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STRUCTURE INVESTIGATION OF METAL COMPLEXES BY MEANS OF X-RAY EMISSION AND PHOTOELECTRON SPECTROSCOPY

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ABSTRACT

The ability of the Ni L α , β , S KB, O K α , and Ni 2p spectra to distinguish between chemical states of atoms and their various environments is applied for structural characterization of nickel coordination compounds. In addition to the well documented influences of metal oxidation state and the electronegativity, the dependence of the energy shifts and intensity ratios upon the coordination geometry and the chelate ligand structure is discussed.

INTRODUCTION

A large number of experimental and theoretical studies during the last twenty years has shown that much could be learned about chemical bonding from X-ray emission (XES) and X-ray photoelectron spectroscopy (XPS). Much of this work was associated with electronic structure calculations which have been used to interpret the experiments as well as to establish the validity of theoretical models /1/. The potential of XES and XPS for probing the electronic structure of transition metal compounds has been demonstrated also in numerous contributions to the conference proceedings of this series. The intention of our early experiments /2-4/ was to find the correct explanation for the fine structure of X-ray emission bands using semiempirical as well as ab initio and SW X α MO calculations. New instrumentation for fluorescence excitation in the ultrasoft X-ray region enabled us now to record all the X-ray emission bands of interest with high resolution, necessary for identification of the electronic charge fractions contributing to the individual molecular orbitals.

Most of the XES investigations are combined with the results of photoelectron spectroscopy because core-hole initial and final states involved in both methods and complementary valence band information are available. An interesting and even now controversial topic of the XPS research is concerned with the origin of satellite structure in core electron emission. The satellites occurring 5 eV or more higher in binding energies than the main peaks $2p_{3/2}$ and $2p_{1/2}$ in heavy transition metals and their compounds are not predicted by ligand field theory and can be attributed to two-bound hole final states. To account for the satellites, interaction of 3d with the ligand p orbitals has been examined. With Ni compounds, screening by ligand-to-metal charge transfer causes the main line which is to be attributed to $3d^9 L$ valence electron configuration with a hole L in an appropriate ligand level /5,6/. The satellite line is due to unscreened $3d^8$ core hole electron emission with a HOMO-LUMO transition /7/. In every case the metal 3d - ligand p mixing influences substantially the satellite structure.

The scope of this report is limited to the interpretation of the XES and XPS intensity distribution in terms of details of chemical bonding. The effects of composition and geometry of the coordination sphere and the oxidation state of the Ni ion in complex compounds with mono- and bidentate ligands, the latter chelating via N, O, P, and S, on the O $K\alpha$, S $K\beta$, and Ni $L\alpha, \beta$ emission bands and the Ni 2p spectra are analysed. In order to confirm the interpretation by ligand-field arguments and the calculation of component peak areas, the molecular orbital energies and the electronic charge fractions of the individual molecular orbitals have been calculated by means of an iterative EHT method.

EXPERIMENTAL

The Ni L and O K emission bands are located in the soft X-ray region. Therefore, the spectrometer SARF-1 has to exhibit several sophisticated parameters such as a high-vacuum system, very thin window foils at the flow counter (Ar and CH_4), and a high-power X-ray tube with primary currents up to 1 A to generate sufficient secondary X-ray intensity. In the present measurement RbAP ($2d = 2.612$ nm) was used as analysing crystal. The samples were cooled by liquid nitrogen inside of the secondary anode to prevent high-temperature decomposition, and excited by X-rays from the tube operated at 6 kV with currents between 200 mA and 1 A. The self-absorption effects which are to be expected in the short-wavelength region of the bands, are assumed to be small because the Ni $L\alpha$ band profile of the metal coincides with the band profile obtained by us by primary excitation at low voltage between 2 and 3 kV /8/. The energy scales were calibrated using the Ni $L\alpha$ energy of the metal /9/ and the O $K\alpha$ energy of Li_2SO_4 /10/. The accuracy of the energy values was better than 0.2 eV. Depending on the slit width the experimental broadening of the peaks was in the case of Ni $L\alpha, \beta$ in the range 0.1 - 0.9 eV, and for O $K\alpha$ 0.3 - 0.6 eV. From the band profile fit with a deconvolution program (Marquardt's approach) Gauss/Lorentz (1/1) components have been obtained.

The XPS experiments have been carried out by means of the spectrometer VG ESCA 3 using unmonochromatized Al $K\alpha$ radiation. The binding energies are referenced to the C 1s peak at 285 eV.

