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# Note

## Synthesis and molecular structure of two crystalline forms of hydrated cerium(III) picrate

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### Abstract

The compound of formula $Ce(pic)_3 \cdot 12H_2O$ (pic = picrate, $C_6H_2N_3O_7$) has been synthesized and crystallized in two different forms. The X-ray structure of both forms has been determined; form 1 is monoclinic, space group $P2_1/n$, $a = 7.799(2)$, $b = 26.925(2)$, $c = 17.465(2)$ Å, $\beta = 98.93(3)°$, $V = 3623(2)$ Å$^3$, $Z = 4$, $D_x = 1.908$ g cm$^{-3}$; form 2 is monoclinic, space group $C2/c$, $a = 40.225(5)$, $b = 8.008(4)$, $c = 24.351(9)$, $\beta = 111.46(2)°$, $V = 7300(8)$ Å$^3$, $Z = 8$, $D_x = 1.893$ g cm$^{-3}$. The molecular structure of the two forms is essentially the same, with the $Ce^{3+}$ ion coordinated to six water molecules, one phenolic oxygen from one picrate ion and two oxygens, one from a phenolic and the other from a nitro group of a second picrate giving a coordination number nine; a third picrate ion and six additional water molecules (in different positions in the two forms) complete the crystal packing through a complex network of hydrogen bonds.

*Key words:* Crystal structures; Cerium complexes; Picrate complexes

### Introduction

The coordination of lanthanoids has been studied by several authors [1–3]. The common coordination numbers of the lanthanoids are 7, 8 and 9. The coordination numbers and the coordination polyhedra are determined mainly by mutual repulsions of ligands and the constraints imposed when ligands other than monodentate are employed [1–3].

The molecular structure of ytterbium and yttrium hydrated picrates [4] has shown eight coordinated metal ions, each being bonded to five water molecules, a phenolic oxygen of one picrate and a phenolic oxygen and a nitro oxygen from a second picrate. A third picrate completes the crystal structure and takes part in a number of hydrogen bonds linking the symmetrically related molecules in the lattice. The synthesis and some properties of other hydrated lanthanide picrates have also been described [5, 6], but they were not fully characterized.

In this article the preparation, characterization and structure determination of two crystalline forms of cerium(III) picrate-dodecahydrate are described.

### Experimental

The hydrated cerium(III) picrates were prepared by reaction of the hydrated cerium(III) carbonate with picric acid in aqueous solution. The solution was partially evaporated and left to stand at room temperature. *Anal.* Calc.: C, 20.76; H, 2.90; N, 12.10. Found: C, 20.74; H, 2.80; N, 11.88%. The resulting crystals were separated and dried in air. Two crystalline forms were obtained in the preparation, one of them (form 1) being proportionally dominant.

IR spectra were recorded in a Perkin-Elmer model 1750 spectrophotometer, using Nujol mulls between KBr plates. The following bands were observed in the IR: $\nu_{as}(NO_2)$ 1612s, 1570m, 1542s, 1492m, $\nu_s(NO_2)$ 1427s, 1342s; $\nu(CO)$ 1280s; $\delta$(CH in plane) 1169m, 1088m; $\nu(CN)$ 919m; $\delta(NO_2)$ 846w; $\nu(CN)$ 790m; $\delta(NO_2)$ 744w, 712m. The bands attributed to $\nu(OH)$ from water molecules were found at 3527m, 3441m, 3373m and 3086m. The multiple bands attributed to $NO_2$ stretching and deformation modes and also those attributed to $\nu(OH)$ are related to the different environment of these groups in the crystal structures.

Details of data collection and refinement parameters for the two crystalline forms are summarized in Table 1. The structures were solved using standard direct methods and difference Fourier techniques. In the final cycles all non-hydrogen atoms were treated anisotropically. The H atoms were not localized and the relatively large residual electron density in the final difference map was near to the cerium atom. Scattering factors for non-H atoms were taken from Cromer and Mann [8] with corrections for anomalous dispersion from Cromer and Liberman [9]. Programs used: SHELX76 [10], SHELXS86 [11] and ORTEP [12]. Atomic coordinates for non-H atoms of the two crystalline forms are given in Table 2. See also 'Supplementary material'.

