

X-ray Photoelectron Spectroscopy Studies of some Cobalt(II) Nitrate Complexes

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Abstract

X-ray photoelectron spectra of $\text{Co}(\text{NO}_3)_2 \cdot 2\text{L}$ with $\text{L} = \text{tdpo}$, tpo and tpyrp , were recorded and interpreted. It seems that in these complexes tpyrp is the strongest electron donor, followed by tdpo and then tpo . In these complexes a stronger electron donor ligand results in a more ionic Co–nitrate bond, and it could thus result in a less stable complex. Paramagnetic Co^{II} satellite structures were observed. The modified Auger parameters (α') were calculated and used to compare the polarizability of the compounds to each other. $\text{Co}(\text{NO}_3)_2 \cdot 2\text{tpyrp}$ seems to be the most polarizable of the three complexes, and $\text{Co}(\text{NO}_3)_2 \cdot 2\text{tpo}$ the least polarizable.

Introduction

Since the advent of XPS (X-ray photoelectron spectroscopy) there has been considerable interest in studying transition metal complexes using this technique. The complexes chosen for the present study are neutral donor ligand cobalt(II) nitrate complexes, $\text{Co}(\text{NO}_3)_2 \cdot 2\text{L}$, with L three different phosphorous ligands: tpo (triphenyl phosphine oxide), tdpo (tris(dimethylamino) phosphine oxide) and tpyrp (trispyrrolidino phosphine oxide). The influence of these different $\text{P}=\text{O}$ ligands on the electronic structure of the cobalt ion has been investigated. The donor properties (Lewis basicity) of the neutral donor ligands must be among the more important chemical factors in determining the stability of these compounds, as it is likely to affect the energies of the metal–nitrate bonds. Strivastava [1] concluded in a study of *cis*-bis ethylenediamino alkyl amino nitrito cobalt(III) nitrate complexes that as electron transfer from RNH_2 to the metal ion increases, the electron transfer from the metal ion to nitrogen (NO_2) through π -back bonding also increases.

Experimental

Sample Preparations

The complexes $\text{Co}(\text{NO}_3)_2 \cdot 2\text{tpo}$, $\text{Co}(\text{NO}_3)_2 \cdot 2\text{tdpo}$ and $\text{Co}(\text{NO}_3)_2 \cdot 2\text{tpyrp}$ were prepared as described in the literature [2]. $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, tpo , tdpo and tpyrp were obtained from Fluka. $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dehydrated for 48 h in the spectrometer at a pressure of 7×10^{-11} mbar to obtain $\text{Co}(\text{NO}_3)_2$.

XPS Analysis

The X-ray photoelectron spectra were recorded using a VG Scientific ESCALAB Mk.II. Non-monochromatic $\text{Mg K}\alpha$ (1253.6 eV) radiation was used from a X-ray gun operated at 15 kV and 20 mA. The base pressure was better than 7×10^{-11} mbar in the analyser. The Co metal pellets were sputter clean with a VG AG21 argon ion etch gun. The oxygen uptake of Co was measured after bleeding research grade O_2 directly onto the sample at a pressure of 2×10^{-8} mbar for 10 min. All the samples were cooled to liquid nitrogen temperature.

All spectra were recorded using the same spectrometer parameters of 20 eV pass energy and 6 mm split width. Two sets of data were recorded for each of the powdered samples – one set on the as-received powder and one on the powder with a 5–10 Angstrom gold coating. The latter data was used to obtain static charge-corrected binding energies by means of the calibrated energy of 84.0 eV for the $\text{Au } 4f_{7/2}$ line [1, 3, 4]. Such charging corrections varied between 2.85 and 5.65 eV.

Linear background subtraction and a least-squares fitting procedure were used to determine peak positions, linewidths and peak areas.

