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Positronium formation in lanthanide (III) trifluoroacetate with 3-picoline-N-oxide compounds

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Abstract

Positron annihilation lifetime and Doppler broadening annihilation radiation line shape on the salts $Ln(CF_3COO)_3 \cdot xH_2O$ and the adducts $Ln(CF_3COO)_3(3\text{-picNO}) \cdot xH_2O$ (Ln = La–Pr, Sm–Lu and Y, and 3-picNO = 3 picoline-N-oxide, x in the range 0.75–1.33) were performed. Positronium formation in the adducts, except for the europium complex, was observed. These results are discussed in terms of the electronic properties of the central metal ions.

1. Introduction

When injected into molecular solids, positrons can form positronium (Ps), which is the bound state of an electron and a positron: *para*-positronium (*p*-Ps) in which the positron and the electron have opposite spins and *ortho*-positronium (*o*-Ps) in which the spins are parallel. The great interest in the study of Ps formation in ionic and molecular solids lies in the fact that its formation probability, I, and lifetime τ, depend on the physical and chemical properties of the solids [1]. However, only during the two last decades have positron annihilation studies applied to metallic complexes received more attention. Thus, positron annihilation lifetime (PALS) and Doppler broadening annihilation radiation line shape (DBS) measurements on solid pyridine [2] and on a series of lanthanide acetylacetonates [3] and dipivaloylmethanates [4], have shown that Ps is preferentially formed in compounds exhibiting a negative charge stabilization at specific sites. These results also indicated that the positron annihilation parameters are sensitive to the liability of the solids to charge transfer processes. Furthermore, early measurements on coordination and organometallic transition metal complexes of the nickel triad [5] led to the conclusion that the conformation of the complex plays an important role in the interpretation of the experimental data. First one must consider the nature of the central metal ion and second the nature of the ligand. Regarding the ligand, the interpretation is somewhat complicated due to the variety of influencing parameters such as chemical structure, composition, possibility of

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charge transfer processes and electron distribution. In fact, to explain the non-formation of Ps in complexes with ligands containing halogen, Levay [6] proposed the formation of a positron–halogen compound (halogen effect). However, our early results [7,8] showed that the electronic configuration of the central metal ion itself appears to be the more important effect.

These studies suggest that a careful choice of systems could lead to a better understanding of the correlation between positron annihilation parameters and the structure of the metallic complexes. In this way the $Ln(CF_3COO)_3(3\text{-picNO})\cdot xH_2O$ complexes seem to be a suitable system since it allows a simultaneous study of both the halogen effect and the consequences of changing the electronic density on the central ion site due to the adduct formation.

In general, if Ps is formed, the experimental lifetime spectra consist of three exponential components representing *p*-Ps ($\tau_1 = 120$ ps) free and bound positrons ($\tau_2 = 150$–500 ps) and *o*-Ps ($\tau_3 > 900$ ps), with the associated formation probabilities I_1, I_2 and I_3, respectively.

The positron lifetime is measured experimentally as the time delay between the 1.28 MeV γ-ray, emitted by the positron source, ^{22}Na radionuclide, immediately after the positron emission, and the 0.51 MeV annihilation radiation. This measurement may be performed using a conventional 'fast-fast' coincidence system.

Ps formation may also be studied by a complementary DBS technique. In this case the momentum distribution associated with the positron/electron pair for the various positron-containing species will be different at the moment of annihilation. The momentum distribution results in a small deviation from the colinearity of the two annihilation photons and in a broadening of the annihilation ray (Doppler broadening). The positron and *o*-Ps contribute to the lineshape with broad components and the *p*-Ps with a very narrow component.

2. Experimental

The adducts were synthesized and characterized by the Zinner method [9] and the reagents (lanthanide oxides, trifluoroacetic acid and 3-picoline-N-oxide) were purchased from Aldrich company and used without any further purification.

The PALS measurements were carried out using a fast-fast coincidence system (ORTEC), with time resolution of 280 ps, given by the ^{60}Co prompt curve. The ^{22}Na positron source with approximately 4.0×10^5 Bq activity was sandwiched between two identical 3.5 μm thick foils of Mylar. The source correction was approximately 10%. The lifetime spectra were analyzed for three components using the POSITTRONFIT-EXTENDED program [10].

The time resolution of the apparatus (280 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, τ_1 was fixed at 120 ps [11]. On this basis, the fit quality of the spectra (its reduced chi-square and the corresponding excess of probability) is not significantly altered and the derived parameters are close to those obtained when the analysis is made without any constraints.

DBS measurements were performed using an intrinsic Ge detector (Intertechnique) with a resolution of 1.23 keV, at the 514 keV ^{85}Sr photopeak. For calibration (52.5 eV/canal), the sources of ^{133}Ba ($E_\gamma = 356$ and 383.8 keV) and ^{207}Bi ($E_\gamma = 570$ keV) were counted simultaneously with the samples. The positron source used in DBS and PALS experiments was the same.

