Structure of Tris(tetrabutylammonium) Hexaisothiocyanatoerbate(III)

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Abstract. $[C_{16}H_{36}N]_3[Er(NCS)_6]$, $M_r = 1243·13$, triclinic, $A\bar{1}$, $a = 22·72$ (1), $b = 16·80$ (1), $c = 18·87$ (1) Å, $\alpha = 88·00$ (1), $\beta = 89·15$ (1), $\gamma = 92·47$ (1)°, $V = 7190·6$ Å^3, $Z = 4$, $D_m = 1·13$ (1), $D_x = 1·15$ g cm^{-3}, $\lambda(Mo\ K\alpha) = 0·7107$ Å, $\mu = 13·85$ cm^{-1}, $F(000) = 2636$, $T = 297$ K, $R(F) = 0·076$ and $wR(F) = 0·119$ for 5397 unique reflections with $I > 3\sigma(I)$. The asymmetric unit consists of a complex ion containing an Er atom that is octahedrally coordinated to six thiocyanate ligands through the N atoms and three tetra-*n*-butylammonium cations.

Introduction. Complexes of the lanthanide ions having a coordination number of six and octahedral geometry are relatively rare. In 1968, it was first shown that such discrete complexes with the thiocyanate ion could be formed with the tetrabutylammonium cation as the counter ion (Martin, Thompson, Radonovich & Glick, 1968). Since that report there has been renewed interest in the thiocyanate (and cyanate) ion as a ligand with the lanthanides (Burmeister, Patterson & Deardorff, 1969; Dieck & Moeller, 1973). The six-coordinate basically octahedral coordination has been confirmed in several studies of the spectral and magnetic properties of $[Ln(NCS)_6]^{3-}$ and $[Ln(NCO)_6]^{3-}$ (Amberger, Fischer & Rosenbauer, 1976; Bünzli & Klein, 1978; Auzel, DeSá & Azevedo, 1980; Malta, Azevedo, Gouveia & DeSá, 1982; Strek, Mugeński, Cywiński, Hanuza & Jezowska-Trzebiatowska, 1987). That the coordination number and stoichiometries are dependent on the counter ion is shown by the isolation of $[(C_2H_5)_4N]_3Eu(NCS)_6$ (Bünzli & Klein, 1978), $[(C_2H_5)_4N]_4[M(SCN)_7(H_2O)]$ ($M =$ La–Er) (Tateyama, Kunigasu, Suzuki & Ouchi, 1988) and $[(CH_3)_4N]_4[M(NCS)_7]$ ($M =$ Dy, Er and Yb) (Matsumura & Ouchi, 1988).

Although a preliminary report of the synthesis and structure of $[(C_4H_9)_4N]_3[Er(NCS)_6]$ has been communicated (Martin, Thompson, Radonovich & Glick, 1968), details of the structure determination

have not yet been reported. Recently, as a prerequisite to a detailed spectroscopic study, Hiltunen, Hölsä, Strek & Jezowska-Trzebiatowska (1987) determined the structure of the isomorphous praseodymium complex. Because a precise knowledge of the structural parameters in the coordination sphere is necessary for the interpretation of the spectral properties and because the preliminary paper on the erbium complex is often cited as the prototype of this class of rare-earth complexes (Palenik, 1983), we now report the details of an X-ray structure determination recently carried out on a larger crystal of $[(C_4H_9)_4N]_3[Er(NCS)_6]$.

Experimental. The compound was synthesized by mixing warm ethanolic solutions of $ErCl_3.6H_2O$ and tetra-*n*-butylammonium thiocyanate in a 1:10 ratio. Upon standing small single crystals of the desired compound were deposited.

