

Photoluminescence of 8-quinolinolatomethylmercury(II)

Horst Kunkely, Arnd Vogler*

Institut für Anorganische Chemie, Universität Regensburg, Universitätsstrasse 31, D-93040 Regensburg, Germany

Received 27 December 2000; accepted 25 April 2001

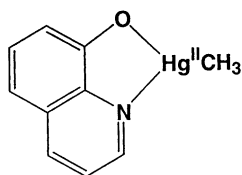
Abstract

The organometallic complex $\text{CH}_3\text{Hg}^{\text{II}}$ (oxinate) with oxine = 8-quinolinol or 8-hydroxyquinoline shows a longest-wavelength absorption at $\lambda_{\text{max}} = 375 \text{ nm}$ ($\epsilon = 1900$) and a red phosphorescence at room temperature ($\lambda_{\text{max}} = 638 \text{ nm}$, $\phi = 5 \times 10^{-3}$ at $\lambda_{\text{exc}} = 420 \text{ nm}$ in benzene). The emitting triplet is of the oxinate intraligand type. It follows that the heavy atom effect of mercury is fully transmitted to the oxinate ligand. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Luminescence; Mercury complexes; Oxinate complexes

1. Introduction

The luminescence of metal complexes is a rapidly expanding research field [1]. Especially optical sensors which rely on luminescent coordination compounds attract much current interest [2–5]. Owing to the toxicity of mercury [6,7], considerable attention has been paid to analytical applications of the luminescence of Hg(II) compounds [8–13]. Surprisingly, simple organometallics of Hg(II) have apparently not been reported to show an emission under ambient conditions. We explored this possibility and selected the complex $\text{CH}_3\text{Hg}^{\text{II}}$ (oxinate) [14] for the present study.



This choice was guided by several considerations. While Hg^{2+} is generally toxic the methylmercuric ion CH_3Hg^+ is particularly dangerous since it is hydrophilic as well as lipophilic and widely proliferated in the environment [6,7,15,16]. The complex CH_3Hg (oxinate) is rapidly formed in aqueous solution [14]. Generally, oxinate (oxine = 8-hydroxyquinoline or 8-quinolinol) forms rather stable chelates with most metals [17,18]. These complexes are characterized by low-energy oxinate intraligand (IL) states which are emissive [19–37] if other excited states

such as metal-centered (MC) or charge transfer (CT) states are not located below the emissive IL states. The IL luminescence of the oxinate ligand is modified by the metal in several ways. Since the electronic structure of the oxinate ligand is influenced by the metal, the emission energies are also metal dependent. Moreover, for oxinate complexes of light metals such as aluminum, only an IL fluorescence appears at r.t. In the case of heavy metals beginning with the second transition row, the IL fluorescence is partly or completely quenched owing to enhanced intersystem crossing. Simultaneously, an IL phosphorescence occurs at r.t. because the lifetime of the emitting IL triplet is reduced by increased spin-orbit coupling [29,34,35]. Since Hg(II) does not provide MC and CT states at low energies [38], a r.t. IL luminescence should be observed. In addition, a heavy atom effect by mercury was expected to attenuate the fluorescence and induce an IL phosphorescence under ambient conditions. While the emission behavior of $[\text{Hg}(\text{dpp})\text{Cl}]_2$ [39] with $\text{dppH} = 2,9$ -diphenyl-1,10-phenanthroline is consistent with this expectation, Hg(II) complexes of various other organic emitters have not been reported to show a r.t. phosphorescence [8–13]. So far no explanation has been given for this surprising observation.

2. Experimental

2.1. Materials

All solvents used were of spectrograde quality. CH_3Hg (OH) (Strem) and 8-hydroxyquinoline or 8-quinolinol

* Corresponding author. Fax: +49-941-943-4488.

E-mail address: arnd.vogler@chemie.uni-regensburg.de (A. Vogler).

(Aldrich) were commercially available and used without further purification. $\text{CH}_3\text{Hg}(\text{oxinate})$ was prepared according to a literature procedure [14].

2.2. Instrumentation

Absorption spectra were measured with a Hewlett Packard 8452 A diode array or an Uvikon 860 absorption spectrometer. The light source used was an Osram HBO 200 W/2 or a Hanovia Xe/Hg 977 B-1 (1 kW) lamp. An additional cutoff filter Schott WG 345/2 was applied to avoid short-wavelength photolysis of chloroform and benzene. Monochromatic light was obtained using Schott PIL/IL interference filters or a Schoeffel GM/1 high-intensity monochromator (band width 23 nm). In all cases the light beam was focused on a thermostated photolysis cell by a quartz lens. Emission and excitation spectra were recorded on a Hitachi 850 spectrofluorometer equipped with a Hamamatsu 928 photomultiplier for measurements up to 900 nm. The luminescence spectra were corrected for monochromator and photomultiplier efficiency variations. Absolute emission quantum yields were determined by comparison of the integrated emission intensity with that of Rhodamine B [40] under identical conditions such as exciting wavelength, optical density, and apparatus parameters. Emission lifetimes were measured on a luminescence analysis system (model LS-100-07) from Photon Technology International.

