

Fig. 2. A projection of the crystal structure along the *a* axis.

The compounds *trans*-dichlorobis(1-methylimidazole)palladium(II) (Navarro-Ranninger, Martínez-Carrera & García-Blanco, 1983) and *trans*-dichlorobis(2-methylimidazole)palladium(II) show very similar structural relations in molecular geometry.

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## Structure of a Cubic Form of Tetraethylammonium Octakis(thiocyanato-*N*)thorate(IV), $[\text{N}(\text{C}_2\text{H}_5)_4]_4[\text{Th}(\text{NCS})_8]$

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**Abstract.**  $M_r = 1217.7$ , cubic,  $Pm\bar{3}m$ ,  $a = 11.589(5) \text{ \AA}$ ,  $V = 1556(2) \text{ \AA}^3$ ,  $Z = 1$ ,  $D_x = 1.300(2) \text{ Mg m}^{-3}$ ,  $\lambda(\text{Mo } K\alpha) = 0.71069 \text{ \AA}$ ,  $\mu(\text{Mo } K\alpha) = 2.74 \text{ mm}^{-1}$ ,  $T = 294 \text{ K}$ . The structure solved from intensities measured on a single crystal was refined to a final  $R = 0.039$ . The Th atom is eight-coordinated in a strictly cubic configuration. The structure is disordered in the sense that occupancy

factors of the tetraethylammonium positions are less than unity given with equal probability. These tetraethylammonium ions are of two kinds: three sandwiched between the faces of adjacent cubic anions occupy two positions related by a unique fourfold axis, while the fourth lies at the center of the cell with six positions given by the three fourfold axes. The cubic structure differs from the tetragonal one in the packing of consecutive layers of cubic anions, which are not translated.

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**Introduction.** Some years ago, the crystal structure of tetraethylammonium octakis(thiocyanato-*N*)uranate(IV),  $[\text{N}(\text{C}_2\text{H}_5)_4]_4[\text{U}(\text{NCS})_8]$  (I) (Countryman & McDonald, 1971), confirmed the exceptional eight-fold cubic coordination of uranium(IV) in the complex. Soon after, the corresponding complexes of Th, Pa, Np, and Pu were reported as isostructural ones by comparison of their powder patterns (Alkazaz, Bagnall, Brown & Whittaker, 1972); unit-cell dimensions were given for all compounds but the Th one.

The unusual cubic coordination was discussed by Bombieri, Moseley & Brown (1975) who found a square-antiprism coordination in the analogous Cs compound  $\text{Cs}_4[\text{U}(\text{NCS})_8]$ . They concluded from spectral studies that (I) also adopts the square-antiprism environment when dissolved in non-aqueous solvents. This fact agrees with the suggestion of Countryman & McDonald (1971) that the cruciform shape of the  $\text{N}(\text{C}_2\text{H}_5)_4^+$  ion may force the  $\text{U}(\text{NCS})_8$  group to adopt cubic coordination in the solid state.

Folcher, Marquet-Ellis, Rigny, Goodman & Soulie (1976), Soulie & Goodman (1976) and Soulie (1977), however, pointed out that the cubic coordination should be maintained in nitromethane solutions. To obtain a better understanding of the NMR spectra and evaluate the chemical shift due to the diamagnetic contribution, crystals of the Th complex  $[\text{N}(\text{C}_2\text{H}_5)_4]_4[\text{Th}(\text{NCS})_8]$ , were prepared in our laboratory and the structure determination was undertaken.

