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X-RAY PHOTOELECTRON SPECTRA OF COBALT(III) COMPLEXES WITH SEVERAL KINDS OF SULFUR DONOR ATOMS

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The X-ray photoelectron spectroscopic data of 25 cobalt(III) complexes of CoN_xS_{6-x} types are reported(x = 6, 5, 4, 3, and 0). The $S2p_{3/2}$ binding energies can readily be distinguished into eight types of sulfur ligands. The $S2p_{3/2}$, $Co2p_{3/2}$, and N1s binding energies are distributed between two extremes; one represents the case of thiolato and sulfenato complexes, and the other sulfinato and sulfito ones. These results are discussed in connection with the structural trans effect.

X-Ray photoelectron spectroscopy(XPS) has been used to distinguish different chemical environments of donor atoms in the complexes with halides or sulfur-containing ligands.[1),2)] Since any comparision of XPS data from different sources is complicated by the variety of calibration techniques, systematic investigation on a series of compounds becomes further fruitful. This letter deals with the XPS data($S2p_{3/2}$, $Co2p_{3/2}$, and N1s binding energies) of 25 cobalt(III) complexes of CoN_xS_{6-x} types(x = 6, 5, 4, 3, and 0) which contain one or two of eight kinds of sulfur donor groups, RS^-, μ-RS^-, R_2S, $(C_2H_5O)_2PS_2^-$, $S_2O_3^{2-}$, RSO^-, RSO_2^-, and SO_3^{2-}. The results will be discussed in connection with the structural trans effect induced by coordinated sulfur atoms.

Ligands and complexes are shown in Tables 1 and 2, respectively. The complexes except **5**, **15**, **19**, and **22**[3)] were prepared according to the published methods.[4)] The X-ray photoelectron spectra were recorded with an AEI ES 200 electron spectrometer at *ca.* 295 K and at 1 × 10^{-5} Pa. The Al Kα X-ray line(1486.6 eV) was used as an X-ray source. The binding energies relative to the Fermi level were determined by referring to the Na2s binding energy(64.0 eV) of anhydrous sodium carbonate mixed with an appropriate amount of each sample. This method reproduces the binding energies within 0.2 eV. The binding energies of $Co2p_{3/2}$ and N1s were taken at a position corresponding to the middle point of the full peak at half-height. The $S2p_{1/2,\ 3/2}$ spin-orbit

Table 1. Abbreviations of Ligands.

Haet	$NH_2CH_2CH_2SH$	**H_2dt**	$HSCH_2CH_2SH$
Haese	$NH_2CH_2CH_2S(O)H$	**H_2dti**	$HS(O)_2CH_2CH_2S(O)_2H$
Haesi	$NH_2CH_2CH_2S(O)_2H$	**Hdpt**	$NH_2CH_2CH(SH)CH_2NH_2$
L-Hcym	$NH_2CH(COOCH_3)CH_2SH$	**Hdtp**	$(C_2H_5O)_2PS_2H$
L-Hcyme	$NH_2CH(COOCH_3)CH_2S(O)H$	**maet**	$NH_2CH_2CH_2SCH_3$
L-H_2cysi	$NH_2CH(COOH)CH_2S(O)_2H$	**L-Hmet**	$NH_2CH(COOH)CH_2CH_2SCH_3$

components are resolved and the $S2p_{3/2}$ binding energy is taken as the peak maximum of the overall band envelope.

The $S2p_{3/2}$ binding energies were plotted against the oxidation numbers of the coordinated sulfur atoms(Fig. 1). The eight kinds of sulfur donor groups are distinguishable from one another and the $S2p_{3/2}$ binding energies of thiolato(RS^-), sulfenato(RSO^-), sulfinato(RSO_2^-), and sulfito (SO_3^{2-}) groups increase in this order in proportion to their oxidation numbers. The $S2p_{3/2}$ binding energy of the μ-thiolato complex 8 is higher than that of the corresponding thiolato complex 4. This relation is analogous to the case of chloro complexes where μ-chloro ligands have a higher $Cl2p_{3/2}$ binding energy than non-bridging chloro ligands.$^{1)}$ In the mixed sulfenato and sulfinato complexes of CoN_3S_3 type, both $S2p_{3/2}$ components of RSO^- and RSO_2^- are well resolved and the RSO^-/RSO_2^- ratios can be deduced exactly from the overall spectral patterns.

