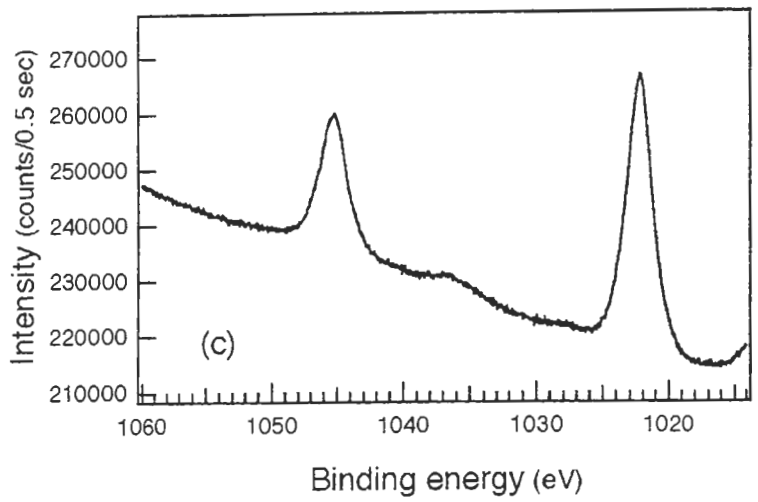
Zn(salen)

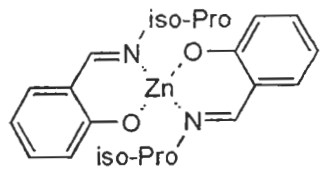
Fig. 6 Zn 2p XPS spectra and chemical structures for zinc(II) complexes (continued).