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TABLE 1. Crystallographic summary

| | Crystalline form 1 | Crystalline form 2 |
|---|---|---|
| *Data collection*$^{a,b}$ | | |
| Mode | $\omega$ | $\omega$ |
| Radiation used | Mo K$\alpha$ | Mo K$\alpha$ |
| Absorption coefficient (cm$^{-1}$) | 14.001 | 13.897 |
| Scan rate (° min$^{-1}$) | 1.98–16.48 | 1.19–16.48 |
| $\theta$ range (°) | 0–25 | 0–25 |
| Range of *hkl* | $-9 \leqslant h \leqslant 9$, $0 \leqslant k \leqslant 31$, $0 \leqslant l \leqslant 20$ | $-47 \leqslant h \leqslant 44$, $0 \leqslant k \leqslant 9$, $0 \leqslant l \leqslant 28$ |
| Total reflections measured | 7380 | 8880 |
| Unique reflections | 5714 | 5489 |
| $R_{\text{int}}$ | 0.048 | 0.029 |
| Crystal dimensions approx. (mm) | 0.10×0.10×0.40 | 0.10×0.10×0.60 |
| *Structure determination and refinement* | | |
| Reflections used ($I > 3\sigma(I)$) | 4111 | 3052 |
| Absorption correction$^c$: max., min. | 1.547, 0.769 | 1.362, 0.772 |
| No. of variables | 550 | 550 |
| $R$, $R_w$$^d$ | 0.089, 0.093 | 0.068, 0.071 |
| Max. shift/e.s.d. | 0.012 | 0.003 |
| Density in final difference map: max., min. (e Å$^{-3}$) | 2.61, −2.22 | 0.95, −1.01 |

[a] Unit cell parameters by least-square refinement of the setting angles of 25 reflections with $10 < \theta < 25°$. [b] Enraf-Nonius CAD4 diffractometer with graphite monochromator. [c] Absorption correction following the DIFABS procedure of Walker and Stuart [7]. [d] $w = 1/[\sigma^2(F_o) + gF_o]$ where $g$ was 0.0015 for crystalline form 1 and 0.00042 for crystalline form 2.

