Direct Evidence for the Formation of One-Dimensional Ni(II)–Ni(IV) Mixed-Valence Complexes by the X-Ray Photoelectron Spectra

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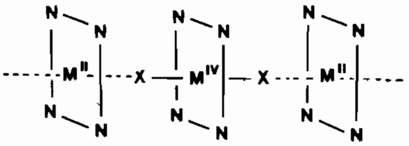
Recently a new type of nickel complex, formulated as $Ni(AA)_2ClY_2$, was reported [AA = ethylenediamine (en), 1,2-propanediamine (pn), 2,3-butanediamine (btn), or 1,2-cyclohexanediamine (chxn); Y = Cl^- or ClO_4^-] [1]. The complexes are apparently tervalent nickel but are diamagnetic, almost black in color, and have electric conductivities of the order of 10^{-7} ~ 10^{-8} Ω^{-1} cm^{-1} at room temperature [1]. We found on the basis of measurements of electronic spectra, magnetic moments and electric conductivities that $NiL^1Br(ClO_4)_2$ and $NiL^2Cl(ClO_4)_2$ also belong to the same class of compounds†, where L^1 = 1,4,7,10-tetraazacyclotridecane ([13]aneN$_4$), 1,4,8,11-tetraazacyclotetradecane ([14]aneN$_4$), or 1,4,8,12-tetraazacyclopentadecane ([15]aneN$_4$) and L^2 = 3,7-diazanonane-1,9-diamine (2,3,2-tet) or 4,7-diazadecane-1,10-diamine (3,2,3-tet). Generally, nickel complexes of this type are very sensitive to moisture and it is difficult to grow single crystals suitable for X-ray analysis.

We now report X-ray photoelectron spectra of $Ni(pn)_2Cl_3$ (*1*) and Ni([14]aneN$_4$)Br(ClO$_4$)$_2$ (*2*), along with those of reference compounds [Ni^{II}([14]aneN$_4$)](ClO$_4$)$_2$, [Ni^{III}Cl$_2$([14]aneN$_4$)](ClO$_4$), and [Ni^{III}Br$_2$([14]aneN$_4$)](ClO$_4$). Complemented with the chemical and physical properties, the spectra provide evidence that the compounds are Ni(II)–Ni(IV) mixed-valence complexes with a structure as shown below.



Square-planar divalent complexes and quadrivalent six-coordinate complexes of the *trans* dihalogeno type are alternately arranged, constructing a linear chain structure as in the well-characterized Pt(II)–Pt(IV) and Pd(II)–Pd(IV) mixed valence complexes [2–7].

Figure 1 shows X-ray photoelectron spectra of Ni2p$_{3/2}$ for *1* and *2*, along with those of Cl2p for *1*. The compounds were very susceptible to X-ray irradiation damage and thereby the spectra changed gradually with time. Spectral measurements were therefore carried out repeatedly at appropriate time intervals to extrapolate to time zero.

The Ni2p$_{3/2}$ spectra of *1* and *2* were resolved into two components by computer simulation (Fig. 1). The higher energy component (857.7 eV for *1* and

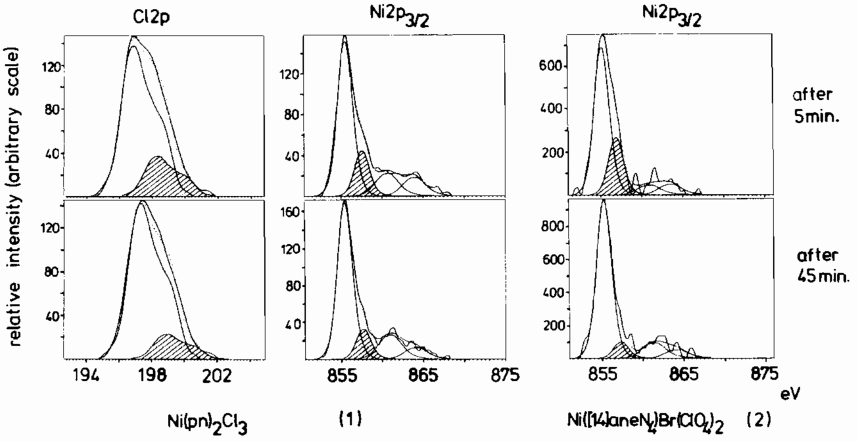


Fig. 1. X-ray photoelectron spectra of *1* and *2* and their time dependencies. Each spectrum is resolved into two components by simulation. Shaded portions correspond to the bridging Cl^- ligand and Ni(IV) species (see text). Top and bottom spectra were recorded 5 and 45 minutes respectively after the sample was placed under the conditions of spectral measurements.

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†The preliminary conductivity measurements were carried out on pellets by the two-probe dc method. The compounds, $NiL^1Br(ClO_4)_2$ and $NiL^2Cl(ClO_4)_2$ have electric conductivities on the order of 10^{-6} and 10^{-8} Ω^{-1} cm^{-1} at room temperature, respectively.

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TABLE I. Binding Energies (eV) of Ni2p$_{3/2}$ and Cl2p.

		2p$_{3/2}$			Cl2p		
		Ni(II)	Ni(III)	Ni(IV)	Cl$^-$		ClO$_4$$^-$
[Ni^{II}([14]aneN$_4$)](ClO$_4$)$_2$		855.1	–	–	–	–	207.6
[Ni^{III}Br$_2$([14]aneN$_4$)]ClO$_4$		–	855.9	–	–	–	
[Ni^{III}Cl$_2$([14]aneN$_4$)]ClO$_4$		–	855.9	–	–	197.6[a]	207.5
Ni(pn)$_2$Cl$_3$	(1)	855.6	–	857.7	196.9[b]	198.4[c]	–
Ni([14]aneN$_4$)Br(ClO$_4$)$_2$	(2)	855.2	–	856.9	–	–	207.9

[a]Axial. [b]Counter anion. [c]Bridged.

