

# Positron Annihilation Studies in Coordination and Organometallic Transition Metal Complexes of the Nickel Triad

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Estudos de aniquilação de pósitrons foram efetuados em uma série de complexos neutros dos tipos  $[MC\ell_2(EPh_3)_2]$  e  $[M(EPh_3)_{3,4}]$  e em seus ligantes  $EPh_3$  ( $M \equiv Ni, Pd, Pt$ ;  $E = P, As, Sb$ ). A probabilidade de formação e o tempo de vida do *ortho*-positrônio nestas séries são dependentes do estado de oxidação dos metais e da geometria dos complexos. Também foi observada a formação de positrônio em um complexo organometálico,  $[Pt(PhC=CH)(PPh_3)_2]$ .

Positron annihilation studies were performed on a series of neutral complexes of the type  $[MC\ell_2(EPh_3)_2]$  and  $[M(EPh_3)_{3,4}]$  and on their  $EPh_3$  ligands ( $M = Ni, Pd, Pt$ ;  $E = P, As, Sb$ ). The formation probability and lifetime of *ortho*-positronium in this series were found to be dependent on the oxidation state of the metals and the geometry of the complexes. It was also observed, positronium formation in an organometallic complex,  $[Pt(PhC\equiv CH)(PPh_3)_2]$ .

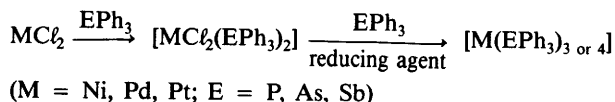
**Key words:** positron annihilation, transition metal complexes.

## Introduction

When injected into molecular solids, positrons can form positronium, Ps, which is the bound state of an electron and a positron. There is a great interest in the study of the Ps behaviour because its formation probability,  $I$ , and lifetime,  $\tau$ , depend on the physical and chemical properties of the solids<sup>1,2</sup>. Nevertheless only during the last decade positron annihilation studies applied to metallic complexes have received more attention. To our knowledge, the first attempt to correlate positron lifetimes with chemical structure of transition metal compounds was performed by Burger and Levay<sup>3,4</sup>, who found very complex relationships between changes in the annihilation parameters and changes in the nature of ligands and geometries of the complexes. Within a series of 44 compounds of Fe(II), Fe(III), Co(III), Ni(II), Cu(II) and Zn(II), these authors only found evidence for the formation of Ps in the zinc complexes  $[Zn\{S_2CN(CH_2C_6H_5)_2\}_2]$  and  $[Zn(pyridine)_2]Cl_2$ . They were unable at that time to interpret the strange behaviour of the zinc compound, although they tried to correlate the quantity of unpaired metal 3d electrons to longer positron lifetimes in the tetrahedral and square planar complexes studied<sup>4</sup>.

More recently, preliminary studies of lifetime measurements on solid pyridines<sup>5</sup> and on a series of lanthanides  $\beta$ -diketonates<sup>6</sup>, showed that Ps formation is favored in a chemical structure that allows a certain negative charge stabilization at preferred sites in the compounds. Moreover, these results showed also that the positron annihilation parameters are sensitive to charge transfer processes.

All these studies pointed out that a careful choice of transition metals and ligands could lead to complexes where the formation of Ps could be observed. We therefore chose planar and tetrahedral metal complexes of the nickel triad, since they can also be reduced to the isoelectronic Zn(II)  $d^{10}$  configuration. The series of compounds studied is particularly interesting, for they represent the basis of the synthetic route to an important class of complexes which have been employed in many catalytic systems.



## Experimental

To form Ps a source of positrons, usually  $^{22}Na$ , is used. This isotope decays into the excited state of  $^{22}Ne$  with the emission of a positron and almost simultaneously ( $10^{-11}s$ ) the emission of a 1,28 MeV gamma quantum which indicates the birth of this positron (Figure 1). Positrons injected into condensed materials will normally slow down to thermal or near-thermal energies within a few picoseconds, at which point they can combine with electrons to form Ps. Two Ps ground states exist, the *para* (or singlet) Ps, *p*-Ps, in which the positron and the electron have opposite spins and *ortho* (or triplet) Ps, *o*-Ps, in which the spins are parallel.

