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Paramagnetic Cobalt(III) Complexes with Organic Ligands. VI. An X-Ray Photoelectron Spectroscopic Study

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Paramagnetic tetraammine-5-nitrosalicylato cobalt complex, paramagnetic μ-hyperoxo-dicobalt complexes and related diamagnetic compounds have been studied by X-ray photoelectron spectroscopy. In all these compounds, the binding energies of Co 2p electrons and their spin-orbit separation were those of usual Co(III) complexes. In the spectrum of paramagnetic tetraammine-5-nitrosalicylatocobalt salt, satellites appeared near the Co 2p peaks showing certain spin density at the cobalt atoms. At the same time, the C 1s spectrum showed that considerable portion of carbon atoms has high binding energy suggesting delocalization of electron hole over the organic ligand. The O 1s peaks in μ-hyperoxo complexes were *ca.* 0.6 eV higher than those in μ-peroxo complexes. Deconvolution of the O 1s peak in the μ-OOH complex gave OH, =O–, and H_2O peaks at the 1:1:1 ratio, supporting the μ-OOH formulation.

Previous papers[1–5] described the preparation and properties of a series of deep green ammine 5-nitrosalicylato cobalt complexes formed from russet ammine salicylato cobalt(III) complexes.[6,7] Inasmuch as these deep green compounds have oxidizing power and are paramagnetic, the earlier papers formally denoted them as cobalt(IV) compounds. However, examination of electric resistivity,[3] ESR,[3] IR,[4] and NMR[4] spectra suggested that the electron deficiency is not centered at cobalt, but is delocalized over the system composed of the cobalt atom and the organic ligand. In this sense we have changed the series title to the present one.[5]

The situation is in a sense similar to the case of some paramagnetic μ-O_2 dicobalt complexes which were formerly described as Co(III)–Co(IV) complexes,[8] but which are now usually formulated as μ-hyperoxo-dicobalt(III) complexes on the basis of structural,[9] ESR,[10] vibrational,[11] and other studies.[12]

The present study has been intended to elucidate the valency and related problems in paramagnetic ammine 5-nitrosalicylato cobalt complexes and μ-O_2 dicobalt complexes by means of X-ray photoelectron spectroscopy (XPS), which is becoming to give useful information as to the state of the constituent atoms.

Experimental

Materials. Tetraammine-5-nitrosalicylatocobalt complexes were prepared after Yamamoto *et al.*,[1–5] whereas μ-O_2 dicobalt complexes were prepared according to the description by Mori *et al.*[13,14]

XPS Measurements. The spectra were obtained by irradiating the compounds with Mg $K\alpha$ X-rays (120 W) in a vacuum at a pressure of less than 3×10^{-7} Pa and at room temperature or around 220 K. The powdered compounds were uniformly mounted on Ni holders by using adhesive tape. The instrument used was a VG ESCA 3 electron spectrometer, and was calibrated with gold and copper, relative to the photoelectron peaks Au $4f_{7/2}$(84.0 eV), Cu $3s_{1/2}$(122.6 eV), and Cu $2p_{3/2}$(932.7 eV); FWHM (full width at half maximum) of the Au $4f_{7/2}$ peak was 1.18 eV, and C 1s peak due to the carbonaceous contamination formed on Au and Cu specimens in the instrument appeared at 284.8 eV. The peak shift caused by charge-up effect was corrected with the contamination C 1s peak.[15]

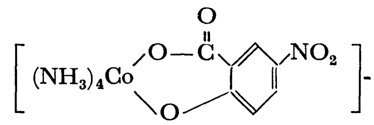
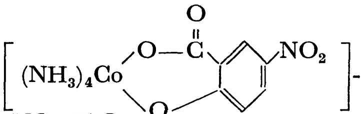
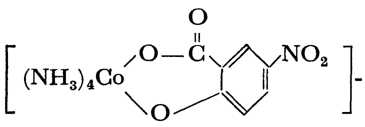
The spectra comprised of several components were deconvoluted with skewed Gaussian shape, where the same FWHM was assigned for components of the same element. The error of binding energy determination was estimated to be ±0.2 eV when the peaks were well-separated, whereas it was estimated to be ±0.4 eV when deconvolution was applied. The error of intensity estimation was around 5% in the former case while it was around 10% in the latter case.

