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XPS Study of Au Bis(mnt) Complexes

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The XPS study has been carried out for the $[Au(mnt)_2]^-$ and $[Au(mnt)_2]^{2-}$ salts. The Au^{III} states were confirmed for both monoanion and dianion salts; although the obtained $Au4f_{7/2}$ peak for the $[Au(mnt)_2]^{2-}$ dianion is at 0.8-1.0 eV higher energy than that for the $[Au(mnt)_2]^-$ salt, this apparent energy shift is explained as arising from the Madelung potential difference between the two. It is concluded that the oxidation state of the central metal Au does not change with reduction.

Transition-metal bis(dithiolene) complexes have unique physicochemical properties owing to having the ligand π electron systems. The discovery of metallic conductivity in $Li_{0.8}(H_3O)_{0.3}$-$[Pt(mnt)_2]\cdot 1.7H_2O$[1] (mnt = 1,2-dicyano-1,2-ethylenedithiolato, $C_4N_2S_2^{\ 2-}$) have motivated the syntheses of new types of bis(dithiolene) complexes having the extended ligand π electron systems. Among them, bis(mnt) comlexes (Fig. 1) are interesting materials in that they have a rather small ligand π electron system and their central metal ions can be more or less concerned in their electronic properties.[2] This means that the central metal can be a key factor of controlling their electronic properties. Our interest lies in understanding the relationship between the central metals and their electronic structures of the bis(mnt) complexes.

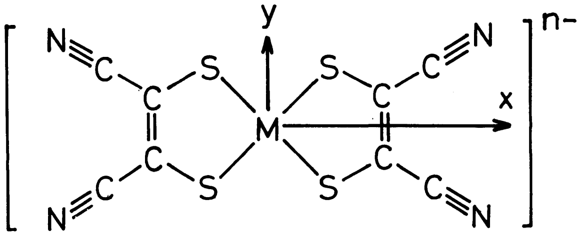

Fig. 1. $[M(mnt)_2]^{n-}$ complex.

In this paper, we chose Au bis(mnt) complexes from the following reasons: Obtaining the information on their electronic structures, we can use the combination of X-ray photoelectron spectroscopy (XPS or ESCA), IR absorpton spectra and Mössbauer spectroscopy. Furthermore, as far as the XPS studies are concerned, little work has been reported even on Au complexes. Thus, we have started to investigate the XPS for two types of complexes, monoanionic $[Au(mnt)_2]^-$ and dianionic $[Au(mnt)_2]^{2-}$ salts. In the latter salt, we measured the XPS of $[Bu_4N]_2[Ni(mnt)_2]$ doped with $[Bu_4N]_2[Au(mnt)_2]$ to minimize the decomposition of the $[Au(mnt)_2]^{2-}$ ion by exposure to air. On this $[Au(mnt)_2]^{2-}$ salt, we can compare the XPS results with the ESR studies.[3,4]

XPS spectra were obtained at room temperature with Mg Kα exciting radiation using VG Scientific ESCA LAB MK II system at Institute for Molecular Science; the source region vacuum was always better than 10^{-8} Torr (1 Torr = 133.322 Pa). Samples were mounted as follows; pressing onto a In foil (method 1) or evaporation of a dilute solution on a compressed BN pellet (method 2). The binding energies (E_b) of the core electrons were calibrated by using the C1s peak from pump oil (method 1) or the B1s and N1s peaks from a BN sample base (method 2). In method 1, the C1s signals did not seem to be a reliable reference because the samples also contain carbon. Therefore, we determined the absolute values of the binding energies from method 2 within an accuracy of 0.3 eV. The spectrum of $CsAuCl_4$ was also measured with method 2 ($E_b(Au4f_{7/2})$=88.0 eV) and was in good agreement with that obtained by Kitagawa et al. ($E_b(Au4f_{7/2})$=87.7 eV).[5] Detailed calibrations using method 2 will be reported in a succeeding paper.[6] Air-sensitive $[Au(mnt)_2]^{2-}$-doped salt $[Bu_4N]_2[Ni_{1-x}Au_x(mnt)_2]$[3] (x = ca. 0.01; as measured by atomic absorption and ESR) was handled under nitrogen in a glove bag.

