Luminescence of Two Dioxo d^0 Transition-Metal Complexes: $K_2MoO_2F_4 \cdot H_2O$ and $NaWO_2PO_4$

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The luminescence properties of $K_2MoO_2F_4 \cdot H_2O$ and $NaWO_2PO_4$ are reported and discussed. The first compound shows only luminescence at low temperatures, but the second also emits efficiently at room temperature. The decay time of the emission at low temperature is much longer for these compounds than for related oxomolybdenum or -tungsten compounds. This is probably due to the relatively low oscillator strength of the first singlet–singlet transition. © 1992 Academic Press, Inc.

Introduction

Luminescence of d^0 transition-metal complexes is well known (1). In a previous paper the luminescence properties of the VOF_4^- complex in $KVOF_4$ and of the $NbOF_5^{2-}$ complex in $K_2NbOF_5 \cdot H_2O$ were reported (2). It was noted that these properties are different from those of related oxo d^0 transition-metal complexes like VO_4^{3-}, NbO_4^{3-}, and NbO_6^{7-}. The oxofluoro complexes show vibrational structure in their emission spectra and the decay times of the emission are much longer than those of the oxo complexes. These different luminescence properties were ascribed to the localization of the excitation in the very short V–O or Nb–O bond which is present in these complexes.

The conclusions from the luminescence measurements on the VOF_4^- complex have been applied in the characterization of silica-supported vanadium oxide catalysts using luminescence spectroscopy (3). The vibrational structure in the emission spec-trum and the long decay time of the lumines-cence of this catalyst suggested that the structure of the luminescent vanadium ox-ide species on the silica surface is similar to that of the VOF_4^- complex (3).

It seems promising to try to identify the structure of molybdenum and tungsten ox-ide species at silica surfaces using lumines-cence spectroscopy as well. It has been sug-gested, based on preliminary luminescence measurements and various other experi-mental techniques ($4, 5$), that in silica-supported molybdenum and tungsten oxide catalysts there are isolated, distorted transi-tion-metal complexes present with two short metal–oxygen bonds sticking out of the surface (dioxo complexes).

In the present paper we report on the lu-minescence of $K_2MoO_2F_4 \cdot H_2O$ and $NaWO_2PO_4$. In both compounds there are dis-torted, isolated dioxo transition-metal com-plexes present. The structures of these two compounds have been well characterized by X-ray diffraction ($6, 7$). The information

from the luminescence measuremens on these two model compounds will be applied in the characterization of molybdenum and tungsten oxide catalysts in a subsequent paper (8).

The crystal structure of $K_2MoO_2F_4 \cdot H_2O$ has been described in Ref. (6). It contains isolated $MoO_2F_4^{2-}$ octahedra with two Mo–O bond lengths of 1.69 and 1.73 Å, which are in the cis position. The water molecule in the crystal structure connects two $MoO_2F_4^{2-}$ octahedra by bonding to an oxygen atom of one octahedron and to a fluorine atom of another one. There is, however, no strong hydrogen bonding: The $O-OH_2$ distance is 3.10 Å and the frequency of the O–H stretching vibration in the IR spectrum is 3620 cm^{-1} (6).

In $NaWO_2PO_4$ two crystallographically distinct WO_6 octahedra are present (7). In both octahedra four oxygens share corners with PO_4 groups and two oxygens are bonded to tungsten only. The W–O distances of the latter oxygens are 1.75 Å for one WO_2 unit and to 1.85 and 1.95 Å for the other WO_2 unit. In addition, we shall briefly discuss the luminescence properties of $NaMoO_2PO_4$, which is isomorphous with $NaWO_2PO_4$.

Experimental

$K_2MoO_2F_4 \cdot H_2O$ was isolated from aqueous hydrofluoric acid solutions following procedures described in Refs. (6) and (9). The phase purity was checked using X-ray powder diffraction (6). The X-ray pattern indicated the presence of a small amount of an unknown second phase.

$NaWO_2PO_4$ and $NaMoO_2PO_4$ were prepared by a solid state method. Firing was in both cases at 650°C. The phase purity was checked by X-ray powder diffraction (7). For $NaWO_2PO_4$ the pattern indicated the presence of a minor amount of WO_3 which may also be responsible for the yellow color of the product. Optical equipment used for

the measurement of spectra and decay curves has been described previously (2, 10).

