An XPS Study of Rh and Co Derivatives of Tetrapyrrole Macrocyles

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Transition metal complexes of polypyrrole macrocycles have been extensively studied because of their possible applications as models for biological systems.

Among other metals, rhodium has received a great deal of attention because of its key role in catalysis and its versatile redox behaviour, while cobalt derivatives of porphyrin and tetradehydrocorrins have been investigated primarily because of their relation to the vitamin B_{12} coenzyme.

During our investigation on the chemistry of rhodium complexes with macrocyclic ligands, we have recently synthesized some Rh(III) corrole derivatives [1]. These compounds are the first examples of Rh(III) corrolates with the metal ion lying in the macrocyclic plane.

We carried out an XPS investigation in order to elucidate the chemical nature of the central metal ions and the electronic and geometrical structures of these compounds. This investigation has been extended to Rh(III) derivatives of *meso*-tetraphenyl- (TPP) and octaethylporphyrin (OEP), some of which have been already studied by XPS, and to some Co(II) species, in order to compare a variety of coordinative structures, from simple 1:1 complexes to mono- and diaxially substituted systems. An example is also reported of a Rh(I) 'open structure' complex with the ligand 1,19-dideoxy-decamethylbiladiene a, c (BD). The complexes investigated and the related XPS binding energy values are reported in Table I.

Experimental

All reported compounds were prepared according to literature methods [2–6] and gave satisfactory elemental analyses.

XPS measurements were carried out on a VG-ESCA 3 photoelectron spectrometer, employing an Al Kα source ($h\nu$ = 1486.6 eV). Samples were cooled to liquid nitrogen temperature. Radiation damage effects were found to be absent for investigated compounds. All reported binding energies (b.e.s) are referred to the contamination carbon signal C 1s (285.0 eV); the uncertainty is ±0.2 eV.

TABLE I. XPS Binding Energies for Reported Compounds

Compound	N 1s	Rh 3d/Co 2p	P 2p
Corrole	397.7 399.9		
Rh corrole (PPh_3)	398.9	309.6	132.6
Rh corrole (PPh_3)(CO)	398.8	309.4	132.0
Rh corrole (t-Bu NC)$_2$	398.4	310.1	
TDHC	400.6		
[CoTDHC]$^+ClO_4^-$	398.8	780.3	
BD	400.1		
Rh(I) BD	398.9	309.8	
H_2TPP^a	398.2 400.1		
RhTPPCl	399.5	310.1	
[RhTPP(PPh_3)$_2$]$^+PF_6^-$	399.3	310.3	131.8 136.0
CoTPP^a	399.1	780.9	
H_2OEP^a	397.8 399.9		
RhOEPCl	398.9	310.2	
RhOEP[(PPh_2Me)$_2$]$^+PF_6^-$	399.1	310.1	131.8 136.6

^{a}The b.e.s of these compounds have already been published (see, for example, ref. 12); we remeasured them for a more homogeneous comparison.

Results and Discussion

The most sensitive XPS structural probe in porphyrins and porphyrin-like systems is the N 1s b.e. On the basis of the differences in this experimental value, reported in Table I, an unequivocal assignment of aza- and pyrrole-type nitrogen is proposed both for free ligands (with b.e.s. respectively found at ≈398 and ≈400 eV) and for coordinated ones, according to the literature [7–9].

After complexation, we always observed a single N 1s peak component, generally shifted to a value in between those obtained for free bases. The difference between observed extreme values (398.4, 399.5 eV) is close to that previously reported for some platinum porphyrinates [10] and attributed to nitrogen hybridization

$>$N–Pt ⟶ 398.6 (sp^3)

$>$N→Pt ⟶ 399.4 (sp^2)

However, in our opinion, the general constancy of observed difference in N 1s b.e. between free and coordinated bases, the presence of only one main component in N 1s peaks in coordinated compounds and the obtained XPS quantitative ratios between Me and N, are clear indications of a quite similar coordinative mode of N functions to the metal, implying sp^2 N donors.

As far as the oxidation state of the central metal atom is concerned, we note that Rh 3d b.e. in the reported complexes is in the expected range for Rh(III) compounds; the only different compound, RhBD (μ-(1,19-dideoxy-1,2,3,7,8,12,13,17,18,19-decamethyl biladienato-a,c)-bis(dicarbonylrhodium-(I)) [4]) has a Rh 3d b.e. which is coincident with the value measured for the parent compound $[Rh(CO)_2Cl]_2$ (309.8 eV).