RESULTS AND DISCUSSION

X-ray Emission Spectra

The X-ray emission process in the investigated Ni(II) compounds corresponds to an electron transition from the d' to the d'' configuration. Near the top of the valence band the X-ray emission intensity is expected to be dominated by transition of d electrons. The metal 3d orbitals can mix with linear combinations of 2p states of the surrounding ligands. Because of the distorted tetrahedral and planar local geometries, dipole selection rules allow numerous final states to contribute to the L emission band with an upper part dominated by the Ni $3d_{\pi}$ levels and a lower part with some d contributions to mainly σ bonded orbitals localized preferably on the ligands (d_{π} and d_{σ} respectively, see Fig. 1).

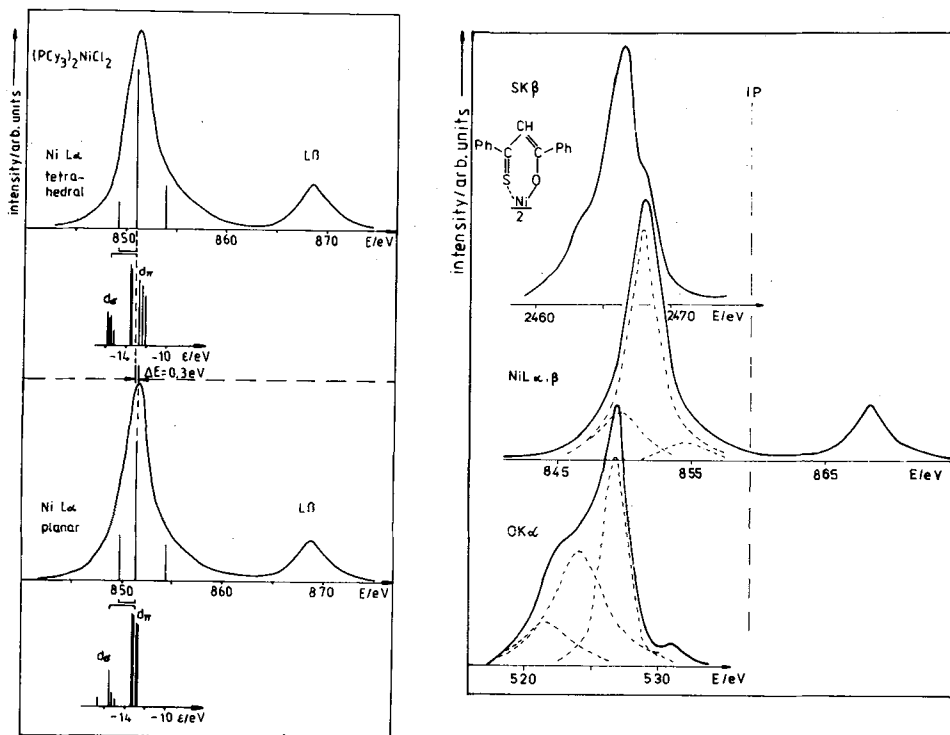


Fig. 1 Comparison of the experimental Ni L emission bands of tetrahedral and planar $(PCy_3)_2NiCl_2$ with calculated 3d charge fractions of molecular orbitals (Cy = cyclohexyle)

Fig. 2 S K β , Ni L α, β , and O K α emission bands of the Ni chelate of monothiodibenzoylmethane aligned to the corresponding ionization potentials IP

For the further discussion it is useful to examine the intensity ratio $I(L\beta)/I(L\alpha)$ too. Investigating different Mn oxides Galakhov et al. /11/ pointed out that this value rises if the number of unpaired electrons increases. This finding correlates with the growing exchange interaction between the core hole and the electrons

in an unfilled 3d shell and consequently with the magnetic properties of the compounds.

Fig. 2 shows the S KB, Ni L α , β , and O K α X-ray emission bands of the Ni chelate with monothiodibenzoylmethane aligned by the appropriate core ionization potentials (binding energy plus 5 eV). The similar energies of the low-energy L α component and the L α maximum on the one hand and the high-energy S KB structure and its band maximum on the other hand indicate the common origin of the respective final states originating from S 3p - Ni 3d orbital mixing.

The shoulder at the high-energy side of the S KB maximum indicates clearly the S 3p - Ni 3d donor-acceptor interaction. The third Ni L α component (at 854 eV) is interpreted as a multiple-ionization satellite structure.

