The refined C—H distances for compound (2) range from 0.88 (2) to 1.01 (2) Å.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989) for (1) and (3); *XSCANS* (Siemens, 1994) for (2). Cell refinement: *CAD*-4 *Software* for (1) and (3); *XSCANS* for (2). Data reduction: *XCAD*4 (Siemens, 1993) for (1) and (3); *XSCANS* for (2). For all compounds, program(s) used to solve structures: *XS* in *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structures: *XLS*3 in *SHELXTL/PC* for (1) and (3); *SHELXL*93 (Sheldrick, 1993) for (2). For all compounds, molecular graphics: *XP* in *SHELXTL/PC*. Software used to prepare material for publication: *XPUBL* in *SHELXTL/PC* for (1) and (3); *SHELXL*93 for (2).

This research was supported by NSERC Canada and the University of Toronto.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, bond distances and angles involving non-H atoms for (1) and (3), and complete geometry for (2) have been deposited with the IUCr (Reference: FG1056). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Strongly Luminescent Organic-Solvent-Soluble Salt of the Tris(dipicolinato)-europium(III) Trianion

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Abstract

The tetraethylammonium salt of the $[\mathrm{Eu(dipic)_3}]^{3-}$ (dipic = 2,6-pyridinedicarboxylate) complex anion, tris(tetraethylammonium) tris(2,6-pyridinedicarboxylato-*N*,*O*,*O*″)europium(III) tetrahydrate, $(\mathrm{C_8H_{20}N})_3[\mathrm{Eu(C_7H_3NO_4)_3}].4\mathrm{H_2O}$, forms monoclinic crystals. The lattice contains alternating columns of the Δ and Λ enantiomeric forms of the trianion, with the water molecules hydrogen bonded to the uncoordinated O atoms of the carboxylate groups and the tetraethylammonium cations forming columns, presumably to optimize electrostatic attractions.

Comment

Luminescence of rare earth cations such as $\mathrm{Eu^{III}}$ and $\mathrm{Tb^{III}}$ is enhanced by the exclusion of water from the metal coordination sphere and by the binding of rigid ligands (Bünzli & Choppin, 1989). Tris(dipicolinato) [dipicolinate (dipic) = pyridine-2,6-dicarboxylate] complexes of rare earth metals, in which the metal is bound with D_3 nine-coordinate stereochemistry to six O- and three N-donor atoms of the ligands, are well known as strong emitters in solution (Riehl & Richardson, 1986; Dong & Flint, 1992). Enantioselective quenching of this emission by chiral transition metal–polyamine complexes in solution has been demonstrated (Metcalf, Bolender, Driver & Richardson, 1993) and we have shown recently that the emission is almost totally quenched in solid salts formed from rare earth complex anions and such cations (Brayshaw, Bünzli, Froidevaux, Harrowfield, Kim & Sobolev, 1995). Structural studies reveal extensive hydrogen-bonding interactions between the NH groups of the cations and the carboxylate O atoms of the anions in these salts (Harrowfield, Kim,

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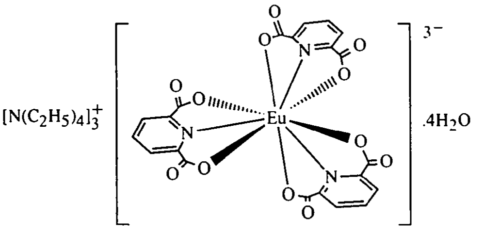
Skelton & White, 1995), and these interactions may explain both the high lattice energy, which is reflected in low solubilities, and the luminescence quenching. Contrasting properties are found for the tetraethylammonium salts of the anions (at least for those involving Eu, Gd and Tb) in that they are rather soluble in water, like the sodium and caesium salts, and are also soluble in moderately polar organic solvents, and exhibit, again like the sodium and caesium salts, strong solid-state luminescence for Eu and Tb. Hence, it was of interest to determine the structure of a tetraethylammonium salt in order to define precisely the points of difference from the non-luminescent solids. We report herein the structural characterization of $[N(C_2H_5)_4]_3[Eu(dipic)_3].4H_2O$, (I).