**Experimental.** Different preparations were examined by powder pattern techniques; curiously they showed variations in the intensity ratios of Debye-Scherrer lines, without extra lines which would have indicated the presence of an impurity. In fact, it has been possible to select, with a microscope, two kinds of crystals: one kind gave the typical diagram of the well known tetragonal phase, while the other had a simpler but closely related diagram (Table 1).<sup>\*</sup> This new phase has all its Debye-Scherrer lines common to those of the tetragonal phase; they were all indexed in a cubic cell with parameter  $a = 11.589$  (5) Å obtained from least-squares adjustment of 25 reflections measured on an automatic diffractometer. This value is close to half the  $c$  value measured under the same conditions for the tetragonal phase [ $a = 11.635$  (4),  $c = 23.150$  (6) Å]. After preliminary photographic examination a crystal (edge  $\sim 0.2$  mm) of the cubic phase was used to collect intensity data: Nonius CAD-4 diffractometer, monochromatized Mo  $K\alpha$  radiation, 1610 reflections measured in one quadrant of the reciprocal sphere, using  $\omega/2\theta$  mode, 1122 reflections with  $I > 3\sigma(I)$  considered observed and retained for structure analysis,

<sup>\*</sup> See deposition footnote.

Lorentz and polarization corrections applied, no absorption correction.

As no systematic extinction was observed, the space group is a primitive one. The equality of intensities of pairs  $hkl/khl$  leads to Laue symmetry  $m\bar{3}m$ . Three space groups are then possible, either the noncentrosymmetric  $P432$  and  $P\bar{4}3m$ , or the centrosymmetric  $Pm\bar{3}m$ . The latter was finally chosen since it gave a better description of the structural disorder, probably rotational, associated with the tetraethylammonium groups.

Structure solved with *SHELX* (Sheldrick, 1976); after averaging symmetry-equivalent reflections, 279 unique reflections remained;  $R_{\text{int}} = 0.024$ ; atomic scattering factors incorporated in the program used for all atoms except Th; the scattering factor of  $\text{Th}^{4+}$  introduced by coefficients for analytical approximation, anomalous-dispersion taken into account (*International Tables for X-ray Crystallography*, 1974); it was clear that the Th position was 000; the structure was then solved from successive difference syntheses; N, C and S atoms of the NCS groups and one of the N atoms of the tetraethylammonium groups were refined anisotropically, the rest isotropically; the C-C bond in the  $\text{N}(\text{C}_2\text{H}_5)_4^+$  ions was constrained to 1.54 Å; H atoms were not located. Final  $R = 0.039$ ;  $F(000) = 538$  (excluding H atoms); unit weights.

**Discussion.** Atomic positional and thermal parameters are given in Table 2. Table 3 lists some characteristic distances.

<sup>\*</sup> Lists of structure factors and anisotropic thermal parameters, and Tables 1 and 4 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38206 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Atomic positional and thermal parameters ( $\text{Å}^2 \times 10^3$ )

	<i>x</i>	<i>y</i>	<i>z</i>	<i>k</i>	$U_{\text{iso}}$ or $U_{\text{eq}}$
Th	0	0	0		32 (1)
N(1)	0.1231 (8)	0.1231 (8)	0.1231 (8)		83 (5) <sup>*</sup>
C(1)	0.180 (1)	0.180 (1)	0.180 (1)		62 (5) <sup>*</sup>
S(1)	0.2599 (3)	0.2599 (3)	0.2599 (3)		108 (2) <sup>*</sup>
N(2)	0	0	$\frac{1}{2}$		82 (16) <sup>*</sup>
C(21)	0.219 (2)	0	$\frac{1}{2}$		145 (9)
C(22)	0.108 (2)	0	0.425 (2)	$\frac{1}{2}$	112 (9)
N(3)	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$		43 (9)
C(31)	0.278 (3)	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{3}$	84 (11)
C(32)	0.391 (3)	$\frac{1}{2}$	0.428 (3)	$\frac{1}{6}$	42 (13)

$$* U_{\text{eq}} = \frac{1}{3}(U_{11} + U_{22} + U_{33}).$$

Table 3. Characteristic distances (Å) and angles ( $^\circ$ )

Th-N(1)	2.47 (2)	N(1)-N(1)	2.85 (2)
N(1)-C(1)	1.15 (2)	C(1)-C(1)	4.17 (3)
C(1)-S(1)	1.59 (2)	S(1)-S(1)	6.02 (1)
N(2)-C(22)	1.53 (2)		
C(22)-C(21)	1.55 (2)	C(22)-N(2)-C(22)	110 (1)
N(3)-C(32)	1.52 (3)	N(2)-C(22)-C(21)	111 (2)
C(32)-C(31)	1.55 (2)	C(32) N(3)-C(32)	113 (3)
		N(3)-C(32)-C(31)	114 (3)