The most intensive component in the O K α band represents the "lone pair" electrons and also π states of the C - O bond /12/. The influence of the changed local geometry of the metal on the Ni L α , β emission bands of tetrahedral and planar (PCy $_3$) $_2$ NiCl $_2$ is demonstrated in Fig. 1. For comparison, the energies and metal 3d populations of the respective molecular orbitals from our iterative EHT calculation are shown. In both cases the Ni L α band exhibits three structures: The high-energy component should be a multiple-ionization satellite; the other two components including the peak maximum are reproduced by the two groups of d $_{\sigma}$ and d $_{\pi}$ states (see above). The experimentally obtained splitting of the L α components $\Delta E_{A/B}$ is 1.8 eV (tetrahedral) and 1.6 eV (planar). The difference between these values is satisfactorily reproduced by the calculation as the separation of the gravity centres of the σ and π states (see Table 1). The theoretical values for the intensities of the low-energy component do not agree with the experiment, reflecting some limitation of the simple EHT procedure. Comparing the energies of the L α peak maxima we found a high-energy shift of 0.3 eV for the planar compound in analogy to other tetrahedral and planar species of compounds with the same ligands. The intensity ratio I(L β)/I(L α) changes in a similar way exhibiting higher values in the spectra of tetrahedral compounds (Table 1).

Configuration		L α components			$\Delta E_{A/B}$ /eV		$\frac{I(L\beta)}{I(L\alpha)}$
		A	B	C	exp.	calc.	
tetrahedral	E(L α)/eV	849.2	851.0	853.9	1.8	2.7	0.22
	I $_{rel}$ (exp.)	31	100	57			
	I $_{rel}$ (calc.)	38	100				
planar	E(L α)/eV	849.7	851.3	854.3	1.6	2.5	0.21
	I $_{rel}$ (exp.)	61	100	46			
	I $_{rel}$ (calc.)	20	100				

Table 1 Experimental and calculated data of the Ni L α , β spectra of (PCy $_3$) $_2$ NiCl $_2$

X-ray Photoelectron Spectra

In Tables 2 and 3 the Ni 2p $_{3/2}$ energies of several complex compounds are given together with the relative intensities of the main components in the satellite region. Fig. 3 shows the strong dependence of the spectra on the chemical environment.

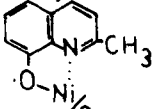
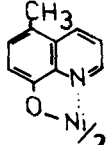
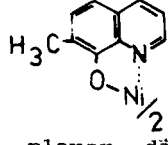
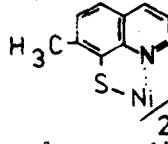
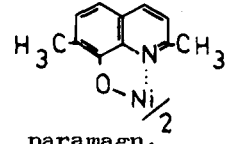
Compound	Ni 2p _{3/2}			L α		
	E _{max} /eV	ΔE_{sat} /eV	$\frac{I_{sat}}{I_{max}}$	A/eV	B/eV	I(LB)/I(L α)
(PCy ₃) ₂ NiCl ₂ tetrah., paramagn.	856.4	5.1	0.60	849.2	851.0	0.22
(PCy ₃) ₂ NiCl ₂ planar, diamagn.	854.5	-	-	849.7	851.3	0.21
(PCy ₃) ₂ NiBr ₂ tetrah., paramagn.	855.6	6.0	0.40	848.0	851.0	0.21
(PCy ₃) ₂ NiBr ₂ planar, diamagn.	854.5	-	-	849.2	851.3	0.19
 tetrah., paramagn.	855.5	5.8	0.44	848.6	851.2	0.29
 octah., paramagn.	855.7	6.0	0.45	849.5	851.1	0.22
 planar, diamagn.	855.1	-	-	848.3	851.5	0.20
 planar, diamagn.	854.8	-	-	850.2	851.4	0.17
 paramagn.	856.3	5.7	0.54			

Table 2 Energies and intensity ratios of the Ni 2p and L α spectra of complex compounds (B and A are referred to peak maximum and the low-energy shoulder of Ni L α resp.)