3. Results

The electronic spectrum of $\text{CH}_3\text{Hg}(\text{oxinate})$ in benzene (Fig. 1) shows absorptions at $\lambda_{\text{max}} = 375 \text{ nm}$ ($\epsilon = 1900 \text{ dm}^3 \text{ M}^{-1} \text{ cm}^{-1}$), 336 nm (1460) and 322 nm (sh, 1180). The spectra are quite similar in various solvents such as benzene, CHCl_3 , CH_2Cl_2 , CH_3CN and methanol. The complex is luminescent in solution at r.t. as well as in the solid state. Solutions of $\text{CH}_3\text{Hg}(\text{oxinate})$ in these sol-

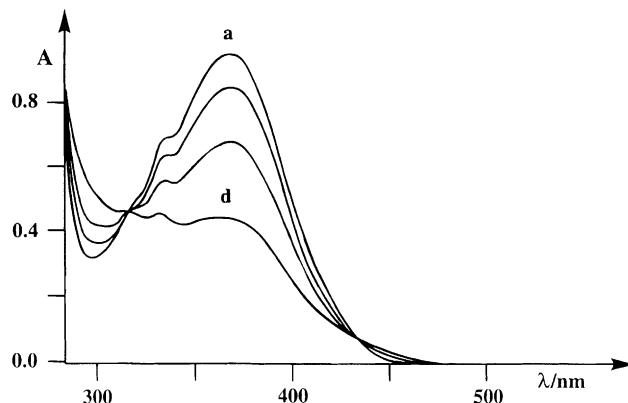


Fig. 2. Spectral changes during the photoysis of $5.47 \times 10^{-4} \text{ M}$ $\text{CH}_3\text{Hg}(\text{oxinate})$ in CH_2Cl_2 at r.t. at 0 (a), 0.5, 1 and 2 (d) min irradiation times with $\lambda_{\text{irr}} = 366 \text{ nm}$ (Hanovia Xe/Hg 977 B-1, 1 kW lamp), 1 cm cell.

vents display a red luminescence which appears in benzene (Fig. 1) at $\lambda_{\text{max}} = 638 \text{ nm}$ with $\phi = 5 \times 10^{-3}$ at $\lambda_{\text{exc}} = 420 \text{ nm}$. Reliable lifetime measurements could not be carried out due to the photoreactivity of the complex. The excitation spectrum of $\text{CH}_3\text{Hg}(\text{oxinate})$ agrees well with the absorption spectrum. The luminescence is not affected by oxygen. The formation of $\text{CH}_3\text{Hg}(\text{oxinate})$ also takes place in rather dilute solution. Upon addition of a ca. 10^{-2} M solution of oxine in methanol to an equal volume of 10^{-5} M $\text{CH}_3\text{Hg}(\text{OH})$ in water the complex is immediately formed as indicated by the appearance of its red emission.

Solutions of $\text{CH}_3\text{Hg}(\text{oxinate})$ are not only luminescent but also light sensitive. Upon irradiation ($\lambda > 320 \text{ nm}$) of $\text{CH}_3\text{Hg}(\text{oxinate})$ in benzene, CHCl_3 , or CH_2Cl_2 , a photolysis takes place. The concomitant spectral changes (Fig. 2) show clear isobestic points indicating a clean photolysis. The photoproduct displays a green luminescence at $\lambda_{\text{max}} = 490 \text{ nm}$ ($\lambda_{\text{exc}} = 400 \text{ nm}$). However, at later stages of the photolysis the isobestic points and the green luminescence disappear owing to efficient secondary reactions.

