

Fig. 2. The crystal packing of the title complex viewed along the  $c$  axis.

$O(5)-C(39)-C(47)-C(48)$  is  $43.6(4)^\circ$ . Other torsion angles are nearly the same for the two aminoalcohol moieties. It should be noted that the structural features of the title complex are similar to those of the phenolic-oxygen-bridged binuclear copper(II) complex (Yanagi & Minobe, 1987). This indicates that the structure of the tridentate Schiff-base ligand plays an important role in the catalytic asymmetric induction. The absolute configuration of the two ligands must be  $R$  since they were synthesized from  $D$ -phenylalanine.

The crystal packing is shown in Fig. 2. The crystal structure is stabilized mainly by van der Waals forces; the shortest intermolecular distances are  $C(28)\cdots C(46)$

$(x-1, y, z-1)$   $3.446(6)$  and  $C(35)\cdots C(43)$   $(x, y, z-1)$   $3.466(5)$  Å.

The authors are grateful to Dr Tadatoshi Aratani of our laboratory for providing a sample of the title complex. We also thank Professor Yoshio Sasada of the Tokyo Institute of Technology and Dr Yuji Ohashi of Ochanomizu University for their valuable discussions and encouragement.

#### References

- ARATANI, T. (1985). *Pure Appl. Chem.* **57**, 1839–1844.  
 ARATANI, T., YONEYOSHI, Y. & NAGASE, T. (1975). *Tetrahedron Lett.* pp. 1707–1710.  
 ARATANI, T., YONEYOSHI, Y. & NAGASE, T. (1977). *Tetrahedron Lett.* pp. 2599–2602.  
 ARATANI, T., YONEYOSHI, Y. & NAGASE, T. (1982). *Tetrahedron Lett.* **23**, 685–688.  
 FRENZ, B. A. (1978). *The Enraf-Nonius CAD-4 SDP - A Real-time System for Concurrent X-ray Collection and Crystal Structure Determination*. In *Computing in Crystallography*, edited by H. SCHENK, R. OLTJOF-HAZEKAMP, H. VAN KONINGSVELD & G. C. BASSI, pp. 64–71. Delft Univ. Press.  
*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)  
 NOZAKI, H., TAKAYA, H., MORIUTI, S. & NOYORI, R. (1968). *Tetrahedron*, **24**, 3655–3669.  
 YANAGI, K., & MINOBE, M. (1987). *Acta Cryst.* **C43**, 1045–1048.

*Acta Cryst.* (1987). **C43**, 2063–2067

## Structural Study of Tris(tetrabutylammonium) Hexaisothiocyanatopraseodymate(III)

BY LASSI HILTUNEN AND JORMA HÖLSÄ\*

*Helsinki University of Technology, Department of Chemistry, SF-02150 Espoo, Finland*

AND WIESLAW STREK AND BOGUSLAWA JEZOWSKA-TRZEBIATOWSKA

*Polish Academy of Sciences, Institute of Low Temperature and Structure Research, PO Box 937, Wrocław, Poland*

(Received 30 June 1986; accepted 16 June 1987)

**Abstract.**  $3C_4H_9N^+.[Pr(NCS)_6]^{3-}$ ,  $M_r = 1216.8$ , triclinic,  $P\bar{1}$ ,  $a = 12.419(5)$ ,  $b = 12.927(3)$ ,  $c = 22.848(6)$  Å,  $\alpha = 90.94(2)$ ,  $\beta = 92.423(4)$ ,  $\gamma = 96.75(4)^\circ$ ,  $V = 3638.26$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.11$  g cm<sup>-3</sup>,  $\lambda(Mo K\alpha) = 0.71069$  Å,  $\mu = 8.13$  cm<sup>-1</sup>,  $F(000) = 1300$ ,  $T = 293$  K,  $R = 0.077$  for 6236 observed unique reflexions [ $F_o > 6\sigma(F_o)$ ]. The structure consists of

praseodymium atoms coordinated to six N atoms from thiocyanate groups. The coordination polyhedron approaches an ideal octahedron with only minor distortions. The thiocyanate groups are nearly linear. The coordination of *n*-butyl groups to the ammonium N atom is tetrahedral and the butyl groups are partly disordered.

\* Author to whom all correspondence should be sent. Present address: University of Dar es Salaam, Chemistry Department, PO Box 35061, Dar es Salaam, Tanzania.