(I)

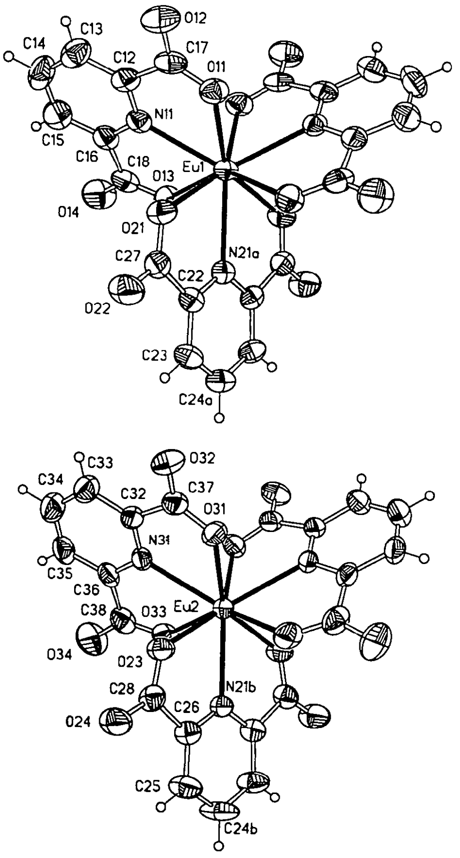


Fig. 1. *ORTEP* (Johnson, 1965) drawings of the anions of title compound. Displacement ellipsoids are shown at the 50% probability level.

Water molecules within the lattice are found sufficiently close to the uncoordinated dipicolinate O atoms to justify the postulation of hydrogen-bonding interactions, which may well be of some significance in the vibrational deactivation of the europium ion when excited,

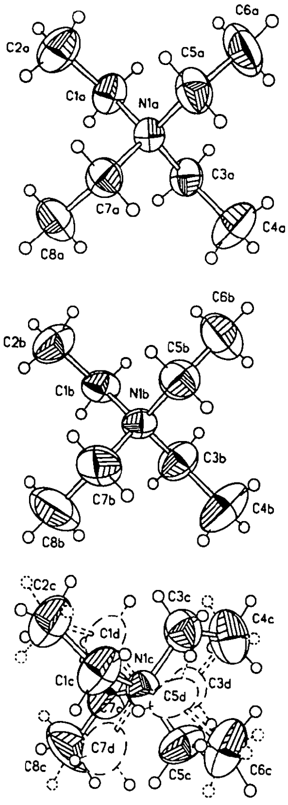


Fig. 2. *ORTEP* (Johnson, 1965) drawings of the cations of title compound. Displacement ellipsoids are shown at the 50% probability level.

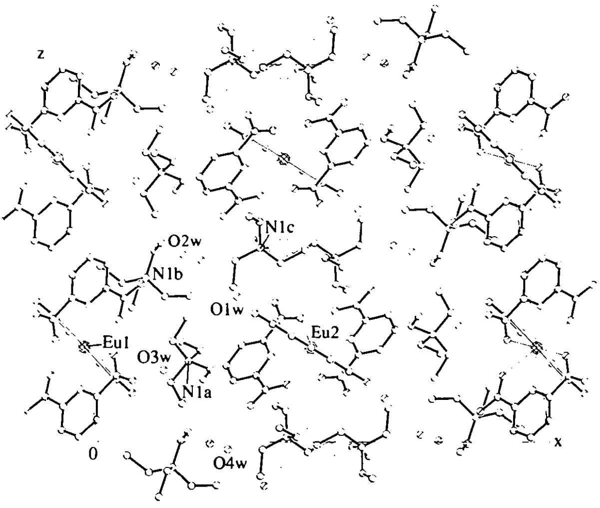


Fig. 3. Packing diagram viewed down the *b* axis.

even though the compound still shows strong solid-state luminescence. Here, of course, the associated cations have no low-lying excited states for energy acceptance from europium. Unsurprisingly, the dimensions of the dipicolinate ligands do not differ outside experimental error in the various salts of the anionic $[Eu(dipic)_3]^{3-}$ complex. Though differences in the exact site symmetry of the emitting metal centre might be expected to be of some significance, detection of such differences would seem to be outside the limit of determination by standard X-ray crystallography, at least in crystals of the quality obtained to date. The lattice contains both Δ and Λ forms of the complex anion, columns containing one form alternating through the lattice, the only difference in europium sites being the result of a mirror-image relationship.

