Volume 34
Number 15
July 19, 1995

Inorganic Chemistry

© Copyright 1995 by the American Chemical Society

Communications

Spectroscopic Observation of Coupled Metal−Ligand Vibrational Modes in the Luminescence Spectrum of *trans*-[ReO_2(1-methylimidazole)$_4$]I

Carole Savoie, Christian Reber,* Suzanne Bélanger, and André L. Beauchamp

Département de chimie, Université de Montréal, Montréal, Québec, Canada H3C 3J7

Received November 17, 1994

Coordination compounds and doped materials containing metal centers with the nd^2 electron configurations ($n = 3-5$) have received much interest with regard to their potential for photochemical applications and as optical materials.[1−6] In this communication, we present the near-infrared luminescence properties of single crystals of *trans*-[ReO_2(1-methylimidazole)$_4$]I. The synthesis and crystal structure of this compound are reported elsewhere.[7] Compounds containing the *trans*-[ReO_2L_4]$^+$ unit are known to show electronic spectra with resolved vibronic structure.[8,9] Two types of metal−ligand vibrations are easily distinguished because of their different vibrational energies, typically on the order of 900 and 200 cm^{-1} for modes with mainly Re−O and Re−N(ligand) characters, respectively.

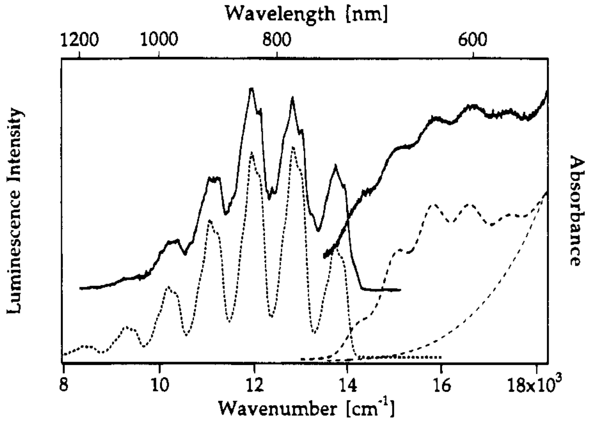

Figure 1. Single-crystal luminescence and absorption spectra of *trans*-ReO_2(1-methylimidazole)$_4$I at 15 K. Experimental spectra are shown as solid lines; calculated spectra using the harmonic model are shown as dotted lines, including the baseline added to the calculated absorption spectrum.

The low-temperature single-crystal luminescence and absorption spectra of the title compound are shown in Figure 1 and were obtained with instruments described in ref 10. No resolved hot bands or major changes of the band shape are observed in the luminescence spectrum between 4.2 and 100 K, in contrast to the spectrum of [ReO_2(pyridine)$_4$]$^+$.[9] Two progressions with average spacings of 900 ± 10 and 200 ± 10 cm^{-1} are clearly discernible in the luminescence spectrum, corresponding to the Re−O and Re−N vibrational modes, respectively. The Re−O vibration is observed at 905 cm^{-1} in the Raman spectrum. Each member of the high-frequency progression consists of a cluster of bands in the low-frequency progression. The absorption spectrum is less resolved; only one progression with an average separation of 770 ± 10 cm^{-1} is observed, corresponding to the Re−O vibrational energy in the emitting state. The exact point group symmetry of the *trans*-[ReO_2(1-methylimidazole)$_4$]$^+$ units in the title compound is C_1,[7] allowing progressions in all vibrational modes. In the following, we limit our discussions to the two modes observed in the luminescence spectrum, likely mainly Re−O and Re−N(imidazole) stretching vibrations in character, since the potential energy surfaces along these modes are most affected by the different electron configurations of the initial and final states of the electronic transition. The deviations from an idealized D_{4h} symmetry are larger than in *trans*-[ReO_2(CN)$_4$]$^{3-}$ and *trans*-[ReO_2(pyridine)$_4$]$^+$.[9] There is no spectroscopic evidence for multiple absorption bands corresponding to transitions to the individual states arising from the ^3E_g lowest energy excited state in D_{4h} symmetry.[9] We will therefore use D_{4h} labels for consistency with the literature reports on analogous compounds. The lowest energy absorption band has an extinction coefficient ϵ of 10 cm^{-1} M^{-1} in solution, typical for the spin-forbidden $^1A_{1g} \rightarrow {}^3E_g$ transition.[9]

