NN-Dimethyl- and *NN*-Diethyl-propionamide Complexes of Uranium Tetrachloride; Crystal Structure† of Trichlorotetrakis(*NN*-diethylpropionamide)uranium(IV) Pentachloro(*NN*-diethylpropionamide)uranate(IV), $[UCl_3(EtCONEt_2)_4]^+[UCl_5(EtCONEt_2)]^-$

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The complexes $UCl_4{\cdot}xL$ [x = 2 or 2.5, L = $EtCONMe_2$ (dmpa) and $EtCONEt_2$ (depa)] have been prepared and their u.v.–visible and i.r. spectra are reported. The crystal and molecular structure of $UCl_4{\cdot}2.5$depa has been determined from single-crystal, *X*-ray diffractometer data and refined by least squares to *R* 0.0478 for 3 386 independent reflections. Crystals of $U_2Cl_8{\cdot}5$depe are monoclinic, space group $P2_1$ (no. 4), with $Z = 2$, $a = 16.817(2)$, $b = 10.339(1)$, $c = 16.400(2)$ Å, and $\beta = 104.99(1)°$. The compound is ionic, $[UCl_3(depa)_4]^+[UCl_5(depa)]^-$, and the co-ordination geometry about the seven-co-ordinate uranium atom in the cation is pentagonal bipyramidal, while that about the six-co-ordinate uranium atom in the anion is octahedral.

The stoicheiometry of the known complexes of uranium tetrachloride with the smaller *NN*-dimethylamides is commonly $UCl_4{\cdot}2.5L$ [L = $HCONMe_2$ [1,2] and $MeCONMe_2$ (dma)[3]], while with the more bulky ligands of this type, bis-complexes $UCl_4{\cdot}2L$ [L = $Me_2CHCONMe_2$, $Me_2CHCH_2CONMe_2$, and $Me_3CCONMe_2$ (dmpva)[4]] are formed. The molecular structure of $[UCl_4(dmpva)_2]$ is reported[5] to be *trans* octahedral, but no structural information is available for any of the complexes of composition $UCl_4{\cdot}2.5L$. The compound $UCl_4{\cdot}2.5$dma exists in three distinguishable crystal modifications,[6] but single crystals decompose in an *X*-ray beam. Dimeric structures involving Cl bridging have been suggested[7] for the compound on the basis of its reactions with sodium iodide in non-aqueous media, but the u.v.–visible spectrum of the compound in non-aqueous media suggests that the anion $[UCl_5(dma)]^-$ is formed, although the attempted isolation of salts of this anion with large cations (*e.g.* PPh_4^+) was unsuccessful.[8] Complex anions of this type have also been postulated[4] as intermediates in the reaction in non-aqueous media of complexes of the type $[UX_4L_4]$ (X = Cl or Br) with R_4NX and of $Cs_2[MCl_6]$ (M = U, Np, or Pu) with amide ligands. Since dma[9] and *NN*-dimethylpropionamide (dmpa)[10] form complexes of the type $U(NO_3)_4{\cdot}2.5L$, both of which are thermally unstable, it was of interest to investigate the formation of *NN*-dialkylpropionamide complexes of UCl_4 in an attempt to obtain further structural information for complexes of this stoicheiometry.

Experimental

The complexes were prepared and handled under dry nitrogen in glove-boxes. Uranium tetrachloride[11] and the amide ligands were prepared by standard methods.[4] Spectroscopic measurements and the drying of solvents were carried out as described previously.[4]

Preparations.—(*a*) $UCl_4{\cdot}2.5$dmpa. A large excess of dmpa (1.5—2.5 g, 15—20 mmol) was added to a solution of UCl_4 (1.2614 g, 3.32 mmol) in tetrahydrofuran (thf) (30 cm^3). After stirring for 24 h the supernatant was slowly evaporated under vacuum to *ca.* 5 cm^3, when toluene (5 cm^3) was added to precipitate the green *product*. This was washed with toluene (5 cm^3), followed by a toluene–n-pentane mixture (1 : 1, 2 × 5 cm^3) and n-pentane (2 × 5 cm^3), after which the complex was vacuum dried (8 h); yield, 70%. The complex with *NN*-diethylpropionamide (depa) was prepared in the same way. During the vacuum evaporation a part of the green product crystallised out; yield, 70%.