Perhaps the most common non-oxygen donor atom in rare-earth compounds is nitrogen. A classical group of six-coordinated rare-earth nitrogen coordination compounds is the hexaisothiocyanato complexes. These compounds have been the subject of structural (Martin, Thompson, Radonovich & Glick, 1968; de Almeida Santos & Lechat, 1980) and optical studies (Malta, Azevedo, Gouveia & de Sa, 1982).

Martin, Thompson, Radonovich & Glick (1968) found the erbium compound to crystallize in the triclinic crystal system with  $A\bar{1}$  as the space group. The unit-cell dimensions reported by them are:  $a = 22.63$  (3),  $b = 16.73$  (2),  $c = 18.82$  (2) Å,  $\alpha = 87.97$  (2),  $\beta = 89.08$  (3) and  $\gamma = 92.47$  (3)°. The final  $R$  value was rather poor, 12%. Only approximate average values for the Er–N bond distances and angles were reported.

Another incomplete study of the crystal structure of these complexes was conducted by de Almeida Santos & Lechat (1980) who found the corresponding europium compound to belong to the triclinic crystal system with  $P\bar{1}$  as the space group. The unit-cell dimensions obtained by them are:  $a = 12.415$  (2),  $b = 12.893$  (2),  $c = 22.783$  (2) Å,  $\alpha = 90.93$  (1),  $\beta = 92.37$  (1) and  $\gamma = 96.76$  (1)°. The value of the agreement factor  $R$  (13%) showed no improvement when compared to the results of Martin, Thompson, Radonovich & Glick (1968). However, de Almeida Santos & Lechat (1980) confirmed in principle the sixfold coordination of europium to the N atoms of the thiocyanate groups. No further structural details were given.

One study of the optical properties of the hexaisothiocyanato complexes has been carried out. Malta, Azevedo, Gouveia & de Sa (1982) concentrated on explaining the hypersensitive nature of the  $^5D_0 \rightarrow ^7F_0$  and  $^5D_0 \rightarrow ^7F_2$  transitions of the  $\text{Eu}^{3+}$  ion with the aid of the pseudomultipolar effect.

As a consequence of the well shielded spatial position of the  $4f$  electron core of  $\text{RE}^{3+}$  ions, the interactions with the environment affect the energy-level structure of  $\text{RE}^{3+}$  ions only slightly. The  $4f-4f$  transitions then appear as very sharp lines in both the absorption and the luminescence spectra of the RE compounds. This phenomenon offers an excellent opportunity to probe the symmetry of the RE-ion surroundings since the energy-level schemes are very sensitive to changes in the symmetry in spite of the weakness of the effect. The interpretation of the modifications in energy-level schemes requires, however, in low-symmetry cases the knowledge of the exact crystal structure.

The present study of tris(tetrabutylammonium) hexaisothiocyanatopraseodymate(III) was undertaken in order to elucidate the crystal structure of this compound and to remove the uncertainties in the matter. This investigation was carried out at the same time as an optical study, the results of which will be reported later in a separate paper.

**Experimental.** Single crystals of tris(tetrabutylammonium) hexaisothiocyanatopraseodymate(III),  $[(\text{C}_4\text{H}_9)_4\text{N}]_3[\text{Pr(NCS)}_6]$ , were obtained from a 1:1 solution of ethyl alcohol–*tert*-butyl alcohol containing a mixture of lanthanide thiocyanate and tetra-*n*-butylammonium thiocyanate in a 1:3 molar ratio.

X-ray intensity data were collected with a Syntex  $P2_1$  single-crystal diffractometer at ambient temperature. Two standard reflexions, 551 and 058, were chosen to check the crystal and electronics stability. The intensity of these reflexions remained practically constant throughout the whole measurement. The intensities were corrected for Lorentz, polarization and absorption effects. Additional information on the data collection can be found in Table 1.

The position of the Pr atom was determined from a Patterson map and those of the S, N and C atoms were found from subsequent difference electron density calculations with the aid of *MITHRIL* (Gilmore, 1983). The atomic scattering factors were obtained from *International Tables for X-ray Crystallography* (1974) and the anomalous-dispersion correction factors from Cromer & Liberman (1970). No H atoms were found. The atomic positions were refined in two alternating blocks with *SHELX76* (Sheldrick, 1976). This refinement was based on 6236 reflexions with  $F_o$  greater than  $6\sigma(F_o)$  and the reflexions were weighted inversely proportional to the estimated variance. Pr, S and N atoms of the thiocyanate groups were refined with anisotropic temperature factors whereas all C and H atoms and the N atoms belonging to the tetra-*n*-butylammonium groups were refined with isotropic temperature factors. H atoms belonging to the  $\text{CH}_2$  groups were included in the refinement with restricted orientation but free C–H distance. Details of structure refinement are given in Table 1.