Results and Discussion

The measured binding energies of some peaks on the XPS spectra of the complexes $\text{Co}(\text{NO}_3)_2 \cdot 2\text{tpo}$, $\text{Co}(\text{NO}_3)_2 \cdot 2\text{tdpo}$, $\text{Co}(\text{NO}_3)_2 \cdot 2\text{tpyrp}$, as well as $\text{Co}(\text{NO}_3)_2$, Co_3O_4 , Co metal and Co metal + O_2 are

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TABLE 1. XPS Peak Binding Energy Values (eV) of some Cobalt-containing Compounds

Peaks	Co(NO ₃) ₂ ·2tppo	Co(NO ₃) ₂ ·2tdpo	Co(NO ₃) ₂ ·2tpyrp	Co(NO ₃) ₂	Co ₃ O ₄	Co metal	Co metal + O ₂
Co 2p _{5/2}	796.05	796.55	796.85	796.50	794.15	793.55	793.40
Co 2p _{3/2}	780.85	780.70	781.40	780.90	780.30	778.55	778.50
Co 3s	101.90	103.20	103.10	102.60	103.10	101.35	nd
Co 3p	61.15	61.55	61.55	61.30	61.70	59.70	nd
Co 3d	3.1	3.4	3.4	2.7	2.2	1.6	2.1
O 1s	531.25	531.25	531.60	531.70	532.40	nd	nd
O 2s	24.8	24.1	24.2	24.6	22.5		22.2
O 2d	[9.2]	[9.9]	[8.9]	[5.8]	[6.5]		
P 2p	132.45	133.50	133.85				
P 3s	17.4	17.0	18.5				
P 3p	[13.4]	[9.9]	[14.6]				
N 1s	399.25	399.40	399.65	399.20			
N 2p	[9.2]	[9.9]	[8.9]	[10.1]			
C 1s	284.55	286.20	285.80	284.80	286.00	285.10	286.70
C 2p	[9.2]	[9.9]	[8.9]	[5.8]	[10.4]		
Co 2p _{5/2} satellite	803.20	802.00	802.85	802.95	803.70		803.40
Co 2p _{3/2} satellite	787.00	786.90	787.40	786.75	789.30		787.55
LMM Auger	482.85	482.60	482.90	482.85	482.80	480.20	480.20
Kinetic energy of LMM Auger	770.75	771.00	770.70	770.75	770.80	773.40	773.40
Modified ^a Auger parameter	1551.60	1551.70	1552.10	1551.65	1551.10	1551.95	1551.90
Co 2p multiplet splitting	15.20	15.85	15.45	15.60	15.05	15.00	14.90

[]: denotes less certain data; nd: not determined.

^aThe Auger line for all but Co and Co₃O₄ is broad, and accuracy of the line energy is therefore limited.

listed in Table 1. A visual comparison between the Co 2p_{5/2} and Co 2p_{3/2} peaks are given in Fig. 1, while Fig. 2 represents the valence band peaks of these compounds. All values and figures were corrected for static charging.

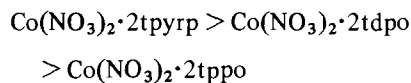
The Co 2p Region

The Co 2p peaks at 793.55 and 778.55 eV for the metal (Table 1) compared very well with tabulated values of 794 and 779 eV [5]. Raaen [6] observed two very weak satellite structures in the 2p core levels in Co, that are due to a two-hole final state in the d band of Co. The first peak occurred at approximately 4.5 eV and the second at 28 eV from the main emission. The first satellite structure can clearly be distinguished on the XPS spectrum of Co metal and is labelled S in Fig. 1. Raaen [6] also observed a 2p spin-orbit splitting of 15.1 eV, that compared well with the value of 15.00 eV observed in this study (Table 1).