The characteristics of Ps in this condensed matter are somewhat changed due to its overlap with surrounding

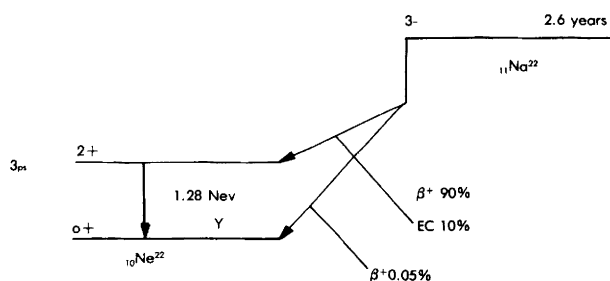


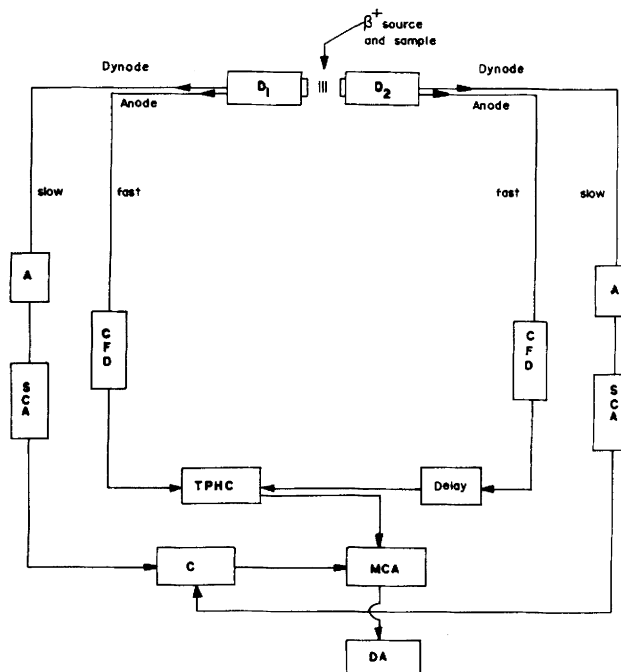
Figure 1. The dominant decay scheme of  $^{22}\text{Na}$

electrons<sup>7</sup>. The effect of this overlap is particularly important: the so called pick off annihilation process by which the positron in the *o*-Ps annihilates with one of the molecular electrons that has its spin opposite to that of the positron. On this process two gamma quanta are emitted and the *o*-Ps lifetime is strongly reduced from the vacuum value (140ns) to a few nanoseconds. The exact magnitude of the lifetime is determined by the amount of overlap between *o*-Ps and the electrons, since the annihilation probability increases (and the *o*-Ps lifetime therefore decreases) with increasing electron density at the positron site. Therefore if Ps is formed, the lifetime spectra obtained is believed to consist of three exponential components standing for *p*-Ps ( $\tau_1 = 120$  ps), free and bound positrons ( $\tau_2 \sim 200$ -500 ps) and *o*-Ps ( $\tau_3 > 1000$  ps), with formation probability  $I_1$ ,  $I_2$  and  $I_3$ , respectively.

Experimentally, the lifetime of the positron is measured as the time delay between the signal of 1,28 MeV gamma quantum and that of 0.51 MeV gamma quantum from the positron annihilation in the studied material. This is performed using conventional "fast-fast" or "fast slow" coincidence systems. The latter is shown schematically in Figure 2.

The apparatus basically consists of two detectors ( $D_1$ ,  $D_2$ ) for both signals of 1,28 MeV (birth) and 0,51 MeV (annihilation) gamma quanta; two electronic circuits, which record the delayed coincidence between signals, and a data analyzer.

The lifetime measurements were performed using a fast-slow coincidence spectrometer whose time resolution taken



$D_1$ ,  $D_2$ : Detectors

A: Amplifiers

SCA: Single - channel analyser

CFD: Constant fraction discriminator

C: Coincidence

TPHC: Time to pulse-height converter

MCA: Multichannel analyser

DA: Data analyser

Figure 2. Schematic diagram of the fast-slow coincidence system used in positron lifetime measurements.

as the full width at half maximum (fwhm) of the  $^{60}\text{Co}$  prompt spectrum was 340 ps. The  $^{22}\text{NaCl}$  source ( $4 \times 10^5 \text{ Bq}$ ,