The parameter chosen to report the DBS results is the FWHM (full width at half-maximum of the annihilation line) determined using the ANNPEAK program [12].

All the experiments were performed at 294 K and atmospheric pressure, on sample powders. The experimental errors for the PALS parameters τ_3 and I_3, determined over multiple measurements, were found to be 50 ps and 1.0%, respectively, defining a confidence limit with a probability content 68.3%. For FWHM, the errors are approximately 0.01 keV.

3. Results and discussion

No Ps formation was observed in significant quantities ($I_3 < 2\%$) for the salts $Ln(F_3CCOO)_3$

$\cdot xH_2O$ (Ln = Pr(III), Sm(III), Eu(IIII), Gd(III), Tb(III), Dy(III), Er(III) and Yb(III)), while for the adducts of general formula $Ln(F_3CCOO)_3 \cdot 2(3\text{-picNO}) \cdot xH_2O$, the PALS experiments showed Ps formation with I_3 values from 8% to 41%, except for the europium compound, as shown in Table 1.

The longest lifetime component, τ_3, observed in adducts is ascribed to the pick-off annihilation of *o*-Ps. Since I_3 is very low for the europium complex, we do not attribute any physical significance to this compound. The assignment of *o*-Ps to the longest lifetime component observed in the adducts was confirmed by DBS experiments (Table 2).

As it can be seen from Table 2, the FWHM value for the europium complex is remarkably broader than those values observed for the other complexes. This result is in very good agreement with the PALS data (Table 1) that show no Ps formation for the europium adducts.

Two features of positron annihilation parameters are especially noteworthy; (i) non-Ps formation in the salts and high I_3 values for the adduct compounds and (ii) absence of Ps formation in europium compounds, as observed early for two different β-diketonates [3,4]. This behavior was explained supposing a charge transfer process (CTP) from the HOMO of the ligand to the 4f orbital of the central metal ion. In fact this process changes the $4f^6$ electronic structure of the Eu^{3+} to the more stable half-filled ($4f^7$) configuration. For the same reason the low value observed for the Yb complex could be attributed to the charge transfer process that changes the electronic configuration from $4f^{13}$ to $4f^{14}$ [13].

Two hypotheses can be put forward to explain the non-formation of Ps in the complexes: (i) the halogen effect, as suggested by Levay [6], and (ii) the electronic delocalization on the central ion stimulated by the inductive effect of the halogen. This second hypothesis is based on early experiments performed on coordination metal complexes of the nickel triad [5], for which it was shown that the positron capture and Ps formation depend on charge localization. As suggested by the authors [6] the hardening of the d^{10} metal centers on changing their oxidation state from 0 to 2^+ may explain the non-formation of Ps in the complexes $[NiM(PPH_3)]$ (M = Ni, Pt, Pd). So the strong difference observed between I_3 values in both series of compounds (salts and adducts) could be explained the same way. Certainly the adduct formation minimizes the hardening effect in the central ion by the inductive halogen effect and so, the addition of the ligand in the original complex is followed by an enhancement of Ps formation. It is interesting to note that, according to the halogen effect hypothesis, there is no reason to suppose that the addition of a ligand to the original salts would inhibit the formation of a so-called positron–halogen compound. Contrarily, the Ps formation was observed.

Table 1
PALS parameters for the adducts of general formula $Ln(F_3CCOO)_3 \cdot 2(3\text{-picNO}) \cdot xH_2O$[a]

Ln^{3+}	τ_2 (ps)	I_2 (%)	τ_3 (ps)	I_3 (%)
La	376	63	1768	23
Ce	366	71	1670	20
Pr	367	64	1918	24
Sm	364	55	1210	30
Eu	336	90	1821	01
Gd	338	47	1019	41
Tb	353	48	1041	36
Dy	396	60	1184	23
Ho	379	54	1197	29
Er	365	47	1106	35
Tm	375	56	1156	27
Yb	354	84	1289	08
Lu	359	55	1324	28

[a] For pure 3picoline-3-N-oxide $\tau_3 = 1641$ ns and $I_3 = 17\%$.

4. Conclusions

First of all we can conclude that Ps formation in metallic complexes is mainly related to the elec-

Table 2
FWHM of compounds of general formula $Ln(F_3CCOO)_3 \cdot 2(3\text{-picNO}) \cdot xH_2O$

Ln^{3+}	La	Ce	Pr	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
FWHM (keV)	2.76	2.77	2.70	2.59	2.98	2.45	2.50	2.60	2.57	2.53	2.57	2.78	2.64

tronic structure of the central metal ion but, on changing the electronic density of this ion by changing the nature of the ligand, the positron annihilation parameters may be changed.

Finally a new important conclusion obtained from the analysis of these results is that the softening of the central metal ion only will be effective for Ps formation, if the electronic structure of the ion is favorable as it was confirmed through the europium adduct results. So we are strongly convinced that the positron behavior in metallic complexes is mainly governed by the central metal ion.

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