Cochran and Larkins [7] reported that the Co^{II} and Co^{III} peaks are not resolved on the XPS spectrum of Co₃O₄, resulting in asymmetric Co 2p peaks. The Co 2p_{3/2} peak at 780.30 eV on the XPS spectrum of Co₃O₄ in this study compared well with the peak at 779.5 eV reported by Cochran and Larkins [7]. The Co 2p_{3/2} peaks between 780.70 and 781.40 eV (Table 1) for all the Co^{II} complexes in this study also

compared well with the Co 2p_{3/2} peak at 781 eV for paramagnetic Co^{II}, reported in ref. 7.

The generalization by Siegbahn *et al.* [8] that the higher the binding energy, the greater the effective positive charge is on a metal ion, is used to compare the three different neutral donor ligand cobalt(II) nitrate complexes to each other. According to this generalization the maximum effective positive charge on the cobalt ion is in the Co(NO₃)₂·2tpyrp complex with a binding energy value of 796.85 eV for the Co 2p_{5/2} peak. The lowest Co 2p_{5/2} binding energy is for the tppo complex (796.05 eV) and it thus seems to have the smallest effective positive charge on the cobalt ion. The decreasing order of effective positive charge, according to the Co 2p_{5/2} peak binding energy values, is



The Co 2p_{3/2} binding energies for the tppo and tdpo complexes are approximately the same, with that of the tpyrp complex higher at 781.40 eV (Table 1). When comparing the Co 2p peaks of the neutral donor ligand complexes to that of Co₃O₄, it is clear that the Co bonds in the complexes are more ionic in character than the more covalent bonds in the Co^{II}-Co^{III} oxide, Co₃O₄ (Table 1 and Fig. 1).

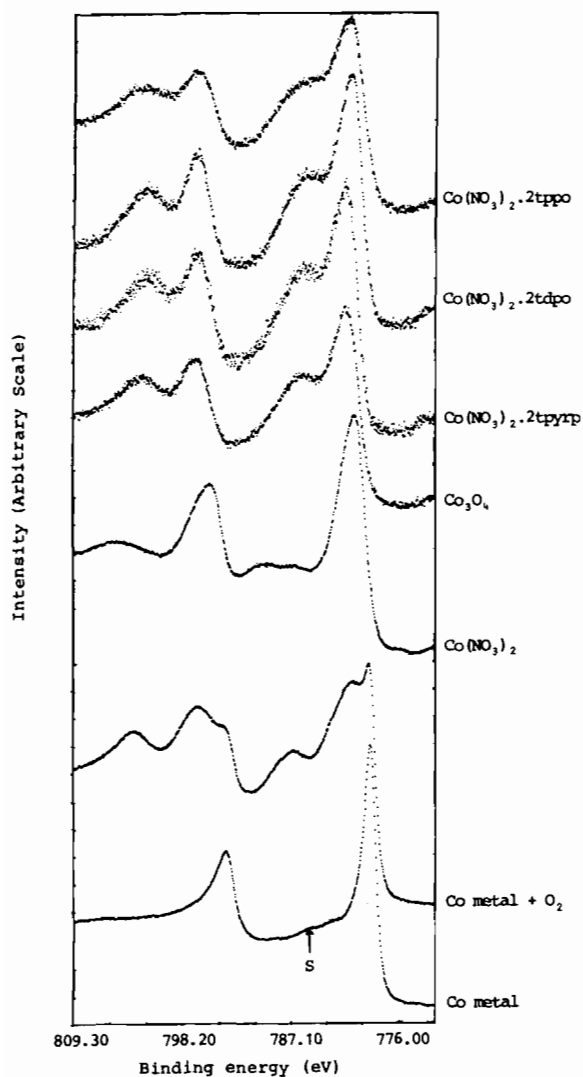


Fig. 1. XPS peaks in the Co 2p binding energy region.

The Co 2p Satellites

Atoms or molecules containing unpaired electrons exhibit paramagnetism. The satellites associated with the 2p photoelectron lines of transition metal are interpreted to be due to the excitation of a metal 3d electron into an unoccupied metal orbital (predominantly of 4s character), concurrently with the emitted photoelectron [4]. The most pronounced satellites are observed in elements (ions) with almost filled 3d shells, such as Co, Ni and Cu. No shake-up satellites are observed in diamagnetic compounds or compounds with filled 3d shells [9].

