Luminescence of the Nonclassical Homoleptic Metal Carbonyl Complex [Rh(CO)$_4$]$^+$

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The nonclassical [Rh(CO)$_4$]$^+$ cation is luminescent at low temperature with a peak maximum at 19640 cm^{-1} and a full-width at half-maximum of 2900 cm^{-1}. Both the solution absorption and low-temperature solid-state luminescence spectra of the [Rh(CO)$_4$](1-Et-CB$_{11}$F$_{11}$) salt are reported. The cesium salt of the [1-Et-CB$_{11}$F$_{11}$]$^-$ counterion is also luminescent (with a peak maximum at 22650 cm^{-1}), but the emission maximum of [Rh(CO)$_4$]$^+$ is lower in energy. The Rh–C bond length changes of ~0.07 Å in the excited state are calculated. The calculated bond length changes in the nonclassical [Rh(CO)$_4$]$^+$ ion are not very different from those in classical complexes.

Luminescence from homoleptic metal carbonyl compounds is rare.[1−4] Radiationless deactivation or photochemical reactions are common sources of excited-state depopulation in metal carbonyl compounds that prevent luminescence spectroscopy from being used to characterize the lowest energy excited electronic state, but when luminescence is observed, the spectrum can provide detailed information. As part of our interest in excited-state distortions of organometallic compounds, we are continuing to investigate the luminescence spectra of metal carbonyls.[5−10]

The rhodium tetracarbonyl cation is "nonclassical" because the vibrational frequency of the symmetric CO stretch, and

ν(CO)$_{av}$, are higher than that of the free, uncoordinated CO.[11,12] Luminescence from a nonclassical homoleptic metal−carbonyl complex has not been reported.

In this communication we report the first example of luminescence from the homoleptic nonclassical metal carbonyl compound [Rh(CO)$_4$][1-Et-CB$_{11}$F$_{11}$].[11,13] The counterion, 1-Et-CB$_{11}$F$_{11}$$^-$, is also luminescent, but the emission maximum of [Rh(CO)$_4$]$^+$ is lower in energy. Bond length changes in the excited ligand field electronic state are calculated and, surprisingly, are similar to those in classical metal carbonyl compounds.

The 20 K luminescence spectrum of [Rh(CO)$_4$][1-Et-CB$_{11}$F$_{11}$] shown in Figure 1 (top panel, solid line) consists of a broad unresolved band beginning at approximately 23000 cm^{-1} with a peak maximum at 19640 cm^{-1} and a full-width at half-maximum (fwhm) of 2900 cm^{-1}. Luminescence spectra were obtained from powders in sealed capillaries and excited by the 350.7 nm line from a krypton ion laser. The room temperature solution absorption spectrum of [Rh(CO)$_4$][1-Et-CB$_{11}$F$_{11}$] in methylene chloride displayed in Figure 1 (top panel, dashed−dotted line) shows three broad and unresolved bands. The lowest energy band has its peak maximum at 26300 cm^{-1} with an extinction coefficient of 155 M^{-1} cm^{-1} and a fwhm of 2400 cm^{-1}. A less intense peak is observed at a higher energy at 31600 cm^{-1} with an extinction coefficient of 80 M^{-1} cm^{-1}. A third absorption band is observed at 36700 cm^{-1} with an extinction coefficient of 290 M^{-1} cm^{-1} and a fwhm of 4900 cm^{-1}. The low-energy edge of the absorption band overlaps the high-energy edge of the luminescence band.

The 1-Et-CB$_{11}$F$_{11}$$^-$ anion also luminesces. The 20 K luminescence spectrum of Cs[1-Et-CB$_{11}$F$_{11}$] shown in Figure

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(1) Wrighton, M. S.; Handell, D. I.; Morse, D. I. *Inorg. Chem.* **1976**, *15*, 434.
(2) McHugh, T. M.; Narayanaswamy, R.; Rest, A. J.; Salisbury, K. *J. Chem. Soc., Chem. Commun.* **1979**, 208.
(3) Bitner, T. W.; Zink, J. I. *J. Am. Chem. Soc.* **2000**, *122*, 10631.
(4) Lees, A. *Chem. Rev.* **1987**, *87*, 711.
(5) Tutt, L.; Tannor, D.; Heller, E. J.; Zink, J. I. *Inorg. Chem.* **1982**, *21*, 3859.
(6) Tutt, L.; Tannor, D.; Schindler, J.; Heller, E. J.; Zink, J. I. *J. Phys. Chem.* **1983**, *87*, 3017.
(7) Tutt, L.; Zink, J. I.; Heller, E. J. *Inorg. Chem.* **1987**, *26*, 2158.
(8) Tutt, L.; Zink, J. I. *J. Am. Chem. Soc.* **1986**, *108*, 5830.
(9) Larson, L. J.; Oskam, A.; Zink, J. I. *Inorg. Chem.* **1991**, *30*, 42.
(10) Chang, T. H.; Zink, J. I. *J. Am. Chem. Soc.* **1987**, *109*, 692.

