N1	−0.1494 (4)	0.5766 (3)	0.8466 (4)	0.0284 (6)
N2	−0.3474 (5)	0.8220 (4)	0.7930 (4)	0.0341 (7)
N3	0.0163 (4)	0.8071 (4)	0.7810 (4)	0.0298 (6)
C1	−0.3290 (5)	0.5602 (5)	0.7987 (5)	0.0400 (10)
C2	−0.4042 (5)	0.6807 (5)	0.7122 (5)	0.0362 (8)
C3	−0.2576 (5)	0.9261 (4)	0.7246 (5)	0.0343 (8)
C4	−0.1168 (5)	0.8662 (4)	0.6695 (4)	0.0315 (7)
C5	0.0717 (5)	0.6647 (4)	0.7359 (5)	0.0335 (8)
C6	−0.0647 (5)	0.5523 (4)	0.7288 (4)	0.0322 (7)
C7	−0.0908 (5)	0.4888 (4)	0.9671 (5)	0.0324 (8)

Table 2. *Selected geometric parameters (Å, °)*

Cd—Cl3	2.4293 (13)	N2—C2	1.510 (6)
Cd—Cl4	2.4430 (15)	N3—C5	1.501 (5)
Cd—Cl1	2.4700 (13)	N3—C4	1.503 (5)
Cd—Cl2	2.5044 (13)	C1—C2	1.515 (6)
N1—C7	1.468 (5)	C3—C4	1.505 (6)
N1—C1	1.469 (5)	C5—C6	1.527 (6)
N1—C6	1.480 (5)	C7—C7^{i}	1.511 (8)
N2—C3	1.497 (6)		
Cl3—Cd—Cl4	114.77 (5)	C3—N2—C2	118.1 (3)
Cl3—Cd—Cl1	112.36 (4)	C5—N3—C4	113.7 (3)
Cl4—Cd—Cl1	112.37 (5)	N1—C1—C2	112.8 (3)
Cl3—Cd—Cl2	108.37 (5)	N2—C2—C1	110.2 (4)
Cl4—Cd—Cl2	108.22 (5)	N2—C3—C4	114.8 (3)
Cl1—Cd—Cl2	99.48 (5)	N3—C4—C3	114.8 (3)
C7—N1—C1	109.9 (3)	N3—C5—C6	109.4 (3)
C7—N1—C6	113.6 (3)	N1—C6—C5	111.8 (3)
C1—N1—C6	112.8 (3)	N1—C7—C7^{i}	113.3 (4)

Symmetry code: (i) $-x, 1-y, 2-z$.

The H atoms on all C atoms were located on Fourier difference maps, but were fixed at ideal positions (0.96 Å) with common isotropic displacement parameters (U_{iso} = 0.08 Å) and refined using a riding model. The four amino H atoms were found in difference maps and refined with fixed isotropic displacement parameters (U_{iso} = 0.08 Å); N—H distances varied from 0.79–0.99 Å with an average e.s.d. of 0.08 Å. The largest peaks and holes in these maps were located near Cd.

Data collection: *P3/PC* (Siemens, 1989*a*). Cell refinement: *P3/PC*. Data reduction: *XDISK* (Siemens, 1989*b*). Program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1991). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXL*93.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1194). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The β Form of the Macrocyclic Complex $[Eu(NCS)_3(C_{22}H_{26}N_6)]$

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Abstract

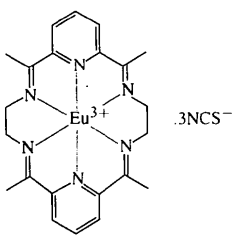
In the β form of tris(thiocyanato-*N*)[2,7,13,18-tetramethyl-3,6,14,17,23,24-hexaazatricyclo[17.3.1.1^{8,12}]tetracosa-1(23),2,6,8(24),9,11,13,17,19,21-decaene-N^3,N^6,N^{14},N^{17},N^{23},N^{24}]europium, the nine-coordinate Eu^{III} ion is bound to the N atoms of three monodentate isothiocyanate ligands and to the six N atoms of the macrocyclic ligand *L* ($C_{22}H_{26}N_6$), which has an 18-membered six-N-atom donor cavity, with a coordination geometry analogous to that of the α form.

