ELSEVIER

Intraligand phosphorescence of lead(II) β-diketonates under ambient conditions

Andreas Strasser, Arnd Vogler*

Institut für Anorganische Chemie, Universität Regensburg, D-93040 Regensburg, Germany

Abstract

The lead(II) β-diketonates $Pb(acac)_2$, $Pb(hfac)_2$, $Pb(tta)_2$, $Pb(dbm)_2$ and $Pb(dpm)_2$ with acac = acetylacetonate, hfac = hexafluoro-acetylacetonate, tta = thenoyltrifluoroacetonate, dbm = dibenzoylmethanate and dpm = dipivaloylmethanate show an intraligand (IL) phosphorescence in low temperature glasses. With the exception of $Pb(dpm)_2$ this emission appears also at room temperature (r.t.) for the solid compounds while in solution this phosphorescence is rather weak.
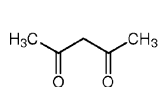© 2004 Elsevier B.V. All rights reserved.

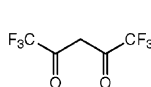*Keywords:* Lead complexes; β-Diketonate complexes; Phosphorescence

1. Introduction

Optical sensing of Pb^{2+} by luminescence spectroscopy has attracted much attention in recent years [1]. Various approaches have been developed. Owing to its intrinsic emission which originates from metal-centered (MC) sp triplets [2], Pb^{2+} can be used as its own sensor [3]. However, most procedures rely on the selective interaction of Pb^{2+} with suitable organic fluorophores [1]. Generally, a fluorescence is shifted or changes its intensity in the presence of Pb^{2+} which modifies the environment of the fluorophore. This occurs by various influences including steric effects, variation of the microscopic polarity, inhibition or enhancement of excited state electron transfer. In most cases a direct electronic interaction between Pb^{2+} and the fluorophore does apparently not take place. Since Pb^{2+} is a heavy metal an electronic coupling should lead to a fluorescence quenching of the organic fluorophore by increased
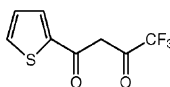
intersystem crossing (heavy atom effect). As a further consequence the lifetimes of the lowest energy triplet of the organic probe should be reduced and a phosphorescence may appear. Indeed, $Pb(qu)_2$ with qu = 8-quinolinolate (or oxinate) displays this behaviour [4]. However, at room temperature (r.t.) the intraligand (IL) phosphorescence is hardly detectable. In contrast, the complex $Pb(hfac)_2$ with hfac = hexafluoroacetylacetonate has been recently shown to exhibit a strong IL triplet emission at r.t. [5]. It it suspected that this type of IL phosphorescence of Pb(II) diketonates is a very general phenomenon. We explored this possibility and selected the complexes $Pb(acac)_2$, $Pb(hfac)_2$, $Pb(tta)_2$, $Pb(dbm)_2$ and $Pb(dpm)_2$ with acac = acetylacetonate, tta = thenoyltrifluoroacetonate, dbm = dibenzoylmethanate and dpm = dipivaloylmethanate for the present study.
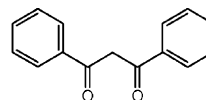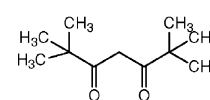

The emissions of these complexes were expected to cover different regions of the visible spectrum. They are not only of interest in the area of optical sensors. As triplet emitters they might find application in organic light emitting diodes (OLED) technology.

* Corresponding author. Tel.: +49-941-943-4485;
fax: +49-941-943-4488.
E-mail address: arnd.vogler@chemie.uni-regensburg.de (A. Vogler).

2. Experimental

2.1. Materials

The compounds Pb(acac)$_2$ (Strem), Pb(hfac)$_2$ (Strem), Pb(dpm)$_2$ (ABCR), Hdbm (ABCR) and Htta (Aldrich) were commercially available and used without further purification. Ethanol (Merck, Uvasol) was used as received, 2-methyltetrahydrofuran (Aldrich, 99+) was distilled from its blue sodium benzophenone ketyl solution.