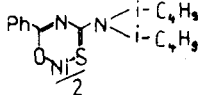
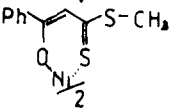
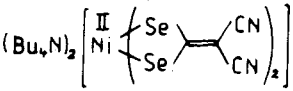
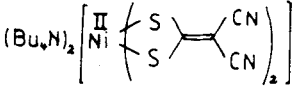
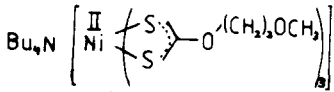
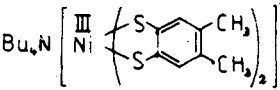
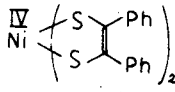
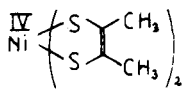
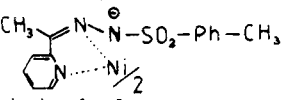
Compound	Ni 2p _{3/2}			S 2p	
	E _{max} /eV	ΔE _{sat} /eV	I _{sat} /I _{max}	N 1s	(Se 3d)
 planar, diamagn.	854.6	-	-	399.2	163.1
 planar, diamagn.	854.7	-	-	-	-
 planar, diamagn.	853.3	-	-	398.6	55.4
 planar, diamagn.	853.9	-	-	398.5	162.1
 octahedr., paramagn.	853.4	5.4	0.24	401.4	161.6
 planar, paramagn.	854.9	-	-	402.5	162.5
 planar, diamagn.	855.5	-	-	-	163.6
 planar, diamagn.	855.1	-	-	-	163.3
 tetrahedr., param.	856.0	5.6	0.32		
		8.2	0.14		

Table 3 Energies and intensity ratios of Ni 2p-, N 1s- and S 2p-spectra of complex compounds

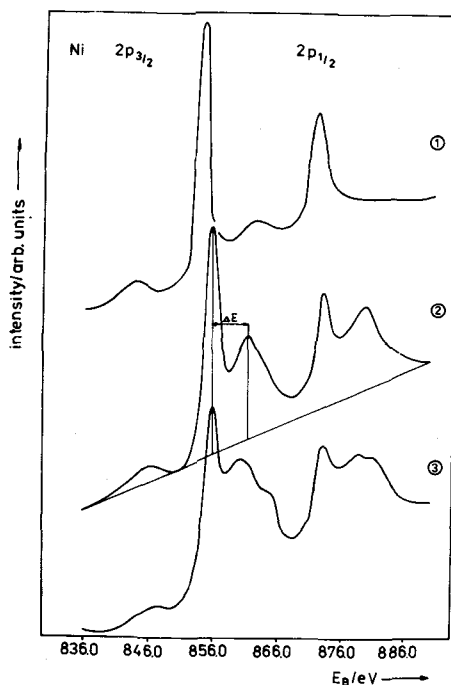


Fig. 3 Ni 2p photoelectron spectra of the diamagnetic monomeric Ni chelate of 7-methylchinoline-8-ol (1) and the paramagnetic chelates of 2-methylchinoline-8-ol (2) and acetylpyridine-p-tolyl-sulfonylhydrazone (3)

Summarizing the features we find the following connections between the parameters of the spectra and the bonding which confirm earlier results /14-16/ and reveal some new aspects:

- In all paramagnetic Ni(II) compounds one or more satellites on the high-binding energy side of the main line with varying intensity are observed.
- There is no satellite emission in planar Ni(III) and Ni(IV) compounds.
- The averaged energy difference of the Ni $2p_{3/2}$ main lines of planar Ni compounds with oxidation states II and IV with a sulfur coordination sphere is 1.6 eV.
- The Ni $2p_{3/2}$ lines of compounds with tetrahedral or octahedral coordination sphere around the Ni ion are shifted by ligand-field effects about 1.7 eV to higher binding energy with respect to the line of comparable compounds with planar geometry.
- The energy difference between the $2p_{3/2}$ main line and the satellite is larger for $(PCy_3)_2NiBr_2$ than for $(PCy_3)_2NiCl_2$ by 0.9 eV. This is in accordance to the situation found for Cu^2 dihalides /5/: The more electronegative the ligand is, the larger the energy difference between the $3d^9$ configuration and the $3d^{10}L$ configuration with a hole in an appropriate ligand level is, the smaller is the separation ΔE between the main line and the satellite. These findings contradict to the increasing satellite separation ΔE with increasing ligand electronegativity and HOMO-LUMO separation in numerous transition metal compounds /7/. For lack of optical data and theoretical results for the complex compounds studied by us, this fact remains open for discussion.

CONCLUSIONS

It has been demonstrated that the X-ray emission bands of the metal ion and all ligand atoms give more detailed information on the valence level structure of Ni complexes with mono- and bidentate ligands than studies of XPS valence bands. Otherwise, the XPS data of core electrons are more suitable to recognize the coordination geometry of the metal ion than the XES data. Therefore, the potential of both XES and XPS for structure investigations of transition metal compounds should remain useful for a long time.

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