

rameters.¹⁴ Each manganese has only four ligands. Two iodines and two phosphines are arranged such that a crystallographic twofold axis passes through the metal bisecting the angles I-Mn-I* and P-Mn-P*. The resulting distorted tetrahedron is the most simple type of a manganese dihalide phosphine adduct structurally characterized so far. All other known adduct structures contain hexacoordinated manganese,^{4,5} in one case alternating with tetracoordinated centers.¹⁰ As a consequence of the low coordination number the bond lengths in **1/2** are considerably smaller than most of their counterparts in ref 4, 5, and 10.

A solution of **1/2** in (deuterated) benzene yields ¹H and ¹³C signals for the ethyl groups of the phosphine. The room-temperature paramagnetic shifts, $\delta_{298}^{\text{para}}$, are -36.8 (CH₂), -654.2 (CH₂), -5.5 (CH₃), and -158.8 (CH₃) (negative sign to high frequency). The shifts are very similar to those found for phosphine-stabilized manganese half-sandwich compounds which contain five unpaired electrons.^{9b} The electron spin delocalization most probably proceeds through σ bonds with a hyperconjugative contribution to the large α -carbon shift. With small amounts of oxygen, the benzene solution turns dark green while in THF a blue to violet color is seen. The original pink solutions can be regenerated by bubbling argon through them. This supports earlier reports and is indicative for a reversible binding of dioxygen.⁶

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Supplementary Material Available: Listings of further crystal structure data and atomic coordinates and anisotropic temperature factors (4 pages). Ordering information is given on any current masthead page.

(14) Bond lengths in picometers and angles in degrees for **1/2**: Mn-P = 252.8 (4)/253.9 (4); Mn-I = 266.2 (2)/267.0 (2); I-Mn-I* = 120.1 (1)/119.9 (1); P-Mn-P* = 115.1 (2)/116.4 (2); I-Mn-P = 105.2 (1)/105.5 (1); I-Mn-P* = 105.8 (1)/105.1 (1).

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"Photoinduced" Complex Formation

Sir:

Luminescence properties of crown ether complexes with divalent europium ions have been studied recently, and the crown ether complexes are known to exhibit a remarkably intense blue emission under UV irradiation.¹⁻³

During the course of our studies, we found that Eu(II) complex formation⁴ with crown ethers having a bromoalkyl

- (1) Adachi, G.; Tomokiyo, K.; Sorita, K.; Shiokawa, J. *J. Chem. Soc., Chem. Commun.* **1980**, 914.
- (2) Sabbatini, N.; Ciano, M.; Dellonte, S.; Bonazzi, A.; Balzani, V. *Chem. Phys. Lett.* **1982**, *90*, 265.
- (3) Adachi, G.; Sorita, K.; Kawata, K.; Tomokiyo, K.; Shiokawa, J. *J. Less-Common Met.* **1983**, *93*, 81.
- (4) The solutions of the divalent europium crown ether complexes used in this study were obtained by dissolving anhydrous EuCl₂ and crown ethers in anhydrous degassed methanol. The molar ratio method was applied to establish the stoichiometry of the complexes and gave values of 1:1 for Eu-2. For Eu-1 no accurate value has been obtained so far. A mixture of 1:4 (Eu(II):1) was then used for most of the measurements.

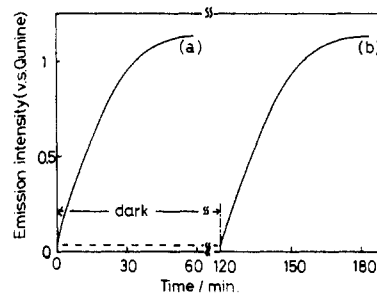


Figure 1. Time dependence of emission intensities for the complex with **1** (excitation 370 nm, emission 440 nm). See text for an explanation of curves a and b.

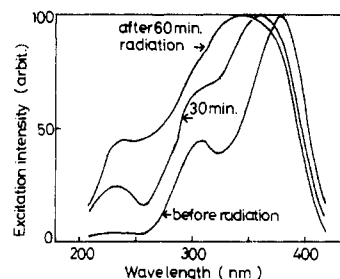


Figure 2. Time dependence of excitation spectra for the complex with **1** (emission 440 nm).

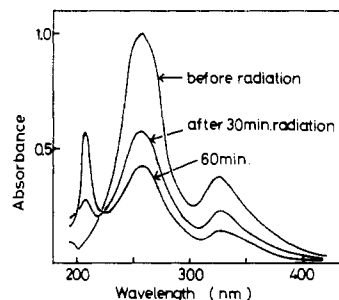


Figure 3. Time dependence of absorption spectra for the complex with **1**. (Concentration of **1**, 8×10^{-4} mol dm⁻³).

side chain was extraordinarily induced by UV irradiation and that the Eu(II) luminescence intensity in the complex increased significantly.

