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Short communication

Optical properties of bis(2,6-diphenylphenolate)niobium(V) trichloride Luminescence from a phenolate to metal charge transfer state

Horst Kunkely, Arnd Vogler*

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

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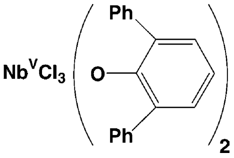
Abstract

The electronic spectra of $Nb^V(dpp)_2Cl_3$ (dpp^-: 2,6-diphenylphenolate$^-$) in the solid state under ambient conditions are reported. The scattered transmission spectrum shows a long-wavelength band ($\lambda_{max} = 415$ nm) which is assigned to a spin-forbidden (phenolate $\rightarrow$ Nb^V) ligand-to-metal charge transfer (LMCT) transition. The complex displays a luminescence ($\lambda_{max} = 522$ nm; $\tau \sim 10^{-5}$ s) which is suggested to originate from the LMCT triplet.

Keywords: Electronic spectra; Luminescence; Charge transfer; Niobium complexes; Phenolate complexes

1. Introduction

A variety of aryl–imido complexes of the d^0 metals tantalum(V) and niobium(V) have been reported to show a luminescence which originates from ligand-to-metal charge transfer (LMCT) states [1–3]. Owing to the reducing character of aryl–imides ($Ar–N^{2-}$) LMCT transitions occur at relatively low energies. It is thus quite surprising that the optical properties of analogous complexes with phenolate ligands ($Ar–O^-$) which are isoelectronic to $Ar–N^{2-}$ have not yet been examined. We explored this possibility and selected the complex $Nb^V(dpp)_2Cl_3$ with dpp^-: 2,6-diphenylphenolate$^-$ for the present study.



In this context, it should be emphasized that metal–phenolate chromophores play a very important role in biochemistry [4,5]. The colors of various metallo enzymes which contain oxidizing metals such as Fe(III) and Cu(II) and tyrosinate as phenolate ligands are caused by long-wavelength phenolate-to-metal LMCT absorptions [6]. In contrast to the general importance of these electronic transitions very little is known on the properties of such LMCT excited states. Quite recently, it has been shown that Fe(III) [7] and Cu(II) [8] phenolates are photoactive. They undergo a metal reduction which is initiated by a LMCT excitation. A luminescence originating from phenolate-to-metal LMCT excited states has apparently not yet been observed. Accordingly, the present study was expected to provide further inside into the excited behavior of LMCT states involving phenolates as CT donor ligands. In a related study, the complex ethylenebis(indenyl)zirconium(IV) binolate with binol: 1,1′-binaphthyl-2,2′-diol was recently examined [9]. In this case, however, the luminescence is not of the LMCT but of the intraligand (IL) type.

2. Experimental

2.1. Materials

For spectroscopic measurements the solvents were of spectrograde quality. They were rigorously dried and saturated with argon. The compounds 2,6-diphenylphenol and trichlorobis(2,6-diphenylphenolate)niobium(V) were commercially available from Aldrich and used without further purification.

2.2. Instrumentation

Absorption spectra were measured with a Varian Cary 50 or a Kontron Uvikon 860 absorption spectrophotometer.

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* Corresponding author. Tel.: +49-941-943-4484; fax: +49-941-943-4488.
E-mail address: arnd.vogler@chemie.uni-regensburg.de (A. Vogler).

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Emission and excitation spectra were recorded on a Hitachi 850 fluorescence spectrometer equipped with a Hamamatsu 928 photomultiplier for measurements up to 900 nm. The luminescence spectra were corrected for monochromator and photomultiplier efficiency variations. Emission lifetimes were measured on a luminescence analysis system (Model LS-100-07) from Photon Technology International.

3. Results

The electronic spectrum of dppH in C_2H_5OH (Fig. 1) shows absorptions at $\lambda_{max} = 296$ ($\varepsilon = 5490\,M^{-1}\,cm^{-1}$) and 237 nm (26 200). This phenol displays a fluorescence ($\lambda_{max} = 364$ nm) at RT while an additional phosphorescence ($\lambda_{max} = 460$ nm) appears at 77 K (Fig. 1).

The complex $Nb(dpp)_2Cl_3$ is extremely sensitive to moisture and undergoes also a facile decomposition in various other solvents. In order to avoid any interference by impurities which may be formed by solvolysis the electronic spectra of $Nb(dpp)_2Cl_3$ were examined in the solid state.

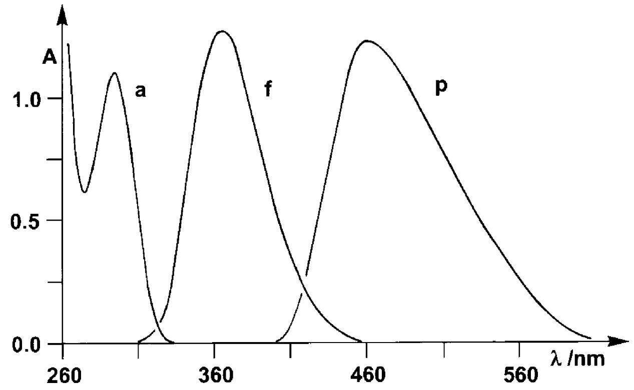

Fig. 1. Electronic absorption (a), fluorescence (f) and phosphorescence (p) spectra of 1.98×10^{-4} M 2,6-diphenylphenol (dppH) in ethanol under argon. (a, f) At room temperature, 1 cm cell; (p) at 77 K, $\lambda_{exc} = 300$ nm, intensity in arbitrary units.

