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Electronic Spectroscopy of $(CO)_5W{-}Al[(R)Do_2]$ Complexes

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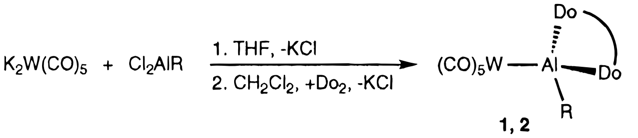
Transition metal stabilized complexes of Al(I) with the formula $(CO)_5W{-}Al[(R)(TMPDA)]$ (R = Cl (**1**), isobutyl (**2**); TMPDA = $Me_2N(CH_2)_3NMe_2$) show luminescence in the visible spectral region. The band maxima observed at 10 K are at 18 070 cm^{-1} (553 nm) for **1**, and at 17 630 cm^{-1} (567 nm) for **2**. Large Stokes shifts of 4150 and 4300 cm^{-1} are determined for **1** and **2**, respectively. The low intensity of the first absorption band and the long lifetimes of 130 μs for **1** and 210 μs for **2** (10 K) indicate a d−d transition. Luminescence spectra of microcrystalline samples of **1** show a resolved progression with an average spacing of 530 ± 10 cm^{-1} (10 K) resulting from excited-state distortions along several different vibrational coordinates.

Introduction

The electronic structure of tungsten carbonyl complexes with the stoichiometry $W(CO)_5$(N-donor) has been studied extensively with a variety of spectroscopic techniques.[1−7] Many of these compounds are luminescent, and the resolved vibronic structure in their low-temperature spectra has led to a detailed characterization of the emitting state. In the following, we describe the electronic spectroscopy of two new tungsten carbonyl complexes with aluminum(I) fragments as donor ligands and compare our results to the spectroscopy of the established compounds with nitrogen-donor ligands.

Subvalent halides and organometallic compounds of aluminum and gallium are receiving much current interest as preparative challenges and as new synthetic starting materials.[8] We described recently the synthesis, structure, and bonding of $[(\eta^5\text{-}C_5Me_5)Al{-}Fe(CO)_4]$, the first example of a compound with a Cp*Al unit strongly bonded to a transition metal fragment in a terminal nonbridging fashion.[9] We also have used a Lewis base adduct stabilized congener, $(CO)_5Cr{-}Ga[(Et)$(tetramethylethylenediamine)], as a volatile single-source precursor to deposit stoichiometric intermetallic CrGa thin films through organometallic chemical vapor deposition.[10]

Scheme 1. Synthesis and Schematic View of Compounds **1** and **2**



1, 2

1 R = Cl, **2** R = iso-Butyl

$(Do)_2 = Me_2N(CH_2)_3NMe_2$

We were thus led to investigate in more detail both the structure and bonding of transition metal stabilized Al(I) and Ga(I) complexes of the general formula $(CO)_nM{-}E[(R)Do_2]$ (M = Cr, Mo, W; n = 5. M = Fe; n = 4. E = Al, Ga. R = Cl, alkyl. $Do_2 = Me_2N(CH_2)_3NMe_2$, abbreviated as TMPDA in the following).[11] We present and discuss electronic spectra of the metal carbonyl stabilized Al(I) complexes $(CO)_5W{-}Al[(R)Do_2]$, typical representatives of this new category of subvalent aluminum compounds.

We use luminescence and absorption and Raman spectroscopy to characterize the low-energy excited states. This approach was successfully applied to a large number of photochemically relevant $W(CO)_5$(N-donor) compounds with nitrogen donors such as pyridine and substituted pyridines.[12] We use these literature results to interpret our spectra.

Experimental Section

The synthesis and analytical and structural characterization of the target molecules **1** and **2** are described in detail in the literature.[11] All materials for this study were synthesized as shown in Scheme 1. Samples for spectroscopic measurements were washed with pentane

