Phosphorescence of Manganese(II) in Single Crystals of $[Mn(CO(NH_2)_2)_6](ClO_4)_2$

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The $^4T_{1g}(t_{2g}^4\ e_g^1) \rightarrow {}^6A_{1g}(t_{2g}^3\ e_g^2)$ phosphorescence spectrum of manganese(II) in single crystals of $[Mn(CO(NH_2)_2)_6](ClO_4)_2$ has been recorded in the temperature range of 4.2 to 298 K. With decreasing temperature the emission maximum is shifted from 17138 cm^{-1} (298 K) to 16809 cm^{-1} (4.2 K). This red shift points to a linear thermal expansion coefficient of $\alpha = 24 \cdot 10^{-6}\ K^{-1}$. Crystal field parameters of $Dq = 748\ cm^{-1}$ and $B = 827\ cm^{-1}$ have been calculated from the room temperature absorption and excitation spectra.

The luminescence behaviour of high-spin Mn(II) in cubic complexes with ionic ligands has frequently been observed and is attributed to the $^4T_1 \rightarrow {}^6A_1$ transition [1 – 6]. Luminescence is rarely detectable in complexes with molecular ligands because of the competition from radiationless deactivation processes [2, 7].

The urea molecule seems to be an exception, since the $[Mn(urea)_6](ClO_4)_2$ complex compound exhibits strong luminescence already at room temperature with the 457.9 nm exciting line of an Ar^+ laser. We have studied the phosphorescence spectra of $[Mn(urea)_6](ClO_4)_2$ as a function of temperature in the range of 298 K to 4.2 K.

Experimental

$[Mn(CO(NH_2)_2)_6](ClO_4)_2$ was prepared by addition of stoichiometric amounts of $NaClO_4$ and urea to an ethanolic solution of $MnCl_2 \cdot 4\,H_2O$. Single crystals of $[Mn(urea)_6](ClO_4)_2$ were grown from aqueous solutions containing 600 g of urea/l. Phosphorescence spectra were measured by use of a Spex 14018 double beam spectrometer with holographic gratings of 1800 grooves per mm in conjunction with a Spectra Physics modes 164-09 argon ion laser. Absorption spectra were recorded on a Cary 14 spectrophotometer (1.47 mole/l of $[Mn(urea)_6](ClO_4)_2$) in a 10 m aqueous solution of urea (cell of 5 cm path-length).

Excitation spectra were taken by illuminating the sample with light from a 150 W xenon lamp in conjunction with a Jarrell Ash 0.25 m grating monochromator, and selecting the luminescence light with the Spex 14018 double spectrometer.

Results

The room temperature phosphorescence and absorption spectra of $[Mn(urea)_6](ClO_4)_2$ are shown in Fig. 1 (range 16000 to 30000 cm^{-1}). The corresponding maxima of emission and absorption are listed in Table 1.

Figure 2 shows the temperature shift (298 – 4.2 K) of the phosphorescence maximum.

Discussion

The crystal structure of $[Mn(urea)_6](ClO_4)_2$ is not known. But in accordance with the coordination chemistry of urea [8, 9] it is reasonable to assume that the manganese ion is octahedrally surrounded by six oxygens from six urea ligands.

In a weak crystal field of O_h symmetry the configuration d^5 of Mn^{2+} gives rise for the following terms [10]:

$$^6A_{1g}(^6S,\ t_{2g}^3\ e_g^2) < {}^4T_{1g}(^4G,\ t_{2g}^4\ e_g^1) < {}^4T_{2g}(^4G,\ t_{2g}^4\ e_g^1) < {}^4E_g,\ {}^4A_{1g}(^4G,\ t_{2g}^3\ e_g^2) < {}^4T_{2g}(^4D,\ t_{2g}^4\ e_g^1).$$

The energy of the degenerate states ^4E_g, $^4A_{1g}$, which arise from the ground-state configuration $t_{2g}^3\ e_g^2$ is independent of the crystal field strength

Table 1. Absorption and phosphorescence excitation bands of $[Mn(CO(NH_2)_2)_6](ClO_4)_2$ at 298 K.