2.1.1. Synthesis of Pb(tta)$_2$

To a solution of Pb(NO$_3$)$_2$ (660 mg, 2.0 mmol) and sodium acetate (1 g) in 10 ml water was added dropwise under stirring a solution of 889 mg (4.0 mmol) Htta in 6 ml ethanol, 50 ml of water was added. The yellow precipitate was collected by filtration, washed with water and dried over P$_2$O$_5$. Yield: 1.16 g.

Analytical calculation for C$_{16}$H$_8$O$_4$F$_6$S$_2$Pb: C, 29.59; H, 1.24%. Found: C, 29.86; H, 1.24%.

2.1.2. Synthesis of Pb(dbm)$_2$

Pb(NO$_3$)$_2$ (600 mg, 1.81 mmol), sodium hydroxide (1.7 g) and Hdbm (817 mg, 3.64 mmol) were stirred in 80 ml of water over night. The product was collected by filtration, washed with NaOH solution (0.5 mol l^{-1}) and water. It was dried over P$_2$O$_5$. Yield: 869 mg.

Analytical calculation for C$_{30}$H$_{22}$O$_4$Pb: C, 55.12; H, 3.39%. Found: C, 55.07; H, 3.39%.

2.2. Methods

Absorption spectra were measured with a Kontron Uvikon 932 double beam spectrophotometer. Emission and excitation spectra were recorded on a Hitachi 850 spectrofluorometer equipped with a Hamamatsu 928 photomultiplier. The luminescence spectra were corrected for monochromator and photomultiplier efficiency.

3. Results

Of the investigated diketonates of Pb(II) only the fluorine containing chelates Pb(tta)$_2$ and Pb(hfac)$_2$ are soluble in ethanol without decomposition. As indicated by concomitant spectral changes Pb(acac)$_2$, Pb(dbm)$_2$ and Pb(dpm)$_2$ decompose in wet solvents.

In solution all five Pb(II) diketonates show long-wavelength absorptions (Figs. 1–4, Table 1) in the near UV spectral region. In low temperature glasses they display a blue or green emission (Figs. 1–4, Table 2). The solid compounds exhibit this luminescence also at r.t. However, under ambient conditions the emissions are slightly shifted and occasionally supplemented by a short-wavelength component. In the case of Pb(acac)$_2$ the emission of the solid material is quite different from that in the glassy medium

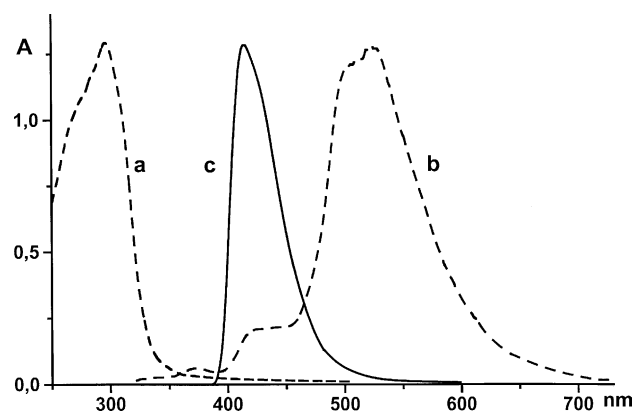Fig. 1. Electronic absorption (a) and emission (b, c) spectra of Pb(acac)$_2$. Absorption: $d = 1$ cm, 2-methyltetrahydrofuran. Emission: solid, room temperature, $\lambda_{exc} = 270$ nm (b); 2-methyltetrahydrofuran, 77 K, $\lambda_{exc} = 290$ nm (c).