Table 2. Complexes investigated.

No.	type	Complex
0	N_6	Λ-$[Co(en)_3]Br_3\cdot H_2O$
	thiolato	
1	N_5S	$[Co(aet)en_2](ClO_4)_2$
2	N_4S_2	*trans*-$[Co(dpt)_2]Cl$
3	N_4S_2	*cis*-$[Co(dpt)_2]Cl\cdot H_2O$
4	N_3S_3	*fac(S)*-$[Co(aet)_3]$
5	N_3S_3	*fac(S)*-$[Co(L\text{-}cym)_3]$
6	S_6	$Na_3[Co(dt)_3]\cdot H_2O$
	thionothiolato	
7	S_6	$[Co(dtp)_3]$
	μ-thiolato	
8	N_3S_3, S_6	$[Co_3(aet)_6]Br_3\cdot 1.5H_2O$
	thioether	
9	N_5S	$[Co(maet)en_2]Cl_3\cdot H_2O$
10	$N_2O_2S_2$	*trans(O)*-$[Co(L\text{-}met)_2]Cl\cdot 0.5H_2O$
	thiosulfato	
11	N_4S_2	*trans*-$Na[Co(S_2O_3)_2en_2]$
	sulfenato	
12	N_5S	$[Co(aese)en_2](ClO_4)_2$
13	N_3S_3	*fac(S)*-Λ-*(R,R,S)*-$[Co(aese)_3]\cdot 0.5H_2O$
14	N_3S_3	*fac(S)*-Λ-*(R,R,R)*-$[Co(aese)_3]\cdot 2.5H_2O$
15	N_3S_3	*fac(S)*-Δ-*(S,S,S)*-$[Co(L\text{-}cyme)_3]\cdot 1.5H_2O$
	sulfinato	
16	N_5S	$[Co(aesi)en_2](ClO_4)_2$
17	N_3S_3	*fac(S)*-$[Co(aesi)_3]$
18	N_3S_3	*fac(S)*-Δ-$K_3[Co(L\text{-}cysi)_3]\cdot 9H_2O$
19	S_6	Λ-$K_3[Co(dti)_3]\cdot 2.5H_2O$
	sulfito	
20	N_4S_2	*trans*-$Na[Co(SO_3)_2en_2]\cdot H_2O$
21	N_4S_2	*cis*-$Na[Co(SO_3)_2en_2]\cdot NaClO_4\cdot H_2O$
22	N_3S_3	*fac(S)*-$Na_3[Co(SO_3)_3dien]\cdot NaClO_4\cdot 4H_2O$
	mixed sulfenato and sulfinato	
23	N_3S_3	*fac(S)*-Λ-*(R,R)*-$[Co(aese)_2(aesi)]\cdot 2H_2O$
24	N_3S_3	*fac(S)*-Λ-*(R)*-$[Co(aese)(aesi)_2]\cdot H_2O$

As shown in Fig. 2, the $Co2p_{3/2}$ binding energies of the thiolato complexes decrease with the increase of the number of the sulfur donor atoms: $N_6 > N_5S > N_4S_2 > N_3S_3 > S_6$. The binding energies of $Co2p_{3/2}$(Fig. 2) and N1s(Fig. 3) also depend on the kinds of sulfur donor groups. In the series of CoN_3S_3 type complexes, the binding energies of both $Co2p_{3/2}$ and N1s increase in the order RSO^-(14) $\leq$ RS^-(4) < RSO_2^-(17) $\leq$ SO_3^{2-}(22), and stepwise by displacing RSO^- to RSO_2^-(14 < 23 < 24 < 17). All complexes containing coordinated sulfur atoms show lower $Co2p_{3/2}$ binding energies than the tris(ethylenediamine)cobalt(III) complex 0. This fact implies that the sulfur donor atom generally donate the more electron pair to the cobalt(III) ion than the amino group.

