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Dichlorobis(1,10-phenanthroline)europium(II) and Dichloro(2,2′6′,2″-tripyridyl)europium(II): Syntheses and Properties

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Although binary europium(II) compounds are quite stable in the absence of air ($Eu^{3+} + e \rightarrow Eu^{2+}$; E = –0.43 v), europium(II) complexes have been rarely investigated. Reported work includes the investigation of Eu(II)–edta complexation in solution [1] and the isolation of $Eu(C_5H_5)_2$ [2]. Eu(II) is of course a large (1.10 Å) Class A ion, which would be expected to form complexes with only halide, oxygen or nitrogen ligand atoms, and such complexes would be expected to be of a rather labile nature.

We now report an investigation of complexes of europium dichloride with 1,10-phenanthroline, 2,2′-bipyridyl and 2,2′6′,2″-tripyridyl. Solid complexes $EuCl_2(phen)_2$ and $EuCl_2(tripy)$ were obtained, but no well-defined product could be isolated from reactions involving 2,2′-bipyridyl.

Experimental

Solvents were dried by distillation from calcium hydride (dimethylsulphoxide and acetonitrile) or magnesium (ethanol) and stored over 4A molecular sieve. 1,10-phenanthroline hydrate was dehydrated at 35 °C *in vacuo*; 2,2′-bipyridyl was purified by sublimation, and A.R. grade 2,2′6′,2″-tripyridyl was used as such. Europium dichloride was obtained by reduction of the anhydrous trichloride (itself obtained by dehydration of $EuCl_3 \cdot 6H_2O$ by $SOCl_2$) using an HCl/H_2 mixture at 150–700 °C. All operations involving europium(II) were carried out under a nitrogen atmosphere.

Dichlorobis(1,10-phenanthroline)europium(II)

To $EuCl_2$ (0.224 g, 1 mmol) was added a solution of 1,10-phenanthroline (0.870 g, 4.8 mmol) in acetonitrile (15 ml). The suspension was stirred for 48 hours, after which time all the $EuCl_2$ appeared to have dissolved, and a purple precipitate had formed. The product was collected by filtration, washed twice with acetonitrile and dried *in vacuo* at room temperature (Found: C, 49.5; H, 3.0; N, 9.7; Cl, 12.1%. $C_{24}H_{16}N_4Cl_2Eu$ requires: C, 49.4; H, 2.8; N, 9.6; Cl, 12.15%). The yield was essentially quantitative. The complex decomposes on heating in nitrogen over a temperature range 150–250 °C giving a yellow-brown residue. The compound is air-sensitive, starting to lose its purple colour on exposure to air for about 30 minutes. It is instantly decolourised by air in the presence of solvent. The complex is sparingly soluble in methanol and ethanol, but dissolves in dimethylsulphoxide to give a purple solution whose electronic spectrum shows a peak at 498 nm, with a second, much more intense, absorption peak beginning at about 435 nm and extending to shorter wavelength. Measurements in the same solvent of the absorbance of the 498 nm peak of a total concentration of 0.059 *M* gave a Job's plot which showed a sharp maximum at a 1:1 phenanthroline: $EuCl_2$ ratio. The stability constant

$$K = \frac{[Eu^{2+}phen]}{[Eu^{2+}]\,[phen]}$$

was evaluated from the plot by matching with theoretical curves, giving log K = 3.9 ± 0.3 l mol^{-1} and $\epsilon_{498} = 85$ l mol^{-1} cm^{-1}.

The infrared spectrum (Nujol mull) of this complex is a follows (cm^{-1}): 1621 w, 1590 m, 1570 w, 1513 m, 1496 w, 1425 m, 1348 w, 1224 w, 1141 m, 1095 w, 864 m, 850 s, 775 w, 735 s, 719 m, 634 w, 416 w. Relative to the free ligand there are comparatively small changes in intensity and wavelength, *e.g.* the ligand ring stretching modes at 1611, 1585 and 1554 cm^{-1} are shifted to higher wavenumber by 5–16 cm^{-1} in the complex.