We analyze the spectra with two-dimensional harmonic oscillator potential energy surfaces $V_{\mathrm{harm,gs}}$ (eq 1) and $V_{\mathrm{harm,es}}$ (eq 2) for the electronic ground state and the emitting state, respectively. Dimensionless normal coordinates $Q_{\mathrm{Re-O}}$ and

---

(1) Liu, W.; Thorp, H. H. *Inorg. Chem.* **1994**, *33*, 1026.
(2) Brunold, T. C.; Hauser, A.; Güdel, H. U. *J. Luminesc.* **1994**, *59*, 321.
(3) Jia, W.; Liu, H.; Wang, Y.; Hömmerich, U.; Eilers, H.; Hoffman, K.; Yen, W. M. *J. Luminesc.* **1994**, *59*, 279.
(4) Hoffman, K. R.; Hömmerich, U.; Jacobsen, S. M.; Yen, W. M. *J. Luminesc.* **1992**, *52*, 277.
(5) Herren, M.; Güdel, H. U.; Albrecht, C.; Reinen, D. *Chem. Phys. Lett.* **1991**, *183*, 98.
(6) Oetliker, U.; Herren, M.; Güdel, H. U.; Kesper, U.; Albrecht, C.; Reinen, D. *J. Chem. Phys.* **1994**, *100*, 8656.
(7) Bélanger, S.; Beauchamp, A. L. *Inorg. Chem.*, submitted for publication.
(8) Winkler, J. R.; Gray, H. B. *J. Am. Chem. Soc.* **1983**, *105*, 1373.
(9) Winkler, J. R.; Gray, H. B. *Inorg. Chem.* **1985**, *24*, 346.
(10) Davis, M. J.; Reber, C. *Inorg. Chem.*, in press.

0020-1669/95/1334-3851$09.00/0 © 1995 American Chemical Society

$Q_{\text{Re-N}}$ represent the two vibrational modes observed in the luminescence spectrum.

$$V_{\text{harm,gs}}(Q_{\text{Re-O}},Q_{\text{Re-N}}) = {}^{1}/_{2}k_{\text{Re-O}}Q_{\text{Re-O}}^{2} + {}^{1}/_{2}k_{\text{Re-N}}Q_{\text{Re-N}}^{2} \quad (1)$$

$$V_{\text{harm,es}}(Q_{\text{Re-O}},Q_{\text{Re-N}}) = {}^{1}/_{2}k'_{\text{Re-O}}(Q_{\text{Re-O}} + \Delta Q_{\text{Re-O}})^{2} + {}^{1}/_{2}k'_{\text{Re-N}}(Q_{\text{Re-N}} + \Delta Q_{\text{Re-N}})^{2} + E_{0} \quad (2)$$

The values for the vibrational energies $k_{\text{Re-O}}$, $k_{\text{Re-N}}$, and $k'_{\text{Re-O}}$ were determined directly from the spectra. A value of 14 140 cm^{-1} for the electronic origin E_0 and line widths of 60 and 160 cm^{-1} were used for calculating emission and absorption spectra, respectively. The time-dependent theory of absorption and luminescence spectroscopy[11,12] was used for the calculations. The differences ΔQ along the Re−O and Re−N totally symmetrical normal coordinates and the excited state vibrational energy $k'_{\text{Re-N}}$ in eq 2 are adjustable parameters, and values of 2.27, 1.53, and 215 ± 10 cm^{-1} were obtained for $\Delta Q_{\text{Re-O}}$, $\Delta Q_{\text{Re-N}}$, and $k'_{\text{Re-N}}$, respectively. Emitting state distortions of 0.077 and 0.035 Å for the Re−O and Re−N(imidazole) bonds were estimated from the dimensionless distortions using masses of 16 and 82 g/mol for the two ligands and assuming pure metal−ligand stretching modes.[9,12] The distortions are similar to those reported for *trans*-$[\text{ReO}_2(\text{pyridine})_4]^+$ and *trans*-$[\text{ReO}_2(\text{CN})_4]^{3-}$,[9] but these compounds have emitting states higher in energy by approximately 2400 cm^{-1}, possibly due to their shorter Re−O bond lengths and higher symmetry compared to those of the title compound.

