Large variation of the luminescence energy from rhenium(V) complexes with oxo and nitrido ligands

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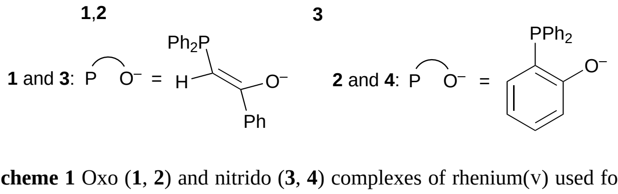
We observe visible and near-IR luminescence from oxo and nitrido compounds of rhenium(V) with chelating ligands combining soft (P) and hard (O) donors and show that the emitting state energy of the nitrido complexes is higher in energy by a factor of *ca.* two (8300 cm^{-1}) than for the oxo compounds, an unusually large difference.

Complexes of Re^{V} with metal–ligand multiple bonds have received considerable attention due to their reactivity, photochemical and spectroscopic properties.[1–4] We have studied a series of *trans*-dioxo complexes of Re^{V} and Os^{VI} with imidazole, carboxylate and ethylenediamine ligands[5,6] and have discovered near-IR (NIR) luminescence bands that are lower in energy by several thousand wavenumbers than the luminescence maximum of the well known *trans*-[ReO$_2$(py)$_4$]$^+$, a representative *trans*-dioxorhenium(V) compound.[7,8] Oxorhenium(V) complexes with low-energy emissions could lead to a novel spin-crossover transition expected for tetragonal 5d^2 complexes.[4]

A detailed comparative study of nitrido and *trans*-dioxo complexes of rhenium(V) reports a difference of 3000 cm^{-1} between the luminescence maxima of related *trans*-dioxo and nitrido compounds.[9] We report here that a significantly larger energy range is accessible to complexes of 5d^2 ions with metal–ligand multiple bonds. We present luminescence spectra of related Re≡O and Re≡N complexes with only one metal–ligand multiple bond and two chelating ligands.

The compounds used for our spectroscopic experiments are shown in Scheme 1. All Re^{V} centers have a triple bond to either an oxo or nitrido ligand and two anionic P–O$^-$ chelating ligands, 2-(diphenylphosphino)phenolate (**2**, **4**) or 1-phenyl-2-(diphenylphosphino)ethanolate (**1**, **3**). The distorted octahedral coordination sphere of the oxo compounds **1**, **2** is completed by chloride ligands.[10,11] The nitrido compound **3** has a triphenylphosphine ligand in its first coordination sphere[10,11] and compound **4** has a square-pyramidal structure, proposed from ^{31}P NMR, IR and elemental analysis data.

The instrumentation for luminescence measurements in the visible and near-IR wavelength range has been described previously.[12,13]‡



Scheme 1 Oxo (**1**, **2**) and nitrido (**3**, **4**) complexes of rhenium(V) used for spectroscopic measurements

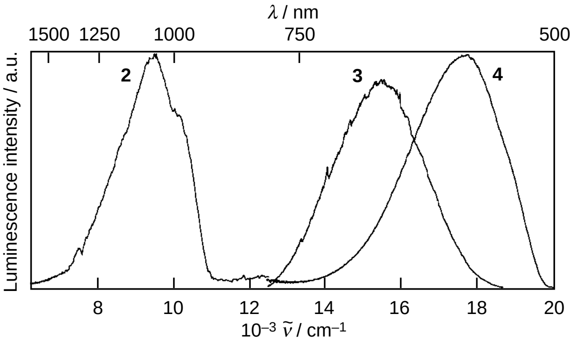


Fig. 1 Solid-state luminescence spectra of the oxorhenium(V) complex **2** and of the nitridorhenium(V) complexes **3**, **4** measured at 10 K

Fig. 1 shows low-temperature luminescence spectra of compounds **2**–**4**. Luminescence spectroscopy allows us to directly determine the energy of the lowest energy excited state for each compound. Band maxima and widths of all emission spectra are summarized in Table 1. The spectra of the oxo complexes **1** and **2** are almost identical and only the spectrum of **2** is shown. The band maxima of the oxo compound **2** and the nitrido compound **4** are separated by more than 8000 cm^{-1}, corresponding to emitting state energies that vary by a factor of two. The solid-state emissions are still observed at 200 K, but their integrated intensity decreases by approximately an order of magnitude for the compounds in Fig. 1. The spectrum of the oxo complex **2** shows barely resolved vibronic structure with a separation of *ca.* 800 cm^{-1} between peaks. This progression involves mainly the Re≡O vibrational mode observed at 958 cm^{-1} in the Raman spectrum. The nitrido compounds **3**, **4** do not show resolved structure involving the Re≡N vibrational mode, but their large bandwidths indicate that this high-frequency mode contributes significantly to the bandshape. The nitrido compound **4** shows weak vibronic structure with peaks separated by *ca.* 130 cm^{-1}. Progressions involving similar low-frequency modes have been observed for nitrido complexes of the isoelectronic Os^{VI}.[14]