Table 1. Analytical data (%) *

Compound	U	C	H	N	Cl
$UCl_4{\cdot}2.5$dmpa	36.6	24.0	4.4	5.6	21.7
	(37.6)	(23.7)	(4.4)	(5.5)	(22.4)
$UCl_4{\cdot}2$dmpa	41.3	21.0	3.8	4.8	24.7
	(40.9)	(20.6)	(3.8)	(4.8)	(24.4)
$UCl_4{\cdot}2.5$depa	33.1	30.2	5.4	4.7	19.8
	(33.9)	(29.9)	(5.4)	(5.0)	(20.2)
$UCl_4{\cdot}2$depa	37.0	26.1	4.8	4.3	21.7
	(37.3)	(26.4)	(4.7)	(4.4)	(22.2)

* Calculated values in parentheses.

(*b*) $UCl_4{\cdot}2$dmpa. The complex $UCl_4{\cdot}2.5$dmpa (*ca.* 2 g) was suspended in thf and stirred for 24 h. After centrifugation, the supernatant, which contained free dmpa, was decanted and the treatment with thf was repeated (3 times). The *product* was washed with n-pentane and vacuum dried (8 h); yield, 50%. Alternatively, $UCl_4{\cdot}2.5$dmpa (*ca.* 2 g) was dissolved in CH_2Cl_2 (30 cm^3) and n-pentane was added to precipitate the complex. After centrifuging, the dissolution/precipitation cycle was repeated (3 times) and the product was then treated as above; yield, 45%. The bis-complex is also formed on leaving $UCl_4{\cdot}2.5$dmpa to stand in thf for 7 d without stirring. The compound $UCl_4{\cdot}2$depa was prepared in the same way as $UCl_4{\cdot}2$dmpa with similar yields.

The analytical results are summarised in Table 1.

Single-crystal Data Collection.—The crystals were air-sensitive and of irregular shape. An equidimensional block of average size 0.4 mm was wedged inside an inert gas-filled, thin-walled capillary, sealed, and mounted on the CAD4 diffractometer system. Data were collected to θ = 24° using (Mo-K_α) radiation (λ = 0.710 69 Å). Owing to the weak diffracting power, each reflection was measured for up to 600 s in order to obtain 3 386 reflections for which $F > 3\sigma(F)$. No

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† *Supplementary data available* (No. SUP 23274; 36 pp.): observed and calculated structure factors, thermal parameters. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 2. Fractional atomic co-ordinates for $[UCl_3(depa)_4][UCl_5(depa)]$ with estimated standard deviations in parentheses