(11) Lupinetti, A. J.; Havighurst, M. D.; Miller, S. M.; Anderson, O. P.; Strauss, S. H. *J. Am. Chem. Soc.* **1999**, *121*, 11920.
(12) Lupinetti, A. J.; Frenking, G.; Strauss, S. H. In *Progress in Inorganic Chemistry*; Karlin, K. D., Ed.; Wiley: New York, 2001; Vol. 49, p 1.
(13) Ivanov, S. V.; Rockwell, J. J.; Polyakov, O. G.; Gaudinski, C. M.; Anderson, O. P.; Solntsev, K. A.; Strauss, S. H. *J. Am. Chem. Soc.* **1998**, *120*, 4224.
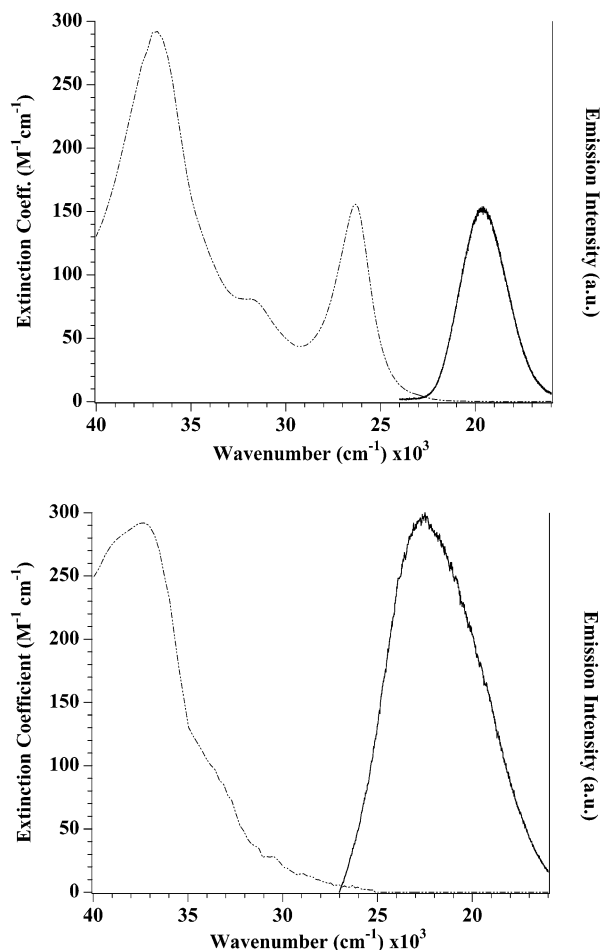
Figure 1. Electronic absorption and emission spectra. Top: Room temperature absorption spectrum of [Rh(CO)$_4$][1-Et-CB$_{11}$F$_{11}$] in methylene chloride (dashed−dotted line) and low-temperature luminescence spectrum of solid [Rh(CO)$_4$][1-Et-CB$_{11}$F$_{11}$] excited at 350.7 nm (bold line). Bottom: Room temperature absorption spectrum of Cs[1-Et-CB$_{11}$F$_{11}$] in methylene chloride (dashed−dotted line) and low-temperature luminescence spectrum of Cs[1-Et-CB$_{11}$F$_{11}$] excited at 350.7 nm (solid line).

1 (bottom panel, solid line) contains a broad band at higher energy than that from [Rh(CO)$_4$]$^+$ beginning at approximately 26500 cm^{-1} with a peak maximum at 22650 cm^{-1} and a fwhm of 5800 cm^{-1}. The room temperature solution absorption spectrum of Cs[1-Et-CB$_{11}$F$_{11}$] displayed in Figure 1 (bottom panel, dashed−dotted line) contains a broad band at 37100 cm^{-1} with an extinction coefficient of 290 M^{-1} cm^{-1}. A shoulder is observed to lower energy at approximately 33500 cm^{-1}. Comparison of these absorption spectra shows that the low-energy bands at 31600 and 26320 cm^{-1} are from the [Rh(CO)$_4$]$^+$ complex and that the high-energy peak at 36700 cm^{-1} is associated with the 1-Et-CB$_{11}$F$_{11}$$^-$ anion.

The spectra in Figure 1 show that the emission from [Rh(CO)$_4$][1-Et-CB$_{11}$F$_{11}$] originates from the lowest energy excited state of [Rh(CO)$_4$]$^+$. The emission (and absorption) band maxima from the lowest excited state of [1-Et-CB$_{11}$F$_{11}$]$^-$ are higher in energy. The lowest energy absorption band of [Rh(CO)$_4$][1-Et-CB$_{11}$F$_{11}$], absent in Cs[1-Et-CB$_{11}$F$_{11}$], overlaps the emission band of [Rh(CO)$_4$][1-Et-CB$_{11}$F$_{11}$].