**Discussion.** The final position parameters of the non-H atoms are presented in Table 2.\* The crystal structure of  $[(\text{C}_4\text{H}_9)_4\text{N}]_3[\text{Pr(NCS)}_6]$  is depicted in Figs. 1 and 2. Selected bond angles and distances are listed in Table 3. The stereoscopic view of the unit-cell contents in Fig. 1 shows the presence of separate  $[(\text{C}_4\text{H}_9)_4\text{N}]^+$  and  $[\text{Pr(NCS)}_6]^{3-}$  groups.

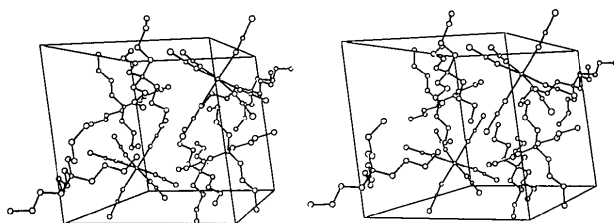
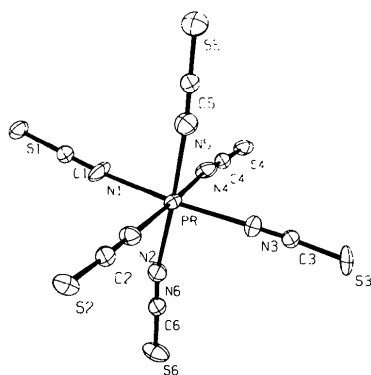
The most interesting information obtained in this work concerns the coordination of the  $\text{Pr}^{3+}$  ions. This information is especially important since the distortions in the praseodymium coordination determine the optical properties of  $[(\text{C}_4\text{H}_9)_4\text{N}]_3[\text{Pr(NCS)}_6]$ .

The crystal-structure determination shows that the immediate surroundings of the Pr ion contain only six

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44153 (34 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Details of the structure refinement for  $[(C_4H_9)_4N]_3[Pr(NCS)_6]$ .

Crystal size (mm)	0.2 × 0.2 × 0.5
Scan type	$\omega$
Scan speed ( $^\circ \text{ min}^{-1}$ )	Variable, from 1 to 29.3
Cell-constant determination	25 reflections ( $20 < 2\theta < 25^\circ$ )
$2\theta$ range ( $^\circ$ )	$0 < 2\theta < 50$
Absorption correction	Empirical ( $\omega$ -scan data); transmission factor from unity to 0.75
$[(\sin \theta)/\lambda]_{\text{max}}$ ( $\text{\AA}^{-1}$ )	0.6
$h, k, l$ range	$18, \pm 15, \pm 27$
Number of reflexions collected	12 918
Number of unique reflexions	12 834
Number of observed reflexions	$6236 [F_o > 6\sigma(F_o)]$
$R_{\text{int}}$	0.025
Function minimized	$\sum w( F_o  -  F_c )^2$
Weighting scheme	$w = 3.7245/[(\sigma^2(F_o) + 0.00992F_o^2)]$
Number of variables	266 and 155
$R$	0.077
$wR$	0.082
$(\Delta/\sigma)_{\text{max}}$	0.558
Final $\Delta\rho$ excursions ( $e \text{\AA}^{-3}$ )	From $-0.57$ to $1.05$

Fig. 1. Stereoscopic view of the atoms within the unit cell of  $[(C_4H_9)_4N]_3[Pr(NCS)_6]$ . The  $xy$  plane of the figure corresponds to the  $ab$  plane of the crystal system.Fig. 2. The immediate environment of the  $Pr^{3+}$  ion in  $[(C_4H_9)_4N]_3[Pr(NCS)_6]$ . Thermal ellipsoids are drawn at 15% probability.