Experimental

$[N(C_2H_5)_4]_3[Eu(dipic)_3].4H_2O$ was obtained as a mixture of pseudo-hexagonal rods and fine needles after two recrystallizations by vapour diffusion of acetone into a methanolic solution. A pseudo-hexagonal rod was used for the present structure determination. As originally prepared, the complex was formulated as a decahydrate, but we presume recrystallization from organic solvents in the present case to be the cause of some loss of water. As the crystals are apparently polymorphic, it is also possible that we selected a lower hydrate from a mixture.

Crystal data

$(C_8H_{20}N)_3[Eu(C_7H_3NO_4)_3].4H_2O$
$M_r = 1110.09$
Monoclinic
$P2/c$
$a = 24.096\,(5)$ Å
$b = 10.692\,(2)$ Å
$c = 20.188\,(4)$ Å
$\beta = 98.36\,(2)°$
$V = 5146\,(2)$ Å^3
$Z = 4$
$D_x = 1.433$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 6 reflections
$\theta = 18.6$–$24.7°$
$\mu = 1.291$ mm^{-1}
$T = 293\,(2)$ K
Pseudo-hexagonal rod
0.25 × 0.25 × 0.25 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$2\theta/\theta$ scans
Absorption correction: Gaussian (*SHELX*76; Sheldrick, 1976)
$T_{min} = 0.731$, $T_{max} = 0.773$
9031 measured reflections
9031 independent reflections
6645 observed reflections $[I > 2\sigma(I)]$
$\theta_{max} = 24.98°$
$h = -28 \rightarrow 28$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 23$
6 standard reflections
frequency: 60 min
intensity decay: 3.0%

Refinement

Refinement on F^2
$R(F) = 0.0417$
$wR(F^2) = 0.0975$
$S = 1.064$
9031 reflections
628 parameters
H atoms were located but not refined
$w = 1/[\sigma^2(F_o^2) + (0.0362P)^2 + 4.4863P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.129$
$\Delta\rho_{max} = 0.884$ e Å^{-3}
$\Delta\rho_{min} = -0.588$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.00022 (8)
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)