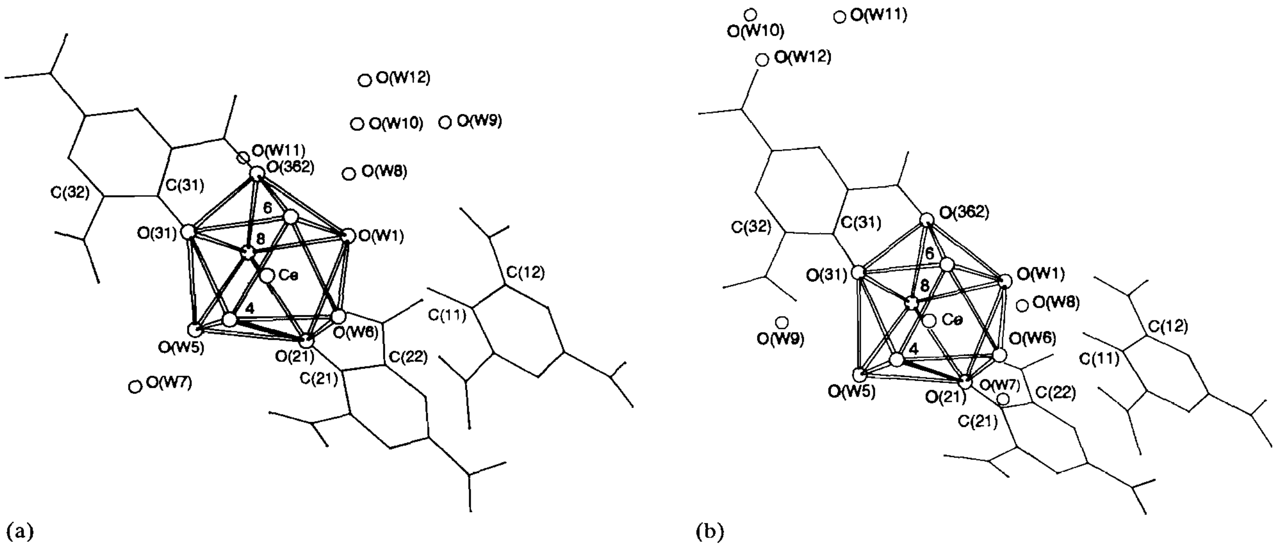

Fig. 1. Perspective view of the molecules of crystalline (a) form 1 and (b) form 2 showing the atom labeling and the coordination polyhedra. Open line is mono-capped square antiprism and line is the diagonal that defines tri-capped trigonal prism. Labels used: 4, O(W4); 6, O(W3); 8, O(W2). (Thermal ellipsoids omitted for clarity reasons.)

## Results and discussion

Figure 1(a) and (b) gives the perspective views of the two crystalline forms, showing the atom numbering scheme; the coordination polyhedra are shown in thick lines. The values of the distance between the central ion $Ce^{3+}$ and the coordinated atoms are shown in Table 3.

In the two crystal forms, the $Ce^{3+}$ ion is nine-coordinated, with six water molecules, one phenolic oxygen from one picrate ion and another phenolic oxygen and a nitro oxygen from a second picrate. In

TABLE 2. Final atomic coordinates and equivalent isotropic temperature factors (Å²)