Bond length changes that occur when the excited state is populated can be determined from the resonance Raman intensities.[14] Resonance Raman spectra were taken using the 406.7 nm line from a krypton ion laser, and Raman (nonresonance) spectra were obtained from samples in sealed glass capillaries using the 514.5 nm line from an argon ion laser. The relative integrated intensities of the normal modes in the resonance Raman spectrum are related to the change in the kth normal coordinate Δ_k multiplied by the vibrational frequency ω_k, $I_k = \Delta_k^2\omega_k^2$.[15] The normal modes with the largest I_k/ω_k^2 values in the [Rh(CO)$_4$]$^+$ complex are associated with the 455 cm^{-1} ($I_{Rh-C}/\omega_{Rh-C}^2 = 1.0$) and 2215 cm^{-1} ($I_{CO}/\omega_{CO}^2 = 0.15$) modes. The 2215 cm^{-1} vibration has been assigned as the totally symmetric ν_s(CO), while the 455 cm^{-1} vibration is the symmetric ν_s(Rh−C) stretching mode.[12,16,17] The relative distortions are converted to dimensionless distortions Δ by using the bandwidth in the electronic spectrum, and the dimensionless distortions into distortions in Å, δ, by using the equation

$$\delta_i = \left[(6.023 \times 10^{23})\frac{\hbar}{2\pi c\omega m}\right]^{1/2}(10^8\Delta_i)$$

where m is the mass involved in the vibration in units of gram atomic weight, ω is the wavenumber of the vibrational mode in cm^{-1}, $\hbar = h/2\pi$, where h is Planck's constant in g cm^2 s^{-1}, c is the speed of light in cm s^{-1}, δ is the displacement in Å, and Δ is the dimensionless distortion.

The luminescence spectrum, including the bandwidth, is fitted by using the time dependent theory of electronic spectroscopy[18−20] and the split operator technique of Feit and Fleck.[21,22] The dimensionless distortions that best fit the emission are $\Delta = 2.78$ for the 455 cm^{-1} Rh−C mode and $\Delta = 0.42$ for the 2215 cm^{-1} CO mode. The calculated emission spectrum is superimposed on the experimental spectrum in Figure 2. These dimensionless distortions can be converted to bond length changes in angstroms when the normal coordinates and the potential energy distributions are known. The changes can be estimated if some simplifying assumptions are made about the normal coordinates. For example, if it is assumed that the 455 cm^{-1} normal mode is entirely Rh−C stretching and that the normal mass is the mass of the CO ligand, then the excited-state normal mode changes are 0.14 Å for the Rh−C mode and 0.01 Å for the CO mode. In the four-coordinate rhodium complex the excited-state normal coordinate changes correspond to individual bond

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

(15) The relative distortions are calculated by using Savin's formula, $I_k/I_{k'} = \Delta_k^2\omega_k^2/(\Delta_{k'}^2\omega_{k'}^2)$, where I_k is the resonance Raman intensity, Δ_k is the dimensionless bond distortion, and ω_k is the vibrational frequency of the kth mode.

(16) Jones, L. H.; McDowell, R. S.; Goldblatt, M. *J. Chem. Phys.* **1968**, *48*, 2663.

(17) Jones, L. H.; McDowell, R. S.; Goldblatt, M. *Inorg. Chem.* **1969**, *8*, 2349.

(18) Heller, E. J. *J. Chem. Phys.* **1978**, *68*, 2066.

(19) Heller, E. J. *J. Chem. Phys.* **1978**, *68*, 3891.

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

(21) Feit, M. D.; Fleck, J. A.; Steiger, A. *J. Comput. Phys.* **1982**, *47*, 412.
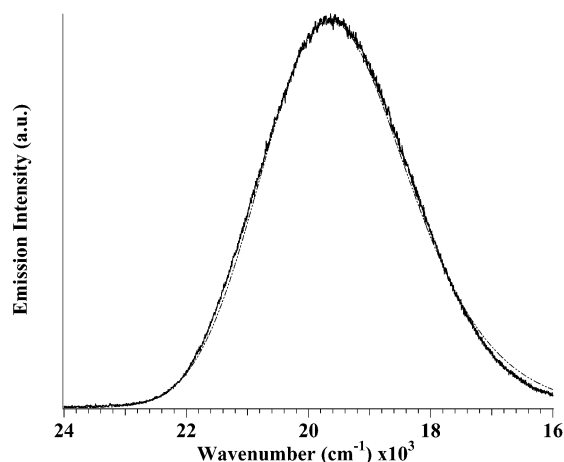
(22) Tannor, J. *J. Chem. Educ.* **1990**, *67*, 917.