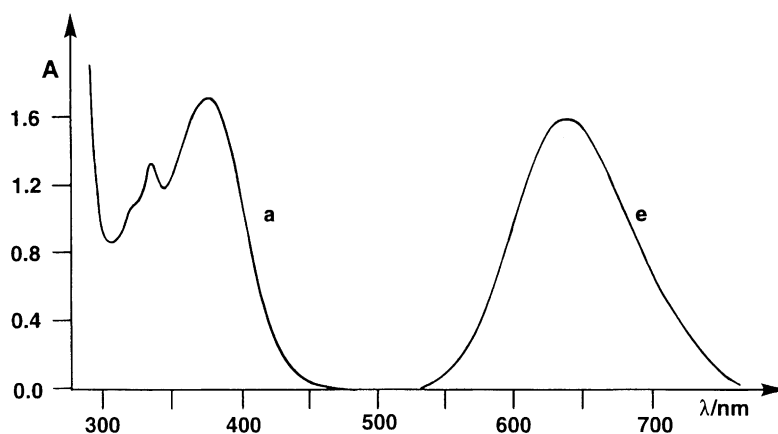
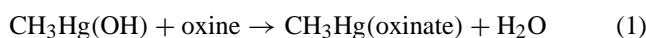


Fig. 1. Electronic absorption (a) and emission (e) spectra of $9.05 \times 10^{-4} \text{ M}$ $\text{CH}_3\text{Hg}(\text{oxinate})$ in benzene at r.t., 1 cm cell. Emission: $\lambda_{\text{exc}} = 420 \text{ nm}$, intensity in arbitrary units.

4. Discussion

Many metal cations react with oxine to form chelate complexes with the deprotonated oxine anion (oxinate) as bidentate ligand [17,18]. However, owing to its tendency to metalate phenyl rings Hg^{2+} reacts with oxine to undergo metal–carbon bond formation at the 5-position of oxine [17]. In distinction to Hg^{2+} , the CH_3Hg^+ cation forms $\text{CH}_3\text{Hg}(\text{oxinate})$ as a regular chelate [14].



Since $\text{Hg}(\text{II})$ has a variable coordination number [38] coordinating solvent molecules may be weakly attached to $\text{CH}_3\text{Hg}(\text{oxinate})$ as additional ligands [14]. For the same reason a dimerization of the complex can take place in non-coordinating solvents, but it has been shown that at least in benzene $\text{CH}_3\text{Hg}(\text{oxinate})$ remains monomeric [14]. Irrespective of these effects the electronic spectra of $\text{CH}_3\text{Hg}(\text{oxinate})$ are very similar in various solvents such as benzene, CHCl_3 , CH_2Cl_2 , CH_3CN and methanol.

The absorption spectra of oxinate complexes are characterized by two long-wavelength bands which are attributed to oxinate IL transitions [29,34–36]. The shorter-wavelength band which shows some vibrational structure is assigned to a $\pi\pi^*$ transition. $\text{CH}_3\text{Hg}(\text{oxinate})$ displays this band at $\lambda_{\text{max}} = 336 \text{ nm}$. The longer-wavelength IL absorption of metal oxinates belong to a $\pi\pi^*$ transition with an IL charge transfer (ILCT) contribution. This ILCT is associated with a shift of electron density from the phenolate oxygen of the oxinate to the π^* orbitals of the aromatic ring. The corresponding absorption of $\text{CH}_3\text{Hg}(\text{oxinate})$ occurs at rather short wavelength ($\lambda_{\text{max}} = 375 \text{ nm}$, Fig. 1) and is hardly solvent dependent indicating only a small ILCT contribution to this transition in analogy to $\text{ReO}_3(\text{oxinate})$ [36].

Dependent on the metal, oxinate complexes show an IL emission which consists of a green fluorescence and a red phosphorescence [29,34,35]. In distinction to $\text{ReO}_3(\text{oxinate})$ which shows the fluorescence and only a very weak phosphorescence at r.t. [36] $\text{CH}_3\text{Hg}(\text{oxinate})$ displays exclusively the IL phosphorescence under ambient conditions. It follows that the heavy atom effect of mercury is fully transmitted to the oxinate ligand. Although the triplet state lifetime could not be measured (see above) it seems to be exceptionally short as indicated by the absence of any phosphorescence quenching by oxygen. In the case of other heavy metal oxinates such as $\text{Pt}(\text{oxinate})_2$ [29], $\text{Re}(\text{CO})_4(\text{oxinate})$ [34] and $\text{Th}(\text{oxinate})_4$ [35], the IL phosphorescence is partially or completely absent in air-saturated solution.

The facile formation of $\text{CH}_3\text{Hg}(\text{oxinate})$ even in rather dilute aqueous solution ($\sim 10^{-5} \text{ CH}_3\text{HgOH}$), the long-wavelength absorption ($\lambda < 460 \text{ nm}$), the high extinction coefficient at its maximum, and finally the appearance of a r.t. phosphorescence which is not quenched by oxygen suggest that the luminescence of $\text{CH}_3\text{Hg}(\text{oxinate})$ may be considered for analytical applications. Unfortunately, the

light sensitivity of $\text{CH}_3\text{Hg}(\text{oxinate})$ is a certain drawback for this application. However, if the samples are not exposed to intense light at $\lambda < 460 \text{ nm}$ the photolysis is rather slow.