thiocyanate groups which are coordinated through N atoms (Fig. 2). The N atoms around the Pr atom form a distorted octahedron. The shortest Pr–N distance is 2.422 (11) Å and the longest is 2.465 (11) Å with an average of 2.436 (11) Å (*cf.* Table 3). The mean Pr–N distance is somewhat shorter than the sum of either the ionic or the covalent radii of Pr and N atoms (Shannon, 1976). The axial Pr–N2 and Pr–N4 distances are clearly elongated when compared with the distances

Table 2. Fractional positional parameters and the equivalent ( $U_{\text{eq}}$ ) and isotropic ( $U_{\text{iso}}$ ) temperature factors for  $[(C_4H_9)_4N]_3[Pr(NCS)_6]$ 

	$x$	$y$	$z$	$U^* (\text{\AA}^2)$
Pr	0.0658 (1)	0.2057 (1)	0.2486 (0)	6.88 (4)
N1	−0.0424 (10)	0.2990 (8)	0.1815 (5)	11.9 (1)
N2	−0.0350 (8)	0.2712 (8)	0.3283 (5)	9.1 (1)
N3	0.1887 (9)	0.1204 (8)	0.3114 (5)	9.8 (1)
N4	0.1609 (10)	0.1459 (9)	0.1641 (5)	10.6 (1)
N5	0.1957 (10)	0.3624 (9)	0.2542 (5)	11.2 (1)
N6	−0.0684 (8)	0.0538 (8)	0.2378 (5)	9.5 (1)
C1	−0.0874 (10)	0.3548 (9)	0.1536 (5)	7.5 (3)
C2	−0.0911 (11)	0.2969 (10)	0.3635 (6)	8.3 (4)
C3	0.2437 (10)	0.0823 (9)	0.3425 (5)	7.5 (3)
C4	0.2043 (9)	0.1090 (9)	0.1287 (5)	7.2 (3)
C5	0.2539 (11)	0.4367 (11)	0.2494 (5)	8.2 (4)
C6	−0.1210 (11)	−0.0267 (11)	0.2388 (6)	8.7 (4)
S1	−0.1513 (3)	0.4298 (3)	0.1113 (2)	10.1 (3)
S2	−0.1701 (3)	0.3382 (3)	0.4112 (2)	10.2 (3)
S3	0.3188 (3)	0.0236 (4)	0.3890 (2)	13.4 (4)
S4	0.2654 (3)	0.0574 (3)	0.0759 (2)	10.8 (3)
S5	0.3349 (4)	0.5428 (3)	0.2447 (2)	12.6 (3)
S6	−0.1955 (4)	−0.1368 (4)	0.2396 (2)	14.2 (4)
N11	0.0589 (6)	0.2569 (6)	0.9632 (3)	5.9 (2)
N12	0.8849 (7)	0.3504 (7)	0.6079 (4)	7.0 (2)
N13	0.5450 (7)	0.1772 (7)	0.2549 (4)	8.1 (3)
C111	0.1660 (8)	0.2238 (8)	0.9445 (5)	6.3 (3)
C112	0.2388 (9)	0.3073 (9)	0.9118 (5)	7.9 (3)
C113	0.3427 (10)	0.2703 (10)	0.8975 (6)	9.0 (4)
C114	0.4177 (16)	0.3519 (16)	0.8721 (9)	15.6 (7)
C121	0.0795 (8)	0.3573 (8)	1.0017 (4)	6.2 (3)
C122	0.1526 (11)	0.3530 (10)	1.0547 (5)	8.9 (4)
C123	0.1754 (12)	0.4582 (11)	1.0878 (6)	10.4 (4)