Results and Discussion

$K_2MoO_2F_4 \cdot H_2O$

$K_2MoO_2F_4 \cdot H_2O$ does not show luminescence at room temperature, but a red emission appears under long wavelength UV excitation at low temperatures. At 4.2 K a broad and structureless emission band is observed at 680 nm. The excitation spectrum of this emission shows two bands peaking at 290 and 330 nm. There is a slight shift of the emission maximum upon varying the excitation wavelength. This may be due to emission of the unknown second phase and/ or to emission of defect molybdate groups in the crystal structure of $K_2MoO_2F_4 \cdot H_2O$. At 120 K the emission intensity has dropped to 50% of its value at 4.2 K.

The optical transitions involved are ascribed to charge-transfer transitions (1) involving the oxygen ligands and the molybdenum ion, since charge transfer from the more electronegative fluorine ligands is expected to take place at higher energies. The absorption is due to singlet–singlet transitions and the emission to a triplet–singlet transition (1, 2, 11).

The positions of the emission and excitation bands are not uncommon for molybdates with six coordination (12). The relatively low efficiency at 4.2 K and the low quenching temperature are ascribed to the low energy position of the first absorption band (12).

At 4.2 K the decay curve of the emission under 280 nm excitation is nonexponential. The tail of the curve is exponential with a decay time of 4.5 ms. The nonexponential behavior may be due to the second phase and/or defect molybdate groups. The decay time of the tail of the curve is ascribed to the intrinsic luminescence of $K_2MoO_2F_4 \cdot H_2O$. The temperature dependence of this
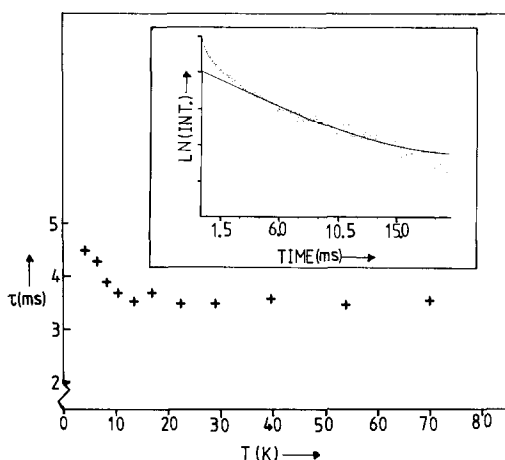
FIG. 1. Temperature dependence of the decay time of $K_2MoO_2F_4 \cdot H_2O$. The inset presents the decay curve at 50 K. The solid line in this curve is a fit to an exponential function.

decay time is plotted in Fig. 1. The inset in this figure presents the decay curve at 50 K.

For most molybdates the decay time shows a strong dependence on the temperature in the low temperature region, but above ca. 20–30 K usually a plateau is reached (*1, 12, 13*). In Table I the decay time of $K_2MoO_2F_4 \cdot H_2O$ in the plateau region is compared with those of other molybdates in their plateau regions.

From this table it appears that the decay time of $K_2MoO_2F_4 \cdot H_2O$ is anomalously

TABLE I

DECAY TIMES OF SOME LUMINESCENT
MOLYBDATE COMPLEXES

Compound	Luminescent Complex	$\tau(ms)$ at 50 K	Reference
$K_2MoO_2F_4 \cdot H_2O$	$MoO_2F_4^{2-}$	3.5	This work
$CaMoO_4$	MoO_4^{2-}	0.25	1
Ba_2CaMoO_6	MoO_6^{6-}	0.1	12
$Na_2Mo_2O_7$	$(Mo_2O_7)^{2-}$ chains	0.77	13
MoO_3/SiO_2	"$(Si-O)_2MoO_2$"	1.8	8

long compared with those of pure oxomolybdates. A similar situation was observed before for the decay time of $KVOF_4$ compared with those of pure oxovanadates (*2*). In the latter case the unusually long decay time was ascribed to the localization of the excited state in the short V–O bond (*2*). In the present case the excitation is expected to be localized in the short Mo–O bonds (see above). Hence, a very long decay time is observed. The present result indicates that the observation of such anomalously long decay times is not restricted to monooxo d^0 transition-metal complexes but that dioxo complexes show the same behavior.

Only the decay time for silica-supported molybdenum oxide catalysts is of the same order of magnitude as that of $K_2MoO_2F_4 \cdot H_2O$. This suggests that the structure of the luminescent species on the silica surface is similar to that of the $MoO_2F_4^{2-}$ complex. A more detailed discussion of the luminescent properties of silica-supported molydenum oxide catalysts will appear elsewhere (*8*).