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Table 1. Summary of Spectroscopic Data for $(CO)_5W-Al[(Cl)(TMPDA)]$ **1** and $(CO)_5W-Al[(isobutyl)(TMPDA)]$ **2**

	environment, temperature	**1**	**2**
absorption maxima λ_{max} (nm)	glass, 10 K	450 (22222, 204)	456 (21930, 1077)
($\hbar\omega$ (cm^{-1}), ϵ (M^{-1} cm^{-1}))		413 (24213, 838)	418 (23923, 2951)[a]
emission onset (cm^{-1})	glass, 10 K	21000	19990
maximum (cm^{-1})	glass, 10 K	18070	17630
lifetime (μs)	glass, 10 K	130	210
Stokes shift (cm^{-1})	glass, 10 K	4150	4300
emission onset (cm^{-1})	powder, 10 K	21030	20200
maximum (cm^{-1})	powder, 10 K	17680	18250
progression interval (cm^{-1})	powder, 10 K	530	
lifetime (μs)	powder, 10 K	1.4	3.6
emission onset (cm^{-1})	powder, 100 K	21090	20230
maximum (cm^{-1})	powder, 100 K	16120	18540
progression interval (cm^{-1})	powder, 100 K	560	
Raman band positions (cm^{-1})	powder, 300 K	326 (Al−Cl)	
		448 (W−C)	452 (W−C)
		502 (Al−N)	510 (Al−N)
		1874 (CO)	1890 (CO)
		1925 (CO)	1919 (CO)
		2028 (CO)	2010 (CO)

[a] 300 K, solution.

to remove excess $W(CO)_6$ and were repeatedly recrystallized from dichloromethane. The resulting crystals were stored under argon in Schlenk tubes and handled in a drybox under an inert atmosphere.

Luminescence Spectra. Polycrystalline samples and the solutions of **1** and **2** were cooled in an Oxford Instruments CF-1204 helium gas-flow cryostat. Typical concentrations for the solution and low-temperature glass spectra were on the order of 1 mM in dried and freshly distilled CH_2Cl_2 and THF (1:1). Exposure to air for a few seconds was sufficient to quench the luminescence from both solutions and solid samples of the title compounds. A 150 W Xe arc lamp filtered through a copper sulfate solution and a Schott UG1 filter were used as excitation sources. The spectra were recorded with a Spex 1800-II 0.75-m monochromator. A long-pass filter (Schott KV418) was placed in front of the entrance slit of the monochromator. The luminescence was detected with a Hamamatsu R4632 photomultiplier and a Stanford Research SR400 photon counter. All luminescence spectra are unpolarized and were corrected for system response. A detailed description of the instrumentation and the correction procedures is given in ref 13.

Luminescence Lifetimes. Samples were cooled to low temperature in the gas-flow cryostat and excited with the 308-nm line of a XeCl excimer laser (Lumonics Hyperex 420 SMB, 20-ns pulse width). The laser power did not exceed 5 mJ/pulse measured at the exit window of the laser. The time-dependent luminescence signal was dispersed by a Spex 500M 0.5-m monochromator set to a spectral bandwidth of 3.2 nm and detected by a cooled Hamamatsu R928 photomultiplier and a digital oscilloscope (Tektronix TDS 380) triggered by a Si photodiode (Thorlabs FDS 100) detecting the excitation pulse.

Absorption Spectra. Solution and low-temperature glass spectra were measured on a Varian Instruments Cary 5E spectrometer with the samples mounted in the helium gas-flow cryostat. Concentrations of 1.29 mM and 0.93 mM were used for **1** and **2**, respectively.

Raman Spectra. Room-temperature Raman spectra were measured with the 488.2-nm line of an Ar^+ ion laser and a Spex 1401 0.85-m double monochromator. The scattered light was detected by a photomultiplier (Hamamatsu R955) and a photon counter. The Raman transitions in Table 1 are assigned according to the literature.[14,15]

Spectroscopic Results

We report steady-state luminescence spectra, luminescence lifetime measurements, and absorption and Raman spectra of the target compounds. The main results of these measurements are summarized in Table 1.