| Atom | x/a | y/b | z/c | $B_{eq}$[a] |
|---|---|---|---|---|
| Crystalline form 1 | | | | |
| Ce | 0.0844(1) | 0.22364(3) | 0.05218(4) | 2.30(2) |
| O(W1) | 0.356(2) | 0.2372(4) | 0.1449(6) | 3.9(4) |
| O(W2) | −0.008(2) | 0.2048(5) | 0.1840(6) | 4.9(4) |
| O(W3) | 0.313(1) | 0.1803(4) | −0.0153(5) | 3.2(3) |
| O(W4) | −0.031(2) | 0.2313(4) | −0.0894(6) | 4.1(4) |
| O(W5) | −0.242(1) | 0.2347(4) | 0.0476(6) | 3.3(3) |
| O(W6) | 0.255(2) | 0.2876(4) | −0.0084(6) | 3.6(3) |
| O(W7) | −0.449(2) | 0.2432(6) | −0.0905(8) | 6.3(5) |
| O(W8) | 0.396(3) | 0.1960(5) | 0.2940(8) | 7.4(6) |
| O(W9) | 0.771(4) | 0.2027(6) | 0.338(1) | 10.7(9) |
| O(W10) | 0.618(2) | 0.1446(7) | 0.1133(9) | 8.0(7) |
| O(W11) | 0.100(3) | 0.1300(7) | 0.2998(9) | 10.9(9) |
| O(W12) | 0.648(3) | 0.1225(6) | 0.266(1) | 10.7(9) |
| O(11) | 0.524(2) | 0.3161(4) | 0.0932(6) | 4.1(4) |
| O(121) | 0.713(2) | 0.2741(4) | 0.2151(7) | 4.5(4) |
| O(122) | 0.772(2) | 0.32220(5) | 0.3132(6) | 4.8(4) |
| O(141) | 0.872(2) | 0.4947(5) | 0.2808(8) | 6.8(6) |
| O(142) | 0.868(2) | 0.5238(5) | 0.1663(9) | 7.2(6) |
| O(161) | 0.440(2) | 0.4429(5) | −0.0239(7) | 5.2(5) |
| O(162) | 0.496(2) | 0.3671(5) | −0.0416(6) | 5.3(5) |
| N(12) | 0.728(2) | 0.3157(5) | 0.2431(7) | 3.2(4) |
| N(14) | 0.836(2) | 0.4917(4) | 0.2094(8) | 4.1(4) |
| N(16) | 0.505(2) | 0.4042(5) | −0.0029(7) | 3.4(4) |
| C(11) | 0.602(2) | 0.3557(5) | 0.1176(8) | 2.9(4) |
| C(12) | 0.709(2) | 0.3595(5) | 0.1955(8) | 2.8(4) |
| C(13) | 0.774(2) | 0.4026(5) | 0.2255(8) | 2.9(4) |
| C(14) | 0.761(2) | 0.4450(5) | 0.1781(8) | 3.1(4) |
| C(15) | 0.673(2) | 0.4456(5) | 0.1040(8) | 2.9(4) |
| C(16) | 0.602(2) | 0.4014(5) | 0.0766(8) | 2.7(4) |
| O(21) | 0.038(2) | 0.3042(3) | 0.1100(6) | 3.4(3) |
| O(221) | 0.115(2) | 0.3086(4) | 0.2655(6) | 4.6(4) |
| O(222) | 0.371(2) | 0.3405(5) | 0.2869(6) | 4.8(4) |
| O(241) | 0.359(2) | 0.5131(5) | 0.1876(8) | 6.7(6) |
| O(242) | 0.223(2) | 0.5260(4) | 0.0725(8) | 5.1(4) |
| O(261) | 0.011(2) | 0.3856(5) | −0.0811(7) | 6.4(5) |
| O(262) | −0.134(2) | 0.3349(8) | −0.0257(8) | 7.5(7) |
| N(22) | 0.226(2) | 0.3381(5) | 0.2495(6) | 3.4(4) |
| N(24) | 0.258(2) | 0.4996(5) | 0.1260(9) | 4.5(5) |
| N(26) | −0.029(2) | 0.3644(5) | −0.0237(7) | 4.0(5) |
| C(21) | 0.083(2) | 0.3474(5) | 0.1124(7) | 2.6(4) |
| C(22) | 0.187(2) | 0.3700(5) | 0.1826(7) | 2.6(4) |
| C(23) | 0.244(2) | 0.4184(5) | 0.1875(9) | 3.3(5) |
| C(24) | 0.211(2) | 0.4481(5) | 0.1254(9) | 3.2(5) |
| C(25) | 0.112(2) | 0.4315(6) | 0.0558(8) | 3.6(5) |
| C(26) | 0.060(2) | 0.3830(5) | 0.0533(7) | 2.6(4) |
| O(31) | −0.039(1) | 0.1452(3) | 0.0094(5) | 2.8(3) |
| O(321) | −0.358(2) | 0.1382(4) | −0.0735(7) | 4.9(4) |
| O(322) | −0.344(2) | 0.0711(5) | −0.1367(7) | 5.6(5) |
| O(341) | −0.308(2) | −0.0711(5) | 0.0456(9) | 6.0(5) |
| O(342) | −0.092(2) | −0.0718(5) | 0.1353(8) | 5.5(5) |
| O(361) | 0.277(2) | 0.0645(6) | 0.166(1) | 7.8(6) |
| O(362) | 0.212(2) | 0.1380(4) | 0.1259(6) | 4.0(4) |
| N(32) | −0.314(2) | 0.0952(5) | −0.0791(7) | 3.8(4) |
| N(34) | −0.186(2) | −0.0505(5) | 0.085(1) | 4.3(5) |
| N(36) | 0.179(2) | 0.0926(5) | 0.1299(7) | 3.8(4) |
| C(31) | −0.073(2) | 0.1013(4) | 0.0284(8) | 2.6(4) |
| C(32) | −0.210(2) | 0.0726(5) | −0.0118(8) | 2.9(4) |
| C(33) | −0.250(2) | 0.0248(5) | 0.0033(8) | 2.9(4) |