Table 1. $Au4f_{7/2,5/2}$ and S2p Binding Energies in Au bis(mnt) Complexes

Compounds	Binding energies/eV (Method 2 [a])			Method of syn ref
	$Au4f_{7/2}$	$Au4f_{5/2}$	S2p	
$K[Au(mnt)_2]$	86.7	90.3	163.1	6
$[Et_4N][Au(mnt)_2]$	86.6	90.3	163.0	7
$[Bu_4N][Au(mnt)_2]$	86.6	90.3	162.9	7
$[Bu_4N]_2[Ni_{1-x}Au_x(mnt)_2]$ [b]	87.7	91.1	——	3
	$Ni2p_{3/2}$	Ni3p		
$[Bu_4N]_2[Ni(mnt)_2]$	854.0	67.9	162.6	8
$[Et_4N]_2[Ni(mnt)_2]$	853.6	67.5	162.3	8

a) Calibrated by using the B1s and N1s peaks from the sample base, which were assumed to be at 190.3 and 397.9 eV,[9] respectively.

b) Averaged value of three samples from method 1 ; calibrated by using the $Ni2p_{3/2}$ peak, which was assumed to be at 854.04 eV.

Table 2. Binding Energies of Some Other Au Compounds

Compounds	Formal oxidation state	$Au4f_{7/2}$ / eV	Ref.
Au metal	0	83.8	9
$[Bu_4N][AuCl_2]$	I	84.4	5
AuCl	I	84.8	5
$Me_2C(Ph_2PAuCl)_2Cl_2$	II	85.7	10
$[Au\{(CH_2)_2PEt_2\}Br]_2$	II	86.4	11
$[Bu_4N][AuCl_4]$	III	87.1	5
$K[AuCl_4]$	III	87.6	10
$Cs[AuCl_4]$	III	87.7	5

The experimental data for the Au bis(mnt) complexes are given in Table 1.

Some literature data of Au4$f_{7/2}$ binding energies of other Au compounds are listed in Table 2. As seen in Table 1, the Au4$f_{7/2}$ energies of three monoanionic $[Au(mnt)_2]^-$ salts are almost the same; changing the cation, which will cause some change in arrangement of the $[Au(mnt)_2]^-$ ions, has little effect on these energies. The values of the Au4$f_{7/2}$ binding energies of these complexes indicate that they are situated at the borderline between Au^{II} and Au^{III} compounds; using the Au4$f_{7/2}$ binding energy, their electronic structures can be described as $[Au^{III}(d^8)][(mnt)_2{}^{4-}]$ in the first approximation. On the other hand, the XPS for the Ni bis(mnt) complexes[12)] shows that the Ni binding energies are almost the same as that of Ni metal. These results may be explained by the following: Replacing Ni by a heavier atom Au, the metal d orbitals rise in energy and become closer to the important ligand π MO's (B_{1u} and B_{2g} ; according to Schrauzer's MO scheme[13)]).