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

	x	y	z	U_{eq}
Eu1	0	0.59348 (3)	1/4	0.03482 (11)
O11	0.06272 (14)	0.4231 (3)	0.2293 (2)	0.0469 (9)
O12	0.0961 (2)	0.2837 (3)	0.1628 (2)	0.0632 (11)
O13	−0.08429 (14)	0.6610 (3)	0.1771 (2)	0.0487 (9)
O14	−0.1450 (2)	0.6522 (4)	0.0831 (2)	0.0759 (13)
N11	−0.0217 (2)	0.4823 (4)	0.1381 (2)	0.0390 (10)
C12	0.0128 (2)	0.3943 (4)	0.1212 (3)	0.0426 (12)
C13	0.0042 (2)	0.3375 (5)	0.0586 (3)	0.0557 (15)
C14	−0.0409 (3)	0.3736 (6)	0.0132 (3)	0.066 (2)
C15	−0.0766 (3)	0.4650 (6)	0.0309 (3)	0.060 (2)
C16	−0.0661 (2)	0.5176 (5)	0.0946 (3)	0.0441 (13)
C17	0.0619 (2)	0.3637 (5)	0.1761 (3)	0.0447 (13)
C18	−0.1018 (2)	0.6190 (5)	0.1199 (3)	0.0482 (13)
O21	0.05255 (14)	0.6968 (3)	0.1694 (2)	0.0465 (9)
O22	0.0913 (2)	0.8661 (4)	0.1297 (2)	0.0660 (12)
N21*A*	0	0.8326 (5)	1/4	0.0350 (13)
C22	0.0290 (2)	0.8944 (4)	0.2092 (2)	0.0373 (11)
C23	0.0292 (2)	1.0248 (5)	0.2073 (3)	0.0437 (12)
C24*A*	0	1.0881 (7)	1/4	0.047 (2)
C27	0.0605 (2)	0.8128 (5)	0.1656 (3)	0.0451 (13)
Eu2	1/2	0.76940 (3)	1/4	0.03339 (11)
O23	0.43129 (14)	0.6665 (3)	0.3087 (2)	0.0460 (9)
O24	0.3860 (2)	1/2	0.3400 (2)	0.0714 (12)
N21*B*	1/2	0.5300 (5)	1/4	0.0371 (13)
C24*B*	1/2	0.2741 (7)	1/4	0.068 (3)
C25	0.4611 (3)	0.3389 (5)	0.2804 (3)	0.057 (2)
C26	0.4625 (2)	0.4684 (5)	0.2800 (2)	0.0406 (12)
C28	0.4230 (2)	0.5515 (5)	0.3124 (2)	0.0437 (12)
O31	0.48576 (14)	0.9384 (3)	0.3285 (2)	0.0468 (9)
O32	0.4350 (2)	1.0876 (3)	0.3680 (2)	0.0557 (10)
O33	0.4355 (2)	0.7030 (3)	0.1529 (2)	0.0503 (9)
O34	0.3483 (2)	0.6923 (5)	0.0981 (2)	0.089 (2)
N31	0.40786 (15)	0.8883 (4)	0.2280 (2)	0.0372 (9)
C32	0.3974 (2)	0.9826 (4)	0.2676 (3)	0.0399 (12)
C33	0.3474 (2)	1.0489 (5)	0.2557 (3)	0.0542 (14)
C34	0.3080 (2)	1.0136 (6)	0.2028 (3)	0.064 (2)
C35	0.3183 (2)	0.9152 (6)	0.1632 (3)	0.058 (2)
C36	0.3696 (2)	0.8527 (5)	0.1773 (3)	0.0452 (13)
C37	0.4432 (2)	1.0064 (5)	0.3265 (3)	0.0421 (12)
C38	0.3858 (2)	0.7405 (5)	0.1387 (3)	0.0526 (14)
N1*A*	0.2257 (2)	0.5461 (4)	0.2148 (2)	0.0411 (10)
C1*A*	0.1795 (2)	0.5755 (6)	0.1575 (3)	0.060 (2)
C2*A*	0.1979 (3)	0.6538 (7)	0.1026 (3)	0.079 (2)
C3*A*	0.1973 (2)	0.4821 (5)	0.2670 (3)	0.0552 (15)
C4*A*	0.2356 (3)	0.4419 (7)	0.3293 (3)	0.089 (2)
C5*A*	0.2708 (3)	0.4656 (6)	0.1920 (3)	0.068 (2)
C6*A*	0.2519 (3)	0.3377 (6)	0.1662 (4)	0.102 (3)
C7*A*	0.2546 (2)	0.6642 (5)	0.2423 (3)	0.0548 (15)
C8*A*	0.2157 (3)	0.7607 (6)	0.2647 (3)	0.083 (2)
N1*B*	0.1567 (2)	0.0345 (4)	0.4334 (2)	0.0487 (11)
C1*B*	0.1441 (2)	0.1725 (5)	0.4239 (3)	0.061 (2)
C2*B*	0.1173 (3)	0.2090 (6)	0.3540 (3)	0.082 (2)
C3*B*	0.1844 (3)	0.0201 (6)	0.5048 (3)	0.078 (2)
C4*B*	0.2021 (4)	−0.1141 (7)	0.5257 (4)	0.112 (3)
C5*B*	0.1034 (3)	−0.0436 (6)	0.4200 (3)	0.072 (2)
C6*B*	0.0600 (3)	−0.0160 (8)	0.4645 (4)	0.106 (3)
C7*B*	0.1930 (3)	−0.0102 (6)	0.3833 (4)	0.080 (2)
C8*B*	0.2480 (3)	0.0607 (8)	0.3848 (5)	0.124 (3)