Atom	*x/a*	*y/b*	*z/c*
U(1)	0.956 9(0)	0.2500	0.758 9(0)
Cl(1)	0.989 9(4)	0.177 6(6)	0.616 8(4)
Cl(2)	0.918 4(4)	0.328 2(7)	0.893 8(4)
Cl(3)	0.954 0(4)	−0.003 1(6)	0.802 8(5)
U(2)	0.551 4(0)	0.268 7(1)	0.247 9(0)
Cl(4)	0.552 3(8)	0.502 3(7)	0.298 5(6)
Cl(5)	0.628 5(7)	0.320 6(10)	0.134 9(5)
Cl(6)	0.689 0(4)	0.221 9(10)	0.357 5(5)
Cl(7)	0.471 8(5)	0.191 1(7)	0.355 8(5)
Cl(8)	0.413 2(5)	0.293 4(13)	0.135 6(6)
O(1)	0.821 6(10)	0.181 2(17)	0.705 3(10)
O(2)	1.086 7(10)	0.201 4(18)	0.832 1(10)
O(3)	0.877 0(9)	0.419 7(15)	0.685 5(9)
O(4)	1.037 9(8)	0.423 8(14)	0.762 5(8)
O(5)	0.556 5(10)	0.054 9(18)	0.212 8(11)
N(1)	0.727 6(14)	0.055 4(24)	0.640 6(15)
N(2)	1.164 8(20)	0.101 1(34)	0.932 2(23)
N(3)	0.767 7(18)	0.463 7(31)	0.595 0(20)
N(4)	1.071 7(13)	0.592 9(22)	0.699 7(14)
N(5)	0.555 1(13)	−0.125 6(21)	0.141 3(13)
C(11)	0.751 6(17)	0.117 2(28)	0.701 5(18)
C(12)	0.649 2(21)	−0.023 5(34)	0.624 5(21)
C(13)	0.578 0(26)	0.053 2(45)	0.564 9(27)
C(14)	0.774 4(17)	0.042 7(28)	0.568 2(18)
C(15)	0.742 6(21)	0.036 3(37)	0.839 3(22)
C(16)	0.708 7(22)	0.137 6(38)	0.772 5(23)
C(17)	0.814 8(24)	−0.075 0(44)	0.573 8(25)
C(21)	1.146 3(22)	0.113 4(39)	0.857 7(25)
C(22)	1.178 4(19)	0.028 7(33)	0.802 7(20)
C(23)	1.226 2(28)	0.094 4(49)	0.768 5(28)
C(24)	1.109 7(24)	0.157 5(44)	1.003 9(26)
C(25)	1.145 9(26)	0.275 5(49)	1.015 4(27)
C(31)	0.800 0(23)	0.457 9(40)	0.661 0(25)
C(32)	0.817 0(16)	0.426 1(27)	0.530 0(16)
C(33)	0.858 6(23)	0.538 5(39)	0.504 5(24)
C(34)	0.677 8(16)	0.497 7(27)	0.557 1(17)
C(35)	0.754 9(17)	0.507 5(28)	0.725 5(18)
C(36)	0.771 2(21)	0.655 5(36)	0.739 5(22)
C(37)	0.625 6(20)	0.394 7(35)	0.557 7(20)
C(41)	1.046 9(14)	0.544 7(24)	0.755 0(15)
C(42)	1.094 3(19)	0.733 4(36)	0.694 9(20)
C(43)	1.023 2(23)	0.800 2(42)	0.624 3(23)
C(44)	1.091 4(18)	0.500 9(30)	0.635 4(19)
C(45)	1.108 6(25)	0.631 3(42)	0.903 5(26)
C(46)	1.025 5(16)	0.631 0(26)	0.822 7(17)
C(47)	1.180 8(30)	0.422 7(54)	0.679 0(29)
C(51)	0.545 6(15)	−0.071 6(26)	0.206 7(16)
C(52)	0.572 6(15)	−0.054 2(26)	0.072 0(16)
C(53)	0.661 6(21)	−0.043 1(35)	0.082 7(21)
C(54)	0.546 4(15)	−0.264 6(28)	0.131 3(15)
C(55)	0.456 5(20)	−0.302 0(37)	0.099 9(20)
C(56)	0.525 4(15)	−0.135 6(24)	0.278 3(15)
C(57)	0.601 0(20)	−0.147 3(33)	0.356 9(20)

significant intensity drift was observed in standard reflection monitoring. No absorption correction was applied.

The two uranium and six of the chlorine atoms were found from a Patterson synthesis, which was interpretable on the basis that the space group was $P2_1$. Successive Fourier syntheses revealed the whole structure, although, not surprisingly, some difficulty was experienced with the terminal ethyl groups, one of which was omitted from the final refinement because of apparent disorder. No hydrogen atoms were assigned. The uranium and chlorine atoms were refined using anisotropic temperature factors. Scattering factors for neutral atoms were applied in structure factor calculations.

The final *R* value was 0.0478, after convergence with a parabolic weighting scheme to give uniform $w \,.\, 0.003\,52\ (\Delta F)^2$ distributions over the ranges of *F* and $(\sin\theta)/\lambda$ of the form $w^{-1} = (15.12 - 0.322\ F_o + 0.003\,52\ F_o^2)$.

Examination of the calculated bond lengths and angles showed that in the case of the cation the two apical U–Cl distances gave an average value of 2.62(2) Å and the third U–Cl distance was 2.72 Å. In the case of the anion, the four equatorial U–Cl distances averaged to 2.59(2) Å, a value only marginally changed to 2.58 Å when the fifth U–Cl distance (2.55 Å) was included. We place no importance on these differences because the crystal was of relatively poor quality and, because of air-sensitivity, the crystal was coated with grease when incorporated into the *X*-ray capillary. This precluded measurement of the sizes of the crystal faces as a prerequisite for absorption corrections. However, since the bond distances do not show any major variation, the lack of absorption corrections does not seem to be of any structural importance.