Since the triplet–singlet emission transiton is spin-forbidden, it has to "steal" intensity from a singlet–singlet transition of suitable symmetry by spin–orbit coupling (*2, 11*). Therefore, the following expression for the oscillator strength of the triplet–singlet transition $f(TS)$ is valid.

$$f(TS) \propto |\langle \Phi (T)|H (s.o.)|\Phi (S)\rangle|^2 \cdot (1/\Delta E)^2 \cdot f(SS) \quad (1)$$

Here the matrix element determines the spin–orbit coupling, ΔE is the energy difference between the excited triplet and singlet levels involved, and f (SS) is the oscillator strength of the singlet–singlet transition from which the triplet–singlet transition steals intensity.

The value of f (SS) is measured from the absorption spectrum of a solution of MoO_3 in aqueous hydrofluoric acid. Since the product $K_2MoO_2F_4 \cdot H_2O$ is isolated from such a solution upon addition of potassium
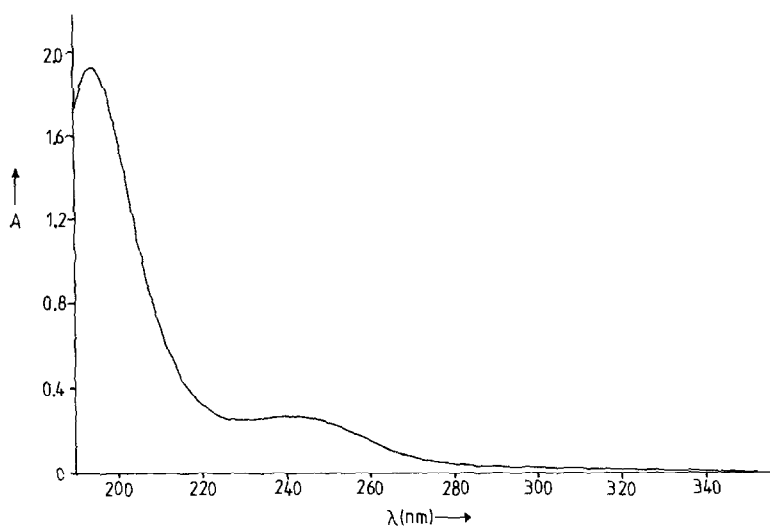
FIG. 2. Absorption spectrum of a 5×10^{-4} M MoO$_3$ solution in 25% HF.

ions it is assumed that it contains MoO$_2$F$_4^{2-}$ ions. The forbidden singlet–triplet transitions are not observed in the spectrum.

The absorption spectrum of a 25% HF solution containing 5×10^{-4} mole molybdenum per liter is presented in Fig. 2. Two bands are observed at 245 and 195 nm, respectively. The tail of the first absorption band toward longer wavelength might be a separate band. The oscillator strengths of the two high intensity bands are estimated to be 0.01 and 0.10, respectively. For comparison, the oscillator strengths of the two lowest absorption bands of the MoO$_4^{2-}$ ion in solution amount to 0.06 and 0.2 (*14*).

If we assume that the first singlet–singlet transition is the relevant one in the spin–orbit coupling, it is clear that the oscillator strength of this transition is considerably smaller for MoO$_2$F$_4^{2-}$ than for MoO$_4^{2-}$. This suggests that the small absorption strength of the singlet–singlet transition is an important factor determining the anomalously slow decay rate of the triplet–singlet transition of K$_2$MoO$_2$F$_4$ · H$_2$O. A similar conclusion was drawn for the long decay

time of KVOF$_4$ (*2*). Ab initio calculations which are carried out at the moment will possibly clarify the backgrounds of the low oscillator strength of these lowest singlet–singlet transitions.

NaWO$_2$PO$_4$

NaWO$_2$PO$_4$ shows an efficient yellow luminescence at room temperature and below. The excitation spectrum of the emission shows two bands at 260 and 305 nm. The emission band is situated at 550 nm. These positions hardly change with temperature. At 260 K the emission intensity has dropped to 50% of its value of 4.2 K. The bands are broad and structureless, which is usually observed for tungstates (*1, 13*). However, the emission maximum is at unusually long wavelength for a tungstate complex.