C124	0.2492 (12)	0.5424 (12)	1.0522 (7)	10.9 (5)
C131	0.0088 (8)	0.1664 (8)	0.9986 (5)	6.3 (3)
C132	−0.1014 (9)	0.1780 (9)	1.0219 (5)	7.2 (3)
C133	−0.1317 (10)	0.0863 (10)	1.0620 (6)	8.5 (4)
C134	−0.2423 (13)	0.0897 (12)	1.0882 (7)	11.8 (5)
C141	−0.0144 (8)	0.2795 (8)	0.9133 (4)	6.1 (3)
C142	−0.0443 (9)	0.1895 (9)	0.8684 (5)	7.0 (3)
C143	−0.1257 (10)	0.2206 (10)	0.8235 (5)	8.3 (4)
C144	−0.1488 (10)	0.1381 (10)	0.7721 (6)	8.7 (4)
C211	0.9432 (10)	0.2710 (9)	0.5763 (5)	8.3 (4)
C212	0.9494 (11)	0.1685 (10)	0.6056 (6)	9.0 (4)
C213	1.0129 (15)	0.1002 (13)	0.5697 (8)	12.8 (6)
C214	1.0130 (13)	−0.0119 (13)	0.5928 (7)	11.9 (5)
C221	0.9362 (9)	0.3771 (9)	0.6700 (5)	7.6 (3)
C222	1.0596 (10)	0.4075 (10)	0.6696 (5)	8.8 (4)
C223	1.1043 (13)	0.4373 (14)	0.7316 (7)	11.6 (5)
C224	1.2247 (14)	0.4681 (13)	0.7332 (8)	13.0 (6)
C231	0.7670 (9)	0.3096 (10)	0.6181 (5)	7.8 (3)
C232	0.6993 (10)	0.2853 (11)	0.5601 (6)	9.5 (4)
C233	0.5804 (13)	0.2433 (14)	0.5748 (7)	11.9 (5)
C234	0.5045 (19)	0.2298 (18)	0.5212 (10)	18.3 (8)
C241	0.8936 (10)	0.4489 (9)	0.5707 (5)	8.1 (3)
C242	0.8319 (12)	0.5335 (10)	0.5922 (6)	9.5 (4)
C243	0.8369 (15)	0.6280 (14)	0.5459 (8)	13.4 (6)
C244	0.7666 (29)	0.6165 (27)	0.5029 (15)	27.2 (15)
C311	0.4656 (10)	0.0787 (9)	0.2348 (6)	8.5 (4)
C312	0.5184 (12)	0.0082 (11)	0.1941 (7)	11.2 (5)
C313	0.4451 (14)	−0.0998 (13)	0.1857 (7)	12.4 (5)
C314	0.4578 (14)	−0.1678 (14)	0.2389 (8)	13.5 (6)
C321	0.6419 (10)	0.1446 (11)	0.2900 (6)	9.1 (4)
C322	0.6217 (15)	0.0835 (15)	0.3420 (8)	13.6 (6)
C323	0.7118 (15)	0.0469 (15)	0.3724 (8)	13.5 (6)
C324	0.6875 (17)	−0.0049 (17)	0.4328 (10)	17.0 (8)
C331	0.5825 (11)	0.2418 (11)	0.2037 (6)	9.9 (4)
C332	0.4954 (12)	0.2791 (12)	0.1647 (7)	10.9 (5)
C333	0.5379 (20)	0.3319 (21)	0.1088 (10)	18.8 (9)
C334	0.4726 (26)	0.3639 (26)	0.0709 (14)	25.2 (14)
C341	0.4767 (10)	0.2373 (9)	0.2951 (5)	8.3 (4)
C342	0.5380 (11)	0.3366 (10)	0.3198 (6)	9.5 (4)
C343	0.4695 (12)	0.3822 (12)	0.3670 (7)	11.2 (5)
C344	0.5309 (15)	0.4816 (15)	0.3990 (8)	14.4 (6)