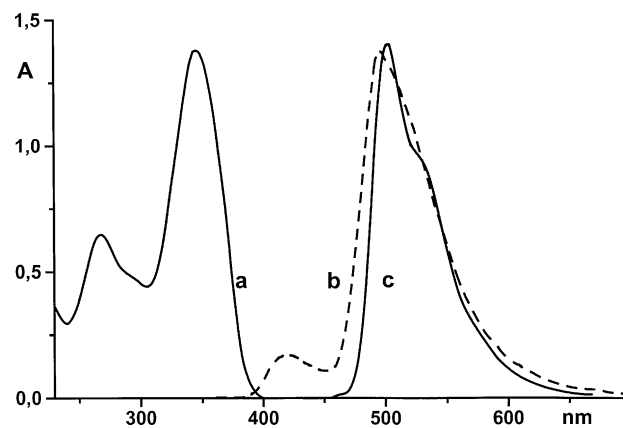

Fig. 2. Electronic absorption (a) and emission (b, c) spectra of Pb(tta)$_2$. Absorption: $c = 4 \times 10^{-5}$ mol l^{-1}, $d = 1$ cm, ethanol. Emission: solid, room temperature, $\lambda_{exc} = 330$ nm (b); ethanol, 77 K, $\lambda_{exc} = 340$ nm (c).
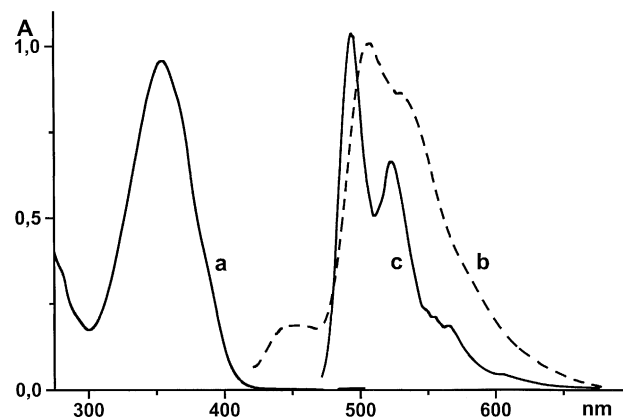

Fig. 3. Electronic absorption (a) and emission (b, c) spectra of Pb(dbm)$_2$. Absorption: $d = 1$ cm, 2-methyltetrahydrofuran. Emission: solid, room temperature, $\lambda_{exc} = 300$ nm (b); 2-methyltetrahydrofuran, 77 K, $\lambda_{exc} = 350$ nm (c).
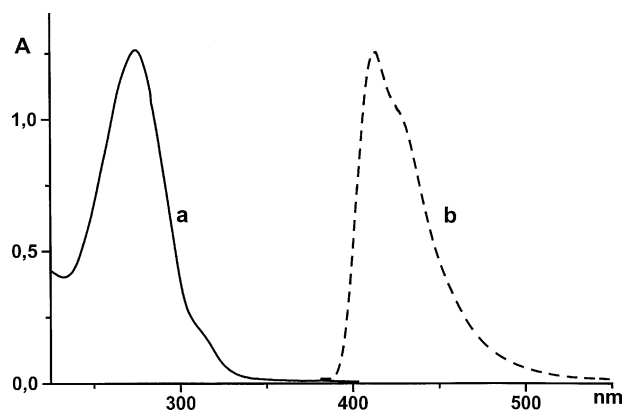
Fig. 4. Electronic absorption (a) and emission (b) spectrum of Pb(dpm)$_2$. Absorption: $c = 6 \times 10^{-5}$ mol l^{-1}, $d = 1$ cm, ethanol. Emission: ethanol, 77 K, $\lambda_{exc} = 270$ nm (b).

Table 1
Absorption band maxima and extinction coefficients in ethanol

	λ_{max}/nm (ε/l mol^{-1} cm^{-1})
Pb(acac)$_2$	297[a]
Pb(hfac)$_2$	312 (12000)
Pb(tta)$_2$	267 (15000), 344 (33000)
Pb(dbm)$_2$	354[a]
Pb(dpm)$_2$	274 (21000)

[a] 2-Methyltetrahydrofuran.