856.9 eV for *2*) and the lower energy component (855.6 eV for *1* and 855.2 eV for *2*) are assigned to Ni2p$_{3/2}$ for Ni(IV) and Ni(II) species, respectively, by comparison with the reference compounds (Table I).

The Cl2p spectrum of *1* can also be resolved into two components. In view of the relative intensity ratio, binding energies, and discussion given below, it is reasonable to assign the higher- and lower-energy components to the bridging ligand Cl2p (198.4 eV) and the counter anion Cl2p (196.9 eV), respectively. This assignment is also supported by the fact that Cl2p binding energy of axial chloro ligands bound to Ni(III) in [Ni^{III}Cl$_2$([14]aneN$_4$)](ClO$_4$) is 197.6 eV (Table I).

For both *1* and *2* the integrated intensities of the resolved Ni(IV) spectra decreased, whereas those of the Ni(II) spectra increased with time of X-ray irradiation. Decreases of the Ni(IV) species were roughly equal to those of the increases of the Ni(II) species, indicating that the Ni(IV) states decompose to produce the Ni(II) states. Figure 2 shows time-dependence of the abundance of the Ni(IV) and Ni(II) species in *2*, which are estimated from the integrated spectral intensities. It can be seen that when the curves are extrapolated the composition ratio between Ni(II) and Ni(IV) reaches 1:1 at time zero.

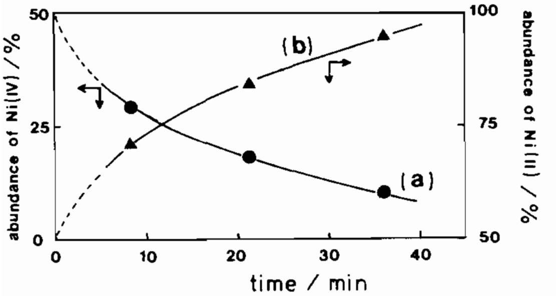

Fig. 2. Change in the abundance of the Ni(IV) species in *2* due to X-ray irradiation damage (a) and the concomitant increase in the Ni(II) species (b).

Likewise, in the resolved Cl2p spectra of *1*, spectral intensity of the bridging Cl2p was found to decrease with time with a concomitant increase in the intensity of the spectrum around the counter anion Cl2p. The rate of the spectral decrease of the bridging Cl2p was approximately equal to that of the Ni^{IV}2p$_{3/2}$. An intensity ratio of the bridging Cl2p to the counter anion Cl2p extrapolated to time zero was approximately 1:2.

Binding energies obtained from peak-top positions of the resolved spectra varied very slightly with time. Values for *1* and *2* in Table I were obtained from the spectra recorded *ca.* five minutes after the samples were placed under the conditions of spectral measurements.

Very similar spectral changes due to X-ray irradiation damage have been observed in 3d$_{5/2}$ and 3d$_{3/2}$ spectral measurements of Pd(II) and Pd(IV) species in Pd([14]aneN$_4$)X(ClO$_4$)$_2$ (X = Cl* [8] and Br) [9].

The difference in the binding energies of Ni2p$_{3/2}$ between Ni(II) and Ni(IV) in *1* (2.1 eV) is larger than that in *2* (1.7 eV). This suggests that the electronic interaction between Ni(II) and Ni(IV) in the bromo-bridged complex is stronger than that in the chloro-bridged complex, as reported for the Pt(II)–Pt(IV) and Pd(II)–Pd(IV) analogs [10, 11]. The fact is also evidenced by the electric conductivities and electronic spectral data of *1* and *2*. The electric conductivity of *1* on a pellet at room temperature is smaller by at least one order of magnitude than the corresponding value of *2*. Compound *1* in nujol-mull shows a charge transfer band from Ni(II) to Ni(IV) at 15300 cm^{-1} while *2* shows it at 10000 cm^{-1}.

The X-ray photoelectron spectral patterns of *1* and *2* are consistent with that expected for the halogen-bridged Ni(II)–Ni(IV) mixed valence

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*An X-ray study shows that [Pd([14]aneN$_4$)][PdCl$_2$([14]aneN$_4$)](ClO$_4$)$_4$ assumes such a halogen bridged linear chain structure [8].

complex having the linear chain structure. In all respects, including the diamagnetism, strong color, analytical and conductivity data, compounds *1* and *2* are properly formulated as $[Ni^{II}(pn)_2][Ni^{IV}Cl_2(pn)_2]Cl_4$ and $[Ni^{II}([14]aneN_4)][Ni^{IV}Br_2([14]aneN_4)](ClO_4)_4$.

Experimental

$Ni(pn)_2Cl_3$ (*1*) was prepared according to the reported method [1]. $Ni([14]aneN_4)Br(ClO_4)_2$ (*2*) was prepared by dropwise addition of Br_2 to a stirred solution of $[Ni([14]aneN_4)](ClO_4)_2$ in 70% $HClO_4$. *Anal.* Calcd % (Found %): $NiBrCl_2O_8N_4C_{10}H_{24}$, C, 22.59 (22.33); H, 4.52 (4.50); N, 10.10 (10.42).

X-ray photoelectron spectra were obtained with an Al Kα exciting irradiation on a VG Scientific ESCALAB-5 at -30 °C. The source vacuum was 2×10^{-8} mbar. Binding energies were calibrated as δ-(Cls) = 284.6 eV.

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