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Positronium formation in solid acetylacetonate complexes

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ABSTRACTS

Positron annihilation lifetime (LS) and Doppler broadening annihilation radiation lineshape (DBARL) were measured at room temperature in a series of solid acetylacetonate chelates involving metals of different groups. The LS and DBARL obtained parameters were associated with the electronic configuration of the central metal ions and their electronic spectra.

INTRODUCTION

Preliminary studies on a series of lanthanide acetylacetonates and dipivaloylmethanates (1,2), and on coordination and organometallic transition metal complexes of the nickel triad (3), have shown that the positron annihilation parameters are sensitive to the liability of the solids to charge transfer process, conformation of the complexes, as well the nature of both the central metal ion and the ligand.

With the purpose to obtain more information about these subjects, we performed the study on a series of solid acetylacetonate chelates of the groups IIA, IIIB, VB, VIB, VIIB, VIIIB, IB, IIB and IIIA metals, using both LS and DBARL techniques.

EXPERIMENTAL

The metal acetylacetonates were synthesized as described in the literature (4), with some modifications, when necessary. The complexes were purified by column chromatographic method, using cellulose as stationary phase and benzene as eluent. The characterization of the compounds was made by I.R. and powder X-ray spectroscopies, by comparison with published data, and elemental analysis.

The lifetime spectrometer and positron source were described elsewhere (5). The lifetime spectra were satisfactorily analysed in three components, using the POSITRONFIT-EXTENDED program (6),

leading to the intensities (I_i) and lifetimes (τ_i) of the various positron states: subscripts 1, 2, and 3 will refer to para-positronium (p-Ps), free-positron and ortho-positronium (o-Ps), respectively. The superscript "o" denotes the parameters measured in the pure solid phase. The source correction was 10%. In all cases, τ_1^0 was fixed to 120 ps, the value for p-Ps self-annihilation. The intrinsic Ge detector (INTERTECHNIQUE) used for DBARL measurements has a resolution of 1.22 keV (FWHM of the Sr-85, 514 keV line) with an efficiency of 15.9% at 1.33 MeV. The parameter chosen for reporting DBARL results is the FWHM (full width at half maximum of the annihilation line), determined using the ANNPEAK program (7).

RESULTS AND DISCUSSION

The o-Ps yields (I_3^0), FWHM, and electronic configuration of the central metal ion of the studied complexes are summarized in Table 1.

Table 1 - LS and DBARL parameters of metal acetylacetonates and the electronic configuration of the central metal ions (E.C.).

Compound Class 1	I_3^0 (%)	FWHM (keV)	E.C.	Compound Class 2	I_3^0 (%)	FWHM (keV)	E.C.
VO(acac) ₂	1.8	2.88	[Ar]3d ¹	Al(acac) ₃	44.0	2.44	[Ne]
Cr(acac) ₃	2.6	2.76	[Ar]3d ³	Ga(acac) ₃	46.4	2.44	[Ar]3d ¹⁰
Mn(acac) ₃	0.9	2.85	[Ar]3d ⁴	In(acac) ₃	46.2	2.50	[Kr]4d ¹⁰
Fe(acac) ₃	0.7	2.88	[Ar]3d ⁵	Be(acac) ₂	27.0	2.46	[He]
Co(acac) ₃	1.3	2.90	[Ar]3d ⁶	Sc(acac) ₃	26.2		[Ar]3d ⁰
Rh(acac) ₃	0.4	2.88	[Kr]4d ⁶	Zr(acac) ₄	29.4	2.51	[Kr]4d ⁰
Co(acac) ₂ ^(a)	1.0	2.91	[Ar]3d ⁹	Y(acac) ₃ ^(b)	38.9	2.49	[Kr]3d ⁰
Ru(acac) ₃	1.5	2.83	[Kr]4d ⁵	Cd(acac) ₂ ^(a)	10.4	2.66	[Kr]4d ¹⁰

(a) Dihydrate compound ; (b) Trihydrate compound

As can be seen in Table 1 we can separate the studied metal acetylacetonates in two classes :

Class 1 - Ps formation is not observed in appreciable amount and I_3^0 values for this class are extremely small, as compared with the corresponding values for the other class. The τ_3^0 values for these compounds are larger than 1.8 ns and poorly

reproducible. This kind of behaviour have been already observed in many solids with $I_3^0 < 5\%$; therefore, little significance is ascribed to these parameters (5). The experimental FWHM values obtained for this class, in the range of 2.76 - 2.90 keV, are compatible with many other results in solid (8,9) and liquid phases (10) where the Ps formation is very low, or no Ps is formed.

Class 2 - Ps formation is observed in appreciable amount. The I_3^0 values are very large, and the τ_3^0 values are in the range 1.00 - 1.40 ns. The experimental FWHM values for the compounds of this class are smaller than the corresponding value for the water (2.66 keV) indicating the presence of a narrow component attributed to p-Ps.

The metal ions of the complexes of the Class 1 have incompletely filled 3d or 4d orbitals in contrast with the completely filled or empty 3d or 4d orbitals of the metal ions of the chelates of the Class 2. The experimental UV-visible spectra for the compounds of Class 1 show two characteristic types of electronic transition: charge tranfer and d-d transitions, inexisting in the electronic spectra of the compounds of the Class 2 (see Fig.1a and Fig.1b, as typical examples). These results suggest that the electronic transitions observed in the metal complexes of Class 1, particularly the d-d transitions, may be closely associated with the inability of Ps formation in this class of compounds.

Fig.1a - The electronic absorption spectrum $\text{Rh}(\text{acac})_3$ (Class 1)

Fig.1b -The electronic absorption spectrum of $\text{Ga}(\text{acac})_3$ (Class 2)

The only found exception is the $\text{Ir}(\text{acac})_3$ (not showed in Table 1). This complex presents all spectroscopic characteristics of the compounds of Class 1: incompletely filled 5d orbitals ($[\text{Xe}] 5d^6$), charge transfer and d-d transitions. However, this complex shows significative Ps yields ($I_3^0 = 27.0\%$ and $\text{FWHM} = 2.57 \text{ keV}$). The shielding effect promoted by the filled 4f orbitals may be responsible for this peculiar behaviour. Moreover, differently from the complexes of Class 1 which are inhibitors or quenchers, the $\text{Ir}(\text{acac})_3$ is rather inert as inhibitor or quencher when diluted with $\text{Al}(\text{acac})_3$ matrix in the binary solid solution $\text{Al}_{(1-x)}\text{Ir}_{(x)}(\text{acac})_3$ (see reference 11).

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