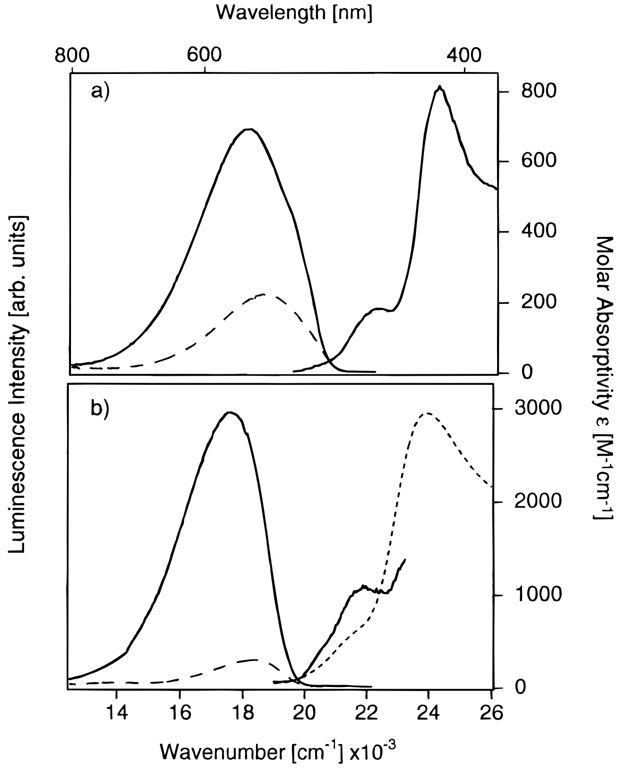

Figure 1. Luminescence and absorption spectra for (a) $(CO)_5W-Al[(Cl)(TMPDA)]$ (**1**) and (b) $(CO)_5W-Al[(isobutyl)(TMPDA)]$ (**2**) as low-temperature glasses. Luminescence and absorption spectra measured at 10 K are shown as solid lines, long dashes indicate luminescence spectra measured at 50 K, and short dashes denote the absorption spectrum of **2** measured at 300 K.

Intense green luminescence is observed from both $(CO)_5W-Al[(Cl)(TMPDA)]$ (**1**) and $(CO)_5W-Al[(isobutyl)(TMPDA)]$ (**2**) in low-temperature glasses. Both compounds show similar broad-band spectra without resolved vibronic structure. The luminescence maxima are at 18070 and 17630 cm^{-1} for **1** and **2**, respectively. The onset of the luminescence bands is at the same energy as the onset of the lowest-energy absorption bands and is higher in energy by 1010 cm^{-1} for **1** than for **2**. Luminescence and absorption spectra are compared in Figure 1. The low-temperature absorption spectra show a weak first maximum at approximately 22 000 cm^{-1} for both **1** and **2**. At

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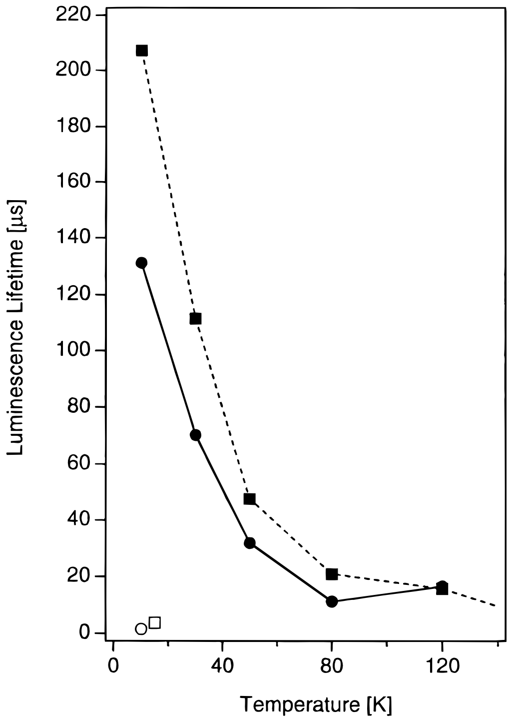

Figure 2. Luminescence lifetimes of **1** (solid circles) and **2** (solid squares) in THF/CH_2Cl_2 glasses as a function of temperature. The open symbols denote low-temperature lifetimes for microcrystalline samples of **1** and **2**.

room temperature, this maximum appears as a weak shoulder on the intense band with a maximum near 24 000 cm^{-1} in both compounds, illustrated for **2** in Figure 1. The Stokes shifts at 10 K are 4150 and 4300 cm^{-1} for **1** and **2**, respectively, determined from the lowest-energy absorption and emission maxima.

The luminescence intensity decreases with temperature for both compounds, as illustrated by the comparison of spectra measured at 10 and 50 K in Figure 1. The signal for both compounds is still observable at 130 K, but no signal was detected from solutions at temperatures above 200 K, higher than the melting point of the low-temperature glass.

The lowest-energy absorption transition broadens with temperature, and its maximum is less defined at room temperature than at 10 K. The band is superposed to the onset of the more intense absorption band; it is difficult to accurately determine its intensity as a function of temperature, but it appears to vary only weakly between 10 K and room temperature. The molar absorptivity of the more intense band near 24 000 cm^{-1} decreases from 650 M^{-1} cm^{-1} at 200 K to 490 M^{-1} cm^{-1} at 300 K in **1**. For compound **2**, the molar absorptivity changes by less than 20% over the same temperature interval.