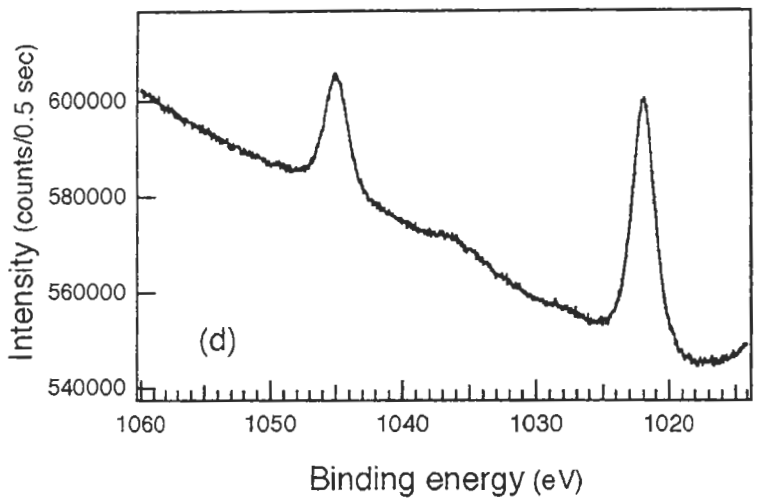


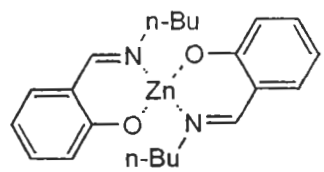
Zn(*N*-n-Pro sal)$_2$





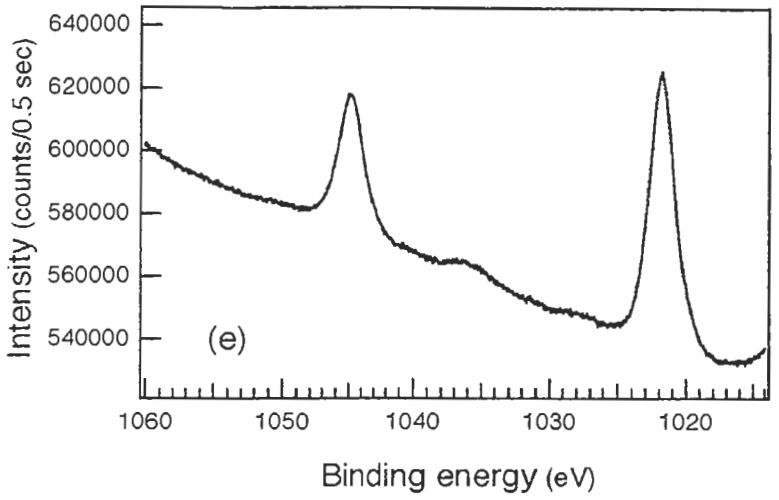
Zn(*N*-iso-Pro sal)$_2$

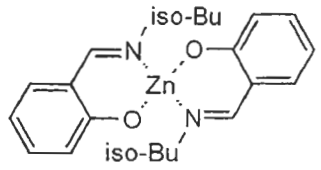




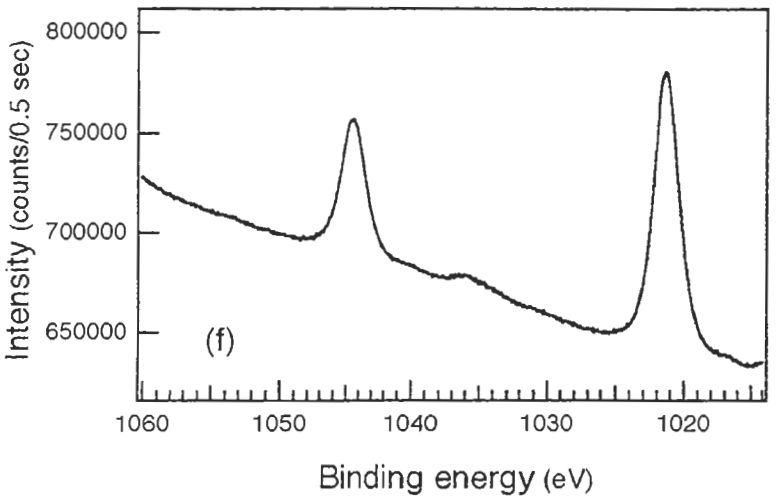
Zn(*N*-n-Bu sal)$_2$

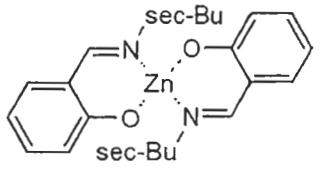
Fig. 6 Zn 2p XPS spectra and chemical structures for zinc(II) complexes (continued).



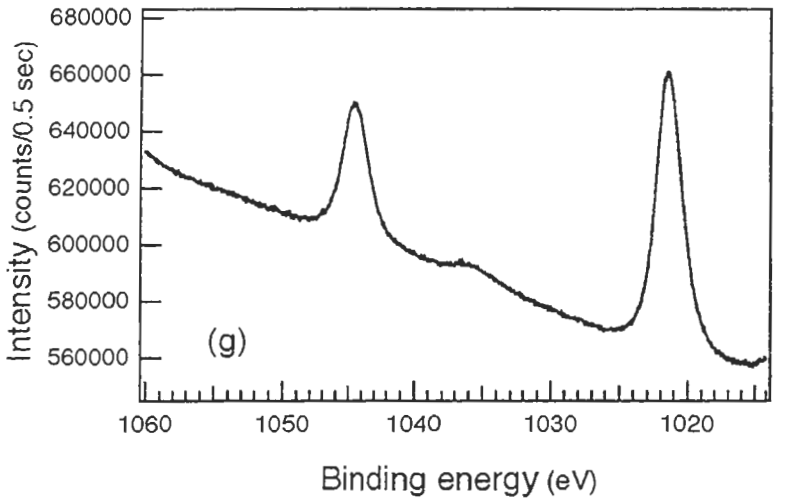


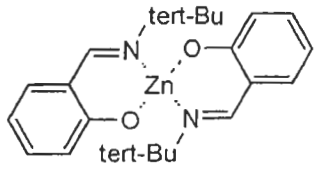
Zn(*N*-iso-Bu sal)$_2$





Zn(*N*-n-Bu sal)$_2$





Zn(*N*-tert-Bu sal)$_2$

Fig. 6 Zn 2p XPS spectra and chemical structures for zinc(II) complexes.

In the case of the manganese(III) and iron(III) complexes, the satellite on the higher binding energy side could not be separated from main peak, as the energy separation between the $2p_{1/2}$ and the $2p_{3/2}$ peak is about 12 to 14 eV, and causes the overlapping between main and satellite peak. The magnetic susceptibilities are roughly 4.8 BM for three manganese(III) complexes, and about 5.9 BM for three iron(III) complexes.