| C(34) | −0.155(2) | 0.0012(5) | 0.0648(7) | 2.6(4) |
| C(35) | −0.012(2) | 0.0239(5) | 0.1078(8) | 3.2(4) |
| C(36) | 0.027(2) | 0.0727(5) | 0.0885(8) | 2.6(4) |
| Crystalline form 2 | | | | |
| Ce | 0.11419(2) | 0.0561(1) | −0.11954(4) | 3.48(3) |
| O(W1) | 0.0825(3) | 0.279(2) | −0.1926(5) | 6.0(5) |
| O(W2) | 0.0709(3) | −0.112(2) | −0.2043(5) | 6.2(5) |
| O(W3) | 0.1026(3) | 0.274(2) | −0.0529(5) | 5.6(4) |
| O(W4) | 0.1638(3) | 0.038(2) | −0.0207(4) | 5.4(4) |
| O(W5) | 0.1389(3) | −0.235(2) | −0.1039(5) | 6.1(5) |
| O(W6) | 0.1570(3) | 0.298(1) | −0.1076(4) | 4.0(3) |
| O(W7) | 0.2167(4) | 0.403(2) | −0.0081(6) | 9.0(6) |
| O(W8) | 0.1617(4) | 0.570(3) | −0.0053(6) | 11.6(8) |
| O(W9) | 0.2702(4) | 0.382(3) | 0.4673(7) | 11.2(8) |
| O(W10) | 0.0000 | 0.252(5) | 0.2500 | 16.0(1) |
| O(W11) | −0.0083(5) | 0.436(3) | 0.161(1) | 15.0(1) |
| O(W12) | 0.0786(8) | 0.446(3) | 0.385(1) | 20.0(1) |
| O(11) | 0.1313(3) | 0.496(2) | −0.2048(5) | 5.3(4) |
| O(121) | 0.0697(4) | 0.483(4) | −0.2900(8) | 22.0(1) |
| O(122) | 0.0597(3) | 0.572(2) | −0.3701(6) | 6.7(5) |
| O(141) | 0.1511(3) | 0.816(2) | −0.4233(6) | 8.9(6) |
| O(142) | 0.2023(3) | 0.871(2) | −0.3587(5) | 6.3(5) |
| O(161) | 0.2342(3) | 0.628(2) | −0.1678(5) | 6.0(4) |
| O(162) | 0.1939(3) | 0.593(2) | −0.1305(4) | 4.7(4) |
| N(12) | 0.0804(3) | 0.546(2) | −0.3220(6) | 5.2(5) |
| N(14) | 0.1730(4) | 0.811(2) | −0.3724(6) | 4.7(5) |
| N(16) | 0.2022(3) | 0.618(2) | −0.1731(5) | 3.5(4) |
| C(11) | 0.1408(3) | 0.570(2) | −0.2430(6) | 3.2(4) |
| C(12) | 0.1169(4) | 0.597(2) | −0.3036(6) | 3.2(4) |
| C(13) | 0.1269(4) | 0.675(2) | −0.3471(6) | 3.3(5) |
| C(14) | 0.1621(4) | 0.732(2) | −0.3288(6) | 3.3(5) |
| C(15) | 0.1866(3) | 0.713(2) | −0.2723(6) | 2.9(4) |
| C(16) | 0.1756(3) | 0.633(2) | −0.2314(6) | 3.0(4) |
| O(21) | 0.1394(3) | 0.021(1) | −0.1956(4) | 4.3(3) |
| O(221) | 0.0914(3) | −0.039(2) | −0.3036(6) | 6.1(5) |
| O(222) | 0.0888(4) | 0.147(3) | −0.3658(7) | 11.4(8) |
| O(241) | 0.1944(3) | 0.387(2) | −0.3716(5) | 5.8(5) |
| O(242) | 0.2390(3) | 0.429(2) | −0.2900(5) | 5.0(4) |
| O(261) | 0.2370(3) | 0.203(2) | −0.1098(5) | 5.7(4) |
| O(262) | 0.2074(3) | −0.017(2) | −0.1149(6) | 7.1(5) |
| N(22) | 0.1054(3) | 0.075(2) | −0.3188(6) | 4.7(5) |
| N(24) | 0.2097(3) | 0.365(2) | −0.3195(6) | 3.6(4) |
| N(26) | 0.2142(3) | 0.106(2) | −0.1373(5) | 3.7(4) |
| C(21) | 0.1558(3) | 0.089(2) | −0.2243(6) | 3.0(4) |
| C(22) | 0.1409(3) | 0.128(2) | −0.2869(6) | 2.8(4) |
| C(23) | 0.1580(3) | 0.217(2) | −0.3171(6) | 3.0(4) |
| C(24) | 0.1927(3) | 0.268(2) | −0.2873(6) | 2.9(4) |
| C(25) | 0.2110(3) | 0.228(2) | −0.2266(6) | 2.9(4) |
| C(26) | 0.1931(4) | 0.145(2) | −0.1986(6) | 3.0(4) |
| O(31) | 0.0809(3) | −0.086(2) | −0.0722(5) | 5.7(4) |
| O(321) | 0.1192(3) | −0.190(2) | 0.0346(6) | 7.6(6) |
| O(322) | 0.0966(3) | −0.429(2) | 0.0435(7) | 7.6(6) |
| O(341) | −0.0250(3) | −0.355(2) | 0.0363(6) | 6.8(5) |
| O(342) | −0.0615(3) | −0.189(2) | −0.0288(5) | 5.4(4) |
| O(361) | −0.0174(4) | 0.089(3) | −0.1669(8) | 14.0(1) |
| O(362) | 0.0373(4) | 0.112(3) | −0.1490(7) | 10.0(7) |
| N(32) | 0.0936(3) | −0.292(2) | 0.0252(6) | 4.8(5) |
| N(34) | −0.0321(4) | −0.255(2) | −0.0058(6) | 4.2(5) |
| N(36) | 0.0113(4) | 0.055(2) | −0.1383(7) | 6.2(6) |