\* The equivalent temperature factors ( $U_{\text{eq}}$ ) for the Pr atom and the N and S atoms of the thiocyanate groups were calculated from the anisotropic temperature factors with the aid of the following formula:

$$U_{\text{eq}} = \frac{1}{3} \sum_{ij} U_{ij} a_i^* a_j^* a_i a_j$$

The other  $U$  values are isotropic ones. The  $U$  values presented above are multiplied by a factor of 100.

Table 3. Selected bond distances (Å) and angles (°) for  $[\text{Pr}(\text{NCS})_6]^{3-}$  and  $[(\text{C}_4\text{H}_9)_4\text{N}]^+$  groups

Pr-N3	2.422 (11)	Pr-N5	2.434 (11)
Pr-N1	2.425 (12)	Pr-N2	2.448 (11)
Pr-N6	2.424 (10)	Pr-N4	2.465 (11)
N1-Pr-N2	87.8 (4)	N1-Pr-N3	174.7 (4)
N1-Pr-N4	88.7 (4)	N1-Pr-N5	86.8 (4)
N1-Pr-N6	89.9 (4)	N2-Pr-N3	95.6 (4)
N2-Pr-N4	176.5 (4)	N2-Pr-N5	91.1 (4)
N2-Pr-N6	89.7 (3)	N3-Pr-N4	87.9 (4)
N3-Pr-N5	89.0 (4)	N3-Pr-N6	94.2 (4)
N4-Pr-N5	88.6 (4)	N4-Pr-N6	90.4 (4)
N5-Pr-N6	176.6 (4)		
N1-C1	1.149 (17)	Pr-N1-C1	171.0 (10)
N2-C2	1.155 (18)	Pr-N2-C2	173.6 (9)
N3-C3	1.124 (16)	Pr-N3-C3	177.1 (10)
N4-C4	1.121 (17)	Pr-N4-C4	172.7 (10)
N5-C5	1.142 (17)	Pr-N5-C5	171.3 (11)
N6-C6	1.163 (17)	Pr-N6-C6	168.6 (10)
C1-S1	1.626 (13)	N1-C1-S1	177.2 (12)
C2-S2	1.621 (14)	N2-C2-S2	177.3 (12)
C3-S3	1.638 (13)	N3-C3-S3	177.3 (11)
C4-S4	1.627 (13)	N4-C4-S4	178.3 (12)
C5-S5	1.611 (13)	N5-C5-S5	178.1 (13)
C6-S6	1.605 (14)	N6-C6-S6	178.9 (13)
N11-C111	1.519 (13)	C111-N11-C121	110.2 (7)
N11-C121	1.546 (12)	C111-N11-C131	104.6 (7)
N11-C131	1.521 (13)	C111-N11-C141	113.5 (7)
N11-C141	1.483 (13)	C121-N11-C131	110.4 (7)
		C121-N11-C141	106.7 (7)
		C131-N11-C141	111.5 (7)
N12-C211	1.514 (16)	C211-N12-C221	111.7 (9)
N12-C221	1.548 (14)	C211-N12-C231	112.2 (8)
N12-C231	1.526 (14)	C211-N12-C241	107.0 (8)
N12-C241	1.538 (15)	C221-N12-C231	104.5 (8)
		C221-N12-C241	109.7 (8)
		C231-N12-C241	111.7 (9)
N13-C311	1.567 (14)	C311-N13-C321	110.0 (9)
N13-C321	1.522 (16)	C311-N13-C331	111.8 (9)
N13-C331	1.506 (17)	C311-N13-C341	103.6 (8)
N13-C341	1.538 (16)	C321-N13-C331	110.4 (9)
		C321-N13-C341	109.6 (9)
		C331-N13-C341	111.2 (9)

within the equatorial N1-N5-N3-N6 plane yielding the tetragonal distortion as the dominant one. The equatorial and axial angles differ only slightly from the ideal 90 and 180°, respectively.

Six-coordinated RE atoms can frequently be found among the smaller, *i.e.* heavier, lanthanides as well as for yttrium and scandium. The lighter lanthanides possessing coordination number six are less common. However, at least in the perovskite-related mixed oxide of barium, praseodymium and molybdenum,  $\text{BaPrMoO}_6$  (Brandle & Steinfink, 1971), and in trichlorotris(hexamethylphosphoramidate)praseodymium(III) (Radonovich & Glick, 1973), six-coordinated Pr atoms are found. The RE thiocyanate complexes are thus marked - though not unique - exceptions in the general trend.

The alignment of the thiocyanate groups towards the praseodymium ion is slightly distorted from linear. The mean value of 172.4 (10)° for the Pr-N-C angle remains well within the limits (between 160 and 180°) found for other nitrogen-bonded thiocyanate-metal complexes (Wells, 1984). The internal thiocyanate N-C-S chain is close to linear [average 177.8 (12)°]

and does not vary much from one group to another. The average C-N and C-S distances are 1.142 (17) and 1.622 (13) Å; the latter corresponds well to a typical C-S bond distance, whereas the C-N length is slightly below the typical value of 1.16 Å (Wells, 1984).

The tetra-*n*-butylammonium cation contains a tetrahedrally coordinated N atom. The mean C-N distances are in agreement with the corresponding values found for other tetra-*n*-butylammonium salts (Bonamico, Jeffrey & McMullan, 1962; McMullan, Bonamico & Jeffrey, 1963). In contrast to  $\text{Bu}_4\text{N}(\text{Ag}_3\text{I}_4)$  (Gilmore, Tucker & Woodward, 1971),  $(\text{Bu}_4\text{N})_2[\text{Mo}_2\text{O}_3\text{S}(\text{C}_4\text{O}_2\text{S}_2)_2]$  (Altmeppen & Mattes, 1980) and  $\text{Bu}_4\text{NIO}_4$  (Carpy, Goursolle, Leger & Nivaud, 1977), the inner coordination sphere of the N atom is not disordered. In the *n*-butyl chains, however, the thermal parameters of some of the C atoms (*cf.* Table 2) as well as some C-C distances suggest orientational disorder. The bulk of the C-C distances correspond to a single bond (1.53 to 1.56 Å) with a slight tendency to increase towards the end of the chain. The rather high *R* and *wR* values, 7.7 and 8.2%, respectively, reflect the structural disorder in the *n*-butyl chains.