Crystal Data.—$C_{35}H_{75}Cl_8N_2O_5U_2$, $M = 1\,544.4$, Monoclinic, $a = 16.817(2)$, $b = 10.339(1)$, $c = 16.400(2)$ Å, $\beta = 104.99(1)°$, $U = 2\,754.4$ Å^3, $D_c = 1.86$ g cm^{-3} for $Z = 2$, $F(000) = 1\,360$, $\mu(\text{Mo-}K_\alpha) = 110.7$ cm^{-2} ($\lambda = 0.710\,69$ Å), space group $P2_1$ (no. 4).

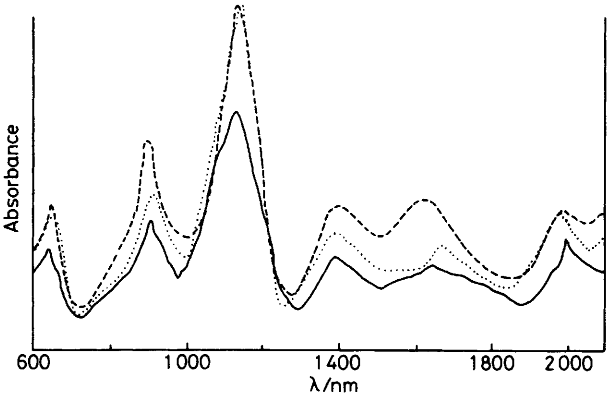

Figure 1. Solid reflectance spectra of the compounds $UCl_4 \cdot 2.5L$: L = dma (– – –), dmpa (· · ·), and depa (——)

Table 2 contains final atomic positional parameters for all non-hydrogen atoms with their estimated standard deviations derived from the last cycle of least-squares refinement.

All calculations were carried out on the ICL/CDC 1906A/7600 computers of the University of Manchester Regional Computer Centre using our own programs.

Results and Discussion

The solid complexes $UCl_4 \cdot 2.5L$ (L = dmpa or depa) were obtained by treating a solution of UCl_4 in thf with a large excess of ligand, followed by evaporation of the solution under vacuum (slowly, in order to avoid trapping excess ligand in the crystals of the product). The solid reflectance spectra of these complexes (600—2 100 nm) were very similar to that of $UCl_4 \cdot 2.5$dma (Figure 1) and clearly show that there is one U^{IV} centre with co-ordination greater than six (broad feature at 1 130 nm), but the six-co-ordination U^{IV} feature which should appear[4] at about 1 050 nm is obscured by the former broad

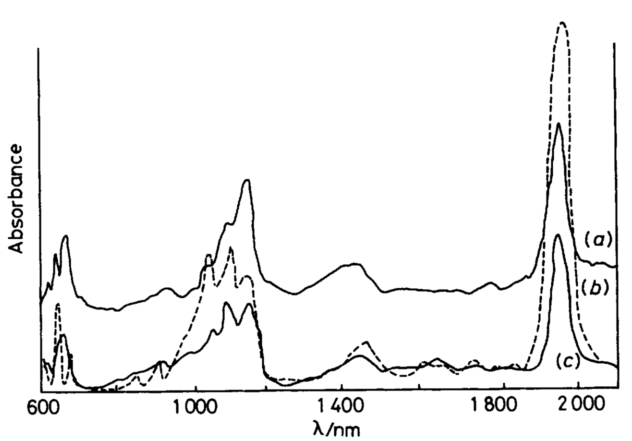

Figure 2. U.v.–visible spectrum of UCl_4·2.5dmpa in different solvents (spectra for UCl_4·2.5depa are similar): (*a*) in thf, (*b*) CH_2Cl_2 (dotted line), and (*c*) MeCN