Figure 2. Low-temperature luminescence spectrum of solid [Rh(CO)$_4$]-[1-Et-CB$_{11}$F$_{11}$] (solid line) and calculated best fit luminescence spectrum (dashed line). The values used to calculate the spectrum are $\Delta_{RhC} = 2.78$, $\Delta_{CO} = 0.42$, $E_{00} = 21120$ cm^{-1}, and $\Gamma = 540$ cm^{-1}.

length changes of 0.07 Å for a Rh−C bond and 0.005 Å for a CO bond.

The excited-state normal coordinate changes in the nonclassical complex are remarkably similar to those previously determined for classical metal carbonyl complexes. Vibronic progressions were observed in the luminescence spectrum of [Ta(CO)$_6$]$^-$.[3] The excited-state normal coordinate changes are 0.14 Å for the Ta−C coordinate and 0.026 Å for the CO coordinate. The normal coordinate changes for Mo(CO)$_6$ and W(CO)$_6$ that were calculated from the absorption spectrum were 0.15 and 0.04 Å for the W−C and C−O stretching coordinates, respectively, and 0.16 and 0.03 Å for the Mo−C and C−O coordinates, respectively.[23] (The lowest energy excited states of these compounds were recently reassigned as MLCT states.)[24,25] Distortions have also been calculated for some substituted metal carbonyl complexes. An electronic and resonance Raman spectroscopic study of W(CO)$_5$(pyridine) and W(CO)$_5$(piperidine) found that the W−C bond trans to the amine changes by 0.12 and 0.25 Å, respectively.[8] TRIR analysis of the same compounds showed that the CO bond distances increased by 0.006 Å for the trans CO in the pyridine complex and 0.005 Å for the piperidine complex.[26] Analysis of the bond length change in the ligand field excited state of [PtCl$_3$(CO)]$^-$ showed that the metal−carbon distance increased by 0.18 Å.[10] All of the above bond length changes,

with the exception of those in Mo(CO)$_6$ and W(CO)$_6$,[24,25] occur in excited states assigned as primarily d−d in character. The picture that is emerging is that the changes in the metal−carbon bond lengths in ligand field excited states of metal−carbonyl complexes are between about 5% and 10% of the bond length. Changes in the CO bond lengths are much smaller, on the order of several hundredths of an angstrom. It is interesting to note that the distortions in charge transfer states of Mo(CO)$_6$ and W(CO)$_6$ are similar to those in ligand field states.

The lowest energy excited electronic state in the nonclassical [Rh(CO)$_4$]$^+$ ion probably arises from a d−d (ligand field) transition, but a metal to ligand charge transfer assignment cannot be ruled out. The molar absorptivity of the lowest energy absorption band, 155 M^{-1} cm^{-1}, is in the normal range of molar absorptivities for d−d bands of metal carbonyls and favors a d−d assignment, but it could also be consistent with a forbidden charge transfer transition.[24,25] The energy of the lowest excited state is lower than that expected for charge transfer transitions in metal carbonyls; the lowest energy charge transfer transition in homoleptic metal carbonyls with a formal +1 metal oxidation state is usually greater than about 40000 cm^{-1}.[27] The energy of the metal to ligand charge transfer is expected to be higher in the formally Rh(I) complex than in zerovalent compounds, and the d−d transitions are expected to be lower in energy in four-coordinate d^8 complexes than in six-coordinate d^8 complexes. These transition energy considerations favor a d−d assignment, but electronic structure calculations are needed to assist in assigning the lowest energy state of the nonclassical [Rh(CO)$_4$]$^+$ ion. The metal−carbon bond length change of this ion is very similar to those calculated for both ligand field and charge transfer excited states of classical metal carbonyls. A ligand field transition causes the largest changes in the metal−ligand bond distances because the transition directly affects the metal−ligand bonding, whereas charge transfer transitions affect both the bonds on the ligand involved in the charge transfer and the bonds between the metal and ligand. The calculated bond length changes in the nonclassical [Rh(CO)$_4$]$^+$ ion are not very different from those in classical complexes and are consistent with both assignments.

(23) Trogler, W. C.; Desjardins, S. R.; Solomon, E. I. *Inorg. Chem.* **1979**, *18*, 2131.

(24) Pierloot, K., Tsokos, E., Vanquickenborne, L. G. *J. Phys. Chem.* **1996**, *100*, 16545.

(25) Rosa, A., Baerends, E. J., van Gisbergen, S. J. A., Lenthe, E., Groeneveld, J. A.; Snijders, J. G. *J. Am. Chem. Soc.* **1999**, *121*, 10356.

(26) Johnson, F. P. A.; George, M. W.; Morrison, S. L.; Turner, J. J. *J. Chem. Soc., Chem. Commun.* **1995**, 391.

(27) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic: New York, 1979; p 90.