At this point some previous observations on excited state properties of other $\text{Hg}(\text{II})$ compounds should be mentioned. In particular, the emission behavior of the cyclometalated $\text{Hg}(\text{II})$ complex of dppH is quite intriguing [39]. The dimeric complex $[\text{Hg}(\text{dpp})\text{Cl}]_2$ which is formed from $\text{Hg}(\text{acetate})_2$, LiCl and dppH by reflux in ethanol for extended periods also shows an IL emission which consists of a fluorescence and a r.t. phosphorescence. Accordingly, a heavy atom effect is also in operation but it is apparently not as strong as that of $\text{CH}_3\text{Hg}(\text{oxinate})$. The light sensitivity of $[\text{Hg}(\text{dpp})\text{Cl}]_2$ [39] and $\text{CH}_3\text{Hg}(\text{oxinate})$ is a further common feature of both complexes. Although a closer examination of the photoreactivity of $\text{CH}_3\text{Hg}(\text{oxinate})$ was not within the scope of the present work, it should be noted that organometallic $\text{Hg}(\text{II})$ compounds are generally light sensitive [41,42]. Mercury–carbon bonds undergo a facile photolysis, but usually this requires shorter-wavelength UV irradiation. The CH_3Hg^+ cation which is also light sensitive [16] shows its longest-wavelength absorption at $\lambda_{\text{max}} = 209 \text{ nm}$ [43].

A comparison of the emission of $\text{Cd}(\text{oxinate})_2$ and $\text{CH}_3\text{Hg}(\text{oxinate})$ is a further point of interest. Generally, metals of the second and third transition row exert a similar heavy atom effect. It follows that in both cases the IL fluorescence should be partially or completely quenched and replaced by the IL phosphorescence which may appear at r.t. While this observation indeed applies to $\text{CH}_3\text{Hg}(\text{oxinate})$, the complex $\text{Cd}(\text{oxinate})_2$ shows only a fluorescence [20,25], even at low temperatures [24,44]. We assume that the bonding in $\text{Cd}(\text{oxinate})_2$ is rather ionic and prevents the transmission of the heavy atom effect to the oxinate ligand. On the contrary, $\text{Hg}(\text{II})$ complexes are characterized by a much higher degree of covalency as indicated by the thermal stability of organometallic mercury compounds in general [45].

In conclusion, although the present study may not lead to an immediate analytical application it provides an important insight in the luminescence properties of an organic chromophore coordinated to $\text{Hg}(\text{II})$.

Acknowledgements

Support of this research by the Fonds der Chemischen Industrie is gratefully acknowledged.

References

- [1] A. Vogler, H. Kunkely, *Top. Curr. Chem.* 213 (2001) 143.
- [2] A.W. Czarnik, *Acc. Chem. Res.* 27 (1994) 302.
- [3] C. Fabbrizzi, A. Poggi, *Chem. Soc. Rev.* 24 (1995) 197.
- [4] I. Oehme, O.S. Wolfbeis, *Mikrochim. Acta* 126 (1997) 177.
- [5] A.P. de Silva, H.Q.N. Gunaratne, T. Gunnlangsson, A.J.M. Huxley, C.P. McCoy, J.T. Rademacher, T.E. Rice, *Chem. Rev.* 97 (1997) 1515.