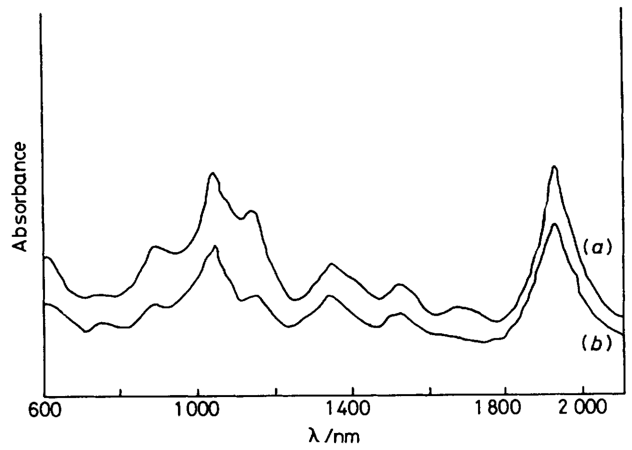

Figure 3. Solid reflectance spectra of the compounds UCl_4·2L: (*a*) L = depa, (*b*) L = dmpa

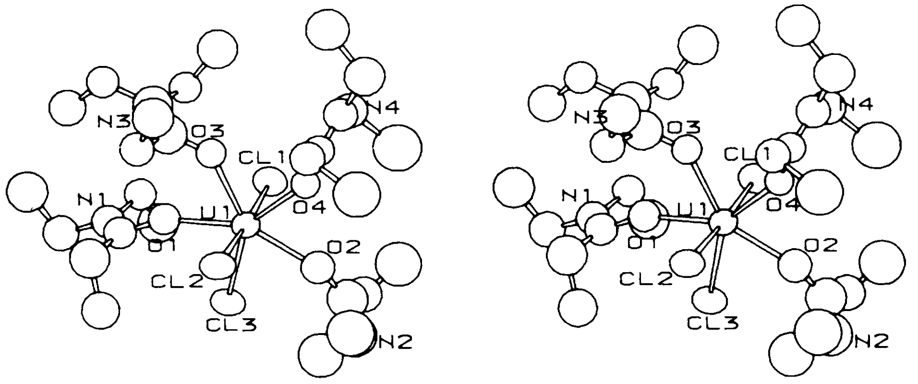

Figure 4. Stereoscopic drawing of the cation $[UCl_3(depa)_4]^+$

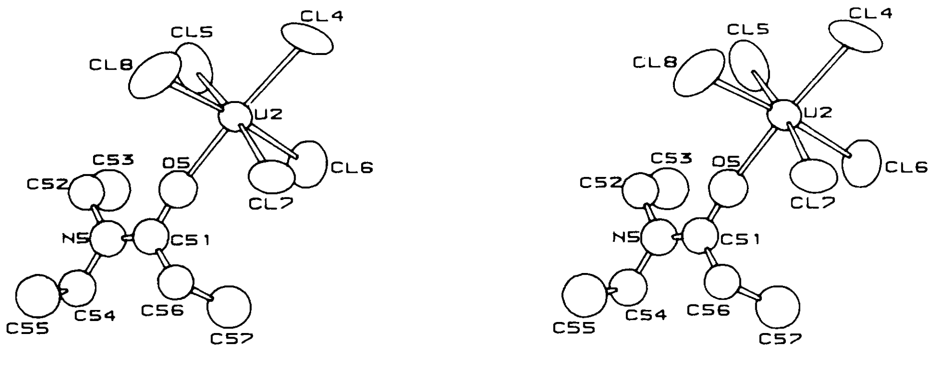

Figure 5. Stereoscopic drawing of the anion $[UCl_5(depa)]^-$

feature. However, the band at 1 990 nm can also be assigned to a six-co-ordinate centre. The solution u.v.–visible spectra of the two complexes in thf, CH_2Cl_2, or MeCN (Figure 2) differ appreciably from their solid reflectance spectra in that the six-co-ordinate uranium(IV) features are much more strongly marked. Thus the most intense band in the spectra now appears at 1 920 nm and the feature at 1 050 nm is clearly resolved. At the same time, the i.r. spectra of the complexes in thf solution exhibit features due to both bonded and free ligand at around 1 600 cm^{-1}. This is probably because of an equilibrium of the form shown below. Treatment with thf was continued until the solution i.r. spectrum no longer showed the presence of free ligand, at which stage the uranium(IV)

$$2\ UCl_4{\cdot}2.5L \rightleftharpoons 2\ UCl_4{\cdot}2L + L$$

feature at 1 130 nm had vanished. In this way, and by repeated dissolution of the complexes UCl_4·2.5L in CH_2Cl_2 and precipitation therefrom with n-pentane, the corresponding bis-complexes were obtained. The solid reflectance spectra of these were the same as their solution spectra (Figure 3). Some

