Luminescence of Divalent Europium Complexes with Crown Ethers and Polyethylene Glycols

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Summary Divalent europium complexes with crown ethers give a remarkably intense, blue emission under u.v. radiation.

WE report here the observation of fluorescence from divalent europium (Eu^{2+})[1] complexes with cyclic and acyclic polyethers including 12-crown-4, 15-crown-5, 18-crown-6, dicyclohexyl-18-crown-6 (DC-18-O-6), dicyclohexyl-24-crown-8 (DC-24-O-8), triethylene glycol (EO3), tetraethylene glycol (EO4), pentaethylene glycol (EO5), hexaethylene glycol (EO6), and heptaethylene glycol (EO7).

The observed intensity of the fluorescence is generally very large; of the crown ether and polyethylene glycol complexes examined, the most intense fluorescence is given by a methanol solution of 15-crown-5 complex with Eu^{2+}, the intensity of which is 600 times greater than that given by a $EuCl_2$–methanol solution of the same Eu^{2+} concentration.† Luminescence properties of the Eu^{2+} complexes are summarized in the Table. The emission is in the region of 400—500 nm which is common for Eu^{2+} fluorescence. Peaks of the luminescence spectra for the complexes shift to the short-wavelength side, compared with that for $EuCl_2$.

TABLE Luminescence properties of Eu^{2+} complexes with crown ethers and polyethylene glycols

Complex (methanol solution)[a]	Eu : ligand	Maximum absorption bands/nm I	Maximum absorption bands/nm II	Maximum emission band/nm	Relative intensity of emission[b]
Eu^{2+}–15-crown-5	1 : 3	248	318	433	620
Eu^{2+}–18-crown-6	4 : 3	257	325	446	150
Eu^{2+}–DC-18-O-6	4 : 3	257	318	439	87
Eu^{2+}–DC-24-O-8	1 : 1	252	327	443	180
Eu^{2+}–EO3	—[c]	250	329	467	2·2
Eu^{2+}–EO4	—[c]	251	327	442	5·0
Eu^{2+}–EO5	1 : 1	252	320	464	4·2
Eu^{2+}–EO6	2 : 1	252	321	467	47
Eu^{2+}–EO7	2 : 1	252	316	458	66
$EuCl_2$	—	250	330	489	1·0

[a] The Eu^{2+} concentration is $4·0 \times 10^{-3}$ mol l^{-1}. [b] Relative intensities of the emission were determined by comparison with the intensity of the emission from a $EuCl_2$–methanol solution (Eu^{2+} concentration $4·0 \times 10^{-3}$ mol l^{-1}). [c] The ratios could not be established.

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† Emission spectra were determined at room temperature on a Shimadzu Absolute Spectrofluorophotometer, Model RF-502, using the automatic compensation and pre-calibration system for the instrumental factors (*cf.* T. Kurita, H. Yamamoto, M. Takada, and Y. Komurasaki, *Shimadzu Rev.*, 1975, **32**, 225). Emission spectra were taken at the maximum peak wavelength of the excitation spectra of the complexes. The emission intensity was calculated from the area of the emission band recorded. Concentration of Eu^{2+} ion in the complex solutions was maintained at $4·0 \times 10^{-3}$ mol l^{-1}.

The metal (Eu^{2+}) to ligand ratio for the complexes (M:L) has been determined by means of molar ratio methods.[2] The ratio (M:L) for the 15-crown-5 complex was 1:3, suggesting that the Eu^{2+} ion was located at the centre of the triangle formed by the three crown ethers' rings, although other possibilities cannot be excluded.

It is not yet clear why the 15-crown-5 complex gives the highest intensity. The Eu^{2+} ion may fit so tightly in the cavity of 15-crown-5 that the intramolecular vibration which causes a non-radiative process may become minimal.

It has been found that the fluorescence of 1,8-naphtho-21-crown-6 and dibenzo-18-crown-6 (DB-18-O-6) is enhanced by the chelation of alkali metal cations.[3] The reason given for this fluorescence enhancement is that DB-18-O-6 complexes have a rigid structure, compared with the uncomplexed crowns. In other words, chelation with metal ions causes the internal quenching rate to become appreciably lower. Although the situation described here is not the same as those previously reported because the Eu^{2+} complexes produce the luminescence from a central ion while the alkali–crown complexes, described above, produce the luminescence from the excited state of the double bonds, the rigid structure model for the enhancement should be sufficiently accurate.

The 18-crown-6 complex with Eu^{2+} is a 4:3 complex which is probably of the 'club sandwich' type.[4] The Eu^{2+} ions in the complex are close to each other, so that concentration quenching of the luminescence would take place to some extent, giving a smaller intensity than that of the 15-crown-5 complex.

Polyethylene glycols loosely encircle one Eu^{2+} in EO5 or two in both EO6 and EO7 and so give a poorer emission. However, in a series of polyethylene glycols, the longer the ligand chain, the more intense the emission becomes, since the longer polyethylene glycol can surround the central cation to greater effect.

The absorption spectra for the complexes are similar and consist of two bands which are due to 'allowed electric dipole' transitions between the 4f and 5d states ($4f^7 \rightarrow 4f^6 5d$) and structure, *i.e.*, the two bands are a result of the crystal field splitting of the 5d orbitals into the excited state. The excitation spectra of the complexes coincide in position with the absorption spectra of the corresponding complexes.

Reactions and measurement of the emission spectra were routinely performed under a nitrogen atmosphere since the complexes are not very stable in air. Complex solutions were obtained by dissolving 0·1 mmol of $EuCl_2$ and a given amount of the ligand in 25 ml of degassed methanol. $EuCl_2$ was prepared by the method described elsewhere.[5]

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[1] The emission is due to a transition from the $4f^6 5d^1$ state to the $4f^7$ state of Eu^{2+}, *cf.* (a) G. Blasse, W. L. Wanmaker, J. W. Ter-Vrugt, and A. Bril, *Philips Res. Rep.*, 1968, **23**, 189; (b) G. Blasse, *Phys. Status Solidi, B*, 1973, **55**, K131.

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