	Absorption			Excitation	Assignment
(Å)	$\bar{\nu}$ (cm^{-1})	*E*	ε	$\bar{\nu}$ (Ph) = 17138	
5100	19610	0.435	0.059	19037	$\vert {}^4G,\ {}^4T_{1g}(t_{2g}^4\ e_g^1) >$
4250	23530	0.685	0.093	23096	$\vert {}^4G,\ {}^4T_{2g}(t_{2g}^4\ e_g^1) >$
4030	24810	0.920	0.125	24673	$\vert {}^4G,\ {}^4A_{1g},\ {}^4E_g(t_{2g}^3\ e_g^2) >$
3575	27972	1.190	0.162		$\vert {}^4D,\ {}^4T_{2g}(t_{2g}^3\ e_g^2) >$
3380	29586	1.280	0.174		$\vert {}^4D,\ {}^4E_g(t_{2g}^3\ e_g^2) >$

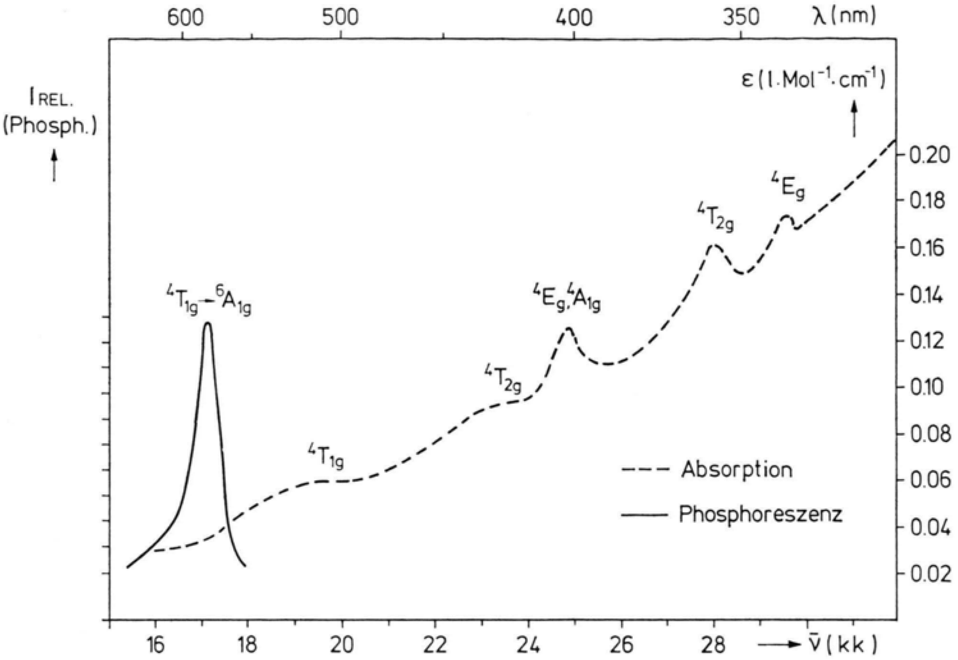

Fig. 1. Single crystal phosphorescence and solution absorption spectra of $[Mn(urea)_6](ClO_4)_2$ at 298 K.

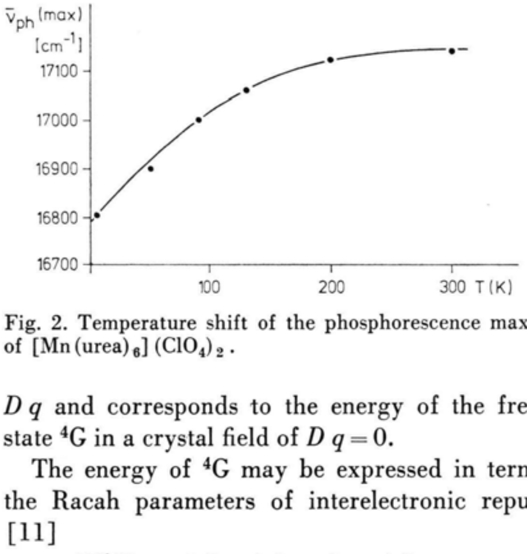

Fig. 2. Temperature shift of the phosphorescence maximum of $[Mn(urea)_6](ClO_4)_2$.

$D\,q$ and corresponds to the energy of the free-ion state ^4G in a crystal field of $D\,q = 0$.

