

Table 2. Bond lengths (Å) and bond angles (°)

Standard deviations are given in parentheses.

Cu—Cl(1)	2.25 (1)	N(1)—C(1)	1.54 (3)	N(2)—C(4)	1.55 (2)
Cu—Cl(2)	2.21 (1)	N(1)—C(2)	1.50 (1)	N(2)—C(5)	1.43 (2)
Cu—Cl(3)	2.23 (1)	N(1)—C(3)	1.49 (4)	N(2)—C(6)	1.46 (2)
Cl(1)—Cu—Cl(2)	101.1 (0.3)	C(1)—N(1)—C(2)	108.8 (1.4)	C(4)—N(2)—C(5)	107.9 (1.8)
Cl(1)—Cu—Cl(3)	132.1 (0.2)	C(1)—N(1)—C(3)	108.8 (1.4)	C(4)—N(2)—C(6)	113.1 (0.9)
Cl(2)—Cu—Cl(2')	126.4 (0.3)	C(2)—N(1)—C(3)	110.3 (1.7)	C(5)—N(2)—C(6)	103.4 (1.1)
Cl(2)—Cu—Cl(3)	100.8 (0.2)	C(3)—N(1)—C(3')	109.7 (1.5)	C(6)—N(2)—C(6')	114.7 (1.3)

differed mainly in the y coordinates of the nitrogen and carbon atoms, and the large thermal parameters of these atoms could certainly be a result of a disordered structure. This tripling is clearly of some importance in the interpretation of spectral and magnetic properties of the solid, but as the superlattice reflexions were very few and weak our average parameters were felt to be a satisfactory approximation to the true structure, at least for the CuCl_4^{2-} tetrahedron.

Bond distances and angles are given in Table 2. The CuCl_4^{2-} tetrahedron is strongly distorted towards D_{2d} symmetry, as in Cs_2CuCl_4 , $(\text{Et}_3\text{NH})_2\text{CuCl}_4$ and other 'tetrahedral' CuCl_4^{2-} ions (see references in Lamotte-Brasseur, Dupont & Dideberg, 1973).

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Europium Dichloride Dihydrate

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Abstract. $\text{EuCl}_2 \cdot 2\text{H}_2\text{O}$, monoclinic, $C2/c$, $a=11.661$ (5), $b=6.404$ (3), $c=6.694$ (3) Å, $\beta=105.37$ (5)°, $V=482.2$ Å³, $Z=4$, $D_c=3.56$, $D_m=3.58$ g cm⁻³. Final R 0.038 for 504 reflexions. $\text{EuCl}_2 \cdot 2\text{H}_2\text{O}$ is isomorphous with $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$.

Introduction. Analogous salts of Eu^{2+} on the one hand and Ba^{2+} or Sr^{2+} on the other are generally supposed to be isomorphous. This has been shown in several cases (*e.g.* McCoy & Pauling, 1937). In this respect we have investigated the dichloride dihydrates of the two elements europium and barium. We report here a structure determination of $\text{EuCl}_2 \cdot 2\text{H}_2\text{O}$. This compound was prepared as indicated in Brauer (1962): a solution of Eu_2O_3 (99.97%, supplied by Th. Goldschmidt, Essen) in 6*N* hydrochloric acid was reduced by amalgamated zinc in an atmosphere of pure nitrogen; $\text{EuCl}_2 \cdot 2\text{H}_2\text{O}$ was precipitated by concentrated hydrochloric acid.

Chemical analysis gave: Cl, 27.41 (27.39); Eu, 58.34 (58.68)%, where figures in parentheses are calculated

values. The density was determined pycnometrically as 3.58 g cm⁻³ with tetraline under N_2 .

A plate-like single crystal of $\text{EuCl}_2 \cdot 2\text{H}_2\text{O}$ with dimensions 0.14 × 0.05 × 0.10 mm was mounted in a thin-walled capillary filled with N_2 . An X-ray investigation by photographic methods showed it could belong to either the triclinic or the monoclinic crystal system. A decision between these could not be made because of strong absorption effects. A Nonius CAD-4 four-circle automatic diffractometer and graphite-monochromated $\text{Mo } K\alpha$ radiation were then used in conjunction with a scintillation detector and pulse-height discrimination. The crystal setting and the triclinic unit cell ($P\bar{1}$, $a=6.410$, $b=6.650$, $c=6.699$ Å, $\alpha=103.46^\circ$, $\beta=90.09^\circ$, $\gamma=118.72^\circ$, $Z=2$) were found by using the program *SEARCH*. 1752 reflexions were collected in the range $2^\circ \leq \theta \leq 35^\circ$. Three reflexions were monitored periodically during the data-collection process. Subsequent analysis of these reflexions indicated no crystal decomposition.