The exact nature and origin of the disorder are not obvious since the extent and actual place of disorder in the  $\text{Bu}_4\text{N}^+$  cation varies from one compound to another as shown, for example, in  $(\text{Bu}_4\text{N})_2(\text{Cu}_2\text{I}_4)$  (Asplund, Jagner & Nilsson, 1982). Asplund & Jagner (1984) have, however, concluded that electrostatic and packing effects are responsible for disorder in  $[(\text{C}_3\text{H}_7)_4\text{N}]_2(\text{Cu}_4\text{Br}_6)$ . A more detailed analysis of this disorder is out of the scope of this work. As far as the optical properties of the  $\text{Pr}^{3+}$  ion are considered, the disorder in the *n*-butyl chains situated far from the Pr atom should have only minor importance.

Financial aid to one of the authors (JH) from the Academy of Finland is gratefully acknowledged.

## References

- ALMEIDA SANTOS, R. H. DE & LECHAT, J. R. (1980). *Quim. Nova*, **1**, 49.
- ALTMEPPEEN, D. & MATTES, R. (1980). *Acta Cryst.* **B36**, 1942-1944.
- ASPLUND, M. & JAGNER, S. (1984). *Acta Chem. Scand. Ser. A*, **38**, 725-730.
- ASPLUND, M., JAGNER, S. & NILSSON, M. (1982). *Acta Chem. Scand. Ser. A*, **36**, 751-755.
- BONAMICO, M., JEFFREY, G. A. & McMULLAN, R. K. (1962). *J. Chem. Phys.* **37**, 2219-2231.
- BRANDLE, C. D. & STEINFINK, H. (1971). *Inorg. Chem.* **10**, 922-926.
- CARPY, A., GOURSOLLE, M., LEGER, J.-M. & NIVAUD, E. (1977). *C. R. Acad. Sci. Sér. C*, **285**, 311-314.
- CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891-1898.
- GILMORE, C. J. (1983). *MITHRIL. A Computer Program for the Automatic Solution of Crystal Structures from X-ray Data*. Univ. of Glasgow, Scotland.

- GILMORE, C. J., TUCKER, P. A. & WOODWARD, P. (1971). *J. Chem. Soc. A*, pp. 1337–1341.
- International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- MCMULLAN, R. K., BONAMICO, M. & JEFFREY, G. A. (1963). *J. Chem. Phys.* **39**, 3295–3310.
- MALTA, O. L., AZEVEDO, W. M., GOUVEIA, E. A. & DE SA, G. F. (1982). *J. Lumin.* **26**, 337–343.
- MARTIN, J. L., THOMPSON, L. C., RADONOVICH, L. J. & GLICK, M. D. (1968). *J. Am. Chem. Soc.* **90**, 4493–4494.
- RADONOVICH, L. J. & GLICK, M. D. (1973). *J. Inorg. Nucl. Chem.* **35**, 2745–2752.
- SHANNON, R. D. (1976). *Acta Cryst.* **A32**, 751–767.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- WELLS, A. F. (1984). *Structural Inorganic Chemistry*. Oxford: Clarendon Press.

*Acta Cryst.* (1987). **C43**, 2067–2069

## Structure du L- $\alpha$ -Alaninate de Cadmium Trihydraté

PAR A. DÉMARET

*Laboratoire de Chimie Physique, Université de Paris VII, 2 place Jussieu, 75005 Paris, France*

ET F. ABRAHAM

*Laboratoire de Cristalochimie et Physicochimie du Solide, Ecole Nationale Supérieure de Chimie de Lille, BP 108, 59652 Villeneuve d'Ascq CEDEX, France*

(Reçu le 8 décembre 1986, accepté le 17 juin 1987)