Comment

Lanthanide(III) complexes of the 18-membered six-N-atom donor macrocyclic ligand *L* ($C_{22}H_{26}N_6$) have been synthesized by the metal-templated cyclic Schiff base condensation of 2,6-diacetylpyridine and 1,2-diaminoethane (De Cola, Smailes & Vallarino, 1986). A representative selection of these complexes has been characterized by single-crystal X-ray diffraction analysis, as well as by infrared (IR) and nuclear magnetic resonance (NMR) spectra (Fonda, Smailes, Vallarino, Bombieri, Benetollo, Polo & De Cola, 1993). All these complexes have, as a common feature, the presence of a highly inert metal–macrocycle entity accompanied by two or three labile exocyclic ligands, linked to the central metal ion on opposite sides of the macrocycle. Most of these complexes were initially isolated as acetates or nitrates, as these coordinating oxygen-donor anions greatly facilitated the metal-template synthesis of the macrocycle. Once the cationic metal macrocycle was formed, salts of other non-coordinating or coordinating counterions were obtained simply by anion metathesis (Bombieri, Benetollo, Polo, De Cola, Smailes & Vallarino, 1986; Bombieri, Benetollo, Polo, Fonda & Vallarino, 1991).

We have previously reported the crystal structures of the tris(isothiocyanato) complexes of the $\{Eu^{III}L\}$ and $\{Y^{III}L\}$ macrocycles, obtained from the corre-

sponding diacetate chlorides by metathesis with sodium thiocyanate in methanol solution at room temperature (Bombieri, Benetollo, Polo, De Cola, Hawkins & Vallarino, 1989). In that work, the Eu^{III} species was selected for its potential as a monochromatic luminescent material; the yttrium(III) analog was studied because it offered the opportunity to correlate the crystal structure with the NMR spectrum in solution. We have now obtained a different crystal form of the $\{Eu^{III}L\}$ tris(isothiocyanato) complex, prepared again by anion metathesis from the diacetate chloride and sodium thiocyanate in methanol, but at a lower temperature (275–277 K). We report here the crystallographic study of this new form, referred to as the β form, (I). For comparison, the previously reported form (α form) is monoclinic and crystallizes in the space group *Cc*, with cell parameters a = 33.244 (3), b = 11.976 (2), c = 14.164 (2) Å, β = 92.72 (5)°, V = 5632.8 (9) Å^3, Z = 8 (two independent molecules as asymmetric units) (Bombieri *et al.*, 1989). The α and β crystal forms of the $[Eu(NCS)_3L]$ complex present many similarities as well as many differences. In the β form, as in the α form, the crystal lattice does not include solvent molecules and the coordination entity is non-ionic. In both forms, the central Eu^{III} atom is linked to the six N atoms of the macrocyclic ligand, which is folded in the 'butterfly' pattern typical of this system. In addition, the Eu^{III} atom is linked to the N atoms of the three exocyclic isothiocyanate counterion ligands, two on the convex side of the folded macrocycle and one on the concave side.



(I)

An *ORTEP*II (Johnson, (1976) view of the complex molecule present in the β form is shown in Fig. 1. The average Eu—N_{py} [2.62 (2) Å] bond length in the β form is comparable to the values [2.60 (2) and 2.64 (2) Å] found in the two slightly different molecules present in the α form. For the Eu—N_{imine} bonds, the values are 2.608 (4) Å in the β form and 2.57 (2)–2.60 (2) Å (average values) in the two molecules of the α form. The Eu—NCS bonds are also quite similar in the α and β forms, with average values of 2.457 (4) Å (β form), and 2.50 (1) and 2.43 (1) Å (α form). A significant difference between the two forms concerns the torsions of the ethylenic side chains. The N8—C22—C23—N9 chain in the molecule of the β form has a torsion angle [55.7 (6)°] similar to that found in one of the two molecules of the α form [55 (1)°]; in the other molecule of the α form, the corresponding angle [50 (1)°] is only slightly smaller. The N5—C11—C12—N6 chain of the β form, in contrast, has a torsion angle [58.6 (5)°] which is significantly larger than the corresponding angles [48 (1) and 43 (1)°] found in the two molecules of the α form. The volume [1423.6 (9) Å^3] of the unit cell of the β form is also slightly larger than the average volume [1408.2 Å^3] of the α form (calculated for two molecules). This difference results from the more efficient crystal packing of the α form, in which the unit cell contains four pairs of somewhat different $[Eu(NCS)_3L]$ molecules, compared to the β form with two equivalent $[Eu(NCS)_3L]$ molecules per unit cell.

