distances are longer than U—O(eq.) as predicted from the covalent radii; they are significantly longer than that found in complex (4). As expected, the Np—O(axial) and Np—O(eq.) distances in (3) are shorter by about 0·05 (1) Å than those in (4) (Alcock, Roberts & Brown, 1982), though *M*—N is greater in (3) than (4). The pyridine ring in complex (1) is twisted out of the equatorial plane, forming an angle with this plane of 36·9 (2)°, whilst in complex (2) it lies parallel to the uranyl group (90·0° twist). In complex (3) the corresponding twist is 49·0 (2)°, whilst in (4) the out-of-plane twist is 48·7 (10)°. These twists presumably reduce interference with the diketonate groups, but must have the effect of increasing repulsions between the *o*-hydrogen atoms on the pyridine and the actinyl oxygen atoms.

We have therefore been surprised to find that none of the O—*M*—O groups in these complexes show substantial non-linearity compared with that found in (4). The pyridine–uranyl repulsions were believed to be responsible for the non-linear O—U—O group in this complex; however, study of the pyridine-H to actinyl-O distances shows that this steric influence is less in (4) than in the other complexes, yet the distortion of the actinyl bond is greatest (Table 7). Furthermore, there is no apparent correlation between O—*M*—O bond angles and *M*—O(axial) bond lengths which could account for this. The one parameter which does show a correlation with the distortion is the U—N distance. It may therefore be that direct O—N repulsion in the actinyl coordination sphere is responsible for the bent O—U—O group in (4). In their turn, the *M*—N distances show an inverse correlation with the *M*—O(eq.) distances, implying that the acac groups in (1)–(3) are rather more strongly held than in (4), leading to steric pressure and slight weakening of the *M*—N bond.

Table 7. *Comparison of M*—N *bond lengths* (Å), O—*M*—O *bond angles* (°), *interplane angles* (°) *and proximity of* (*pyridine*)H—O(*uranyl*) *atoms* (Å)

Atomic numbering as for Table 5.

	(1)	(2)	(3)	(4)
M—N	2·569 (6)	2·595 (2)	2·56 (3)	2·47 (1)
O(11)—*M*—O(12)	177·9 (2)	175·8 (8)	176·5 (19)	173·5 (8)
Equatorial/pyridine angle	36·9 (2)	90·0	49·0 (2)	48·7 (10)
O(11)···H(51)	2·914	2·677	3·074	3·179
O(12)···H(55)	3·145	2·634	—	—

We thank the SERC and AERE Harwell for support to DJF and MP under the CASE scheme.

References

ALCOCK, N. W. (1970). *Crystallographic Computing*, edited by F. R. AHMED, pp. 271–278. Copenhagen: Munksgaard.

ALCOCK, N. W. & FLANDERS, D. J. (1987). *Acta Cryst.* C**43**, 1267–1269.

ALCOCK, N. W., FLANDERS, D. J. & BROWN, D. (1984). *J. Chem. Soc. Dalton Trans.* pp. 679–681.

ALCOCK, N. W., ROBERTS, M. M. & BROWN, D. (1982). *J. Chem. Soc. Dalton Trans.* pp. 869–873.

FRASSON, E., BOMBIERI, G. & PANATTONI, C. (1966). *Coord. Chem. Rev.* **1**, 145–150.

HAGER, K. (1927). *Z. Anorg. Allg. Chem.* **162**, 82–86.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

SHELDRICK, G. M. (1983). *SHELXTL Users Manual*, Revision 4. Nicolet XRD Corporation, Madison, Wisconsin, USA.

STEWART, J. M. (1976). Editor. The *XRAY*76 system. Tech. Rep. TR-466. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.