*(continued)*

TABLE 2. (*continued*)

| Atom | $x/a$ | $y/b$ | $z/c$ | $B_{eq}$[a] |
|---|---|---|---|---|
| C(31) | 0.0545(4) | −0.119(2) | −0.0580(7) | 3.5(5) |
| C(32) | 0.0577(3) | −0.221(2) | −0.0095(7) | 3.5(5) |
| C(33) | 0.0305(3) | −0.271(2) | 0.0070(6) | 3.0(4) |
| C(34) | −0.0036(4) | −0.212(2) | −0.0248(6) | 3.3(4) |
| C(35) | −0.0114(4) | −0.104(2) | −0.0736(6) | 3.5(5) |
| C(36) | 0.0187(4) | −0.063(2) | −0.0882(6) | 3.8(5) |

[a] $B_{eq}=\frac{4}{3}\sum_{i,j}\beta_{ij}(a_i a_j)$.

TABLE 3. Bond distances in the $Ce^{3+}$ coordination spheres for both crystalline forms

| | Form 1 | Form 2 |
|---|---|---|
| Ce–O(W1) | 2.49(1) | 2.52(1) |
| Ce–O(W2) | 2.57(1) | 2.55(1) |
| Ce–O(W3) | 2.57(1) | 2.54(1) |
| Ce–O(W4) | 2.51(1) | 2.50(1) |
| Ce–O(W5) | 2.55(1) | 2.51(1) |
| Ce–O(W6) | 2.51(1) | 2.53(1) |
| Ce–O(21) | 2.44(9) | 2.43(1) |
| Ce–O(31) | 2.39(1) | 2.36(1) |
| Ce–O(362) | 2.75(1) | 2.94(2) |

both structures, a third picrate ion and six additional water molecules complete the crystal packing.

The two crystal forms differ mainly in the position of the non-coordinated water molecules and the resulting network of hydrogen bonds.

The $Ce(pic)_3(H_2O)_6$ moieties are packed in a similar layer arrangement. This seems to indicate that the crystallization process is dominated by the packing of the bulky complexes with the water molecules filling the empty spaces.

In an attempt to rationalize the coordination mode of the two compounds, the typical distances and angles of the different ideal coordination polyhedra have been calculated according to the procedure proposed by Muetterties and Guggenberger [2]. The characteristic values for the relevant distances and angles observed in the present study (see 'Supplementary material'), indicate that the coordination polyhedron in the two crystalline forms is an intermediate between the mono-capped square antiprism (CSAP) and tri-capped trigonal prism (TCTP). This can be associated with steric limitations of the bidentate picrate ion.

## Supplementary material

Lists of interatomic distances and angles, anisotropic thermal parameters, hydrogen bonds distances, structure factor tables, theoretical and experimental values for CSAP and TCTP polyhedrons have been deposited.

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