Figure 2 shows the luminescence lifetimes as a function of temperature for both title compounds in low-temperature glasses. Lifetimes longer than 100 μs are measured at 10 K. The lifetimes decrease to approximately 20 μs at 80 K, a trend similar to the decrease of the luminescence intensities in Figure 1. Luminescence lifetimes were determined at the band maxima for both compounds, and an additional series of measurements at higher energy (19 610 cm^{-1}) for **1** lead to the same lifetimes to within 5%. To our knowledge, these lifetimes are among the longest reported for $W(CO)_5X$ (X = N-donor or Al(I) fragment) compounds. A temperature-independent lifetime, corresponding to the radiative limit, cannot be determined from the data in Figure 2. Microcrystalline samples of **1** and **2** show luminescence lifetimes shorter by 2 orders of magnitude even at the lowest temperatures. These low-temperature lifetimes are included for comparison in Figure 2.

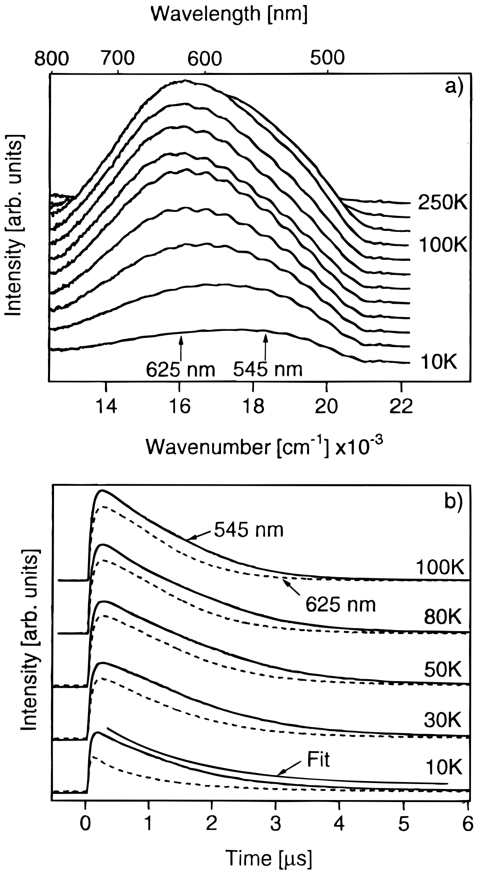

Figure 3. (a) Luminescence spectra of a microcrystalline sample of $(CO)_5W-Al[(Cl)(TMPDA)]$ (**1**) as a function of temperature. The wavelengths at which luminescence decay curves are measured are indicated. Spectra are shown at the following temperatures: 250 K, 200 K, 150 K, 100 K, 80 K, 70 K, 60 K, 50 K, 40 K, 30 K, 20 K, 10 K (top to bottom). (b) Luminescence decay curves for a microcrystalline sample of **1** as a function of temperature. Dotted lines indicate measurements at 625 nm, and solid lines indicate measurements at 545 nm. A single-exponential fit to the decay curve at 10 K is included for comparison.

The luminescence intensities from microcrystalline samples of both compounds are much weaker than those from the low-temperature glasses. Band onsets and maxima at low temperature are at energies similar to those for the glasses, as indicated in Table 1. Luminescence spectra for **1** as a function of temperature are shown in Figure 3a. The lowest-temperature spectrum shows a resolved vibronic structure with an average spacing of 530 ± 10 cm^{-1} near the onset of the band. Several series of measurements with different samples all showed this increase in luminescence intensity between 10 and 100 K. Spectra were measured with the temperature increasing from 10 to 100 K, followed by a control measurement at 10 K which led to a spectrum identical to the original lowest-temperature measurement. The irradiation for several hours, therefore, did not lead to a photochemical degradation of the sample crystals. The band maximum of the 100 K spectrum is at approximately 16 120 cm^{-1}, lower in energy by 1560 cm^{-1} than the maximum at 10 K, and the band shows more distinct vibronic structure with an average spacing of 560 ± 10 cm^{-1}. This behavior is indicative of efficient thermally activated energy transfer and emission from minority sites. No resolved structure was observed for microcrystalline samples of **2** at any temperature.

Three series of measurements on this compound led to identical spectra without variation of the band shape as observed for **1**. The band intensity of compound **2** decreases by 90% between 10 and 100 K.

