

XPS Spectra of Spin-Triplet Cobalt(III) Complexes

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The X-ray photoelectron spectra of cobalt(III) complexes in an unusual spin triplet state are reported. The binding energies in the 2P spectral region are somewhat low and the spectra exhibit rather strong satellite structure. The Co 2P_{1/2}-Co 2P_{3/2} separations and satellite intensities appear to be related to the magnetic moments of the complexes as has been suggested previously for cobalt(II) compounds.

Introduction

The X-ray photoelectron spectroscopy (XPS) of transition metal complexes, especially those of first row transition elements, has received considerable attention in the past few years. In addition to the many experimental contributions, a substantial amount of theoretical work has appeared which is directed at the goal of understanding the details of the XPS spectra of transition metal systems. The XPS properties of a large number of cobalt complexes have been reported, including examples from each of the commonly occurring electronic states for cobalt, high and low spin cobalt(II) and low spin cobalt(III) [1–10]. In general each electronic state demonstrates rather characteristic and distinguishing features in the XPS spectrum. Thus, low spin cobalt(III) shows only a main peak in, for example, the Co 2P_{3/2} region with little evidence of satellite structure on the high binding energy side of this peak. High spin cobalt(II), on the other hand, normally exhibits a rather strong satellite at about 5 eV higher binding energy from the main peak. Low spin cobalt(II) shows satellite structure which is less intense and less well resolved than that for high-spin cobalt(II).

There exists another unusual cobalt(III) electronic configuration. In complexes with ligands derived from biuret, a spin triplet state (two unpaired electrons, $\mu_{\text{eff}} = 3.3\text{--}3.5$ B.M.) has been observed

[11, 12]. It was of interest to measure the XPS spectra of these complexes because this would provide information about a new class of cobalt complexes for which XPS data was not previously available. This would extend to four the number of electronic states (for positive oxidation numbers) for which XPS data have been reported and thus provide new information for those interested in developing a comprehensive theoretical explanation of satellite structure in the XPS spectra of transition metal compounds. We report here, therefore, an XPS spectral investigation of KCo(bi)₂, KCo(en)(bi)₂, and KCo(o-phen)(bi)₂ [13].

Results and Discussion

The preparations of these systems, as well as their characterization, have been satisfactorily reported previously [12]. Each of the complexes appears to have a square-planar coordination geometry, an unusual environment for cobalt(III).

Fig. 1 (curves c and d) show the cobalt 2P_{3/2} XPS spectra for KCo(bi)₂ and KCo(o-phen)(bi)₂. In addi-

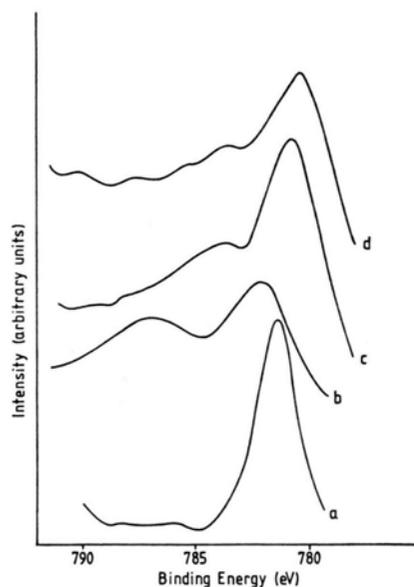


Fig. 1. Cobalt 2P_{3/2} XPS spectra for: a) Co(NH₃)₆Cl₃, b) Co(H₂O)₆Cl₂, c) KCo(bi)₂, and d) KCo(o-phen)(bi)₂.

tion the spectra for two very common species, Co(NH₃)₆Cl₃ (curve a) and Co(H₂O)₆Cl₂ (curve b) are included so that comparison of spectral properties obtained with the same instrument and referencing procedures can be made. Table I summarizes the pertinent cobalt XPS parameters in the 2P spectral region for the complexes studied. The qualitative features of the spectra for the spin triplet complexes are a rather low cobalt binding energy and definite satellite structure at the high binding energy side of the main peak. The splitting

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Table I. Cobalt XPS parameters.

Compound [13]	Co 2P _{3/2} binding energies, eV		$\frac{I_{\text{satellite}}}{I_{\text{total}}}$	Co 2P _{1/2} -Co 2P _{3/2} separation, eV
	main peak	satellite		
KCo(bi) ₂	780.8	783.8	.32	15.3
KCo(<i>o</i> -phenbi) ₂	780.5	784.0	.31 [14]	15.3
KCo(enbi) ₂	780.6	784.6	.30 [14]	15.6
Co(NH ₃) ₆ Cl ₃	781.4	—	—	15.1
Co(H ₂ O) ₆ Cl ₂	782.1	786.8	.41	15.9

between the main peak and the satellite maximum is on the order of 3 eV, less than is normally observed for high spin cobalt(II) (compare, for example, spectra b and c in Fig. 1). In several of the spectra there is evidence of multiplet structure in the satellite peaks in both the Co 2P_{3/2} and Co 2P_{1/2} region. However, this possible fine structure is in general poorly resolved.

The cobalt 2P_{3/2} binding energies for the spin triplet complexes are low, more than 1 eV lower than for Co(NH₃)₆Cl₃. Normally, one observes a higher binding energy for higher oxidation states than for lower oxidation states of the same metal. However, such comparisons are valid only when the complexes of two oxidation states have identical ligand donor atoms. In the spin triplet cobalt(III) complexes, the ligand system contains 4 deprotonated nitrogen atoms which are very strong electron donors. This affords the metal an unusually low actual charge resulting in the low binding energies.