(Fig. 1). The emissions appear also in solution at r.t. but are very weak. In the case of Pb(dpm)$_2$ no luminescence at ambient temperatures is found.

4. Discussion

The long-wavelength absorptions of the Pb(II) diketonates are assigned to spin-allowed IL $\pi\pi^*$ transitions. Such IL absorptions have been previously identified in the electronic spectra of various other diketonate complexes [6].

Metal β-diketonates in low temperature (77 K) glasses are well known to display a photoluminescence which originates from the lowest energy intraligand (IL) $\pi\pi^*$ triplet of the β-diketonate ligands [6–8]. Depending on the substituents at the ligands this phosphorescence ranges from blue to green. Frequently, the emission band shows a diagnostic vibronic structure. However, if other excited states

such as metal-centered (MC) or charge transfer (CT) states are located at lower energies they will be populated by radiationless deactivation from the diketonate IL states. As a consequence such complexes are not luminescent (e.g. Co(β-diketonate)$_3$) [9] or they emit from other excited states. Examples are Cr(acac)$_2$ with a dd emission [9] and Eu(β-diketonate)$_3$ with a ff emission [10].

In low temperature glasses the lead(II) β-diketonates show the typical β-diketonate IL phosphorescence (Figs. 1–4; Table 2). With the exception of Pb(acac)$_2$ a well-discernible vibronic structure can be recognised.

The lead(II) complexes PbCl$_3^-$ and PbCl$_4^{2-}$ exhibit a MC phosphorescence at 538 nm and 518 nm, respectively [2]. Since the Pb(II) β-diketonates emit in the same wavelength region, the IL phosphorescence might be obscured by the MC phosphorescence. However, in their ^{3}MC (sp) excited states lead(II) complexes undergo large structural rearrangements which cause huge Stokes shifts. There is indeed no indication for the appearance of a MC emission of the lead(II) diketonates. Accordingly, the sp triplets may lie well above the emissive β-diketonate IL triplets.

Solid samples of Pb(hfac)$_2$, Pb(tta)$_2$ and Pb(dbm)$_2$ show the IL phosphorescence also at r.t. (Figs. 2 and 3, Table 2). This is certainly a consequence of the heavy-atom effect induced by lead. Increased spin-orbit coupling facilitates intersystem crossing. As a final result, the IL phosphorescence is fast enough to successfully compete with radiationless deactivations.

The solid complexes Pb(tta)$_2$ and Pb(dbm)$_2$ display in addition to the r.t. phosphorescence a weak fluorescence ($\lambda_{max} = 418$ and 448 nm, respectively) which overlaps with the spin-allowed absorption. Such an IL fluorescence of dbm complexes has been observed before [11]. The emission behaviour of solid Pb(dpm)$_2$ and Pb(acac)$_2$ is distinctly different from that of the other lead(II) diketonates. It is quite surprising that solid Pb(dpm)$_2$ does not exhibit any luminescence at r.t. The IL triplet of this complex apparently undergoes a fast radiationless deactivation which must be facilitated by suitable vibrations. The t-butyl substituent of the dpm ligand is well known to induce such a "loose bolt" effect [12]. A further striking result is the observation that the emission spectrum of Pb(acac)$_2$ in the solid state is totally different from that in low temperature glasses. While the emission in the glass is certainly the normal IL phosphorescence which resembles that of various other metal acac complexes, the r.t. emission of solid Pb(acac)$_2$ shows a