Theoretically two emission bands can be expected since there are two crystallographically distinct WO$_6$ octahedra present. This is not observed; the position and the shape of the emission band do not depend on the excitation wavelength. Probably the emis-
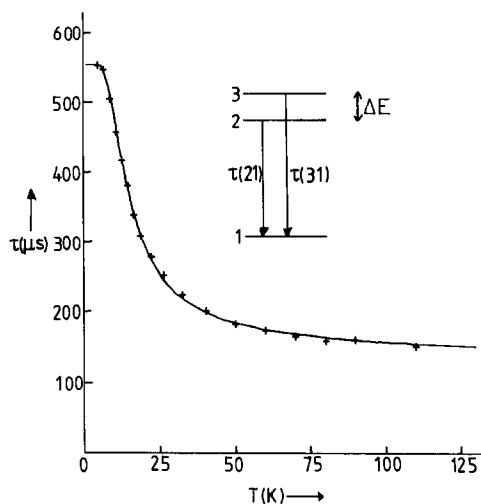
FIG. 3. Temperature dependence of the decay time of $NaWO_2PO_4$. The solid line presents a fit to a three-level scheme which is illustrated in the inset.

sion spectra of the two WO_6 groups coincide more or less.

The decay curves of the emission of Na WO_2PO_4 are one-exponential. Only below 10 K a slight deviation from exponential behavior is observed. In Fig. 3 a graph of the decay time versus temperature is presented. The solid line represents a fit to a three-level scheme as described in Ref. (15). From this fit the decay times of the lower emitting level ($\tau(21)$), the higher emitting level ($\tau(31)$), and the energy difference between these two ex-

cited levels, ΔE, are derived. This is illustrated in Fig. 3. The values for $\tau(21)$, $\tau(31)$, and ΔE for $NaWO_2PO_4$ and other tungstates are given in Table II.

Due to the stronger covalent bonding between phosphorus and oxygen compared to tungsten and oxygen, it is to be expected that the oxygens which are shared between phosphorus and tungsten are more electronegative than the two oxygens which are only bonded to tungsten. Therefore, the lowest optical transition is expected to be localized in the two latter W–O bonds. For one of the two WO_6 groups in the crystal structure these W–O bonds are very short (see above). Hence, the present situation is similar to that for $K_2MoO_2F_4 \cdot H_2O$.

Just as observed for $K_2MoO_2F_4 \cdot H_2O$, both decay times $\tau(21)$ and $\tau(31)$ of Na WO_2PO_4 are longer than those of nearly all other tungstates. Only the decay time of the silica-supported tungsten oxide catalyst is longer, which suggests that the structures of the tungsten oxide species on the silica surface and the $WO_2(O_4P)_4$ complex in Na WO_2PO_4 are similar (8).

The isomorphous compound NaMo O_2PO_4 does not luminesce at room temperature, and even at 4.2 K the emission is weak. The emission maximum is at 710 nm. The excitation spectrum of the emission shows two maxima at 330 and 370 nm. The decay curve at 50 K is nonexponential, but the tail could be fitted to an exponential function

TABLE II

DECAY TIMES OF SOME LUMINESCENT TUNGSTATE COMPLEXES

Compound	Luminescent complex	$\tau(21)/\tau(31)$ (μs)	ΔE (cm^{-1})	Reference
$NaWO_2PO_4$	$WO_2(O_4P)_4$	550/80	24	This work
$CaWO_4$	WO_4^{2-}	330/8	20	16
$Ba_2CaTeO_6:W^{6+}$	WO_6^{6-}	20/10	—	1
$Na_2W_2O_7$	$(W_2O_7)^{2-}$ chains	200/30	12	13
WO_3/SiO_2	"(Si-O)$_2WO_2$"	450 (plateau value at 50 K)	—	8

resulting in a decay time of 5 ms. We do not know the origin of the nonexponential behavior. However, the long decay time of the tail of the curve seems to be in accordance with the observations on $K_2MoO_2F_4 \cdot H_2O$ and $NaWO_2PO_4$.

Conclusions

We have reported the luminescence properties of $K_2MoO_2F_4 \cdot H_2O$ and $NaWO_2PO_4$. In both compounds there are two short metal–oxygen bonds present in the transition metal complex, the oxygens of which are only bonded to the transition metal ion. In both complexes the excited state is more or less localized in the short metal–oxygen bonds due to the higher electronegativity of the additional ligands. The localization in these short bonds results in anomalously long decay times of the emission just as was found before for monooxo transition-metal complexes like VOF_4^- and $NbOF_5^{2-}$ (2).

For the $MoO_2F_4^{2-}$ complex it was shown that the relatively low oscillator strength of the singlet–singlet transition from which the triplet–singlet emission transition steals intensity is an important factor determining the anomalously long decay time.

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