Matienzo *et al.* [4] observed double satellites in more covalent complexes, where considerable delocalization of the metal electrons and consequently more overlap between metal and ligand orbitals are expected. They also reported a strong correlation between the satellite separation from the

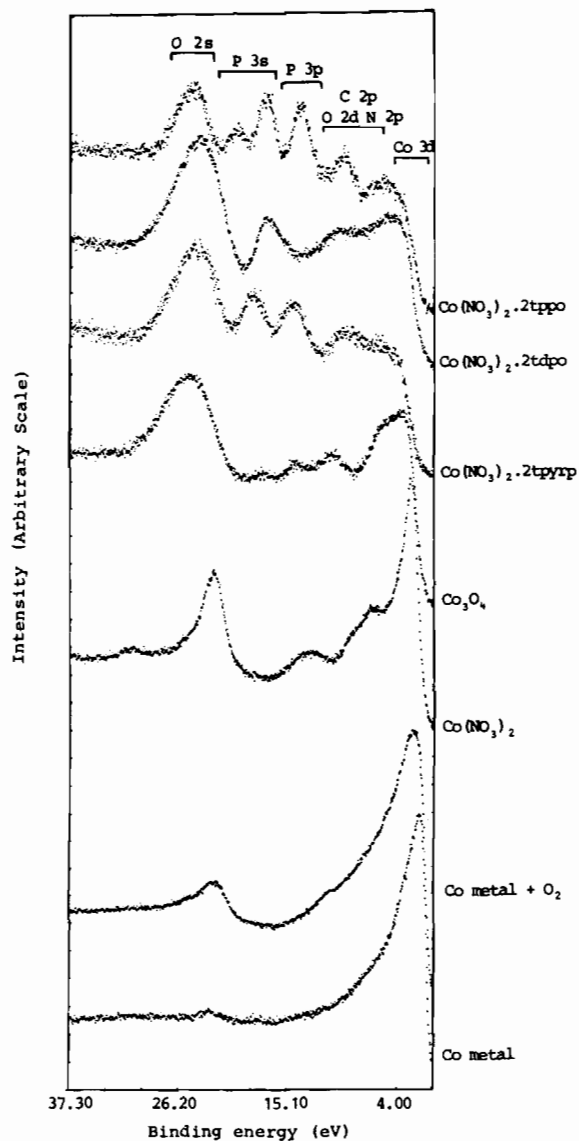


Fig. 2. XPS peaks in the valence band binding energy region.

main line and the degree of covalency in the bonds. The data indicated that the more covalent the bond, the larger the satellite separation [4]. Since no clear double satellites were observed for all the compounds in this study, and since the satellite separation from the main peaks are small, it seems that the Co bonds are more ionic than covalent in character.

The shake-up satellite structures at approximately 787 (Co $2p_{3/2}$) and 803 (Co $2p_{5/2}$) eV on the spectra of the Co(II) nitrate complexes (Table 1 and Fig. 1) are a clear indication of the presence of paramagnetic Co^{II} . After exposing the Co metal to oxygen for 10 min, three distinct Co $2p_{3/2}$ (and three Co $2p_{5/2}$) peaks and satellites were observed (Fig. 1). The cobalt metal Co $2p_{3/2}$ peak appeared at 778.50 eV, the unresolved Co^{II} and Co^{III} oxide peaks at 780.90 eV

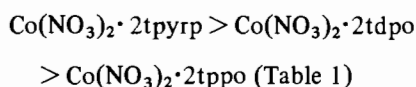
and the paramagnetic Co^{II} satellite at 787.55 eV. These values compared well to results obtained by Cochran and Larkins [7].