Table 1. Positron lifetime parameters for three-component analysis

Compound	$\tau_2$ (ps)	$\tau_3$ (ps)	$I_2$ (%)	$I_3$ (%)
1 - $\text{PPh}_3$	$366 \pm 15$	$1154 \pm 35$	$56.8 \pm 0.7$	$25.2 \pm 1.4$
2 - $\text{AsPh}_3$	$375 \pm 16$	$1238 \pm 18$	$48.7 \pm 0.9$	$27.9 \pm 0.5$
3 - $\text{SbPh}_3$	$389 \pm 12$	$1232 \pm 22$	$54.6 \pm 2.6$	$23.9 \pm 0.9$
4 - $[\text{NiCl}_2(\text{PPh}_3)_2]$	$349 \pm 3$	$979 \pm 400$	$87.1 \pm 0.9$	$0.3 \pm 0.2$
5 - $[\text{PdCl}_2(\text{PPh}_3)_2]$	$358 \pm 3$	$1992 \pm 373$	$89.9 \pm 1.1$	$0.2 \pm 0.1$
6 - $[\text{PtCl}_2(\text{PPh}_3)_2]$	$353 \pm 1$	$3328 \pm 631$	$88.1 \pm 0.4$	$0.5 \pm 0.1$
7 - $[\text{PdCl}_2(\text{AsPh}_3)_2]$	$364 \pm 1$	$2329 \pm 243$	$89.0 \pm 0.6$	$0.1 \pm 0.1$
8 - $[\text{PdCl}_2(\text{SbPh}_3)_2]$	$375 \pm 25$	$763 \pm 329$	$88.5 \pm 3.3$	$0.2 \pm 0.1$
9 - $[\text{Pd}(\text{PPh}_3)_4]$	$379 \pm 4$	$1117 \pm 11$	$60.3 \pm 2.0$	$16.4 \pm 1.0$
10 - $[\text{Pd}(\text{AsPh}_3)_4]$	$383 \pm 6$	$1345 \pm 18$	$67.6 \pm 1.3$	$13.7 \pm 0.5$
11 - $[\text{Pt}(\text{PPh}_3)_4]$	$385 \pm 20$	$1373 \pm 40$	$61.8 \pm 2.0$	$12.3 \pm 0.5$
12 - $[\text{Pt}(\text{SbPh}_3)_3]$	$383 \pm 17$	$1913 \pm 94$	$74.5 \pm 2.3$	$8.2 \pm 0.2$
13 - $[\text{Pt}(\text{PhC}\equiv\text{CH})(\text{PPh}_3)_2]$	$401 \pm 14$	$1319 \pm 26$	$64.9 \pm 1.0$	$12.8 \pm 0.1$

carrierfree) was sealed between two mylar sheets and sandwiched between two identical 2 mm thick samples. The fraction of positrons annihilating in the source was estimated to be 10%. The lifetime spectra were analyzed using the positron fit-extended computer program<sup>8</sup>. Polycrystalline powders were used.

The divalent complexes were prepared by mixing hot ethanolic solutions of the ligands and cold solutions of  $\text{NiCl}_2$ ,  $\text{Na}_2[\text{PdCl}_4]$  or  $\text{H}_2[\text{PtCl}_6]$  in the same solvent. The precipitates were filtered and washed with ethanol and ether and dried under vacuum. The zerovalent compounds were prepared from suspensions of the divalent metal complexes in the same solvent with sodium borohydride as the reducing agent<sup>9</sup>. The purity of the complexes was checked by infrared spectroscopy and by microanalysis.

The lifetime spectra were resolved into three components with lifetimes  $\tau_i$  and intensities  $I_i$ . Table 1 shows mean values of these parameters, obtained from two separate sets of three measurements for each sample.

The resolution of the apparatus (340 ps) makes the data on the shortest-lived component ascribed to *p*-Ps somewhat unreliable. In order to reduce the scatter of the other parameters, the value of  $\tau_1$  was fixed at 120 ps, the intrinsic value of the *p*-Ps lifetime<sup>10</sup>. On this basis, the quality of fit of the spectra is not significantly altered and the derived parameters are close to those obtained when the analysis is made without any constraints. Since  $I_3$  is very small for the compounds 4 to 8, we do not attribute any physical significance to  $\tau_3$  in these compounds.

## Discussion and Conclusions

The longest lifetime component,  $\tau_3$ , is ascribed to the pick-off annihilation of *o*-Ps, while the intermediate lifetime,  $\tau_2$ , is likely to arise from the interaction of positrons in different regions of the solids.

The first interesting result we found is that the complexes bearing divalent, formally  $d^8$  metals do not form Ps, and that this fact is independent of the metal (compounds 4, 5, 6) and is apparently independent also of the ligand (compounds 5, 7, 8), in agreement with Levay's earlier work<sup>4</sup>. However, the ligands (compounds 1, 2, 3) and the zerovalent complexes (compounds 9 to 13) all show unequivocally the formation of *o*-Ps (Table 1). From the latter the most intriguing is  $[\text{Pd}(\text{PPh}_3)_4]$  (compound 9). Earlier observations on zerovalent metal complexes of the nickel triad have shown that they are luminescent when irradiated with ultraviolet light<sup>11,12</sup>. Our own observations showed that their luminescence is time dependent, i.e., the older the sample the weaker the emission of light under u.v. irradiation. Freshly prepared  $[\text{Pd}(\text{PPh}_3)_4]$  emits in the green, but older samples emit in the yellow region of the spectrum. Interestingly they show  $I_3$  values of 20% (green emitting form) and ca. 16% (yellow emitting form: three weeks old sample, value tabulated in Table 1). So far we have not been able to correlate these two observations, but we assume that this phenomenon does not invalidate the subsequent discussion since the average age of the compounds tabulated, their synthesis, storage etc., are the same.