- [6] F.M. D'Itri, *The Environmental Mercury Problem*, CRC Press, Cleveland, 1972.
- [7] K.H. Falchuk, L.J. Goldwater, B.L. Vallee, in: C.A. McAuliffe (Ed.), *The Chemistry of Mercury*, MacMillan Press, London, 1977, p. 261.
- [8] B. Vaidya, J. Zak, G.J. Bastiaans, M.D. Porter, *Anal. Chem.* 67 (1995) 4101.
- [9] J. Yoon, N.E. Ohler, D.H. Vance, W.D. Aumiller, A.W. Czarnik, *Tetrahedron Lett.* 38 (1997) 3845.
- [10] J.D. Winkler, C.M. Bowen, V. Michelet, *J. Am. Chem. Soc.* 120 (1998) 3237.
- [11] G. Hennrich, H. Sonnenschein, U. Resch-Genger, *J. Am. Chem. Soc.* 121 (1999) 5073.
- [12] K. Rurack, M. Kollmannsberger, U. Resch-Genger, J. Daub, *J. Am. Chem. Soc.* 122 (2000) 968.
- [13] L. Prodi, C. Bargossi, M. Montalti, N. Zaccheroni, N. Su, J.S. Bradshaw, R.M. Izatt, P.B. Savage, *J. Am. Chem. Soc.* 122 (2000) 6769.
- [14] R.J. Bertino, G.B. Deacon, J.M. Miller, *Aust. J. Chem.* 31 (1978) 527.
- [15] P.J. Craig, *Organometallic Compounds in the Environment*, Bath Press, Avon, 1986, p. 65.
- [16] P. Sellers, C.A. Kelly, J.W.M. Rudd, A.R. MacHutchon, *Nature* 380 (1996) 694 and references cited therein.
- [17] J.P. Phillips, *Chem. Rev.* 56 (1956) 271.
- [18] R.G.W. Hollingshead, *Oxine and Its Derivatives, Part I*, Butterworths, London, 1954.
- [19] H.M. Stevens, *Anal. Chim. Acta* 20 (1959) 389.
- [20] W.E. Ohnesorge, L.B. Rogers, *Spectrochim. Acta* 14 (1959) 27.
- [21] W.E. Ohnesorge, A. Capotosto Jr., *J. Inorg. Nucl. Chem.* 24 (1962) 829.
- [22] W.E. Ohnesorge, *J. Inorg. Nucl. Chem.* 29 (1967) 485.
- [23] E.A. Bozhevolnov, G.V. Serebryakova, *Opt. Spectrosc. (Engl. Transl.)* 13 (1962) 216.
- [24] D.C. Bhatnagar, L.S. Forster, *Spectrochim. Acta* 21 (1965) 1803.
- [25] F.E. Lytle, D.R. Storey, M.E. Juricich, *Spectrochim. Acta A* 29 (1973) 1357.
- [26] F.E. Lytle, *Appl. Spectrosc.* 24 (1970) 319.
- [27] A.V. Karyakin, T.S. Sorokina, L.I. Anikina, T.G. Akimova, M.G. Ezernitskoya, *Dokl. Akad. Nauk SSSR* 241 (1978) 617, *Engl. Trans.: Dokl. Phys. Chem.* 241 (1978) 667.
- [28] R. Ballardini, M.T. Indelli, G. Varani, C.A. Bignozzi, F. Scandola, *Inorg. Chim. Acta* 31 (1978) L423.
- [29] R. Ballardini, G. Varani, M.T. Indelli, F. Scandola, *Inorg. Chem.* 25 (1986) 3858.
- [30] C. Bartocci, S. Sostero, O. Traverso, A. Cox, T.J. Kemp, W.J. Reed, *J. Chem. Soc. Faraday I* 76 (1980) 797.
- [31] D. Donges, J.K. Nagle, H. Yersin, *J. Luminescence* 72–74 (1997) 658.
- [32] D. Donges, J.K. Nagle, H. Yersin, *Inorg. Chem.* 36 (1997) 3040.
- [33] H. Yersin, D. Donges, J.K. Nagle, R. Sitters, M. Glasbeck, *Inorg. Chem.* 39 (2000) 770.
- [34] H. Kunkely, A. Vogler, *Inorg. Chem. Commun.* 1 (1998) 398.
- [35] H. Kunkely, A. Vogler, *Chem. Phys. Lett.* 304 (1999) 187.
- [36] H. Kunkely, A. Vogler, *Inorg. Chem. Commun.* 3 (2000) 645.
- [37] J.T. Warren, W. Chen, D.H. Johnston, C. Turro, *Inorg. Chem.* 38 (1999) 6187.
- [38] H. Kunkely, O. Horváth, A. Vogler, *Coordin. Chem. Rev.* 159 (1997) 85.
- [39] C.-W. Chan, S.-M. Peng, C.-M. Che, *Inorg. Chem.* 33 (1994) 3656.
- [40] J.N. Demas, G.A. Crosby, *J. Phys. Chem.* 75 (1971) 991.
- [41] V. Balzani, V. Carassiti, *Photochemistry of Coordination Compounds*, Academic Press, New York, 1970, p. 281.
- [42] K.C. Bass, *Organomet. Chem. Rev.* 1 (1966) 391.
- [43] H. Kunkely, Unpublished observations.
- [44] F. Scandola, R. Ballardini, M.T. Indelli, in: D.O. Hall (Ed.), *Photochemical, Photoelectrochemical and Photobiological Processes, Solar Energy R&D Eur. Comm. Ser. D*, Kluwer Academic Publishers, Dordrecht, the Netherlands, 1982, p. 66.
- [45] D. Seyferth, *J. Organomet. Chem.* 203 (1979) 183.