The $Co2p_{3/2}$ and N1s binding energies in Figs. 2 and 3 show a very similar trend. The complexes containing thiolato or sulfenato groups with two or one lone pair(s) of electrons, respectively, have considerably lower $Co2p_{3/2}$ and N1s binding energies than Λ-$[Co(en)_3]Br_3\cdot H_2O$. In these complexes, both $Co2p_{3/2}$ and N1s binding energies

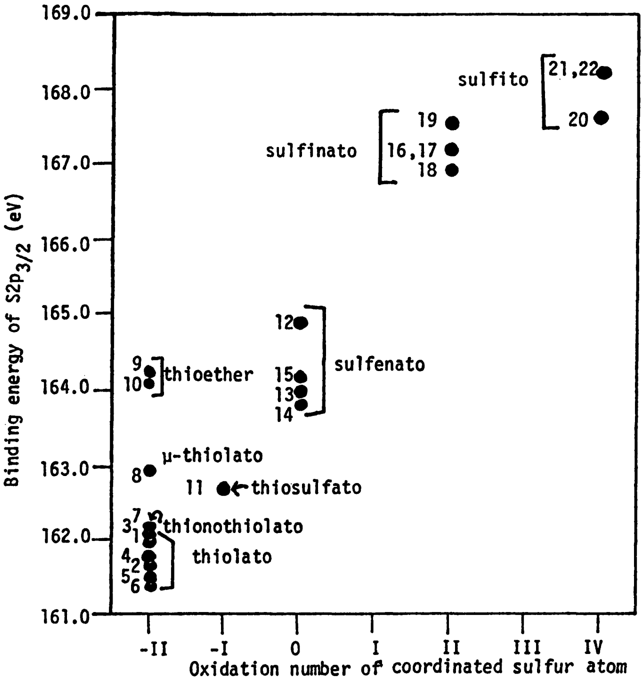

Fig. 1. Binding energies of $S2p_{3/2}$.

decrease with the increase of the number of sulfur donor atoms: (N_6) > N_5S > N_4S_2 > N_3S_3 > S_6 for the thiolato complexes, and (N_6) > N_5S > N_3S_3 for the sulfenato complexes. These results suggest that a significant amount of electrons on sulfur should be transferred to cobalt and concomitantly the Co-N bond distance should be lengthened. On the other hand, the complexes containing sulfinato or sulfito groups which carry no lone pair of electrons show considerably higher $Co2p_{3/2}$ and N1s binding energies than the thiolato or sulfenato complexes. As seen in the complexes of 16-22, neither $Co2p_{3/2}$ nor N1s binding energies depend on the number of sulfur donor atoms.

Our results can be related to the X-ray crystallographic studies. In the sulfur containing cobalt(III) complexes, it has been reported that the structural trans effect(STE) induced by sulfur donor atoms is in the following order: SO_3^{2-} > RSO^- > RSO_2^- > RS^- >> $S_2O_3^{2-}$ ≈ R_2S.[4a] The interpretation of this effect is suggested