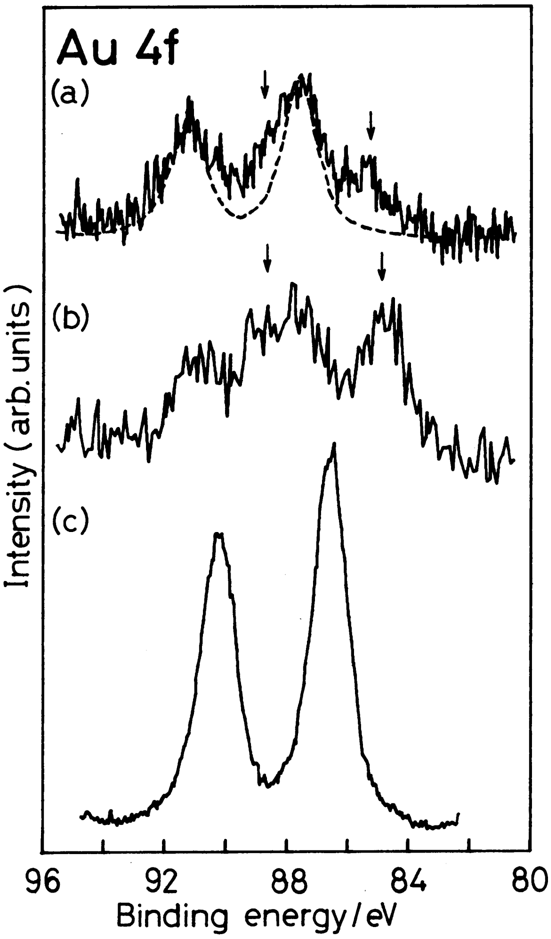

Fig. 2. (a) Spectrum of the Au4f region of $[Bu_4N]_2[Ni_{1-x}Au_x(mnt)_2]$; the broken line shows the Au4$f_{7/2}$-Au4$f_{5/2}$ spin-orbit component determined from the analysis of $[Bu_4N][Au(mnt)_2]$. (b) Spectrum of $[Bu_4N]_2$-$[Ni_{1-x}Au_x(mnt)_2]$ after exposure to air ; the arrows show the peaks assigned to the decomposed species. (c) Spectrum of $[Bu_4N][Au(mnt)_2]$.

Next, we will compare the XPS spectrum of the $[Au(mnt)_2]^{2-}$ dianion with the corresponding monoanionic $[Au(mnt)_2]^-$ salts (Fig. 2). In Fig. 2a, we assigned two peaks at 87.6 and 91.2 eV to the Au4$f_{7/2}$ and Au4$f_{5/2}$ signals for the $[Au(mnt)_2]^{2-}$ ion, respectively. An additional small peak around 85 eV can be assigned to the Au4$f_{7/2}$ signal due to some decomposed Au species, by considering that it became larger after exposure to air (Fig. 2b). In general, the Au4$f_{7/2}$ binding energy becomes higher in energy with the increasing oxidation state of Au. This leaves us in an apparent dilemma because the obtained Au4$f_{7/2}$ peak for the $[Au(mnt)_2]^{2-}$ dianion, whose value is still situated within the Au^{III} region, is at 0.8-1.0 eV higher energy than that for $[Bu_4N][Au(mnt)_2]$ (Fig. 2c). This shift dose not seem to reflect the change in the oxidation state of the central metal Au ion with reduction from $[Au(mnt)_2]^-$ to $[Au(mnt)_2]^{2-}$; we would rather seek for another reason for this energy shift.

A most plausible explanation of this energy shift can be given by considering the marked change in the immediate environment of the anion from the $[Au(mnt)_2]^-$ salts to its dianion-doped salt[14]; in the case of monoanion salts the anions are stacked in a linear chain sided by cations while in the dianion salts each anion is sandwiched between two cations.[15] In fact, it is seen that the Ni2$p_{3/2}$ binding energy of the $[Ni(mnt)_2]^{2-}$ salt becomes 0.4 eV higher when replacing $[Et_4N]^+$ ion by more bulky $[Bu_4N]^+$ ion which more effectively covers the anion plane (see Table 1). Therefore, we can conclude that most of the above 0.8-1.0 eV energy shift is attributed to the Madelung potential difference and that the oxidation state of the central metal Au almost dose not change with reduction from $[Au(mnt)_2]^-$ to $[Au(mnt)_2]^{2-}$. Furthermore, dilute single-crystal ESR studies[3,4] have shown that the ground state of the $[Au(mnt)_2]^{2-}$ dianion is composed of about 80% ligand character. Our conclusion in this study is consistent with the ESR results.

To clarify the above explanation, we are undertaking the Mössbauer specroscopy.

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14) The Madelung potential energy can be separated into two parts: Intramolecular and intermolecular interactins. In the former contribution, increasing the negative charge on the mnt ligands is expected to cause lower energy shift of the Au binding energy. Thus, we believe that the above higher energy shift is mainly due to the difference in the latter contribution, which is caused by the access of two $[Bu_4N]^+$ cations to one Au site.
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