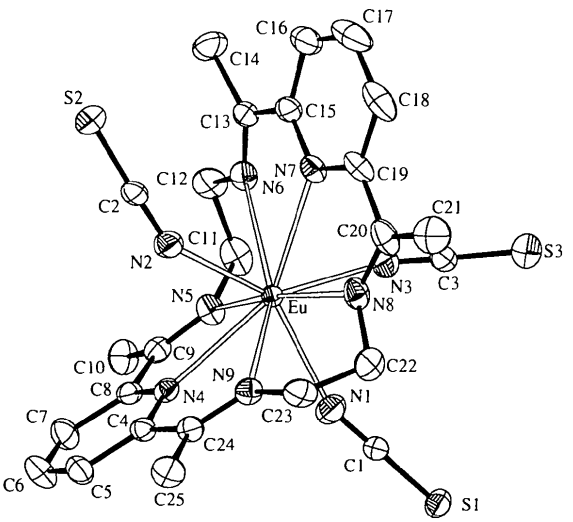


Fig. 1. The molecular structure and atomic labeling scheme for $[Eu(NCS)_3(C_{22}H_{26}N_6)]$. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity.

Different metal–macrocycle conformations have been reported previously for the formally identical coordination entities present in the $[EuL(CH_3COO)_2]Cl.4H_2O$ (Bombieri *et al.*, 1991) and $[EuL(CH_3COO)_2]$-$CH_3COO.9H_2O$ complexes (Fonda *et al.*, 1993), and were attributed to the influence of the different non-coordinated counterions and different numbers of lattice water molecules. In contrast, the α and β forms of $[Eu(NCS)_3L]$ have identical chemical composition and the synthetic procedures by which the two forms were obtained differ only in the temperature of the solutions from which the crystals separated. This pair of crystal structures represents a striking example of the flexibility of the *ML* moiety, which responds not only to variations in chemical environment but also to minor differences in conditions of synthesis.

Experimental

Crystals of the title complex were grown from a water–methanol solution.

Crystal data

[Eu(NCS)$_3$(C$_{22}$H$_{26}$N$_6$)]
M_r = 700.68
Triclinic
$P\bar{1}$
a = 8.131 (3) Å
b = 10.052 (4) Å
c = 18.473 (4) Å
α = 100.75 (4)°
β = 101.52 (4)°
γ = 99.03 (4)°
V = 1423.6 (9) Å^3
Z = 2
D_x = 1.635 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 30 reflections
θ = 9–12.2°
μ = 2.455 mm^{-1}
T = 297 (2) K
Prismatic
0.32 × 0.24 × 0.20 mm
Colorless, transparent

Data collection

Philips PW1100 four-circle diffractometer
Profile-fitted $\theta/2\theta$ scans (Lehmann & Larsen, 1974)
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
T_{min} = 0.766, T_{max} = 0.998
4656 measured reflections

4506 independent reflections
4423 observed reflections [$I > 3\sigma(I)$]
R_{int} = 0.0113
θ_{max} = 25°
h = −9 → 9
k = −11 → 11
l = 0 → 21
3 standard reflections
frequency: 180 min
intensity decay: none

Refinement

Refinement on F^2
$R(F)$ = 0.0276
$wR(F^2)$ = 0.0731
S = 1.103
4423 reflections
348 parameters
$w = 1/[\sigma^2(F_o^2) + 3.1817P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = −1.701
$\Delta\rho_{max}$ = 1.244 e Å^{-3}
$\Delta\rho_{min}$ = −0.775 e Å^{-3}

Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0013 (3)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
Eu	0.51036 (3)	0.25399 (2)	0.245810 (12)	0.03867 (9)
S1	0.1796 (2)	0.41857 (13)	0.02167 (8)	0.0630 (3)
S2	0.8567 (2)	0.05872 (15)	0.43589 (8)	0.0637 (3)
S3	0.3776 (4)	0.7060 (2)	0.29471 (13)	0.1366 (10)
C1	0.2828 (6)	0.3454 (5)	0.0824 (2)	0.0477 (10)
C2	0.7785 (5)	0.1019 (5)	0.3579 (3)	0.0478 (10)
C3	0.3382 (8)	0.5372 (7)	0.2829 (3)	0.071 (2)
N1	0.3557 (6)	0.2924 (5)	0.1255 (2)	0.0641 (11)
N2	0.7236 (6)	0.1353 (5)	0.3029 (2)	0.0629 (11)
N3	0.3270 (6)	0.4220 (5)	0.2760 (3)	0.0716 (12)
N4	0.4904 (4)	0.0270 (3)	0.1438 (2)	0.0402 (7)
N5	0.2493 (4)	0.0561 (4)	0.2187 (2)	0.0521 (9)
N6	0.4009 (5)	0.1952 (4)	0.3641 (2)	0.0543 (10)
N7	0.6544 (5)	0.4073 (4)	0.3836 (2)	0.0521 (9)
N8	0.7233 (6)	0.4804 (4)	0.2607 (3)	0.0619 (11)
N9	0.7241 (5)	0.2510 (4)	0.1548 (2)	0.0492 (9)
C4	0.6175 (5)	0.0114 (5)	0.1080 (2)	0.0441 (9)
C5	0.6232 (7)	−0.1154 (5)	0.0640 (3)	0.0634 (13)
C6	0.4964 (8)	−0.2277 (6)	0.0566 (3)	0.074 (2)
C7	0.3647 (7)	−0.2127 (5)	0.0906 (3)	0.0642 (13)
C8	0.3650 (5)	−0.0835 (4)	0.1339 (2)	0.0441 (9)
C9	0.2253 (5)	−0.0605 (5)	0.1738 (2)	0.0472 (10)
C10	0.0746 (7)	−0.1777 (5)	0.1587 (3)	0.0675 (14)
C11	0.1385 (6)	0.0838 (6)	0.2716 (3)	0.070 (2)
C12	0.2460 (7)	0.0868 (6)	0.3484 (3)	0.071 (2)
C13	0.4874 (7)	0.2409 (5)	0.4313 (3)	0.0588 (12)
C14	0.4594 (9)	0.1821 (8)	0.4981 (4)	0.093 (2)
C15	0.6230 (6)	0.3648 (5)	0.4452 (3)	0.0575 (12)
C16	0.7051 (8)	0.4401 (7)	0.5186 (3)	0.079 (2)
C17	0.8156 (9)	0.5609 (9)	0.5285 (4)	0.095 (2)
C18	0.8459 (8)	0.6065 (7)	0.4663 (4)	0.090 (2)
C19	0.7638 (6)	0.5276 (5)	0.3932 (3)	0.0645 (14)
C20	0.7930 (8)	0.5682 (5)	0.3228 (4)	0.076 (2)
C21	0.9030 (9)	0.7069 (8)	0.3310 (6)	0.158 (5)
C22	0.7549 (8)	0.4995 (5)	0.1875 (3)	0.076 (2)
C23	0.8371 (7)	0.3826 (5)	0.1579 (3)	0.0688 (15)
C24	0.7448 (5)	0.1394 (5)	0.1156 (2)	0.0477 (10)
C25	0.8885 (7)	0.1291 (6)	0.0752 (3)	0.073 (2)

Table 2. *Selected geometric parameters (Å, °)*

Eu—N2	2.434 (4)	Eu—N9	2.648 (4)
Eu—N1	2.455 (4)	S1—C1	1.622 (5)
Eu—N3	2.482 (5)	S2—C2	1.620 (5)
Eu—N5	2.568 (4)	S3—C3	1.641 (7)
Eu—N8	2.568 (4)	C1—N1	1.156 (6)
Eu—N4	2.634 (4)	C2—N2	1.157 (6)
Eu—N6	2.647 (4)	C3—N3	1.128 (7)
Eu—N7	2.647 (4)		
N2—Eu—N1	144.39 (14)	N4—Eu—N9	60.37 (11)
N2—Eu—N3	143.2 (2)	N1—C1—S1	179.5 (5)
N1—Eu—N3	72.3 (2)	N2—C2—S2	178.7 (4)
N5—Eu—N4	60.92 (11)	N3—C3—S3	173.6 (6)
N5—Eu—N6	62.96 (13)	C1—N1—Eu	160.5 (4)
N8—Eu—N7	60.99 (13)	C2—N2—Eu	143.6 (3)
N6—Eu—N7	59.78 (12)	C3—N3—Eu	135.7 (5)
N8—Eu—N9	63.20 (13)		

The H atoms were placed in calculated positions, with isotropic displacement parameters fixed at 1.2U_{eq} of the parent C atom.