The luminescence decay curves measured near the maxima of the high- and low-energy bands also indicate thermally activated energy-transfer processes. We include representative decay data in Figure 3. The decay curves at 10 K can be reasonably well analyzed by a single-exponential function, as illustrated in Figure 3b. The lifetime for the microcrystalline compound **1** shown in Figure 2 is obtained from this fit. The measurements at the two detection wavelengths differ by less than 5% at 10 K. The decay behavior changes significantly with increasing temperature: the decay curves strongly deviate from single exponentials at temperatures as low as 30 K. The intensity at times of approximately 2 μs after the excitation pulse is higher than at 10 K, a clear experimental signature of activated luminescence. The decay curves are similar at both observation wavelengths, and time-resolved luminescence spectra, therefore, cannot be used to separate the different bands contributing to the spectra in Figure 3a. The wide variety of possible minority luminophores and the large number of energy-transfer processes make a quantitative analysis of these decay curves impossible, but they clearly illustrate the presence of different emitting species, in contrast to literature reports on $W(CO)_5$(4-cyanopyridine), where multiple emissions from one type of molecule were observed.[16] The spectra of compounds **1** and **2** are compared to the literature results on related systems in more detail in the following section.

Discussion

Nature of the Lowest-Energy Excited State. Absorption and luminescence spectra of the title compounds lead to a straightforward assignment of the lowest-energy electronic state. The low intensity of the first absorption band in both target compounds and the long luminescence lifetimes observed in glasses at low temperatures indicate a forbidden transition. The corresponding band in $W(CO)_5$(pyridine), the most extensively studied representative of this class of complexes, shows a $d_{x^2-y^2} \rightarrow d_{z^2}$ spin-forbidden transition.[17] This band is observed in luminescence between approximately 21 000 and 16 000 cm^{-1}, an energy range similar to that of our compounds **1** and **2**. The Stokes shifts of our compounds are larger by approximately 1000 cm^{-1} than those for $W(CO)_5$(pyridine).

The spectroscopic similarities indicate that the lowest-energy electronic transition in the title compounds has predominantly d−d character, similar to that of many $W(CO)_5$(N-donor) systems studied in the literature.[12] Our experimental results confirm the analogy between the W−Al- and the W−N-donor bonds, established independently from crystallographic data, vibrational spectra, and quantum chemical ab initio calculations.[11] Density functional calculations on $(CO)_5WAlCl(NH_3)_2$, a model for compound **1**, show highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) with predominant d character, in close analogy to N-donor ligands. Several orbitals centered on the Al(I) fragment are calculated within 1.5 eV of the LUMO, indicating the possibility of low-energy metal-to-ligand charge-transfer bands.[11,18] These results and the electronic spectra presented and discussed here show clearly that the $Al(R)Do_2$ fragment is best described as a very strong $2e^-$ Lewis base donor ligand, isolobal to amines or phosphines. The energy of the lowest excited state is similar for **1** and **2**, but the different R ligands on the aluminum center (**1**, R = Cl**l** **2**, R = isobutyl) lead to a difference of approximately 1000 cm^{-1} for the onset of the luminescence bands for the two compounds, as summarized in Table 1. This difference is comparable to the variations observed for different N-donors such as pyridine and piperidine in $(CO)_5W$(N-donor) complexes.[5] We note that the Al(I) fragment leads to an energetic order of electronic states similar to that reported for $W(CO)_5$(pyridine),[3,19] whereas substitution of electron-withdrawing groups on the pyridine ligand can be used to change the order of excited states. In some compounds, such as $W(CO)_5$(4-cyanopyridine) and $W(CO)_5$(4-acetylpyridine), a charge-transfer state is lowest in energy.[3,19]

Both the luminescence lifetimes and intensities of compounds **1** and **2** decrease rapidly with temperature, in contrast to $W(CO)_5$(4-cyanopyridine) where luminescence is observed in solution at room temperature.[16] The rapid decrease is a likely consequence of the large number of accepting modes available on the aluminum fragment.

The low-temperature luminescence spectra of polycrystalline samples show band onsets and maxima at energies similar to those of the glasses, and we conclude that the lowest-energy electronic transition observed for the concentrated solids also has mainly d−d character.