Results and Discussion

XPS of Ammine 5-Nitrosalicylato Cobalt Complexes. The binding energies of C 1s, N 1s, O 1s, and Co 2p electrons of the cobalt complexes studied in this research are given in Table 1. The binding energies of Co 2p electrons as well as their spin-orbit separation (≈15 eV) in the green paramagnetic complex $[Co(5\text{-}NO_2sal)(NH_3)_4]ClNO_3\cdot H_2O$ fell well within the range of those of cobalt(III) complexes[16] as of course did those of orange diamagnetic complexes $[Co(5\text{-}NO_2sal)(NH_3)_4]NO_3\cdot H_2O$ and $[Co(5\text{-}NO_2sal)(NH_3)_4]Cl\cdot HCl\cdot H_2O$, the latter two being considered to be typical cobalt(III) complexes. This is consistent with the results of studies of electric conductivities, ESR,[3] IR, and NMR spectra[4] and suggests delocalization of the electron hole over the cobalt-ligand system in the former paramagnetic compound.

The following points, however, seem to be worth noting concerning the XPS of the paramagnetic $[Co(5\text{-}NO_2sal)(NH_3)_4]ClNO_3\cdot H_2O$: (1) Cobalt 2p peaks have satellites which show the presence of certain spin density at the cobalt atom (Fig. 1). Somewhat greater FWHM observed for the Co $2p_{3/2}$ peak (Table 1) may also be due to the presence of unpaired spin. (2) There are some carbon atoms (estimated to be 22.2% of the total carbon) that have high binding energies (Fig. 2). (1) is in apparent contradiction to the tervalence of cobalt as concluded from the binding energies and spin-orbit separation. These might be accommodated by assuming that although the unpaired spin is not centered at cobalt in the

TABLE 1. BINDING ENERGIES OBSERVED IN THE XPS OF AMMINE-5-NITROSALICYLATO COBALT COMPLEXES[a)]

Compound	Temp	C 1s	N 1s	O 1s	Co $2p_{3/2}$	$2p_{1/2}$
 $Cl\cdot NO_3\cdot H_2O$[a)]	room	285.1 ring+ contam.[b)] 288.8 ring[c)]+CO shoulder	400.1 NH_3 405.4 NO_2 406.9 NO_3	532.2 max FWHM 3.0	782.1 FWHM 2.6 satellites medium	797.0
	220K	285.4 ring+ contam. 288.6 ring[c)]+CO shoulder	400.2 NH_3 405.6 NO_2 407.2 NO_3	532.4 max FWHM 3.1	782.2 FWHM 2.4 satellites medium	797.0
 $NO_3\cdot H_2O$	room	285.2 ring+ contam. 288.5 =CO shoulder	400.2 NH_3 405.3 NO_2 407.0 NO_3	532.5 max FWHM 2.9	782.3 FWHM 2.1 satellites very weak	797.1
 $Cl\cdot HCl\cdot 2H_2O$[a)]	220K	285.2 ring+ contam. 288.3 =CO shoulder	400.2 NH_3 405.3 NO_2	532.3 max FWHM 3.2	782.1 FWHM 2.3 satellites very weak	796.9

a) In eV. The maximum of Cl $2p_{3/2}$ has been taken to be at 198.2 eV. b) The peak due to ring carbon admixed with that due to contaminating hydrocarbon from instrument.[15)] c) Ring carbon of high binding energy.

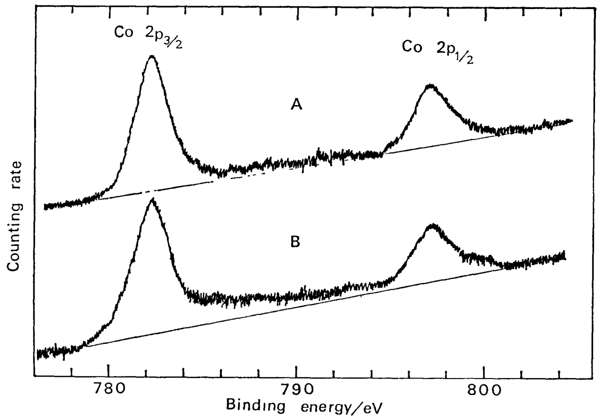
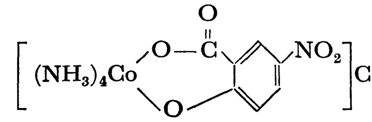
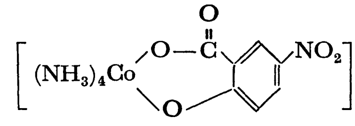


Fig. 1. XPS of



$Cl\cdot HCl\cdot 2H_2O$ (A) and



$Cl\cdot NO_3\cdot 2H_2O$ (B) in the Co 2p region at 220 K.