Table 2
Luminescence band maxima and excitation wavelength

	λ_{max}/nm [λ_{exc}/nm] solid, 298 K	λ_{max}/nm [λ_{exc}/nm] ethanol glass, 77 K
Pb(acac)$_2$	374, 427, 503 (sh), 525 [270]	415[a] [290]
Pb(hfac)$_2$	467, 488 (sh) [300]	460, 485
Pb(tta)$_2$	418, 495 [330]	502, 532 (sh) [330]
Pb(dbm)$_2$	448, 506, 533 (sh) [300]	494[a], 523[a], 565[a] (sh) [350]
Pb(dpm)$_2$	–	413, 430 (sh) [270]

[a] 2-Methyltetrahydrofuran.

complicated pattern including a band at $\lambda_{max} = 525\,nm$ which extends to 700 nm (Fig. 1). Solid In(acac)$_3$ displays also a very broad long-wavelength emission at $\lambda_{max} = 510\,nm$ [8]. It has been suggested that this emission is caused by an intermolecular interaction which is similar to an excimer formation. In the case of the other lead(II) diketonates such an excimer formation could be avoided by the large substituents which may prevent a close approach of the ligands. However, a conclusive explanation can presently not be given.

Finally, it must be emphasised that the lead(II) diketonates are only very weakly emissive in solution at r.t. It is assumed that these complexes are flexible enough to provide a facile radiationless deactivation which is slowed down only by the rigid structures in the solid state.

In summary, it has been shown that lead(II) induces a heavy-atom effect in β-diketonate ligands. As a consequence various Pb(II) β-diketonates exhibit a r.t. phosphorescence. While this phosphorescence is largely restricted to the solid state it should be possible to identify ligands which display a strong phosphorsecence also in solution at r.t. Such phosphorescent complexes might be applied for analytical purposes.

Acknowledgements

References

[1] M.W. Perkovic, Inorg. Chem. 39 (2000) 4962;
S. Deo, H.A. Godwin, J. Am. Chem. Soc. 122 (2000) 174;
J. Li, Y. Lu, J. Am. Chem. Soc. 122 (2000) 10466;
C.-T. Chen, W.-P. Huang, J. Am. Chem. Soc. 124 (2002) 6246;
T. Hayashita, D. Qing, M. Minagawa, J.C. Lee, C.H. Ku, N. Teramae, Chem. Commun. (2003) 2160;
Y. Lu, Chem. Eur. J. 8 (2002) 4589.
[2] H. Nikol, A. Becht, A. Vogler, Inorg. Chem. 31 (1992) 3277;
A. Vogler, H. Nikol, Comments Inorg. Chem. 14 (1993) 245.
[3] S.K. Dutta, M.W. Perkovic, Inorg. Chem. 41 (2002) 6938.
[4] R. Ballardini, G. Varani, M.T. Indelli, F. Scandola, Inorg. Chem. 25 (1986) 3858.
[5] A. Strasser, A. Vogler, Inorg. Chem. Commun. 7 (2004) 528.
[6] W.F. Sager, N. Filipescu, F.A. Serafin, J. Phys. Chem. 69 (1965) 1092;
J.A. Kemlo, T.M. Shepherd, J. Chem. Soc., Faraday Trans. 2 73 (1977) 1850;
J.S. Brinen, F. Halverson, J.R. Leto, J. Chem. Phys. 42 (1965) 4213.
[7] G.A. Crosby, R.J. Watts, S.J. Westlake, J. Chem. Phys. 55 (1971) 4663.
[8] R.H. Clarke, R.E. Connors, Spectrochim. Acta 30 (1974) 2063.
[9] R.L. Lintvedt, in: P.D. Fleischauer, A.W. Adamson (Eds.), Concepts of Inorganic Photochemistry, Wiley, New York, 1975, p. 299 (Chapter 7).
[10] G.E. Buono-Core, H. Li, Coord. Chem. Rev. 99 (1990) 55.
[11] T. Ohno, S. Kato, Bull. Chem. Soc. Jpn. 47 (1974) 1901.
[12] N.J. Turro, Modern Molecular Photochemistry, Benjamin/Cummings, Menlo Park, 1978, p. 170.