Energy Transfer Processes in Microcrystalline Samples. The short luminescence lifetimes of the polycrystalline samples compared to the glasses indicate rapid energy-transfer processes to deep traps that lead to efficient quenching even at the lowest temperatures. The luminescence spectra at 10 K show onsets and maxima at energies similar to those of the glass spectra. We conclude that the nature of the low-temperature luminophore is similar to that of the glass, and therefore, the low-temperature emission is a d−d band. Thermally activated energy-transfer processes to other luminescent species determine the emission spectra at higher temperatures for **1**. The temperature-dependent spectra in Figure 3a illustrate the importance of these effects. The spectrum at 100 K is broader than the low-temperature luminescence band at 10 K, and its maximum is shifted to a lower energy by approximately 1560 cm^{-1}. The spectrum still shows a resolved vibronic structure with a slightly different interval than in the low-temperature spectrum, indicating a well-defined second emitting species with a resolved spectrum. The presence of several luminophores is confirmed by the luminescence decay curves in Figure 3b which deviate very significantly from single exponentials.

We suspect that packing imperfections in the microcrystalline samples could push the first W → (Al fragment) charge-transfer transition to lower energy than the weak d−d band, leading to a faster radiative relaxation and to a higher luminescence intensity, as illustrated in Figure 3a. Similar changes in the temperature-dependent luminescence spectra were observed for many different samples of compound **1** and could not be eliminated or modified by repeated recrystallizations. Luminescence intensities higher by an order of magnitude were reported in the literature for $W(CO)_5$(N-donor) compounds such as $W(CO)_5$(4-cyanopyridine), which are emitting from a charge-transfer state.[3,16] It is therefore tempting to assign the intense lower-energy emission band observed in our spectra at temperatures around 100 K to an emission from a charge-transfer state. The estimated Stokes shift for these luminophores is larger than

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6000 cm^{-1}. Stokes shifts larger than 5500 cm^{-1} were reported for W(CO)$_5$(4-cyanopyridine),[16] again in qualitative agreement with our assignment.

An alternative assignment of the high-temperature luminophore as trace amounts of W(CO)$_6$ can be ruled out because the electronic transitions of this complex occur at energies significantly higher than those in the range of our spectra in Figure 3.[3] Small amounts of (CO)$_4$W(TMPDA), a possible trace impurity, are expected to have the emission maximum close to 18 300 ± 100 cm^{-1}, as observed for (CO)$_4$W(ethylenediamine) and other (CO)$_4$W(N-donor)$_2$ complexes with saturated amines.[3] This expected energy range is higher by 2200 cm^{-1} than that of the observed band maximum in the 100 K spectrum of **1**, and we therefore rule out this type of impurity as responsible for the high-temperature luminescence band.

Vibronic Structure. The intervals observed in the resolved luminescence spectra in Figure 3a do not correspond to a single vibrational frequency in either the Raman or the IR spectra, similar to the situation analyzed for W(CO)$_5$(pyridine), where a missing mode effect (MIME) involving 18 different vibrational modes was used to analyze preresonance Raman and luminescence spectra.[17] Our spectra do not allow a detailed analysis of the MIME because the spectrum for the polycrystalline sample is a superposition of at least two bands even at the lowest temperatures. The observed vibronic spacing does not correspond to any of the vibrational energies summarized in Table 1. The average spacing of 530 cm^{-1} in **1** is larger than the W−(CO) stretching frequency of 448 cm^{-1} but similar to that of the fine structure in W(CO)$_5$(pyridine)[17] where an interval of 550 cm^{-1} was observed in the luminescence spectrum. This qualitative comparison shows spectroscopic similarities between those of the title compounds and of W(CO)$_5$(pyridine), again confirming the donor nature of the Al(I) fragment and our d−d assignment of the lowest-energy electronic transition.

The higher interval between the members of the resolved progression in the 100 K spectrum of **1** in Figure 3 indicates excited-state distortions along the various normal coordinates that are different from those of the emitting state, giving rise to the 10 K spectrum. Such a distinct difference is expected for a charge-transfer excited state with structural properties that vary greatly from those of a metal-centered excited state arising from a d−d transition.

Luminescence and absorption measurements on the new W−Al compounds **1** and **2** indicate a similar nature of the emitting electronic state as observed in systems with N-donor ligands such as W(CO)$_5$(pyridine). We plan to extend our investigation to the photochemistry of these systems and to explore specifically the photochemical generation of the reactive Al(I)Cl fragment, again using the analogy with W(CO)$_5$X complexes, where efficient dissociation of the Lewis base X, typically an N-donor, is often observed in the lowest-energy excited state.[20] In this sense, the (CO)$_5$W fragment can be viewed as a protecting group for subvalent aluminum species. Absorption and luminescence spectra provide strong experimental support for the analogy between the Al(I) fragments of the title compounds and the more traditional N-donors, extensively studied in the literature.

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