Acta Cryst. (1987). C**43**, 1480–1483

Actinide Structural Studies. 14.* Two Uranyl(VI) Complexes Containing 2,4-Pentanedione

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(*Received* 27 *January* 1987; *accepted* 19 *May* 1987)

Abstract. (1) Aquadioxobis(2,4-pentanedionato)-uranium(VI), $[U(C_5H_7O_2)_2(H_2O)O_2]$, $M_r = 486{\cdot}27$, monoclinic, $P2_1/c$, $a = 12{\cdot}895$ (3), $b = 7{\cdot}042$ (2), $c = 16{\cdot}633$ (3) Å, $\beta = 109{\cdot}46$ (2)°, $U = 1424{\cdot}2$ (6) Å^3, $Z = 4$, $D_x = 2{\cdot}27$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 108{\cdot}27$ cm^{-1}, $F(000) = 896$, $T = 290$ K, $R = 0{\cdot}043$ for 1821 unique observed reflections. (2) 2,4,6-Trimethylpyridinium dinitratodioxo(2,4-pentanedionato)-uranate(VI), $[C_8H_{12}N][U(C_5H_7O_2)(NO_3)_2O_2]$, $M_r = 615{\cdot}34$, orthorhombic, $P2_12_12$, $a = 6{\cdot}879$ (2), $b = 15{\cdot}241$ (4), $c = 9{\cdot}613$ (2) Å, $U = 1007{\cdot}9$ (4) Å^3, $Z = 2$, $D_x = 2{\cdot}03$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 78{\cdot}86$ cm^{-1}, $F(000) = 580$, $T = 290$ K, $R = 0{\cdot}039$ for 1936 unique observed reflections. (1) has pentagonal

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* Part 13: Alcock, Flanders, Pennington & Brown (1987).

bipyramidal geometry with considerable puckering of the equatorial plane. The anion in (2) is hexagonal bipyramidal. In both complexes the bonds from U to O(2,4-pentanedione) are shorter than those to the other equatorial ligands. U—O axial = 1·742 (4) (1) and 1·75 (1) Å (2).

Introduction. We have previously reported the structures of four complexes of actinyl(VI) ions with 2,4-pentanedione and its derivatives (acac) (Alcock, Flanders & Brown, 1984; Alcock, Flanders, Pennington & Brown, 1987). One of these, $UO_2(acac)_2$-(pyridine), shows an unusually large deviation from linearity in its UO_2^{2+} group [173·5 (8)°]. Of the two further complexes reported here, the first, $UO_2(acac)_2.H_2O$ (1), has previously been studied but the structural information was based on 2D photographic evidence for a different crystal modification [though with the same space group (Frasson, Bombieri & Panattoni, 1966)]. The second, $[Me_3C_5H_3N][UO_2(acac)(NO_3)_2]$ (2), was formed while attempting to prepare an analogue of the pyridine complex using γ-collidine (2,4,6-trimethylpyridine).

Experimental. Compound (1) was prepared using the method of Comyns, Gatehouse & Wait (1958). A warm dilute aqueous solution (5 cm^3) of sodium hydroxide (1 mol) was added to a warm aqueous solution (10 cm^3) of uranyl(VI) nitrate (2·5 mmol) and 2,4-pentanedione (2·5 mmol). Prismatic crystals formed as the solution cooled and were recrystallized from water. This form is not identical to that studied by Frasson *et al.* (1966). Compound (2) was prepared in a similar manner to $[UO_2(acac)_2py]$ (Alcock *et al.*, 1984) with 2,4,6-trimethylpyridine substituted for pyridine. On concentration of the solution, amorphous lumps of an orange material were precipitated and recrystallization from hot toluene gave thin lath-shaped dark-orange crystals. These were shown by the structure analysis to contain the dinitrato anion rather than being the neutral collidine complex.