The separation between the satellite structure and the parent line increases as the ligand becomes less electronegative [9]. Since for all the cobalt(II) complexes in this study two different types of ligands occur in each complex, *i.e.* the neutral donor ligands (tpo, tdpo or tpyrp) and the nitrate groups, it proved difficult to obtain any useful information from the satellite—parent line separation.

The Auger LMM Lines and the Modified Auger Parameter (α')

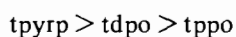
Wagner *et al.* [10] reported that some of the paramagnetic transition metal compounds exhibit wide and blunt Auger peaks and recorded a LMM Auger peak for Co^{II} at a kinetic energy value of 773.2 eV, with an α' value of 1551.2 eV on the XPS spectrum of a Co^{II} compound. The LMM Auger peak binding and kinetic energy values, together with the modified Auger parameter (α'), for the compounds in this study are reported in Table 1.

Changes in the Auger parameter are due principally to changes in extra-atomic relaxation or polarization energy [11]. With core-type Auger lines, polarization effects are more important in determining chemical shifts than are changes in electron density on the atom in the ground state [1]. The greater the Auger parameter, the more polarizable the compound is, giving thus the following order of decreasing polarizability for the studied complexes



The P 2p Peaks

As tpo, tdpo and tpyrp are neutral electron donor ligands, a lone pair of oxygen electrons from the phosphorus groups on each ligand is donated to the cobalt metal ion. Thus the greater the effective positive charge on the P atom in the ligand, the more effective the electron donor ability [8]. When comparing the P 2p binding energy values (Table 1) an order of decreasing electron donor strength for the ligands in the complexes is proposed



The N 1s and C 1s Peaks

Nitrogen occurs in two different chemical environments in the tdpo and tpyrp cobalt complexes, *i.e.* in the nitrate groups and in the neutral donor ligands. These two nitrogen environments result in a broad N 1s peak, with the N 1s peak from the NO_3^- group and that of the neutral ligand unresolved. This is indicated by the FWHM values (full width at half

height) of just above 2 eV for the tdpo and tpyrp complexes in comparison to the FWHM values of just less than 1 eV for the tpo complex and $\text{Co}(\text{NO}_3)_2$.

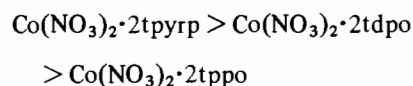
Carbon occurs in different chemical environments in the studied complexes, *i.e.* in phenyl groups in tpo (C is at 284.55 eV), in dimethyl groups in tdpo (C is at 286.20 eV) and in pyrrolidino groups in tpyrp (C 1s at 285.80 eV).

The Valence Bands

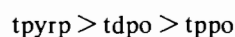
The approximate positions of the Co 3d, O 2s, O 2d, P 3p, C 2p and N 2p peaks are indicated in Fig. 2. Since these peaks are not resolved as good as the core level peaks it proved difficult to compare the binding energy values of the different complexes to each other. The binding energies of the Co 3d peaks in Co_3O_4 (2.2 eV) and Co metal (1.6 eV) compared well with values in the literature [6, 7].

Conclusions

If the stability of the studied cobalt(II) nitrate complexes is dependent on the strength of the Co— NO_3 bonds, as was the case for uranium(IV) nitrate complexes [12], then the more ionic the Co— NO_3 bond the easier it is to rupture. From the Co 2p peak data it seems that the decreasing order of positive charge on the Co ion in the different complexes is



The Auger parameter indicates the same decreasing order of polarizability and according to the P 2p peak binding energy values the decreasing order of electron donor strength is also



It thus seems that a stronger electron donor ligand results in a more ionic cobalt—nitrate bond. Even though tpyrp seem to be the strongest electron donor, the cobalt ion in the tpyrp complex has the biggest positive charge, indicating a greater delocalization of electrons towards the nitrate groups. It is concluded that the ligand groups that result in more covalent type of bonds between a metal ion and the surrounding groups will increase the stability of the molecules.

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