The separation between the cobalt 2P_{1/2} and cobalt 2P_{3/2} main peaks has been discussed with reference to the spin state of the cobalt [1, 3, 4]. Thus, high spin cobalt(III) species appear generally to show a Co 2P_{1/2}-Co 2P_{3/2} separation of about 1 eV larger than is found for the diamagnetic cobalt(III) species. It is suggested that the Co 2P_{1/2}-Co 2P_{3/2} separation will increase with the magnitude of the magnetic moment of the complex. Consistent with this, low spin cobalt(II) complexes with only 1 unpaired electron are reported to exhibit a Co 2P_{1/2}-Co 2P_{3/2} separation intermediate between that found for high spin cobalt(II) and low spin cobalt(III). If there is a qualitative correlation between the magnetic moment and the Co 2P_{1/2}-Co 2P_{3/2} separation, these spin triplet complexes should also demonstrate an intermediate Co 2P_{1/2}-Co 2P_{3/2} separation. Inspection of the data in Table I indicates that this is indeed the case.

The relative intensities of the Co 2P_{3/2} satellite and main peaks in a number of paramagnetic cobalt complexes has also been reported to correlate with the magnetic moment of the complex [7]. This correlation is at best very qualitative but there is at least a trend indicating larger relative satellite intensity with increasing magnetic moment. Al-

though the main and satellite peaks of the compounds investigated here are badly overlapping, we have determined that the satellite intensities account for approximately 30% of the total intensity in the 2P_{3/2} spectral region [14]. With this satellite intensity and an effective magnetic moment of 3.3-3.5 B.M., these complexes appear to lie within the qualitative correlation of Borud'ko *et al.* [7], despite the fact that these complexes have both a different electronic state and different formal oxidation state than those for which the correlation was originally suggested.

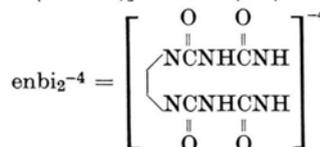
In summary, the XPS spectral properties of these unusual spin triplet cobalt(III) complexes are characterized by a somewhat low binding energy and a strong satellite at about 3-4 eV to high binding energy from the main peak. Both the Co 2P_{1/2}-Co 2P_{3/2} separation and the Co 2P_{3/2} satellite intensity seems to be related to the magnetic moments of the complexes.

Experimental

The complexes were prepared following the procedures of Birker [12]. The free ligands enbi₂H₄ and *o*-phenbi₂H₄ were prepared by reaction of freshly prepared nitrobiuret with ethylenediamine or *o*-phenylenediamine respectively [12]. All chemicals were reagent grade. *o*-Phenylenediamine was recrystallized shortly before use. Spectral measurements were obtained on a Varian V-IEE 15 high-resolution electron spectrometer equipped with a 620-L online computer (8 K). During the course of the measurements the sample was maintained at about 100 K by cooling with liquid nitrogen. The samples were run as finely ground powders dusted onto the backing of a one-sided adhesive Cellotape (Scotch Tape, 3 M Co.) which was attached to the cylindrical sample holder. The spectra were standardized with the C_{1s} aliphatic hydrocarbon line for which a binding energy of 284.0 eV was assigned [15].

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- [1] D. C. Frost, C. A. McCowell, and I. S. Woolsey, *Chem. Phys. Lett.* **17**, 320 (1972).
- [2] J. W. Lauber and J. E. Lester, *Inorg. Chem.* **12**, 244 (1973).
- [3] D. C. Frost, C. A. McDowell, and I. S. Woolsey, *Mol. Phys.* **27**, 1473 (1974).
- [4] D. Briggs and V. A. Gibson, *Chem. Phys. Lett.* **25**, 493 (1974).
- [5] K. Burger, E. Fluck, H. Binder, and Cs. Varhelyi, *J. Inorg. Nucl. Chem.* **37**, 55 (1975).
- [6] J. H. Burness, J. G. Dillard, and L. T. Taylor, *J. Am. Chem. Soc.* **97**, 6080 (1975).
- [7] Yu. G. Borud'ko, S. I. Vetchinkin, S. L. Zimont, I. N. Ivleva, and Yu. M. Shul'ga, *Chem. Phys. Lett.* **42**, 264 (1976).
- [8] K. B. Yatsimirskii, V. V. Nemuskalenko, V. G. Aleshin, Yu. I. Bratushko, and E. P. Moiseenko, *Chem. Phys. Lett.* **52**, 481 (1977).
- [9] H. Binder, E. Fluck, S. Heřmanek, and J. Plešek, *Z. Anorg. Allg. Chem.* **433**, 26 (1977).
- [10] R. Larsson and B. Folkesson, *Phys. Scripta* **16**, 357 (1977).
- [11] J. J. Bour, P. T. Beurskens, and J. J. Steggerda, *J. Chem. Soc., Chem. Commun.* **1972**, 221.
- [12] P. J. M. W. L. Birker, J. J. Bour, and J. J. Steggerda, *Inorg. Chem.* **12**, 1254 (1973).
- [13] Abbreviations used in the text and Table I are as follows: $\text{KCo}(\text{bi})_2$ = potassium *bis*(biureto)cobaltate(III); $\text{KCo}(\text{enbi}_2)$ = potassium[ethylenediamine *bis*(biureto)]cobaltate(III); $\text{KCo}(o\text{-phenbi}_2)$ = potassium[*o*-phenylenediamine *bis*(biureto)]cobaltate(III).



- [14] Because of the fact that the satellite peak overlapped the main peak to a considerable extent, the satellite was resolved by subtracting a linear base-line from the spectrum and assuming that the main peak was then symmetrical. The satellite intensities could contain up to 10% error.
- [15] K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S. E. Karlsson, I. Lindgren, and B. Lindberg, *ESCA, Atomic, Molecular, and Solid State Structures Studied by Means of Electron Spectroscopy*, Almqvist and Wiksells, Uppsala, 1967.