Dichloro(2,2′6′,2″-tripyridyl)europium(II)

A preparative procedure analogous to that described for the phenanthroline complex gave the mono(tripyridyl) complex as a dark blue solid. Changes in the ratio of ligand to metal used in the preparation gave no different products. Yield, 75–80% (Found: C, 39.3; H, 2.7; N, 9.4; Cl, 15.4%. $C_{15}H_{11}N_3Cl_2Eu$ requires C, 39.5; H, 2.4; N, 9.2; Cl, 15.5%). The thermal stability of this compound and its stability on exposure to air resemble the corresponding properties of the phenanthroline complex. $EuCl_2(tripy)$ is sparingly soluble in ethanol but dissolves in Me_2SO to give a deep green solution. The proton n.m.r. spectrum in this solvent showed a single very broad (~100 Hz at half peak height) band at 2.9 τ; that is, the resonance is unshifted but greatly broadened, as expected for an f^7 configuration. The U.V.–visible spectrum in Me_2SO shows an intense broad absorption in the region 260–440 nm,

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together with a weaker absorption at 620 nm. The intense absorption is presumably a combination of ligand bands (260–360 nm for the free ligand in Me_2SO) and the Eu^{2+} $f^7 \rightarrow d^1f^6$ band (290–410 nm, max. at 332 nm, $\epsilon = 1090$ l mol^{-1} cm^{-1} for $EuCl_2$ in Me_2SO). The 620 nm absorption may be an $f^7 \rightarrow {}^*\pi^1f^6$ transition but seems much too weak ($\epsilon = 57$ l mol^{-1} cm^{-1}) for that origin. It is possible it is, a crystal field split $f^7 \rightarrow f^7$ band, in which case the crystal field splitting parameter for the f levels in divalent lanthanide complexes is surprisingly large. The explanation of this band, whatever it may be, presumably applies also to the 498 nm peak of the phenanthroline complex.

The infrared spectrum (Nujol mull) of this complex is as follows (cm^{-1}): 1592 s, 1576 m, 1570 m, 1449 m, 1430 m, 1396 w, 1310 m, 1240 m, 1193 w, 1158 w, 1168 w, 1076 w, 1000 m, 834 w, 800 w, 775 s, 741 w, 652 m, 629 w.

Reaction of Europium Dichloride with 2,2′-Dipyridyl

No reaction took place in acetonitrile, so $EuCl_2$ (100 mg) was stirred with 5 molar proportions of dipyridyl in ethanol (20 ml) yielding a brown solid which was collected, washed and dried at 80 °C under vacuum. Analysis appeared to show however that a considerable replacement of chloride by ethoxide had occurred. Stability towards air and thermal stability were similar to the phenanthroline complex.

Discussion

The structure of $EuCl_2(phen)_2$ is rather unlikely to be monomeric and octahedral as six-coordination would be insufficient for Eu^{2+}. More likely it is a polymeric chain with bridging chloride giving eight-coordination, but any suggestions are of course speculative in the absence of X-ray data, and single crystals could not be obtained. The argument for a polymeric structure applies with even more force to $EuCl_2$(tripy).

The Job's plot shows that the bis(phenanthroline) complex dissociates in dimethylsulphoxide to give a stable mono(phenanthroline) complex in which dimethylsulphoxide doubtless completes the coordination sphere. The association constant value log K = 3.9 represents considerable stability and gives $\Delta G = 21.9 \pm 2$ kJ mol^{-1}. The question arises whether an equilibrium (1) based on reduction rather than on complexation could not equally explain the absorption band at 498 nm or indeed the 620 nm band of the tripyridyl complex (phenanthroline can be reduced by lithium metal in dmso to give a coloured solution).

$$\mathrm{Eu^{2+} + phen \rightleftharpoons Eu^{3+} + phen^-} \tag{1}$$

However, the reduction potential of 1,10-phenanthroline is −2.12 v [3] making it non-reducible by Eu^{2+}; furthermore, the molar conductance of $EuCl_2$ ($\Lambda_m = 33.9$ mol^{-1} cm^2 ohm^{-1} at 0.031 *M*) is almost unaltered by addition of an equimolar quantity of phenanthroline ($\Lambda_m = 32.1$ mol^{-1} cm^2 ohm^{-1}), whereas an increase in Λ_m should result from equation (1). Comparison with other Λ_m values (Table I) suggests that the complex exists in solution mainly as $[EuCl(phen)(dmso)_x]^+$.

TABLE I. Molar Conductances (mol^{-1} cm^2 ohm^{-1}) of Anhydrous Halides and Complexes in Me_2SO at 21 °C.

Compound	Molarity	Λ_m
$EuCl_2$	0.022	33.9
$EuCl_2$	0.031	33.9
$EuCl_2(phen)_2$	0.022	32.2
$EuCl_2(phen)_2$	0.031	32.1
KCl	0.020	29.5
KI	0.020	29.3
$SrCl_2$	0.020	39.9
$EuCl_3$	0.018	57.5
$EuCl_3$	0.0018	88.5

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