Data collection: Philips PW1100 *FEBO* system (Belletti, 1993). Cell refinement: Philips PW1100 *FEBO* system. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1202). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Effects of Cation Interactions on Sugar Anion Conformation in Complexes of Lactobionate and Gluconate with Calcium, Sodium or Potassium

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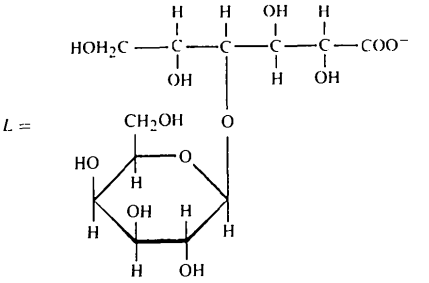
Abstract

In the investigated compounds, the tetrahydrated calcium chloride salt of lactobionic acid ($Ca^{2+}.Cl^{-}.C_{12}H_{21}O_{12}^{-}.4H_2O$), potassium lactobionate ($K^{+}.C_{12}H_{21}O_{12}^{-}$), sodium lactobionate monohydrate ($Na^{+}.C_{12}H_{21}O_{12}^{-}.H_2O$) and calcium galactonate hydrate ($Ca^{2+}.2C_6H_{11}O_7^{-}.5H_2O$), the cations and hydrogen-bonding systems have a strong influence on the geometries and conformations of the carbohydrate anions.

Comment

As a part of an extensive study of the influence of the cation on the conformation of the lactobionate or gluconate anions in carbohydrate–cation complexes (Lis, 1981, 1984; Jeffrey & Fasiska, 1972; Panagiotopoulos, Jeffrey, La Placa & Hamilton, 1974; Cook & Bugg, 1973), we have determined the crystal and molecular structures of the tetrahydrated calcium chloride salt of lactobionic acid, (1), potassium lactobionate, (2), sodium lactobionate monohydrate, (3), and calcium galactonate hydrate, (4). They are of the type of carbohydrate complex in which interactions between the cation and the carbohydrate anion play an important role in a number of physiological processes (Angyal, 1980; Krestinger & Nelson, 1976; Bugg, 1973). X-ray data of structures containing a lactobionate or a galactonate anion have been available only for the bromide analogue of (1) (Cook & Bugg, 1973).



(1) $Ca^{2+}.Cl^{-}.L.4H_2O$
(2) $K^{+}.L$
(3) $Na^{+}.L.H_2O$
(4) $Ca^{2+}.2G.5H_2O$

The asymmetric part of the unit cell of (1) comprises one lactobionate and one Cl^{-} anion, one Ca^{2+} cation and four water molecules. The Ca^{2+} ion binds to three water molecules (O2*W*, O3*W* and O4*W*) and to two lactobionate ions, by O8, O9 and O10 of the first anion and by O7 and O12 of the second symmetry-related anion (Fig. 1). Table 3 presents the intermolecular hydrogen bonding with H···O distances not greater than 2.20 Å. The contacts of the Cl^{-} ion and O1*W* water molecule with the lactobionate moiety are depicted in Fig. 1.

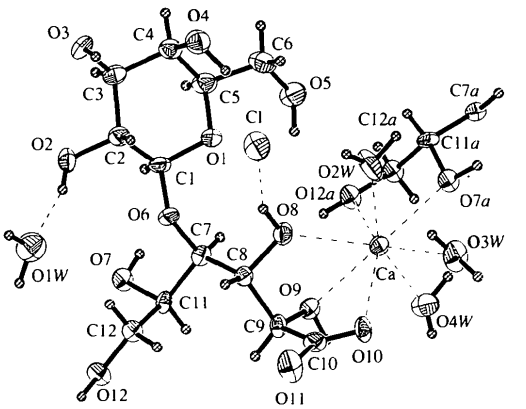


Fig. 1. The environment of the Ca^{2+} cation in (1) showing 50% probability displacement ellipsoids.

Comparison of (1) with the bromide analogue (Cook & Bugg, 1973) shows that the structures are very similar. The bromide analogue crystallizes in the same space group, with similar cell constants. The geometries about the Ca^{2+} ion and the conformations of the