Crystal data and data collection conditions for each compound are given in Table 1. Data were collected with a Syntex $P2_1$ diffractometer for 2θ in the range 3–50°, at 290 K. Background intensities were measured at each end of the scan for 0·25 of the scan time. Three standard reflections, monitored every 200 reflections, showed no significant changes. Unit-cell dimensions and standard deviations were obtained by least-squares fit to 15 reflections ($23 < 2\theta < 28°$). Observed reflections [$I/\sigma(I) \geq 3{\cdot}0$] were corrected for Lorentz, polarization and absorption effects, the last with *ABSCOR* (Alcock, 1970). For complex (1), the systematic absences $h0l$: $l \neq 2n$ and $0k0$: $k \neq 2n$ indicated the space group $P2_1/c$ and the U-atom position was determined from a three-dimensional Patterson map. The non-H atoms were found on successive difference Fourier maps and all were refined anisotropically. H atoms, with the exception of those of the water molecule, were inserted in calculated positions with C—H 0·96 Å and fixed isotropic temperature factors, $U = 0{\cdot}08$ Å^2, and were not refined; methyl groups were treated as rigid bodies. The comparatively large residual peaks on the difference Fourier synthesis were located close to the U atom.

Table 1. *Data collection and refinement*

Compound	(1)	(2)
Formula	$C_{10}H_{16}O_7U$	$C_{13}H_{19}N_3O_{10}U$
Crystal size (mm)	0·36 × 0·11 × 0·10	0·42 × 0·12 × 0·12
Max. transmission factor	0·28	0·65
Min. transmission factor	0·10	0·53
Scan range about $K\alpha_1 - K\alpha_2$(°)	−1·0/+1·1	−1·0/+1·1
Reflections collected	3072	3160
h, k, l range	−14–14, 0–8, 0–19	−6–7, 0–18, 0–12
Reflections observed $[I/\sigma(I) \geq 3{\cdot}0]$	1821	1936
Weighting constant: *g*	0·0044	0·00088
Final *R*	0·043	0·039
Final *wR*	0·047	0·037
Max./min. on ΔF map (e Å^{-3})	+2·0/−4·0	+0·7/−0·8
Final max. shift/e.s.d.	0·3	0·6

For compound (2), the apparent systematic absences $hk0$: $h + k \neq 2n$ suggested the space group *Pmmn* and a three-dimensional Patterson map located the U atom at $0,\frac{1}{2},z$ in special position 2(*b*). The positions of the non-H atoms in the cation were determined from successive difference Fourier maps, but no peaks corresponding to the remaining anion atoms could be discovered and the *R* factor did not behave satisfactorily. Various attempts were made to reduce the symmetry and space groups $Pm2_1n$ and $P2_1mn$ were examined. In both of these space groups the *mm* symmetry at the U atom is relaxed to a mirror plane either parallel or perpendicular to the uranyl group. The former space group produced no improvement in the refinement, but in the latter the position of most non-H atoms of the anion were determined. However, the position of one of the O atoms of the uranyl group could not be found and the temperature factors of a number of atoms in both ions were found to be unsatisfactory. This raised the possibility of the presence of a false symmetry element and a re-examination of the raw data suggested that the systematic absences $hk0$: $h + k \neq 2n$ corresponding to the *n*-glide plane might be spurious.

In order to resolve these difficulties the lower-symmetry space group, $P2_12_12$, was investigated. The U atom was maintained at special position 2(*b*) $(0,\frac{1}{2},z)$ and all non-H atoms were located from a difference Fourier map and, as the refinement proceeded satisfactorily, the space group was taken to be correct. Both anion and cation are located on twofold axes. The thermal parameters of the nitrate group have high values perpendicular to the equatorial plane, suggesting that they may be partly disordered above and below this plane. Non-H atoms were refined with anisotropic

Table 2. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* ($Å^2 \times 10^3$) *with e.s.d.'s in parentheses*