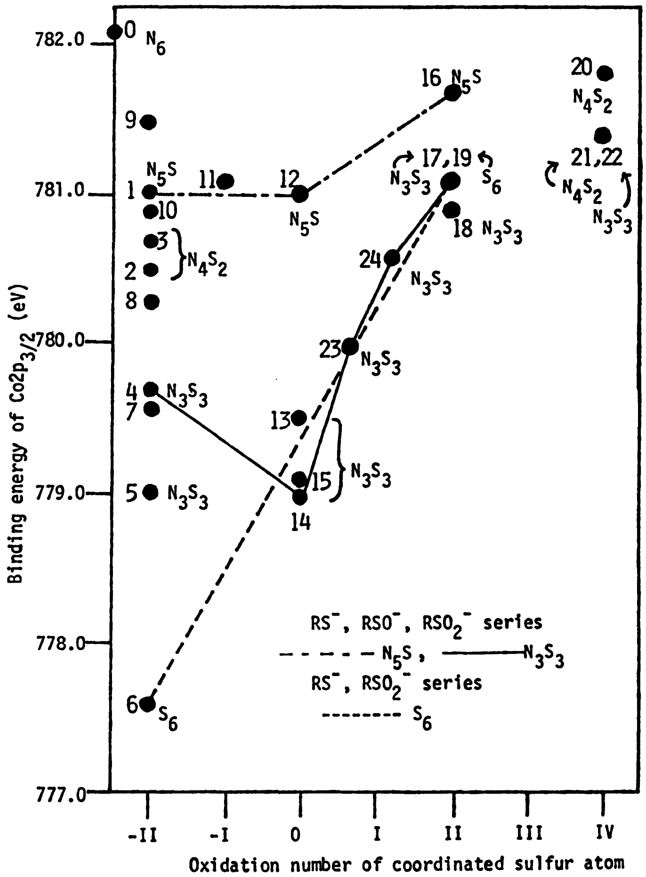

Fig. 2. Binding energies of $Co2p_{3/2}$.

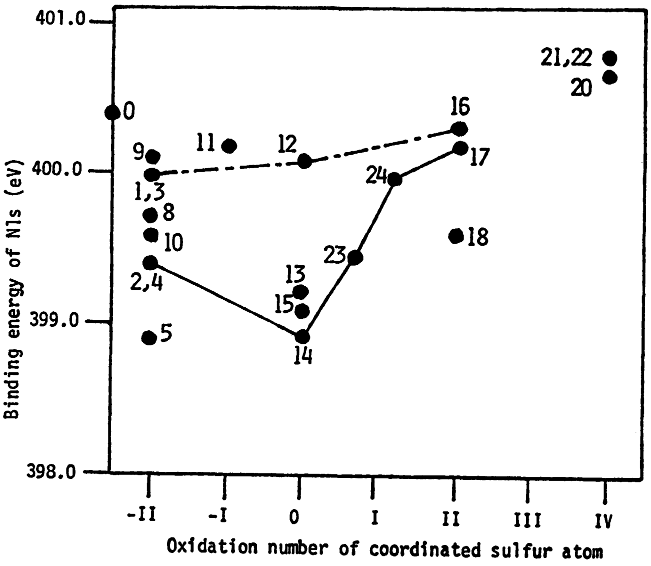

Fig. 3. Binding energies of N1s.

by Nosco *et al.* in terms of the classical σ-trans effect; a shorter and stronger Co-S bond induces a longer and weaker trans Co-N bond.[5)] However, this simple mechanism is not enough to explain the available data. For example, the Co-S bond distance of $[Co(aese)en_2](SCN)_2$(2.253 Å) is significantly longer than that of $[Co(aesi)en_2](NO_3)(ClO_4)$(2.191 Å), though the former complex has a large STE value (0.072 Å) compared with the latter one(0.049 Å). Our XPS data clearly indicate that the large STE induced by coordinated sulfur atoms of SO_3^{2-}, RSO^-, RSO_2^-, and RS^- should be explained by two kinds of mechanisms rather than a single mechanism. One mechanism should be applied to thiolato and sulfenato complexes which have low binding energies of $S2p_{3/2}$, $Co2p_{3/2}$, and N1s. The present result implies a significant amount of electron transfer from the sulfur donor atom to the central cobalt(III) ion. The other mechanism should be applied to sulfinato and sulfito complexes which show higher binding energies of $S2p_{3/2}$, $Co2p_{3/2}$, and N1s than the former group of complexes. The STE of the latter group of complexes will be explained by the mechanism which scarcely contains the electron transfer from the sulfur donor atom to the central cobalt(III) ion.

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References and Notes.

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