The energy of ^4G may be expressed in terms of the Racah parameters of interelectronic repulsion [11]

$$E(^4G) = 10\,B + 5\,C, \quad C \approx 4\,B\,.$$

In the free Mn^{2+} ion ^4G is located at 26 800 cm^{-1}, leading to a value of $B_{\text{free-ion}} = 893\ cm^{-1}$.

Owing to the nephelauxetic effect the transition $^6S(_1A_{1g}) \rightarrow {}^4G(^4E_g, {}^4A_{1g})$ in $[Mn(urea)_6](ClO_4)_2$ is found at 24 810 cm^{-1} (cf. Table 1) suggesting $B_{\text{complex}} = 827\ cm^{-1}$ and $\beta_{35} = 0.93$.

Assuming a nephelauxetic shift of about $-2000\ cm^{-1}$ for all crystal-field terms with respect to the free ion states the absorption energies of Table 1 can be adapted to the Orgel-diagram of Mn^{+2} at $10\,D\,q = 7480\ cm^{-1}$.

Both the crystal field parameter $10\,D\,q$ and the nephelauxetic ratio β_{35} can be factorized according to

$$10\,D\,q = 7480 \approx 8000\ (Mn^{2+}) \times 0.93\ (6\ \text{urea}),$$
$$1\text{-}\beta_{35} = 0.07 \approx 0.06\ (Mn^{2+}) \times 1.2\ \ (6\ \text{urea}).$$

The resulting functions of the central ion and the ligands compare favourably with the values quoted in literature for Mn^{2+} and urea [11].

The phosphorescence transition $^4T_{1g} \rightarrow {}^6A_{1g}$ implies a change in the population of the subcells t_{2g} and e_g: $t_{2g}^4\,e_g^1 \rightarrow t_{2g}^3\,e_g^2$. Consequently the corresponding emission band (cf. Fig. 1) is rather structureless even at low temperatures because the manganese-oxygen equilibrium distance is shorter in the excited state configuration than in the ground state configuration which involves more antibonding electrons.

Since

$$\frac{d}{d(D\,q)}\,(t_{2g}^4\,e_g^1) = -4 \times 4 + 1 \times 6 = -10 \quad \text{and}$$
$$\frac{d}{d(D\,q)}\,(t_{2g}^3\,e_g^2) = -3 \times 4 + 2 \times 6 = 0$$

the $^4T_{1g} \rightarrow {}^6A_{1g}$ phosphorescence is predicted to be moved towards lower wave numbers with increasing ligand field strength, that is on cooling the crystals. This red shift with decreasing temperature is actually observed (cf. Fig. 2) and allows an approximate calculation of the otherwise unknown linear thermal expansion coefficient α of $[\mathrm{Mn(urea)_6}](\mathrm{ClO_4})_2$ to be made [12]:

$$\begin{aligned}&\frac{\mathrm{d}}{\mathrm{d}T}\,[\bar{\nu}(^4T_{1g} - {}^6A_{1g})]\\ &= \frac{\mathrm{d}}{\mathrm{d}(D\,q)}\,[\bar{\nu}(^4T_{1g} - {}^6A_{1g})]\cdot\frac{\mathrm{d}(D\,q)}{\mathrm{d}T}\\ &= -10\,\frac{\mathrm{d}(D\,q)}{\mathrm{d}T}\ .\end{aligned}$$

Since $D\,q \approx \mathrm{const}/R^6$ for dipole ligands and $R \approx R_0(1+\alpha\,T)$:

$$\frac{\mathrm{d}(D\,q)}{\mathrm{d}T} = \frac{\mathrm{d}(D\,q)}{\mathrm{d}R}\,\frac{\mathrm{d}R}{\mathrm{d}T} = -6\,\frac{R_0}{R}\,D\,q$$

assuming $R_0/R \approx 1$, the temperature shift of the emission band is related to the linear thermal expansion coefficient according to:

$$\frac{\mathrm{d}}{\mathrm{d}T}\,[\bar{\nu}(^4T_{1g} \rightarrow {}^6A_{1g})] = 60\,D\,q\,\alpha\,.$$

In the temperature range of 4.2 K to 300 K the average value of $\mathrm{d}/\mathrm{d}t[\bar{\nu}(^4T_{1g} \rightarrow {}^6A_{1g})]$ amounts to $1.1\ \mathrm{cm^{-1}/K}$ (cf. Fig. 2) leading to $\alpha \approx 24\cdot 10^{-6}\ \mathrm{K^{-1}}$.

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