The formation of *o*-Ps in the free ligands (average  $I_3$  ca. 25%) was as expected: they are Lewis bases, the elements P, As and Sb being in their valence state of III. These elements possess a pair of electrons which is used to form bonds with transition metals, but provides also the compounds with localized electron density necessary for positron capture and Ps formation, in analogy to our previous observations on pyridines<sup>5</sup>. Although the  $I_3$  values obtained are not sufficiently accurate to allow distinctions on the preferred ele-

ments site for Ps formation, the absolute values found seem to indicate the order as being  $\text{As} > \text{P} > \text{Sb}$ . This is surprising since the net electronegativity for this series of elements should be  $\text{P} > \text{As} > \text{Sb}$ . However, our results agree with those of Bodner<sup>13</sup>, who found the order of basicity  $\text{As} > \text{P} > \text{Sb}$  for the  $\text{EPh}_3$  ligands, while studying the <sup>13</sup>C NMR chemical shifts of  $[\text{Ni}(\text{CO})_3 \text{EPh}_3]$  complexes.

The interpretation of the data collected for the zerovalent,  $d^{10}$  metal containing compounds is not easy. Compounds 9 to 11 are tetrahedral, 18 electrons species. In this series the average  $I_3$  value is 14%, which is bigger than those found for the trigonal planar compounds 12,  $[\text{Pt}(\text{SbPh}_3)_3]$ , ( $I_3 = 8,2\%$ ) and 13  $[\text{Pt}(\text{PhC}\equiv\text{CH})(\text{PPh}_3)_2]$ , ( $I_3 = 12,8\%$ ), which are both formally 16 electrons complexes.

A qualitative, simple picture of the bonding scheme between the metal and the ligands in both geometries may serve as a guidance in elucidating the differences found. For instance, if it is assumed that metal to ligand back-donation is an important process for the delocalization of excess of electronic density from the metal, then this effects would be enhanced in planar complexes<sup>14</sup>. Distortions from planarity would difficult  $d\pi - d\pi$  interactions up to the limit of tetrahedral symmetry, in which the metal should be richer in electronic density. If this charge localization is important for positron capture and Ps formation, it turns out that the tetrahedral complexes should have greater  $I_3$  values. Moreover the extend  $d\pi - d\pi$  interactions in trigonal planar compounds should difficult the capture of electrons by the formed Ps, and as a consequence these compounds should show greater Ps lifetimes. It is interesting that both the  $I_3$  and  $\tau_3$  values found (Table 1) seem to fit this simple description. The apparent discrepancy of the value  $I_3 = 12,8\%$  of complex 13 may also be indicative of the acetylene acting as a four-electrons donor ligand. Such condition is frequently met in dinuclear complex and has been claimed to be responsible for the high stability of mononuclear, apparently electron-deficient transition-metal acetylene compounds<sup>15</sup>. A description of this concept has been made using extended Hückel molecular orbital calculations<sup>16,17</sup>.

The higher degree of Ps formation in the free ligands, may also be a consequence of the more localized nature of the electrons in the elements P, As, and Sb, than in the softer  $d^{10}$  metal centers in the complexes. In fact, the "hardening" of these centers, on changing their oxidation states from 0 to 2+, may explain the non-formation of *o*-Ps in the complexes 4 through 8. Levay<sup>4</sup> pointed out the possible formation of positron-halide bound states in transition metal complexes and we expect that this effect would decrease the possibility of Ps formation. However this hypothesis does not explain the behaviour of  $[\text{Zn}(\text{pyridine})_2]\text{Cl}_2$ . In fact our data strongly suggest that the electronic configuration at the metal center and the resulting geometry do influence Ps formation in transition metal complexes.

The data presented in this article represent the first study of Ps formation in neutral transition metal complexes. It was observed that *o*-Ps formation was largely dependent on the electronic state of the central metal and secondly, of the adopted geometry of the complex. In the zerovalent complexes studied, the geometry which allowed greater metal-ligand electronic delocalization partially inhibited *o*-Ps formation, but permitted longer *o*-Ps lifetimes. Complexes where the metals were in their higher oxidation states must have offered an alternative route for positron annihilation than Ps formation.

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