A pale-amber crystal of dimensions $0·57 \times 0·53 \times 0·43$ mm was mounted on a glass fiber with silicone adhesive and lattice constants were determined from 55 centered reflections in the range $9·5 \le 2\theta \le 16·5°$. The A-centered unit cell used for the structure determination (see *Abstract*) corresponds to a primitive cell with $a = 12·85$, $b = 22·72$, $c = 12·05$ Å, $\alpha = 92·32$, $\beta = 96·64$ and $\gamma = 90·99°$. The calculated density with $Z = 4$ was $1·15$ g cm^{-3} while the experimental density (by flotation in CCl_4 and benzene) was $1·13$ (1) g cm^{-3}. Intensity data were collected on a Picker diffractometer with a Crystal Logic automation system using Zr-filtered Mo $K\bar{\alpha}$ radiation at a scan rate of $4·5°$ min^{-1}. 6712 data in the range $2\theta \le 40°$ were collected and 5397 data with $I > 3\sigma(I)$ were taken as observed and utilized in the structure determination. Standard deviations were calculated from counting statistics and included an instability factor of $0·04$. Three standard reflections ($3\bar{7}1$, $10,0,0$, $\bar{7}1\bar{7}$) decreased by an average of 3% and a decay correction was applied to the data. $h = 0$ to 21, $k = -16$ to 16, $l = -18$ to 18. Isotropic refinement of the 70 atoms in the asymmetric unit produced $R(F) = 0·107$ and $wR(F) = 0·152$. All refinements

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utilized $1/\sigma^2$ weighting. Absorption corrections, from average path length calculations, were applied in the final cycles of refinement. The linear absorption coefficient was $13{\cdot}85$ cm^{-1} and the transmission factors ranged from $0{\cdot}59$ to $0{\cdot}47$. Full-matrix refinement of the 385 parameters treating the atomic thermal parameters in the $[\text{Er(NCS)}_6]^{3-}$ ion anisotropically and the cations isotropically produced R values of $R(F) = 0{\cdot}079$ and $wR(F) = 0{\cdot}122$. Relatively large thermal parameters were observed for two of the thermal C atoms [C(38) and C(42)] and a difference synthesis revealed well resolved alternate positions for these two C atoms with peaks of $2{\cdot}86$ and $1{\cdot}69$ e Å^{-3}. These two terminal CH$_3$ groups were then treated as half-occupied C atoms [C(38D) and C(42D)] in final full-matrix refinement on F which converged with $R(F) = 0{\cdot}076$ and $wR(F) = 0{\cdot}119$. Thermal parameters for these half-occupied atoms were well behaved on refinement. The shift-to-e.s.d. values for all atoms in the $[\text{Er(NCS)}_6]^{3-}$ anion were less than $0{\cdot}20$. A final difference synthesis revealed some orientational disorder in the cation chains with numerous peaks ranging from $1{\cdot}54$ to $1{\cdot}24$ e Å^{-3}. No simple model that was chemically sensible for the disordered chains and/or H-atom positions was obvious. Indeed the small magnitude of the residual peaks and the fairly well behaved thermal parameters for the existing positions would suggest relatively small fractional occupancy for the residual peaks. Thus no additional partially occupied C- or H-atom positions were included in final refinement and the data-to-parameter ratio was maintained at 14:1. The largest peak not associated with cation chains had a magnitude of $1{\cdot}23$ e Å^{-3} and was $0{\cdot}11$ Å from the Er position. The nature of this structure thus limits any detailed interpretation of the results and our model structure does not attempt to account for the complex disorder of the cation chains. All programs used were those supplied by Crystal Logic (Strouse, 1987). Atomic form factors and anomalous-dispersion corrections were from *International Tables for X-ray Crystallography* (1974). Final atomic coordinates, equivalent isotropic thermal parameters for the anion, and isotropic thermal parameters for the cations are listed in Table 1.*

Discussion. The crystal structure consists of discrete $[\text{Er(NCS)}_6]^{3-}$ ions that are well separated from $[(\text{C}_4\text{H}_9)_4\text{N}]^+$ cations. The asymmetric unit includes one $[\text{Er(NCS)}_6]^{3-}$ ion shown in Fig. 1 and three

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* Lists of structure factors, least-squares planes, anisotropic thermal parameters and bond distances in the cations have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52835 (30 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates for all atoms, equivalent isotropic thermal parameters for the $[\text{Er(NCS)}_6]^{3-}$ ion, and isotropic thermal parameters for the $[(\text{C}_4\text{H}_9)_4\text{N}]^+$ cations*