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
(*a*) For (1)				
U	2922·1 (2)	5086·7 (4)	6976·5 (2)	28
O(1)	2971 (5)	6509 (9)	7853 (4)	47
O(2)	2900 (5)	3677 (9)	6117 (4)	45
O(3)	3528 (5)	2443 (9)	7912 (4)	44
O(4)	1389 (5)	3634 (9)	7165 (4)	42
O(5)	1393 (5)	6643 (9)	6024 (4)	43
O(6)	3546 (5)	7712 (8)	6358 (4)	43
O(7)	4968 (6)	5041 (7)	7469 (7)	48
C(1)	3879 (11)	460 (16)	9131 (8)	59
C(2)	3132 (8)	1711 (12)	8445 (5)	39
C(3)	2069 (8)	2000 (15)	8451 (6)	52
C(4)	1259 (7)	2877 (11)	7797 (6)	40
C(5)	105 (7)	2889 (18)	7826 (8)	64
C(6)	81 (7)	7528 (19)	4736 (8)	62
C(7)	1263 (7)	7497 (12)	5326 (6)	38
C(8)	2084 (8)	8297 (14)	5088 (5)	47
C(9)	3141 (7)	8492 (12)	5613 (6)	38
C(10)	3925 (10)	9626 (16)	5325 (9)	61
(*b*) For (2)				
U(1)	0	5000	3113·1 (9)	49
O(1)	2545 (20)	4899 (23)	3083 (10)	61
O(2)	−131 (72)	4134 (8)	5098 (11)	71
O(3)	−58 (74)	6633 (8)	2641 (13)	114
O(4)	166 (82)	5842 (8)	842 (11)	78
O(5)	−657 (49)	7254 (9)	639 (17)	112
N(1)	−258 (95)	6628 (13)	1298 (19)	103
N(2)	5000	5000	5552 (19)	45
C(1)	115 (80)	3368 (13)	7259 (15)	66
C(2)	232 (80)	4182 (15)	6427 (18)	48
C(3)	0	5000	7107 (22)	61
C(4)	4779 (66)	5768 (12)	6188 (17)	51 (6)*
C(41)	4704 (51)	6579 (11)	5318 (18)	60 (6)*
C(5)	4866 (81)	5817 (12)	7634 (18)	59 (5)*
C(6)	5000	5000	8342 (23)	75
C(61)	5000	5000	9948 (26)	131

* Refined isotropically.

Table 3. *Bond lengths* (Å) *and bond angles* (°) *for* $UO_2(CH_3COCHCOCH_3)_2.H_2O$ (1) *with e.s.d.'s in parentheses*

U(1)—O(1)	1·752 (6)	U(1)—O(5)	2·349 (5)
U(1)—O(2)	1·733 (6)	U(1)—O(6)	2·383 (6)
U(1)—O(3)	2·385 (6)	U(1)—O(7)	2·489 (8)
U(1)—O(4)	2·338 (6)		
C(1)—C(2)	1·51 (1)	C(6)—C(7)	1·51 (1)
C(2)—O(3)	1·27 (1)	C(7)—O(5)	1·27 (1)
C(2)—C(3)	1·39 (1)	C(7)—C(8)	1·37 (1)
C(3)—C(4)	1·38 (1)	C(8)—C(9)	1·36 (1)
C(4)—O(4)	1·24 (1)	C(9)—O(6)	1·30 (1)
C(4)—C(5)	1·51 (1)	C(9)—C(10)	1·49 (2)
O(1)—U—O(2)	179·0 (3)	U—O(3)—C(2)	130·7 (6)
O(1)—U—O(3)	89·4 (3)	U—O(4)—C(4)	131·5 (5)
O(1)—U—O(4)	86·3 (3)	U—O(5)—C(7)	131·6 (6)
O(1)—U—O(5)	94·8 (2)	U—O(6)—C(9)	130·9 (5)
O(1)—U—O(6)	89·5 (3)		
O(1)—U—O(7)	89·6 (3)	O(3)—C(2)—C(1)	117·4 (9)
O(2)—U—O(3)	90·2 (3)	O(3)—C(2)—C(3)	125·0 (8)
O(2)—U—O(4)	94·5 (3)	C(1)—C(2)—C(3)	117·6 (10)
O(2)—U—O(5)	86·1 (2)	C(2)—C(3)—C(4)	123·4 (10)
O(2)—U—O(6)	90·2 (3)	O(4)—C(4)—C(3)	125·5 (9)
O(2)—U—O(7)	89·4 (3)	O(4)—C(4)—C(5)	116·1 (8)
O(3)—U—O(4)	71·2 (2)	C(3)—C(4)—C(5)	118·3 (10)
O(3)—U—O(5)	145·4 (2)	O(5)—C(7)—C(6)	113·4 (9)
O(3)—U—O(6)	143·4 (2)	O(5)—C(7)—C(8)	125·5 (7)
O(3)—U—O(7)	72·2 (2)	C(6)—C(7)—C(8)	121·1 (9)
O(4)—U—O(5)	74·8 (2)	C(7)—C(8)—C(9)	124·3 (8)
O(4)—U—O(6)	145·1 (2)	O(6)—C(9)—C(8)	124·8 (9)
O(4)—U—O(7)	143·2 (2)	O(6)—C(9)—C(10)	115·8 (8)
O(5)—U—O(6)	71·1 (2)	C(8)—C(9)—C(10)	119·4 (9)
O(5)—U—O(7)	142·0 (3)		
O(6)—U—O(7)	71·2 (2)		