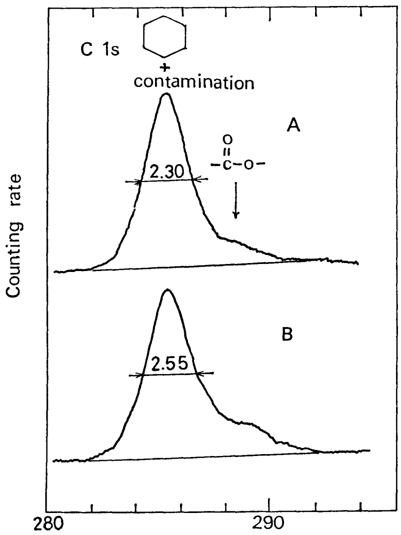
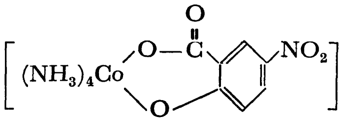
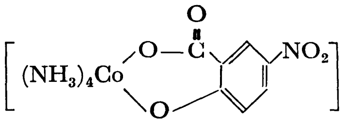


Fig. 2. XPS of



$Cl\cdot HCl\cdot 2H_2O$ (A) and

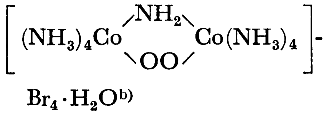
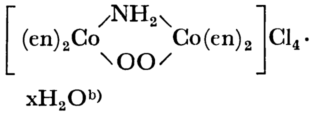
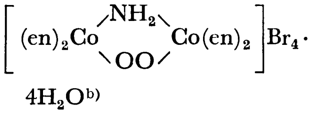
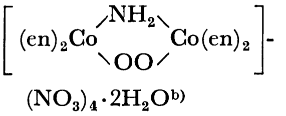
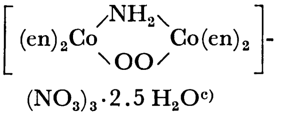
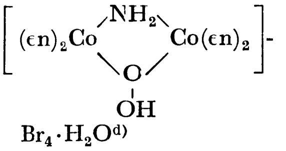


$Cl\cdot NO_3\cdot 2H_2O$ (B) in the C 1s region at 220 K.

sense that cobalt is quadrivalent, yet some fraction of the spin density remains on cobalt. However, a considerable part of the spin density or the electron deficiency seems to be also distributed over some carbon atoms of the 5-nitrosalicylato ligand as evidenced by (2), *i.e.* by the high binding energies observed for certain portion of the carbon atoms. In the case of orange diamagnetic $[Co(5\text{-}NO_2sal)(NH_3)_4](NO_3)\cdot H_2O$, a shoulder appeared at the high energy side of the main C 1s peak, and from its area (estimated to be 6.7% of the total carbon), it is considered to correspond to the carboxylato carbon.

In the green paramagnetic as well as the orange diamagnetic complexes the nitrogen 1s electrons appear as two peaks separated by 6.4—6.8 eV. The peak at *ca.* 400 eV was assigned to NH_3 nitrogen. The peak at higher energy could be deconvoluted to the one at 405—406 eV assignable to NO_2 nitrogen and to the one at *ca.* 407 eV assignable to NO_3 ni-