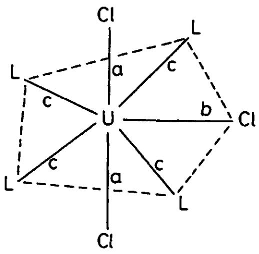

Figure 6. Co-ordination geometry of the cation $[UCl_3L_4]^+$ (L = depa): a = 2.62(2), b = 2.72(4), c = 2.29(5) Å; angles between bonds a,c = a,b = 90.0(2), b,c = 74.0(3), c,c = 70.6(3)°

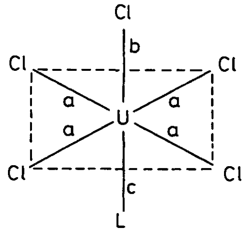

Figure 7. Co-ordination geometry of the anion $[UCl_5L]^-$ (L = depa): a = b = 2.58(3), c = 2.29(5) Å; angles between bonds a,a = 90.0(3), a,b = 92.8(6), a,c = 87.2(12)°

Table 3. Infrared spectral data (cm^{-1})

Compound	ν(CO)	Δν(CO)	ν(U–Cl)
dmpa	1 645		
UCl_4·2.5dmpa	1 600	45	260
UCl_4·2dmpa	1 612	33	262
depa	1 640		
UCl_4·2.5depa	1 580	60	265
UCl_4·2depa	1 590	50	262

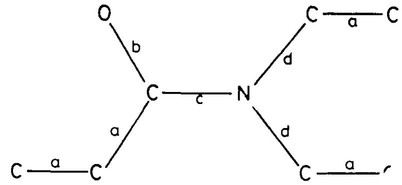

Figure 8. Bond lengths and angles in the ligand depa: a = d = 1.51(12), b = 1.34(5), c = 1.18(5) Å; angles between bonds a,a = a,d = 109(1)°, other angles are 120(4)°

relevant features of the i.r. spectra of both sets of complexes are given in Table 3. However, the attempted degradation of UCl_4·2.5dma to the bis-complex by these procedures was unsuccessful.

The ^1H n.m.r. and Raman spectra of all of these products were also recorded, but did not provide helpful information concerning the structures of these complexes.

Crystal Structure Determination.—The compound UCl_4·2.5depa comprises two complex ions, $[UCl_3L_4]^+$ and $[UCl_5L]^-$ (L = depa), and these are shown in Figures 4 and 5 as stereoscopic drawings. The co-ordination geometry about the uranium atom in the cation is pentagonal bipyramidal, with two chlorine atoms occupying the axial positions; the equatorial pentagon is planar * (all of the six atoms which define the plane are less than 0.03 Å out of the plane) but is not quite regular owing to the presence of the third chlorine atom at one corner (Figure 6). Pentagonal bipyramidal geometry is common in seven-co-ordinate dioxouranium(VI) complexes, in which the linear O=U=O group provides the rigid axis, but in the case of uranium(IV) species it is known only for UBr_4, which is a bromine-bridged polymer,[12] the UF_7^{3-} anion in $K_3[UF_7]$,[13] and in the recently reported neutral complex $[U(NCS)_4(dmiba)_3]$ (dmiba = $Me_2CHCONMe_2$).[14] The anion, $[UCl_5L]^-$, is a near-regular octahedron (Figure 7), the oxygen atom of the ligand occupying less space than any one of the five chlorine atoms. The ligand (Figure 8) is bonded to the uranium atom through its oxygen atom to form an angle U–O–C of 164(2)°. In the case of the cation this angle is 150(5)°. The average U–O bond lengths are 2.29(5) Å in both the cation and the anion, a value which is close to those reported for $[U(NCS)_4(dmiba)_3]$ (2.30 Å [14]) and the cation $[UCl(PMe_3O)_6]^{3+}$ [2.26(1) Å [15]]. The co-ordination geometry about the uranium atom in the latter can be described as a distorted monocapped trigonal antiprism.

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* When referred to an orthogonal set of unit vectors defined by $a' = a$, $c' = a \times b$, and $b' = c' \times a'$ with origin at the centroid, the equation of this plane is $0.447x' - 0.284y' - 0.848z' + 5.157 = 0$.