Table 1 Summary of spectroscopic data for the oxorhenium(V) complexes **1**, **2** and the nitridorhenium(V) complexes **3**, **4**

	Luminescence (crystal, 10 K)		Raman (crystal, 300 K)	Absorption (solution, 300 K)
Complex	E_{max}/ cm^{-1}	Bandwidth/ cm^{-1} [a]	Re≡O,N mode/ cm^{-1}	λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})
Re≡O, **1**	9250	2060	982	840 (10), 635 (75) 400 (260), 280 (3400)
Re≡O, **2**	9500	1990	958	830 (15), 610 (80) 400 (490), 280 (2080)
Re≡N, **3**	15350	2810	1034	450 (sh, 200) 320 (18 000)
Re≡N, **4**	17560	2940	1100	410 (800), 324 (10 200)

[a] Full width at half height.

The luminescence lifetimes of compounds **3**, **4** are shorter than 5 μs at 20 K, indicating a low quantum yield and important non-radiative relaxation processes even at low temperatures. The NIR luminescences from compounds **1**, **2** are too weak to be detected with fast Ge diodes and no lifetimes could be measured.

Absorption spectra of all compounds were measured in Me_2SO or CH_2Cl_2 solution. The onset of the lowest-energy absorption band occurs at wavelengths close to the high-energy onset of the luminescence spectra in Fig. 1, indicating that the observed solid-state emissions are not originating from deep traps. The molar absorptivities of the lowest-energy bands are low, characteristic for d–d transitions, but higher than those typically observed in *trans*-dioxo systems owing to the absence of inversion symmetry in compounds **1**–**4**. Absorption and Raman data for all compounds are included in Table 1.

We rationalize the observed large variation of the luminescence band maxima by comparing spectra and EHMO calculations based on crystal structures for compounds **1**–**3**.[10,11]§ The molecular z axis is chosen to coincide with the metal–ligand multiple bond and the calculations show predominant contributions from the $5d_{xy}$ and $5d_{xz,yz}$ atomic orbitals to the HOMO and LUMO, respectively. The lowest energy electronic transition therefore arises from a $5d_{xy} \rightarrow 5d_{xz,yz}$ orbital excitation, identical to the first electronic transition for *trans*-dioxo complexes of rhenium(v).[4,7] The energy of the HOMO ($5d_{xy}$) orbital depends mainly on the ancillary ligands and varies by less than 400 cm^{-1} within the series of compounds. The different LUMO energies are the most important reason for the variation of the emission energies of oxo and nitrido complexes. The calculated HOMO–LUMO gap for the nitrido compound **3** is 10 621 cm^{-1}, higher by approximately a factor of two than for the oxo complex **2**, where a gap of 4923 cm^{-1} is calculated. These orbital energy differences vary by 5700 cm^{-1}, surprisingly close to the difference of 5850 cm^{-1} between the emission maxima of compounds **2** and **3** given in Table 1. The comparison also indicates that interelectronic repulsions and other physical effects neglected in the EHMO calculations account for the discrepancy between observed transition energies and orbital energy differences. The separation of the $5d_{xz,yz}$ orbitals is calculated to be less than 1000 cm^{-1} for compounds **1**–**3**. These orbitals are degenerate in *trans*-dioxo compounds with D_{4h} symmetry and the small separations calculated for our compounds again underline the close similarity to the *trans*-dioxo systems. The MO calculations therefore confirm our d–d assignment for the lowest-energy electronic transition and are consistent with the spectroscopic data in Fig. 1 and Table 1. In addition, they qualitatively agree with *ab initio* calculations on a series of complexes with metal–ligand multiple bonds.[15]

Electronic spectra and EHMO calculations suggest that the character of the lowest-energy electronic transitions is essentially d–d. We have shown a first example for the large tuning range for the luminescence energies of related oxo and nitrido complexes.

This work was made possible by research grants from the NSERC (Canada) and from the Ministère de l'Enseignement Supérieur et de la Recherche (France).

Notes and References

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‡ Luminescence spectra of polycrystalline samples of all compounds were measured in a helium gas-flow cryostat. A Xe lamp and the 488.0 and 514.5 nm lines of an Ar^+ ion laser were used as excitation sources, and the emitted light was dispersed by either a 0.5 m or a 0.75 m monochromator. Photomultipliers and a photon counting system were used to detect the luminescence from the nitrido compounds, the emission from the oxo systems was measured with a cooled Ge detector and a lock-in amplifier, using an acquisition approach developed in our laboratory to minimize noise in the near-IR region.[13] A pulsed excimer laser and a digital oscilloscope were used to measure luminescence lifetimes. Raman spectra were measured with a Spex Ramalog system and Ar^+ ion laser, solution absorption spectra were recorded on a Varian Cary 5E spectrometer.

§ EHMO calculations were made with the program package YAeHMOP (version 2.0) by G. Landrum, 1997. YAeHMOP is available at http://overlap.chem.cornell.edu:8080/yaehmop.html.

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Received in Bloomington, IN, USA, 25th November 1997; 7/08517F