Table 2. Binding energies observed in the XPS of μ-O_2 dicobalt complexes

Compound	Temp	C 1s	N 1s	O 1s	Co $2p_{3/2}$	$2p_{1/2}$
 $[(NH_3)_4Co(\mu\text{-}NH_2)(\mu\text{-}OO)Co(NH_3)_4]Br_4\cdot H_2O$[b]	room	284.8 contam.[a]	398.2 $-NH_2-$[e] 400.0 NH_3	531.5 -OO- 533.2 H_2O	781.6 FWHM 2.4 satellites very weak	796.5
 $[(en)_2Co(\mu\text{-}NH_2)(\mu\text{-}OO)Co(en)_2]Cl_4\cdot xH_2O$[b]	room	284.8 contam. 286.1 en	398.5 $-NH_2-$[e] 400.3 en	531.9 -OO- 533.4 H_2O	781.9 FWHM 2.4 satellites very weak	796.7
 $[(en)_2Co(\mu\text{-}NH_2)(\mu\text{-}OO)Co(en)_2]Br_4\cdot 4H_2O$[b]	room	284.8 contam. 286.0 en	398.4 $-NH_2-$[e] 400.3 en	531.9 -OO- 533.4 H_2O	781.8 FWHM 2.1 no satellite	796.7
 $[(en)_2Co(\mu\text{-}NH_2)(\mu\text{-}OO)Co(en)_2](NO_3)_4\cdot 2H_2O$[b]	room	284.8 contam. 286.0 en	398.2 $-NH_2-$[f] 400.2 en 407.0 NO_3	531.6 -OO- 532.7 $NO_3 + H_2O$	781.9 FWHM 2.3 satellites very weak	796.6
	220K	284.8 contam. 286.0 en	398.3 $-NH_2-$[e] 400.3 en 406.9 NO_3	531.7 -OO- 532.7 $NO_3 + H_2O$	781.8 FWHM 2.3 no satellite	796.7
 $[(en)_2Co(\mu\text{-}NH_2)(\mu\text{-}OO)Co(en)_2](NO_3)_3\cdot 2.5\,H_2O$[c]	room	284.8 contam. 286.0 en	398.3 $-NH_2-$[f] 400.2 en 406.8 NO_3	530.8 -OO- 532.3 $NO_3 + H_2O$	781.3 FWHM 2.6 satellite weak	795.9
	220K	284.8 contam. 286.0 en	398.2 $-NH_2-$[e] 400.1 en 406.7 NO_3	530.6 -OO- 532.5 $NO_3 + H_2O$	781.1 FWHM 2.6 no satellite	795.9
 $[(en)_2Co(\mu\text{-}NH_2)(\mu\text{-}OOH)Co(en)_2]Br_4\cdot H_2O$[d]	room	284.8 contam. 285.8 en	398.4 $-NH_2-$[e] 400.2 en	531.4 OH 532.2 -O= 533.5 H_2O	781.7 FWHM 2.0 no satellite	796.2

a) The C 1s peak due to hydrocarbon contamination from the instrument has been taken to be at 284.8 eV.[15]
b) Green paramagnetic hyperoxo complex. c) Brown diamagnetic peroxo complex. d) Red diamagnetic hydroperoxo complex. e) I_{NH_2}/I_{NH_3}(or en)$\fallingdotseq 1/8$. f) The above ratio is not equal to 1/8. The reason is not clear.

trogen. It has not so far been possible to deconvolute the peak of O 1s (half width=3.3 eV) into those of different types of atoms in the compound.

XPS of μ-NH_2-μ-O_2 Dicobalt Complexes. Okamoto *et al.* who studied the XPS of various cobalt compounds in connection with the catalytic activities reported that the Co 2p binding energies and their spin orbit separation of $[(NH_3)_5CoO_2Co(NH_3)_5](NO_3)_4$ (diamagnetic) and $[(NH_3)_5CoO_2Co(NH_3)_5]Cl_5$ (paramagnetic) were in the same range as those of usual cobalt(III) complexes.[17] Burness *et al.* studied the XPS of Shiff-base complexes and their O_2 adducts, found similar results,[18] and concluded that the oxygenated compounds contain tervalent cobalt, so that O_2 is a peroxo (diamagnetic) or a hyperoxo (paramagnetic) ligand. The peroxo compounds they studied included both mononuclear and dinuclear (*i.e.* μ-O_2) complexes, whereas the hyperoxo compounds they studied were all mononuclear. They also found that the O 1s binding energies of the hyperoxo complexes are *ca.* 1 eV higher than those of the peroxo complexes in conformity with the reduction of the charge on the O_2 moiety. The result of the present XPS study (Table 2) on the μ-NH_2-μ-O_2 dicobalt complexes also showed a similar trend. A slightly lower binding energies of Co 2p electrons in the peroxo as compared with those in the hyperoxo complex might be accounted for in terms of the donation of the extra antibonding π-electron of O_2 to cobalt in the former. Satellites were either inperceptible or very weak indicating low spin density on the cobalt atom (Fig. 3), again rationalizing the formulation of the paramagnetic compound as μ-hyperoxo-dicobalt(III) complex.