N1*C*	0.4184 (2)	0.7666 (5)	0.5131 (2)	0.0573 (12)
C1*C*†	0.4597 (4)	0.6985 (10)	0.4735 (4)	0.083 (3)
C1*D*‡	0.4747 (12)	0.771 (3)	0.5404 (14)	0.083 (3)
C2*C*	0.5174 (3)	0.6826 (8)	0.5073 (4)	0.103 (3)
C3*C*†	0.4400 (4)	0.9044 (9)	0.5131 (5)	0.084 (3)
C3*D*‡	0.3873 (12)	0.868 (3)	0.5521 (15)	0.084 (3)
C4*C*	0.4053 (4)	0.9981 (8)	0.5372 (4)	0.112 (3)
C5*C*†	0.3602 (4)	0.7575 (10)	0.4796 (5)	0.085 (3)
C5*D*‡	0.4050 (11)	0.777 (3)	0.4387 (14)	0.085 (3)
C6*C*	0.3471 (3)	0.7963 (8)	0.4093 (4)	0.102 (3)
C7*C*†	0.4250 (5)	0.7259 (12)	0.5832 (5)	0.101 (4)
C7*D*‡	0.3931 (14)	0.638 (4)	0.5324 (14)	0.101 (4)
C8*C*	0.4043 (5)	0.6008 (9)	0.5973 (5)	0.163 (5)
O1*W*	0.3527 (2)	0.2731 (4)	0.3832 (2)	0.0769 (13)
O2*W*	0.2465 (2)	0.5821 (6)	0.4957 (3)	0.129 (2)
O3*W*	0.1670 (2)	0.0688 (5)	0.1911 (3)	0.120 (2)
O4*W*	0.2846 (2)	0.6783 (8)	−0.0195 (2)	0.157 (3)

† Occupancy = 0.75.
‡ Occupancy = 0.25.

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

Eu1—O13	2.438 (3)	Eu2—O33	2.424 (3)
Eu1—O11	2.441 (3)	Eu2—O23	2.434 (3)
Eu1—O21	2.463 (3)	Eu2—O31	2.460 (3)
Eu1—N11	2.540 (4)	Eu2—N31	2.541 (4)
Eu1—N21*A*	2.556 (5)	Eu2—N21*B*	2.560 (5)
O13—Eu1—O11	126.84 (12)	O33—Eu2—O23	81.93 (12)
O13—Eu1—O21	86.08 (12)	O33—Eu2—O31	127.07 (12)
O11—Eu1—O21	80.29 (11)	O23—Eu2—O31	81.37 (11)
O13—Eu1—N11	63.60 (12)	O33—Eu2—N31	64.15 (12)
O11—Eu1—N11	63.33 (12)	O23—Eu2—N31	70.87 (12)
O21—Eu1—N11	71.44 (12)	O31—Eu2—N31	62.92 (11)
O13—Eu1—N21*A*	72.78 (8)	O33—Eu2—N21*B*	72.98 (9)
O11—Eu1—N21*A*	138.25 (8)	O23—Eu2—N21*B*	63.13 (8)
O21—Eu1—N21*A*	63.35 (8)	O31—Eu2—N21*B*	137.26 (8)
N11—Eu1—N21*A*	117.90 (9)	N31—Eu2—N21*B*	120.02 (8)

The asymmetric unit of the crystal structure comprises two halves, each containing two independent molecules with the metal atoms on crystallographic twofold axes. During refinement of the structure, the H atoms in the anions and cations were fixed at estimated positions with $U_{\rm iso}$(H) set at $1.5U_{\rm eq}$(C). The H atoms of the water molecules were located from difference syntheses and were not refined by the least-squares procedure.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *PROFIT* (Streltsov & Zavodnik, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL* (Sheldrick, 1983). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1151). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Zinc(II) Chloride–Methanol Complex of 2-[(1,3-Dihydro-1,3-dioxo-2*H*-inden-2-ylidene)amino]-1*H*-indene-1,3(2*H*)-dionate(1–) Sodium Salt: a Complex of Ruhemann's Purple

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Abstract

The title compound, sodium dichloro{2-[(1,3-dihydro-1,3-dioxo-2*H*-inden-2-ylidene)amino]-1*H*-indene-1,3(2*H*)-dionato(1−)}zincate chloro{2-[(1,3-dihydro-1,3-dioxo-2*H*-inden-2-ylidene)amino]-1*H*-indene-1,3(2*H*)-dionato(1−)}(methanol)zinc, Na$\{[ZnCl_2(C_{18}H_8NO_4)][ZnCl(C_{18}H_8NO_4)(CH_3OH)]\}$, is a linear polymer in the solid state. The Na$^+$ ion lies on an inversion centre and is octahedrally coordinated to four keto O atoms, two from each dionate ligand [Na···O 2.280 (3) and 2.286 (4) Å] and to two Cl atoms of adjacent moieties [Na···Cl

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