**Abstract.**  $[\text{Cd}(\text{C}_3\text{H}_6\text{NO}_2)_2] \cdot 3\text{H}_2\text{O}$ ,  $M_r = 342.6$ , trigonal,  $P3_121$ ,  $a = 6.376$  (3),  $c = 25.59$  (2) Å,  $V = 901$  (1) Å<sup>3</sup>,  $Z = 3$ ,  $D_x = 1.86$  (4) g cm<sup>-3</sup>, Mo  $K\alpha$ ,  $\lambda = 0.7107$  Å,  $\mu = 18.4$  cm<sup>-1</sup>,  $F(000) = 516$ ,  $T = 298$  K,  $R = 0.031$ ,  $wR = 0.040$  ( $w = 1$ ) for 1109 independent reflexions. The metal coordination is octahedral; two alanine molecules are coordinated to the Cd atom as a bidentate ligand with a *cis-O,O-trans-N,N* donor set while the other two coordination positions are occupied by oxygen atoms of water molecules. The amino groups, carboxylic groups and the waters of coordination are fully hydrogen bonded to form sheets parallel to the (001) plane. These sheets are hydrogen bonded by the other water molecule.

**Introduction.** Au point de vue médical, il est maintenant établi que l'ion Cd<sup>2+</sup> interfère avec le métabolisme de l'ion Cu<sup>2+</sup> (Sarkar, 1981); Hill, Matrone, Payne & Barber (1963) ont montré la toxicité du cadmium sur les poulets dont le régime alimentaire présentait un déficit en cuivre et en fer. Ces phénomènes ont été attribués (Starcher, 1969) à une compétition (effet antagoniste) entre les ions cuivre, zinc et cadmium au niveau des sites de fixation sur les protéines intestinales.

D'autre part, nos travaux sur la L- $\beta$ -phénylalanine (Démaret, Abello, Fourati & Lapluye, 1978; Démaret, Mhiri, Fourati, Abello & Lapluye, 1979; Mhiri, Démaret & Lapluye, 1983) portant sur neuf ions divalents d'éléments de transition ont montré que les complexes à l'état solide (L-Phe)<sub>2</sub>M.nH<sub>2</sub>O présentaient

un taux d'hydratation maximum correspondant à  $n = 2$ . Ceci a pu être interprété à partir des modèles que constituent les structures des complexes anhydres [(L-Phe)<sub>2</sub>Cu (van der Helm, Lawson & Enwall, 1971)] ou dihydratés [(glycine)<sub>2</sub>Ni.2H<sub>2</sub>O (Freeman, Guss & Sinclair, 1968) et (L- $\beta$ -alanine)<sub>2</sub>Ni.2H<sub>2</sub>O (Jose, Pant & Biswas, 1964)].

Nous avons cherché à établir un parallèle entre L- $\beta$ -phénylalaninates et L- $\alpha$ -alaninates pour mettre en évidence l'influence du noyau benzénique. Parmi les alaninates, nous avons préparé le composé trihydraté (L- $\alpha$ -Ala)<sub>2</sub>Cd.3H<sub>2</sub>O (Démaret & Mercier, 1983). Nous présentons les résultats de la détermination structurale de ce composé.

**Partie expérimentale.** Monocristaux obtenus par la méthode décrite précédemment (Démaret & Mercier, 1983) en forme de prisme à base dodécagonale. Les faces latérales sont les paires (100), (010), (1 $\bar{1}$ 0), (1 $\bar{2}$ 0), (210) et (110) équidistantes de 0,5 mm, les faces latérales (001) sont équidistantes de 0,235 mm. Paramètres de maille affinés à partir de mesures sur poudre, diffractomètre Philips PW 1011, étalon interne Si. Mesures intensités monocristal sur diffractomètre automatique Philips PW 1100. Monochromateur au graphite, radiation Mo  $K\alpha$ . 1242 réflexions mesurées pour  $2 < \theta < 31^\circ$  et  $0 \leq h \leq 8$ ,  $0 \leq k \leq 8$ ,  $0 \leq l \leq 37$ , trois réflexions de contrôle ( $\bar{1}\bar{1}\bar{1}$ ,  $0\bar{1}\bar{1}$ ,  $1\bar{1}\bar{4}$ ) testées toutes les 80 mesures, 1109 réflexions indépendantes telles que  $I \geq 3\sigma(I)$ , corrections d'absorption:  $\mu = 18,4$  cm<sup>-1</sup>,  $T_{\min} = 0,471$  (251),  $T_{\max} = 0,657$  (300).