In $[(en)_2Co(NH_2)(OOH)Co(en)_2]Br_4\cdot H_2O$ spectrum, the O 1s band could be deconvoluted into three peaks at 531.4, 532.2, and 533.5 eV assigned to –OH, $>$O–, and H_2O oxygens, respectively, supporting the μ-OOH structure reported for the corresponding nitrate.[19] The higher binding energy of $>$O– in $>$O–OH as compared with that of usual peroxo oxygen might be due to the lower electron density caused by coordination of one peroxo oxygen to two cobalt ions in the former case. It has also been possible to dif-

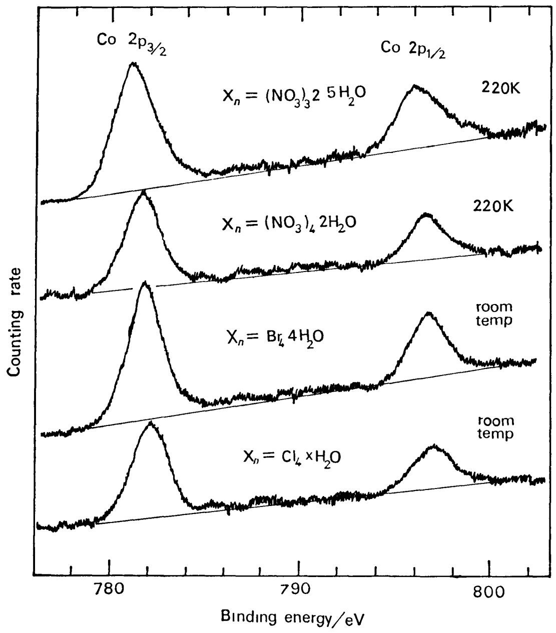
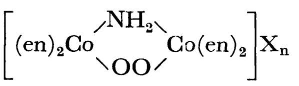


Fig. 3. XPS of  $\left[(en)_2Co\begin{smallmatrix}NH_2\\ OO\end{smallmatrix}Co(en)_2\right]X_n$ in the Co 2p region.

ferentiate the nitrogen atom present as NH_2 from those present as NH_3 or en with the intensity ratio of 1 : 8 in most μ-NH_2-μ-O_2 complexes studied (*cf.* Table 2).

Comparison between the Two Series of Paramagnetic Cobalt Complexes. As discussed above, the deep green ammine-5-nitrosalicylatocobalt complex and the green μ-hyperoxo-dicobalt complex are in a sense similar in that one unpaired spin (an electron hole) has the probability of existence partly on the cobalt atom and partly on some of the ligand molecules. In the case of the paramagnetic μ-O_2 complex, the large hyperfine coupling constant due to ^{17}O nucleus in the ESR spectrum established that the spin density is much higher on the O_2 bridge,[10] rationalizing the μ-hyperoxo nomenclature. This seems to be in line with inperceptible or very weak satellites of Co 2p lines in the XPS of the μ-amido-μ-hyperoxo complex. On the other hand the appearance of satellites in the Co 2p lines in the XPS of the deep green tetraammine-5-nitrosalicylatocobalt complex seems to suggest a higher spin density on cobalt as compared with the μ-hyperoxo-dicobalt case. Yamamoto[3] observed eight hyperfine lines in the aqueous esr spectrum of deep green bis(ethylenediamine)-5-nitrosalicylatocobalt chloride nitrate in the narrow concentration range of ca. 10^{-2}—10^{-3} M, which may possibly be due to ^{59}Co nucleus, but simultaneous appearance of one sharp line leaves some ambiguity as to the state of the complex in aqueous solution. Thus, quantitative estimation of the spin density by use of more stable complex of this series containing isotopically labeled ligand seems to be very desirable.

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