Only the 908 reflexions with $I > 2\sigma(I)$ were used in

the calculations. The atomic coordinates were determined by three-dimensional Patterson and Fourier methods. Anisotropic least-squares refinement of all parameters led to a conventional R of 0.034 in this triclinic setting.

The atomic arrangement in $\text{EuCl}_2 \cdot 2\text{H}_2\text{O}$ is nearly the same as in the structure of $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$ (Jensen, 1942). It is possible to transform [matrix(120/100/001)] the triclinic unit cell of $\text{EuCl}_2 \cdot 2\text{H}_2\text{O}$ to a monoclinic cell described by the space group $C2/c$ (Bärnighausen, 1974)*. The resulting cell parameters are $a=11.661$, $b=6.404$, $c=6.694$ Å, $\beta=105.37^\circ$, $Z=4$, $D_c=3.56$ g cm $^{-3}$. Of the 1752 reflexions measured 962 unique reflexions were used with the program *ORABS-2* (Schwarzenbach, Busing & Levy, 1972) to make absorption corrections ($\mu=138.35$). Only the 504 reflexions with $I>2\sigma(I)$ were used for the structure analysis and Lorentz and polarization corrections were made. Refinement of the positional parameters, isotropic temperature factors and an overall scale factor, with the full-matrix least-squares program *CRYLSQ* and unit weights, reduced R to 0.117 [$R=(\sum|F_o|-|F_c|)/\sum|F_o|$]. Further refinement, varying the temperature factors of the atoms anisotropically and making extinction corrections, resulted in $R=0.038$. The scattering factors used were those for neutral atoms (Hanson, Herman, Lea & Skillman, 1964). The anomalous dispersion corrections, $\Delta f' = -0.4$ and $\Delta f'' = 4.3$ for Eu and $\Delta f' = 0.1$ and $\Delta f'' = 0.2$ for Cl, are given in *International Tables for X-ray Crystallography* (1962).† The programs used in this structure determination were those of the X-RAY 70 system (Stewart, Kundell & Baldwin, 1970) on the 1106-2 UNIVAC computer of the University of Freiburg, Germany. The final positional and thermal parameters are listed in Table 1. Interatomic distances, calculated by the program *BONDLA*, are compared with those of $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ in Table 2. Table 3 shows the valence angles around the Eu atom. From the data it is obvious that $\text{EuCl}_2 \cdot 2\text{H}_2\text{O}$ is isomorphous with $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$ (Jensen, 1942; *Structure Reports*, 1942-44, Vol. 9, p. 161).

* We thank Professor Bärnighausen for suggesting that this transformation be made.

† A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30650 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Interatomic distances of $\text{EuCl}_2 \cdot 2\text{H}_2\text{O}$ compared with $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$*

The e.s.d.'s are in parentheses.

	$\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$ (Jensen, 1942)	$\text{EuCl}_2 \cdot 2\text{H}_2\text{O}$	$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ (Jensen, 1945)
Me-Cl	2.84	2.96 (3)	3.11
	2.84	2.96 (3)	3.16
	2.98	3.00 (1)	3.24
	2.98	3.00 (1)	3.27
	Average	2.91	2.98
Me-O	2.66	2.69 (2)	2.78
	2.66	2.69 (2)	2.80
	2.82	2.74 (2)	2.81
	2.82	2.74 (2)	2.82
	Average	2.74	2.72

Table 3. *Valence angles ($^\circ$) of Eu in $\text{EuCl}_2 \cdot 2\text{H}_2\text{O}$*

E.s.d.'s are in parentheses.

Cl(1)-Eu-Cl(1)	138.8 (1)	O(1)-Eu-O(1)	77.5 (3)
Cl(1)-Eu-Cl(2)	73.4 (1)	O(1)-Eu-O(2)	64.7 (3)
Cl(1)-Eu-Cl(2)	76.1 (1)	O(1)-Eu-O(2)	80.7 (3)
Cl(1)-Eu-O(1)	148.2 (2)	O(1)-Eu-Cl(2)	132.6 (2)
Cl(1)-Eu-O(1)	72.5 (2)	O(1)-Eu-Cl(2)	119.2 (2)
Cl(1)-Eu-O(2)	77.1 (2)	O(2)-Eu-O(2)	135.6 (3)
Cl(1)-Eu-O(2)	119.4 (2)	O(2)-Eu-Cl(2)	74.4 (2)
Cl(2)-Eu-Cl(2)	83.2 (1)	O(2)-Eu-Cl(2)	146.4 (2)