$$U_{eq} = (1/6\pi^2)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{eq}/U_{iso}(\text{Å}^2 \times 10^2)$
Er	0·24794 (3)	0·13882 (4)	0·07125 (4)	69·3 (6)
S(01)	0·2453 (2)	0·4362 (3)	0·1059 (3)	103 (4)
S(02)	0·2379 (2)	−0·1586 (3)	0·0344 (3)	114 (4)
S(03)	0·1141 (2)	0·1383 (3)	0·2887 (2)	76 (3)
S(04)	0·4086 (2)	0·0854 (3)	0·2499 (2)	81 (3)
S(05)	0·3861 (2)	0·1712 (3)	−0·1421 (3)	107 (4)
S(06)	0·0783 (2)	0·1605 (3)	−0·0999 (2)	80 (3)
C(01)	0·2516 (6)	0·3407 (10)	0·0932 (7)	59 (11)
C(02)	0·2393 (7)	−0·0669 (10)	0·0494 (8)	65 (11)
C(03)	0·1566 (7)	0·1331 (8)	0·2171 (9)	58 (10)
C(04)	0·3588 (7)	0·1071 (8)	0·1907 (9)	60 (11)
C(05)	0·3413 (7)	0·1608 (8)	−0·0745 (8)	57 (10)
C(06)	0·1311 (7)	0·1551 (7)	−0·0426 (8)	55 (10)
N(01)	0·2542 (6)	0·2750 (8)	0·0826 (7)	73 (10)
N(02)	0·2378 (6)	−0·0002 (9)	0·0597 (6)	75 (10)
N(03)	0·1850 (6)	0·1318 (8)	0·1665 (7)	73 (10)
N(04)	0·3235 (6)	0·1220 (7)	0·1500 (7)	72 (10)
N(05)	0·3089 (6)	0·1546 (7)	−0·0289 (7)	67 (9)
N(06)	0·1690 (6)	0·1510 (8)	−0·0020 (7)	72 (10)
N(07)	0·0370 (4)	0·3417 (5)	0·4006 (5)	41 (3)
N(08)	0·3934 (5)	0·3831 (6)	0·2669 (5)	54 (3)
N(09)	0·2539 (5)	0·8611 (6)	0·3192 (5)	57 (3)
C(07)	0·0017 (5)	0·4135 (7)	0·4219 (6)	48 (3)
C(08)	−0·0214 (6)	0·4622 (8)	0·3601 (7)	55 (4)
C(09)	0·0616 (7)	0·9783 (9)	0·1093 (8)	74 (4)
C(10)	0·0879 (8)	0·9220 (11)	0·1672 (9)	95 (5)
C(11)	0·0010 (6)	0·2169 (7)	0·1408 (6)	50 (3)
C(12)	0·0545 (6)	0·2524 (8)	0·0999 (7)	61 (4)
C(13)	0·0872 (7)	0·3163 (9)	0·1435 (8)	76 (5)
C(14)	0·0514 (8)	0·3948 (10)	0·1476 (9)	92 (5)
C(15)	0·0892 (6)	0·3673 (7)	0·3525 (6)	50 (3)
C(16)	0·1331 (6)	0·4258 (8)	0·3841 (7)	54 (4)
C(17)	0·1791 (6)	0·4521 (8)	0·3261 (7)	61 (4)
C(18)	0·2286 (7)	0·5045 (9)	0·3586 (8)	71 (4)
C(19)	0·0576 (5)	0·3051 (7)	0·4721 (6)	48 (3)
C(20)	0·0904 (6)	0·2265 (8)	0·4629 (7)	65 (4)
C(21)	0·1015 (7)	0·1939 (9)	0·5414 (8)	69 (4)
C(22)	0·1317 (10)	0·1152 (14)	0·5352 (12)	134 (8)
C(23)	0·4272 (6)	0·3933 (8)	0·3372 (7)	66 (4)
C(24)	0·3953 (7)	0·4430 (9)	0·3927 (8)	70 (4)
C(25)	0·4312 (8)	0·4400 (11)	0·4611 (10)	101 (6)
C(26)	0·4076 (8)	1·0007 (11)	0·0148 (10)	101 (6)
C(27)	0·3828 (6)	0·4631 (8)	0·2308 (7)	58 (4)
C(28)	0·4421 (7)	0·5098 (9)	0·2077 (8)	80 (5)
C(29)	0·4253 (8)	0·5855 (10)	0·1694 (9)	90 (5)
C(30)	0·4838 (10)	0·6328 (14)	0·1403 (12)	135 (8)
C(31)	0·3304 (6)	0·3454 (8)	0·2812 (7)	59 (4)
C(32)	0·3311 (7)	0·2688 (9)	0·3266 (8)	71 (4)
C(33)	0·2670 (8)	0·2322 (10)	0·3372 (9)	89 (5)
C(34)	0·2646 (9)	0·1575 (12)	0·3817 (10)	110 (6)
C(35)	0·4305 (6)	0·3319 (8)	0·2232 (7)	63 (4)
C(36)	0·4067 (7)	0·3194 (9)	0·1487 (8)	72 (4)
C(37)	0·4524 (9)	0·2668 (12)	0·1106 (10)	105 (6)
C(38)	0·5015 (15)	0·3123 (19)	0·0767 (17)	83 (10)
C(39)	0·2035 (7)	0·9119 (9)	0·3301 (8)	76 (5)
C(40)	0·1664 (8)	0·8859 (10)	0·3966 (9)	91 (5)
C(41)	0·1109 (15)	0·9429 (18)	0·4017 (16)	177 (11)
C(42)	0·0585 (27)	0·9087 (35)	0·3754 (32)	168 (20)
C(43)	0·2923 (6)	0·8568 (8)	0·3848 (7)	67 (4)
C(44)	0·3171 (7)	0·9404 (9)	0·4040 (8)	78 (5)
C(45)	0·3694 (8)	0·9241 (11)	0·4587 (9)	94 (5)
C(46)	0·3925 (11)	1·0033 (15)	0·4795 (13)	147 (9)
C(47)	0·2334 (6)	0·7701 (8)	0·3077 (7)	65 (4)
C(48)	0·1896 (7)	0·7623 (10)	0·2490 (8)	81 (5)
C(49)	0·1830 (9)	0·6723 (12)	0·2326 (10)	107 (6)
C(50)	0·2398 (10)	0·6430 (13)	0·1924 (11)	125 (7)
C(51)	0·2875 (7)	0·8925 (9)	0·2532 (8)	74 (5)
C(52)	0·3417 (9)	0·8485 (12)	0·2366 (11)	112 (6)
C(53)	0·3697 (10)	0·8793 (13)	0·1693 (11)	120 (7)
C(54)	0·4351 (14)	0·8448 (18)	0·1596 (16)	190 (12)
C(38D)	0·4535 (17)	0·2590 (22)	0·0386 (20)	103 (12)
C(42D)	0·0701 (20)	0·9209 (25)	0·4467 (24)	117 (14)