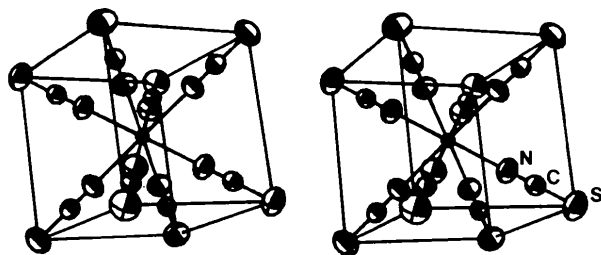


Fig. 1. A stereoview of the cubic environment of thorium(IV) (Johnson, 1965).

The structure is in fact close to that of the tetragonal form: the Th atom lies in a strictly cubic configuration with eight linear N—C—S groups along the diagonals (Fig. 1). The cubic symmetry also implies equivalence of the three tetraethylammonium groups sandwiched between the faces of adjacent cubes. As in the tetragonal form, there are two carbon ( $CH_2$ ) positions related by a  $\pi/2$  rotation around the respective fourfold axes at  $\frac{1}{2}, 0, 0$ ;  $0, \frac{1}{2}, 0$  and  $0, 0, \frac{1}{2}$  which have an occupancy factor of  $\frac{1}{2}$ . Such rotation leaves unchanged the C atom, but not the H atoms, of the  $CH_3$  group.

The center of the cell is occupied by a fourth tetraethylammonium anion lying in one of the six equiprobable positions (occupancy factor =  $\frac{1}{6}$ ) related by rotations around the three fourfold axes.

The essential difference between the cubic and tetragonal crystalline forms is a different packing of

identical layers of cubic anions, the latter being obtained from the former by a  $(\frac{1}{2}, \frac{1}{2}, 0)$  translation of consecutive layers. No evidence was found that the U compound exists in the cubic form: possibly, the variation of the  $c/a$  ratio with the size of the metal ion, and its value very close to 2 for the Th complex, provides justification (Table 4 gives cell dimensions and  $c/a$  ratios in the tetragonal series).\*

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\* See deposition footnote.

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### ( $\eta$ -Allyl)bromodicarbonyl( $N,N'$ -di-*tert*-butyl-ethanediimine)molybdenum(II), $MoBr(C_3H_5)(C_{10}H_{20}N_2)(CO)_2$

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**Abstract.**  $C_{15}H_{25}BrMoN_2O_2$ ,  $M_r = 441.22$ ,  $P2_12_12_1$ ;  $a = 19.850$  (7),  $b = 13.266$  (4),  $c = 7.044$  (3) Å;  $V = 1854.89$  Å<sup>3</sup>;  $Z = 4$ ;  $D_m = 1.574$ ,  $D_c = 1.580$  Mg m<sup>-3</sup>; monochromatic (graphite crystal)  $Cu K\alpha_1$ ,  $\lambda = 1.54051$  Å,  $\mu = 79.71$  mm<sup>-1</sup>,  $F(000) = 888$ , 293 K,  $R = 0.0789$  for 1443 measured reflections.

**Introduction.** This compound is the fifth in a series of the types (I)  $MX(CO)_3(LN=CHCH=NL)$  and (II)  $MX(CO)_2A(LN=CHCH=NL)$ , where  $X = Br, Cl$ ;  $M = Mn, Re, W, Mo$ ;  $L = cyclohexyl, tert-butyl, isopropyl$ ;  $A = \eta$ -allyl,  $\eta$ -2-methylallyl, as prepared by Hsieh & West (1976); it has  $M = Mo$ ,  $X = Br$ ,  $A = \eta$ -allyl and  $L = tert-butyl$ . The previous compounds in the series had  $L = cyclohexyl$  (three com-

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