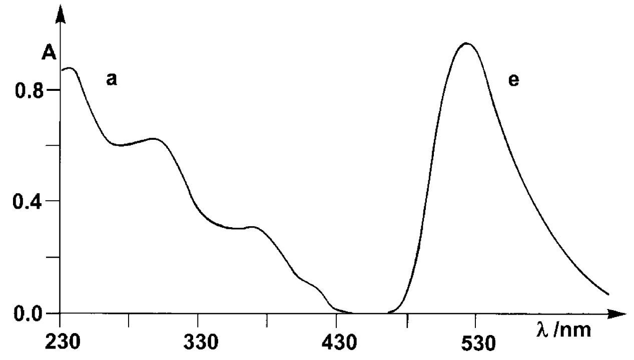

Fig. 2. Scattered absorption (a) and emission (e) spectrum of solid $Nb(dpp)_2Cl_3$ under argon at room temperature. (a) In paraffin oil, 0.1 mm cell; (e) $\lambda_{exc} = 400$ nm, intensity in arbitrary units.

The UV spectrum of solid $Nb(dpp)_2Cl_3$ was measured as scattered transmission spectrum (Fig. 2). It shows bands at $\lambda_{max} = 415$, 370, 300 and 240 nm. The solid complex exhibits a luminescence (Fig. 2) at $\lambda_{max} = 522$ nm which is relatively weak at RT but becomes somewhat more intense at 77 K. Unfortunately, the emission was not strong enough for reliable lifetime measurements. However, the lifetime was estimated to be $\tau \sim 10^{-5}$ s. The excitation spectrum roughly matches the transmission spectrum. The longest-wavelength feature of the transmission spectrum at 415 nm appears as a well resolved band in the excitation spectrum.

4. Discussion

Generally, Ta(V) and Nb(V) complexes are characterized by LMCT transitions owing to empty valence shell (d^0) of these metal centers [1–3,6,10,11]. Acccordingly, it is not surprising that the luminescence of those compounds originates also from LMCT states. As members of the second and third transition series both metals exert a heavy-atom effect which leads to increased spin–orbit coupling. As a consequence these complexes do not show any fluorescence, but only a phosphorescence which appears even at RT. The complex $Nb(dpp)_2Cl_3$ does not seem to be an exception.

Phenolates are certainly stronger CT donors than chloride. It follows that the lowest-energy transitions of $Nb(dpp)_2Cl_3$ are of the LMCT type. A comparison of the UV spectra of $Nb(dpp)_2Cl_3$ and dppH shows that at $\lambda < 350$ nm the spectrum of the complex may also contain IL bands. The emission of $Nb(dpp)_2Cl_3$ occurs at distinctly longer wavelength than that of dppH. It follows that the emission of the complex cannot be attributed to the dpp ligand but should originate from the $dpp^- \rightarrow Nb^V$ LMCT state. In agreement with the relatively long emission life time of $Nb(dpp)_2Cl_3$ and supported by previous observations on numerous other Ta(V) and Nb(V) complexes [1–3,10,11] it is concluded that the emissive LMCT state is a triplet. Since, however, the emission band of $Nb(dpp)_2Cl_3$ slightly overlaps with the longest-wavelength feature of the transmission spectrum, both bands should belong to the same transition. Accordingly, the 415 nm band of $Nb(dpp)_2Cl_3$ must be assigned to a spin-forbidden singlet–triplet LMCT transition. This assumption is in harmony with the observation that the 415 nm band of the transmission spectrum appears as well-pronounced band in the excitation spectrum. Light which is absorbed at 415 nm leads apparently to a direct population of the emitting triplet. The presence of spin-forbidden LMCT absorptions has been also observed in the spectra of Ta(V) and Nb(V) aryl–imide complexes [1–7].

In conclusion, the complex $Nb(dpp)_2Cl_3$ is characterized by a lowest-energy spin-forbidden (phenolate-to-Nb^V)

LMCT transition. The complex shows a RT luminescence which originates from the LMCT triplet.

References

[1] K.S. Heinselman, M.D. Hopkins, J. Am. Chem. Soc. 117 (1995) 12340.

[2] D.S. Williams, D.W. Thompson, A.V. Korolev, J. Am. Chem. Soc. 118 (1996) 6526.

[3] D.S. Williams, A.V. Korolev, Inorg. Chem. 37 (1998) 3809.

[4] L. Que, Coord. Chem. Rev. 50 (1983) 73.

[5] W. Kaim, B. Schwederski, Bioinorganic Chemistry: Inorganic Elements in the Chemistry of Life. An Introduction and Guide, Wiley, Chichester, UK, 1984.

[6] A.B.P. Lever, Inorganic Electronic Spectroscopy, Elsevier, Amsterdam, 1984.

[7] H. Kunkely, A. Vogler, Inorg. Chem. Commun. 6 (2003) 1335.

[8] H. Kunkely, A. Vogler, Inorg. Chim. Acta, in press.

[9] H. Kunkely, A. Vogler, Inorg. Chem. Commun. 7 (2004) 35.

[10] S. Paulson, B.P. Sullivan, J.V. Caspar, J. Am. Chem. Soc. 114 (1992) 6905.

[11] H. Kunkely, A. Vogler, Inorg. Chem. Commun. 4 (2001) 252.