cations. A packing diagram is shown in Fig. 2 while bond distances and angles are listed in Table 2.

The most interesting aspect of the structure is the coordination sphere about the Er^{3+} ion. The Er

atom is coordinated to six NCS⁻ ligands in a slightly distorted octahedral geometry. Planes defined by Er, N(03),N(04),N(05),N(06) (*A*), Er,N(01),N(03),N(02), N(05) (*B*), and Er,N(01),N(04),N(02),N(06) (*C*) have average deviations from planarity of 0·043, 0·015 and 0·023 Å, respectively, and form dihedral angles of 90·2 (*A–B*), 89·8 (*A–C*) and 92·3° (*B–C*). The N—Er—N bond angles in Table 2 also reflect the closeness to the idealized angles of 90 and 180°.

The Er—N bond distances range from 2·28 (1) to 2·35 (1) Å. The average Er—N distance is 2·31 Å with an average deviation from the mean of 0·02 Å. This distance is 0·13 Å smaller than the average Pr—N value reported in the isomorphous Pr com-
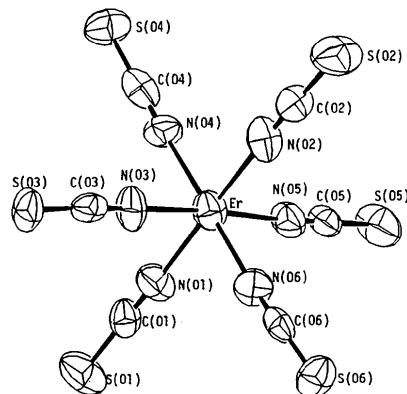
Table 2. *Interatomic distances* (Å) *and angles* (°)