Weak satellites have been reported by various authors to accompany main N 1s lines in free and complexed tetrapyrrole macrocycles [7–9]. They probably represent a $\pi \rightarrow \pi^*$ transition localized on the porphyrin [11]. The relative intensity of these features to the main line has sometimes been observed to vary with the central metal atom [11].

The compounds here reported have generally presented the same N 1s peak shape, *i.e.* a main component plus a weak structure at higher b.e.s. This latter however does not vary appreciably, either in position or in relative intensity.

It is interesting to note that RhBD, which is a Rh(I) open structure complex, presents N 1s satellite peaks (see Fig. 1). Rh 3d lines are not accompanied by satellites, as in Rh(III) corrolates and porphyrinates.

In conclusion, the appearance of N 1s satellite structures in complexed porphyrin-like bases is not strictly related to the presence of a closed macrocyclic ring. We found that the intensity of these satellites depends on the presence of ring substituents in free bases, while it is almost constant and not perturbed by complexation in their derivatives.

A close comparison between strictly related complexes, *i.e.* RhTPPCl and RhOEPCl, clearly evidenced analogies in the behaviour of the two macrocyclic ligands: Rh 3d b.e.s are almost coincident and N 1s differences in b.e.s (free → complexed) are comparable. The positive charge on N 1s is higher in RhTPPCl than in RhOEPCl, an effect which has already [9] been correlated to the electron withdrawal of four phenyl groups with respect to eight electron-donating ethyl groups in the two macrocycles.

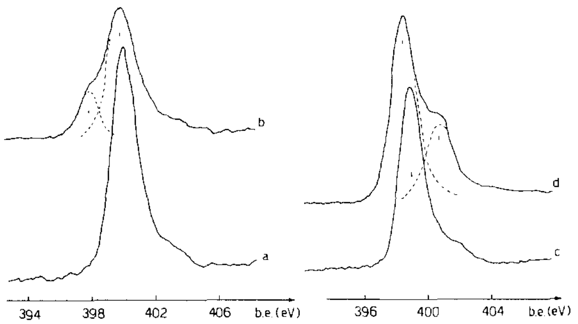

Fig. 1. N 1s spectra of the following compounds: (a) BD; (b) corrole; (c) Rh BD; (d) Rh corrole $(t\text{-}BuNC)_2$.

The presence of one *versus* two axially-coordinated ligands has no major effect on both N 1s and metal ionization peaks, as exemplified by the practically unperturbed b.e. for both Rh 3d and N 1s in the triphenylphosphine derivatives of both TPP and OEP.

On the basis of the last two points, and considering the almost equal values of N 1s b.e.s obtained for OEP and corrole, we can compare the behaviour of rhodium corrolates with that of the analogous rhodium porphyrinates.

In this comparison, [Rh corrole (PPh_3)] and [Rh corrole $(PPh)_3CO$] present less positive Rh atoms and N functions, while P 2p in the triphenylphosphine ligands is more positive (see Table I).

Different effects may contribute to the observed trend, among which the presence of axial ligands and the nature of the corrole molecule itself, which acts as a trinegative ligand and possesses a less-extended π-conjugation system in comparison with TPP and OEP.

The higher values of P 2p b.e. suggest, in our opinion, a larger contribution of the $(PPh)_3$ group to the countermoiety.

[Rh corrole $(t\text{-}buNC)_2$] shows a quite different behaviour with respect to the analogous corrolates and porphyrinates: N 1s b.e. related to macrocycle N functions falls at the lowest obtained value in the entire series of complexes, while Rh 3d b.e. is 0.5 – 0.7 eV higher than the corresponding values for the other corrolates, but it is practically coincident with the values shown by porphyrinates.

The general picture emerging from this comparison is much in favour of a more effective π-back-donation from the central metal ion to the antibonding molecular orbitals of the corrole ligands. In a comparison restricted to Rh corrolates and porphyrinates, this same interpretation was already proposed by us on the basis of the trend of $\nu(C{\equiv}N)$ values of isocyanide ligands in analogous Rh corrolates and porphyrinates [1].

As to the restricted comparison between Rh(III) and Co(II) complexes, our results have evidenced two more significant points:

(i) Rh and Co porphyrinates conform to a more general correlation of increasing N 1s b.e.s with increasing metal ion electronegativity [12].

(ii) The distinction in the N 1s peak shape which has been reported in the literature to be associated with the presence of paramagnetic or diamagnetic metals in porphyrin-like molecules [12], does not apply to the present compounds. However, the presence of satellites accompanying the Co 2p ionization peak has been clearly detected in reported compounds, while rhodium complexes never showed these structures.

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