Discussion. The arrangement of atoms around Eu^{2+} is shown in Fig. 1. The nearest neighbours are four chlorine atoms and four oxygen atoms (water molecules) forming the coordination number 8. In this environment there are two pseudo-square planes on opposite sides of the central Eu atom, the corners of each square being occupied by two chlorine atoms in *cis* positions and by two oxygen atoms. However, the two squares are not parallel and they are rotated against each other by a small amount from corner-to-corner correspondence. This coordination shell of Eu^{2+} may be described as consisting of a hemisphere of four chlorine atoms and a hemisphere of four water molecules. The structures of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{EuCl}_2 \cdot 2\text{H}_2\text{O}$ ($\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$) have CN 8 for the metal atoms, as shown in Fig. 2. Each of these two coordination arrangements is characterized by two pseudo-squares on opposite sides of the central metal atom almost forming an antiprism. In contrast to the distribution of Cl and O atoms around Eu^{2+} (Sr^{2+}), the arrangement around Ba^{2+} does not show atoms of one type in a group on one side of the metal atom.

Table 1. *Final fractional coordinates and thermal parameters with estimated standard deviations in parentheses*

Thermal parameters in the form $\exp[-2\pi^2(U_{11}h^2a^* + \dots + 2U_{12}hka^*b^* + \dots)] \times 10^{-4}$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Eu in 4(e)	0	0.2560 (2)	$\frac{1}{2}$	346 (5)	112 (5)	149 (3)	0	56 (2)	0
Cl in 8(f)	0.1461 (3)	0.0936 (5)	0.6503 (4)	271 (13)	175 (17)	180 (11)	15 (12)	46 (10)	8 (10)
O in 8(f)	0.1101 (8)	0.5826 (16)	0.4708 (14)	244 (40)	202 (49)	285 (40)	0 (40)	62 (33)	-8 (40)

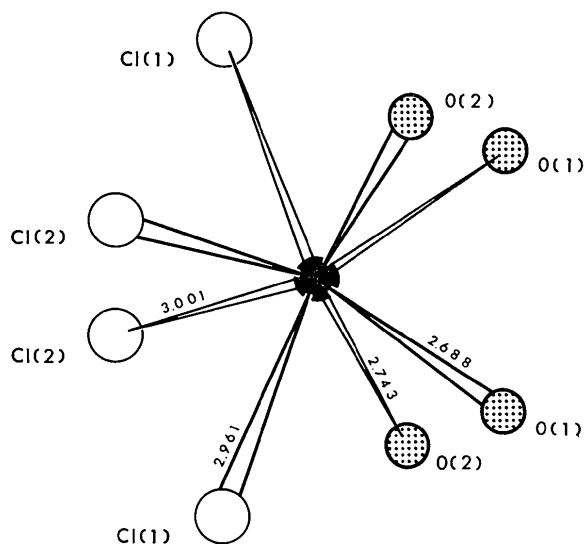


Fig. 1. Arrangement of chlorine and oxygen atoms around Eu. The bond lengths are given in Å.

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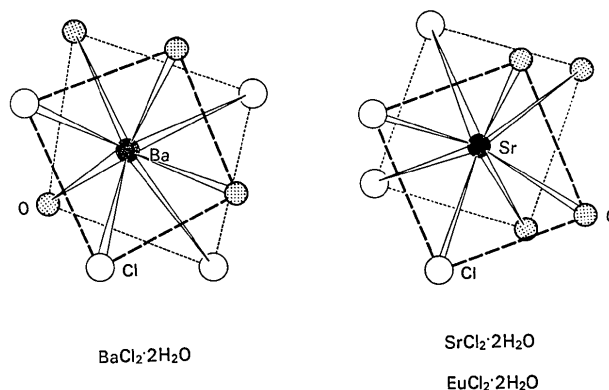


Fig. 2. Comparison of the metal coordination arrangements of $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$ or $\text{EuCl}_2 \cdot 2\text{H}_2\text{O}$ with $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$.

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2,4-Dioxa-5 α -androstan-17 β -ol Acetate

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Abstract. $\text{C}_{19}\text{H}_{30}\text{O}_4$, m.p. 120°C , orthorhombic, space group $P2_12_12_1$, $a = 12.603$ (2), $b = 23.44$ (3), $c = 6.137$ (1) Å, $Z = 4$, $M = 322.45$, $D_x = 1.31$, $D_m = 1.30$ g cm $^{-3}$. The A ring has a symmetrical chair conformation with a mean ring torsional angle of 58.7° . The more perfect chair conformation is associated with the 2,4-dioxa

substitution which relieves the β -face diaxial interactions.

Introduction. Structural features of steroid A rings that are specifically related to activity are being explored through physical and pharmacological studies of a series of synthetic steroids having A rings of varying size and composition (Zanati & Wolff, 1971). The title

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