Er—N(03)	2·28 (1)	S(04)—C(04)	1·65 (2)
Er—N(06)	2·29 (1)	S(05)—C(05)	1·62 (2)
Er—N(01)	2·30 (1)	S(06)—C(06)	1·63 (2)
Er—N(04)	2·31 (1)	C(01)—N(01)	1·13 (2)
Er—N(05)	2·33 (1)	C(02)—N(02)	1·15 (2)
Er—N(02)	2·35 (1)	C(03)—N(03)	1·15 (2)
S(01)—C(01)	1·64 (2)	C(04)—N(04)	1·15 (2)
S(02)—C(02)	1·57 (2)	C(05)—N(05)	1·12 (2)
S(03)—C(03)	1·66 (2)	C(06)—N(06)	1·16 (2)
N(03)—Er—N(06)	89·4 (5)	N(05)—Er—N(02)	92·4 (4)
N(03)—Er—N(01)	87·9 (5)	N(01)—C(01)—S(01)	177·3 (14)
N(03)—Er—N(04)	87·5 (5)	N(02)—C(02)—S(02)	177·1 (15)
N(03)—Er—N(05)	175·7 (4)	N(03)—C(03)—S(03)	177·5 (14)
N(03)—Er—N(02)	90·9 (4)	N(04)—C(04)—S(04)	179·1 (14)
N(06)—Er—N(01)	90·3 (4)	N(05)—C(05)—S(05)	177·9 (14)
N(06)—Er—N(04)	176·4 (5)	N(06)—C(06)—S(06)	179·6 (13)
N(06)—Er—N(05)	88·0 (4)	C(01)—N(01)—Er	172·0 (13)
N(06)—Er—N(02)	88·1 (5)	C(02)—N(02)—Er	171·5 (12)
N(01)—Er—N(04)	91·3 (4)	C(03)—N(03)—Er	174·0 (12)
N(01)—Er—N(05)	88·8 (4)	C(04)—N(04)—Er	173·9 (12)
N(01)—Er—N(02)	178·0 (4)	C(05)—N(05)—Er	175·5 (12)
N(04)—Er—N(05)	95·2 (5)	C(06)—N(06)—Er	175·6 (12)
N(04)—Er—N(02)	90·2 (4)		

Fig. 1. *ORTEP* (Johnson, 1971) diagram at 50% probability of the [Er(NCS)₆]³⁻ ion showing the atomic numbering scheme.
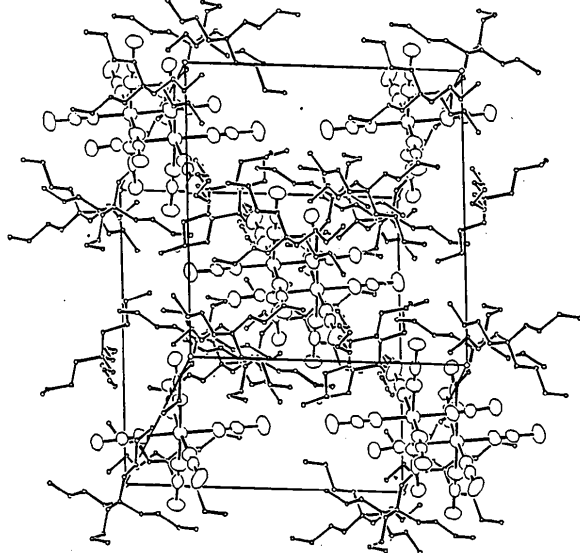

Fig. 2. *ORTEP* (Johnson, 1971) packing diagram. The *c* axis is horizontal and the *b* axis is vertical. Thermal parameters for the [Er(NCS)₆]³⁻ ion are displayed at 50% probability while isotropic thermal parameters of the [(C₄H₉)₄N]⁺ cations have been deliberately reduced to $B = 0·5$ Å² for clarity. The two disordered terminal C atoms are also not displayed for clarity.

pound (Hiltunen, Hölsä, Strek & Jezowska-Trzebiatowska, 1987). Using the Shannon values for the Er³⁺ and Pr³⁺ radii (Shannon, 1976), one would expect Er³⁺ to be 0·10 Å smaller. Thus the observed difference is close but slightly shorter than predicted. Bond-length distortions from octahedral geometry appear slightly different in the two compounds. Whereas two Pr—N bonds that are *trans* to one another are reported as significantly longer than the equatorial bonds (Hiltunen, Hölsä, Strek & Jezowska-Trzebiatowska, 1987) in the praseo-dymium compound, the two longest Er—N bonds in the erbium compound are *cis* to one another but only one distance is greater than 3σ from the average.