In the case of Zn(II) complexes the satellite intensity is almost negligible, as well as the magnetic susceptibility, for various radicals which build up the complex. This is due to the fact that Zn(II) has a basic $3d^{10}$ electron configuration in the valence band, and therefore the number of unpaired electrons is close to zero. In general, the zinc(II) complexes are diamagnetic.

For the Cu(II) complexes, the Cu(II) has a basic $3d^9$ configuration. As the structure of the complex changes with different radical attached to the N atom, from square planar to tetrahedral, although the electronic structure changes, the number of unpaired electrons remains constant. The magnetic susceptibility is about 1.8 BM for all complexes. The relative intensity of the satellite peak is about 60%, except for the secondary-Butyl and the tertiary-Butyl, which show a satellite relative intensity of 13% and 20% respectively. This fact shows that the magnetic moment, which is proportional to the number of unpaired electrons in the valence band, cannot show the exact electron configuration of the valence band on which the intensity of the satellite peak depends. The cause of this discrepancy will be further investigated by means of molecular orbital calculations.

For the Ni(II) complexes, the two unpaired electrons of the Ni which are due to a basic $3d^8$ configuration, the electronic configurations changes with the symmetry of the structure. The number of unpaired electrons changes from zero to two, as the structure changes from square planar to tetrahedral symmetry. Accordingly, the magnetic susceptibility increases from an almost diamagnetic state to 3.2 BM and the satellite relative intensity steadily increases with the increase of the magnetic susceptibility, from about 6% to almost 80%.

The relative intensity of the satellite to the main $2p_{3/2}$ peak, together with the corresponding magnetic susceptibility (μ) and structure symmetry for the nickel(II) and copper(II) complexes are summarized in Table 2.

Table 2 The nickel(II) and copper(II) Schiff base complexes, their structure symmetry, magnetic susceptibilities (μ), and the transition metal satellite relative intensity of the $2p_{3/2}$ peaks.

Ni complex	Ni(*N*-R-sal)$_2$	*Symmetry*	*μ (BM)*	*I*
Radical R	n-Butyl	Planar	Diamagnetic	0.09
	iso-Butyl	Planar	0.07	0.06
	n-Propyl	Planar	0.41	0.15
	iso-Propyl	Tetrahedral	3.18	0.65
	sec-Butyl	Tetrahedral	3.17	0.58
	tert-Butyl	Tetrahedral	3.20	0.80
Cu complex	*Salen or* Cu(*N*-R-sal)$_2$	*Symmetry*	*μ (BM)*	*I*
	Cu(salen)	Planar	1.80*	0.63
Radical R	n-Butyl	Planar	1.79*	0.53
	iso-Butyl	Planar	1.77*	0.45
	n-Propyl	Planar	1.76*	0.56
	iso-Propyl	Tetrahedral	1.92*	0.62
	sec-Butyl	Tetrahedral	1.81*	0.14
	tert-Butyl	Tetrahedral	1.85*	0.20

* Ref.[7]

4. Conclusions

We measured X-ray photoelectron spectra of manganese(III), iron(III), nickel(II), copper(II) and zinc(II) Schiff base complexes with a variety of coordination structure and examined the relation between magnetic susceptibility and satellite peak relative intensity.

From the facts described above, it is found that there is a relation between the value of I and of μ, which is however affected by the electronic structure of the valence band, the symmetry of the structure and binding radical. In near future, we intend to calculate the electronic configuration of these Schiff base complexes by the DV-Xα method and to elucidate the relation between the electronic structure in the valence band and the satellite intensity, and the magnetic susceptibility

Acknowledgments

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(1) Add, if possible, further descriptions and discussions on the relations between satellite intensities and the symmetry around the metal atom, and between satellite intensity and magnetic susceptibility.

Answer: Please see new table 2 and Results and Discussion section.

(2) Did the authors observe radiation (X-ray or electron) damage during the measurement?

Answer: No x-ray or electron radiation damage has been observed during the measurement.

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This paper and the data in it will be very valuable in the field of metal complexes. However, authors should describe more motivations and aims of this paper in the section of 'Introduction', and the description also should be refined. And, it may be better to discuss in the section of 'Results and Discussion'.

1. Introduction: It should be better to describe why the authors refer to the references 1 to 9, how were those references and the opinion of the authors. These descriptions will also refine this section.

Answer: Other parts have been changed or corrected according to the refine indications.