The main discrepancy between the experimental and calculated emission spectra in Figure 1 concerns the shape of the members of the Re−O progression: the shapes of all calculated clusters are identical, but the experimental spectra show systematic changes from cluster to cluster. These changes have been shown recently to arise from coupled vibrational coordinates.[13−15] We therefore include a coupling term in the ground-state potential energy surface:

$$V_{\text{gs}}(Q_{\text{Re-O}},Q_{\text{Re-N}}) = V_{\text{harm,gs}}(Q_{\text{Re-O}},Q_{\text{Re-N}}) + k_{\text{c}}Q_{\text{Re-O}}^{2}Q_{\text{Re-N}} \quad (3)$$

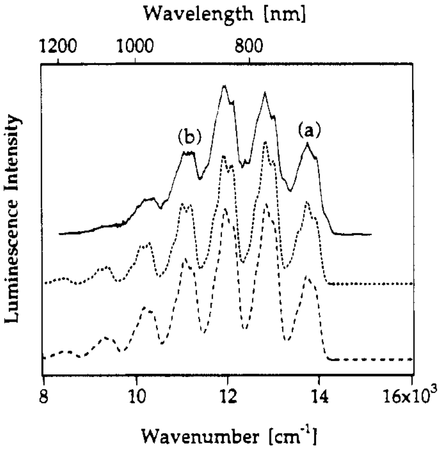

Figure 2. Comparison of the experimental luminescence spectrum with two model calculations, involving harmonic potential energy surfaces with and without coupling between the vibrational coordinates. The experimental spectrum is shown as a solid line (top trace); the calculated spectra with and without coupling are denoted by the middle and bottom dotted lines, respectively.

The fit including a nonzero coupling constant k_c in eq 3 is compared to the experimental spectrum in Figure 2 (middle and top traces). The emission spectrum calculated with the potential energy surface in eq 3 is in better agreement with the experimental data than the uncoupled harmonic calculation, illustrated by the clusters (a) and (b) in Figure 2. All the parameters in eq 3 were held fixed at the values determined for the uncoupled harmonic model, and a value of 11 ± 1 cm^{-1} was obtained for k_c, the only adjustable parameter remaining in eq 3. Our analysis shows a first example of coupling between two metal−ligand vibrational modes involving *different* ligands, in contrast to the literature reports, where coupling occurs between normal coordinates involving a low-energy metal−ligand mode and a high-energy mode on the *same* ligand.[13,14] Compounds with coupling between coordinates involving different ligands are promising candidates for selective photochemistry on the organic ligands via excitation of the *trans*-$[\text{ReO}_2]^+$ unit. In high-symmetry compounds containing this unit, the spectra could be influenced by additional distortions along non-totally symmetric modes due to a Jahn−Teller effect in the emitting state. Highly resolved spectra of transition metal compounds analyzed in the literature show that such distortions can be determined by neglecting coupling with other modes.[16,17] Gas-phase spectra of organic molecules show highly irregular vibronic structure in the low-frequency Jahn−Teller mode only, not comparable to that of the title compound.[18] We are currently examining a series of different 5d^2 compounds in order to find trends in coupling and to establish the importance of other effects.

IC941324P

---

(11) Heller, E. J. *Acc. Chem. Res.* **1981**, *14*, 368.

(12) Zink, J. I.; Kim Shin, K.-S. In *Advances in Photochemistry*; Volman, D. H., Hammond, G. S., Neckers, D. C., Eds.; John Wiley: New York, 1991; Vol. 16, p 119.

(13) Reber, C.; Zink, J. I. *Inorg. Chem.* **1992**, *31*, 2786.

(14) Wexler, D.; Zink, J. I. *J. Phys. Chem.* **1993**, *97*, 4903.

(15) Wexler, D.; Zink, J. I.; Reber, C. In *Electronic and Vibronic Spectra of Transition Metal Complexes I*; Yersin, H., Ed.; Springer: Berlin, 1994; Vol. 171, p 173.

(16) Wilson, R. B.; Solomon, E. I. *Inorg. Chem.* **1978**, *17*, 1729.

(17) Wilson, R. B.; Solomon, E. I. *J. Am. Chem. Soc.* **1980**, *102*, 4085.

(18) Furlan, A.; Riley, M. J.; Leutwyler, S. *J. Chem. Phys.* **1992**, *96*, 7306.