Other average bond parameters between the Pr and Er compounds are remarkably consistent. The average C—N distances in the NCS⁻ ligands are 1·14 (2) Å in both structures while the average S—C distance is 1·63 (2) Å in the Er compound and 1·62 (1) in the Pr compound. Similarly, the average N—C—S angle is 178 (1)° in both structures while the Er—N—C angle is 174 (1)° and the Pr—N—C angle is 172 (1)° (Hiltunen, Hölsä, Strek & Jezowska-Trzebiatowska, 1987).

The relatively large e.s.d.'s, the absence of substantial diffraction data above 2θ of 40°, and the relatively high R value observed for this structure can be attributed to the orientational disorder of the [(C₄H₉)₄N]⁺ cations. As Hiltunen, Hölsä, Strek & Jezowska-Trzebiatowska (1987) point out, this should have little effect on the optical properties associated with the metal coordination sphere.

The most notable difference between the observed results and those reported for the seven-coordinate [(CH₃)₄N]₄[Er(NCS)₇] complex (Matsumura & Ouchi, 1988) is that the average Er—N bond length is 0·04 Å longer in the seven-coordinate complex. An

increase in metal size is certainly expected with an increase in coordination number. How the cation can influence the stoichiometry and coordination number is difficult to assess because complete results were not reported for $[(CH_3)_4N]_4[Er(NCS)_7]$. Packing interactions in $[(C_4H_9)_4N]_3[Er(NCS)_6]$ appear normal and the closest distance between Er atoms is 12·37 Å. From the packing diagram in Fig. 2 it appears that $[Er(NCS)_6]^{3-}$ ions are surrounded by aliphatic carbon chains from $(C_4H_9)_4N^+$ cations. The smaller $(CH_3)_4N^+$ cations would be expected to leave the metal coordination sphere more exposed.

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Structure of Thallium Hydrogen Phthalate*

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Abstract. $[Tl(C_8H_5O_4)]$, $M_r = 369·43$, orthorhombic $P2_1ab$, $a = 6·615$ (2), $b = 10·047$ (2), $c = 12·878$ (2) Å, $V = 855·9$ Å^3, $Z = 4$, $D_x = 2·868$ g cm^{-3}, λ(Mo $K\alpha_1$) $= 0·70926$ Å, $\mu = 190·4$ cm^{-1}, $F(000) = 649·7$, room temperature, final $R = 0·039$ for 613 observed reflections $[I > 2\sigma(I)]$ out of 821 independent reflections. Bond lengths and bond angles are within the normal range. The aromatic ring is planar within 0·01 Å. The planes of the carboxyl groups containing C(1) and C(8) are rotated out of plane from the aromatic ring by 67·9 and 29·3°, respectively.

Introduction. Thallium hydrogen phthalate (I), has been suggested as a possible monochromator for use in soft X-ray spectroscopy (Bohm & Ulmer, 1970). Compound (I) yields 3·7 times the intensity of potas-

sium hydrogen phthalate at the same wavelength and resolution in the region from about 10 to 100 Å (Okaya, 1965). Despite the interest generated by this important application, a single-crystal X-ray structure has not been previously reported.

Experimental. Crystals of (I) were obtained from Quartz Products Co., Plainfield, NJ, and were used as received. Crystal dimensions were 0·16 × 0·13 × 0·11 mm. CAD-4 diffractometer, $\theta-2\theta$ scans. θ-scan range $(0·8 + 0·34\tan\theta)°$. Scan speed 1·0 to 8·2° min^{-1}. Background first and last one-sixth of scan range. Graphite-monochromated Mo $K\alpha$ radiation. Unit cell from 25 reflections, $14 \le \theta \le 21°$. Empirical ψ-scan and spherical absorption corrections, transmission = 0·041–0·012. $(\sin\theta)/\lambda_{max} = 0·353$ Å^{-1}. Index range $-7 \le h \le 7$, $0 \le k \le 11$, $0 \le l \le 15$. Standard reflections 400 and 060 showed max. r.m.s. variation of 1·9% with no obvious trends. R_{int}