The complex of Eu(II) with 2-BrMe-2-Me(15-crown-5) (**1**) gives a strong emission at 423-433 nm with 370-nm excitation. The Eu(II) complex with 2-BrMe-2-Me(18-crown-6) (**2**) shows a 443-nm emission with 376-nm radiation while a simple EuCl₂-methanol solution yields an emission peak at 487 nm. These emissions are due to allowed electric dipole transitions between the 5d and 4f states.⁶

The relation between emission intensity vs. irradiation time for an equimolar methanol solution of EuCl₂ and **2** is shown in Figure 1. Curve *a* in the figure is for a sample whose emission intensity was measured immediately after the sample preparation and curve *b* for a sample whose emission intensity was taken after keeping the sample in a dark place for 120 min.⁷

As has been reported in previous papers,^{1,3} an increase in emission intensity is due to the complex formation of Eu(II)

- (5) The irradiation was done with use of wavelengths of 370 nm for Eu-1 and 376 nm for Eu-2 initially, and then these wavelengths were changed according to changes in the excitation maxima for these complexes. The number of photons at the excitation was measured with a Photodyne 66XLA power meter equipped with a No. 350 sensor head and was 4×10^{15} photons/s at 370 nm after calibration.
- (6) Blasse, G. *Phys. Status Solidi B* **1973**, *55*, K131.
- (7) A concentration of 4×10^{-3} mol dm⁻³ for Eu(II) was employed in most cases.

with crown ethers. For most Eu(II)-crown complexes (such as with 15-crown-5), the intensity is great from the beginning and maintains a constant value during the irradiation.

Emission profiles taken during the irradiation periods indicate that uncomplexed, methanol-solvated Eu(II) gives a 487-nm emission peak, which undergoes blue shifting as the complex formation proceeds.

Excitation spectra in Figure 2 for the complex with **1** also show variations before and after irradiation, suggesting that the inner coordination sphere of Eu(II) is subjected to changes with exposure to UV. Another interesting feature in the excitation spectra is that peak intensities around 240 nm increase with irradiation time. The peak is not observed for other crown ethers that do not have any brominated groups in their side chains. This peak probably is a charge-transfer transition, involving the Eu(II) ion and the brominated side chain.

Figure 3 illustrates the variation in absorption spectra of the complex of **1**. The peak around 200 nm increases with the passage of irradiation time, while other peaks⁸ due to the 4f/5d configuration of Eu(II) become smaller. This phenomenon is not observed for other crown complexes lacking a bromoalkyl group, which maintain the same absorption intensity during the irradiation.

A discrepancy between the absorption and excitation spectra is due to the fact that the concentration of the complex for excitation spectra measurement was too high. Use of a diluted solution (8×10^{-4} mol dm⁻³) narrowed the gap, and every peak shifted to lower wavelength. A tail of an excitation peak that should have been seen at 200 nm was observed at around 220 nm, because the effective wavelength range of our spectro-

fluorometer is from 220 up to 590 nm.

Photochemical decomposition of the bromoalkyl group is not likely, because no free radical was detected in the ESR spectrum taken for the complex irradiated with UV radiation. In addition, there was no change in IR spectra (C-Br stretching 670 cm⁻¹) for the complexes isolated before and after the irradiation.

There is steric hindrance in ligands **1** and **2** exerted by a bromoalkyl side chain, which impedes the ground-state complex formation. The excited Eu(II) ion becomes a strong electron acceptor and is taken into the cavity of the crown ether in spite of the hindrance. Once the complex is formed, it is quite stable and does not dissociate.

Crown ethers having no side chain or having a side chain without a bromoalkyl substituent (such as 2-ethyl-2-methyl or 2-propyl-2-methyl) do not exhibit such changes in emission intensities. The Eu-Br CT must play an important role in the intensity increase.

A mixture of Eu(II) with 2-BrMe-2-Me(12-crown-4) (**3**) in methanol solution showed almost the same emission intensity as that of the EuCl₂-methanol solution and gave no increase in emission intensity even after 2-h irradiation. This is because the cavity of **3** is too small to accommodate an Eu(II) ion, and there can be no complex formation for this case.

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Articles

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Lanthanide Complexes of Ionophores. 2. Spectroscopic Characterization of Lanthanide(III) Ion Binding to Lasalocid A and A23187 in Methanol¹

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Laser luminescence excitation and UV absorption spectroscopy were used to monitor the coordination of the carboxylic ionophores lasalocid A and A23187 to lanthanide(III) ions in methanol. The formation of mono- and bis(ionophore) chelates was demonstrated by monitoring changes in the ⁷F₀ → ⁵D₀ excitation spectrum of Eu(III) in the presence of the ligands. Changes in ligand UV absorption spectra in the presence of Tb(III) indicate that coordination occurs at the salicylate group of lasalocid A and at the α-ketopyrrole and benzoxazole moieties of A23187. The high binding constants imply that both ligands coordinate in a multidentate fashion. A 1:1 complex forms between Ca(II) ions and lasalocid A with a dissociation constant at 1.24×10^{-5} M and ΔH° and ΔS° values of -4.8 ± 0.8 kcal mol⁻¹ and -39 ± 3 cal deg⁻¹ mol⁻¹, respectively, for the dissociation reaction.

Introduction

The characterization of metal ion binding sites in biological molecules is relevant to the understanding of their activity, in terms of structural features and the role of the metal ions. Substitution of trivalent lanthanide ions (Ln(III)) for biologically significant, yet spectroscopically "silent", metal ions

is a well-documented procedure for probing these sites.² The ability of europium(III) to luminesce in solution at room temperature,^{3,4} along with its similarity to calcium(II) in ionic radius and coordination number, has made it one of the more popular Ln(III) probe species.

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(4) Horrocks, W. DeW., Jr.; Albin, M. *Prog. Inorg. Chem.* 1984, 31, 1-104.