Table 4. *Bond lengths* (Å) *and bond angles* (°) *for* $UO_2(CH_3COCHCOCH_3)(NO_3)_2$ (2) *with e.s.d.'s in parentheses*

Primed and unprimed atoms are related by a twofold axis.

(i) Anion			
U(1)—O(1)	1·758 (14)	C(1)—C(2)	1·48 (3)
U(1)—O(2)	2·322 (11)	C(2)—O(2)	1·30 (2)
U(1)—O(3)	2·530 (12)	C(2)—C(3)	1·42 (2)
U(1)—O(4)	2·535 (11)		
		N(1)—O(3)	1·30 (2)
		N(1)—O(4)	1·31 (3)
		N(1)—O(5)	1·18 (3)
O(1)—U—O(1′)	178·1 (6)	U—O(2)—C(2)	140 (2)
O(1)—U—O(2)	90·1 (14)	C(1)—C(2)—C(3)	119 (2)
O(1)—U—O(3)	95·7 (16)	C(1)—C(2)—O(2)	118 (2)
O(1)—U—O(4)	89·2 (14)	C(3)—C(2)—O(2)	119 (2)
O(2)—U—O(3)	134·9 (4)	C(2)—C(3)—C(2′)	125 (2)
O(2)—U—O(4)	175·8 (4)		
O(2)—U—O(2′)	69·5 (6)	U—O(3)—N(1)	100 (1)
O(3)—U—O(4)	49·3 (4)	U—O(4)—N(1)	100 (1)
O(4)—U—O(4′)	61·1 (5)	O(3)—N(1)—O(4)	108 (2)
		O(3)—N(1)—O(5)	124 (2)
		O(4)—N(1)—O(5)	128 (2)
(ii) Cation			
N(2)—C(4)	1·33 (2)	C(5)—C(6)	1·42 (2)
C(4)—C(41)	1·49 (3)	C(6)—C(61)	1·54 (3)
C(4)—C(5)	1·39 (2)		
C(4)—N(2)—C(4′)	125 (2)	C(4)—C(5)—C(6)	116 (2)
N(2)—C(4)—C(5)	120 (2)	C(5)—C(6)—C(61)	119 (1)
N(2)—C(4)—C(41)	118 (2)	C(5)—C(6)—C(5′)	123 (2)
C(41)—C(4)—C(5)	121 (2)		

temperature factors except C(4), C(41) and C(5) which were refined isotropically. H atoms were found and were refined in fixed positions or as rigid groups with fixed isotropic temperature factors, $U = 0{\cdot}07$ Å^2. Refinement of a ($\delta F''$) multiplier gave a reasonably strong indication that the structure had been solved in the correct hand [value 0·64 (15), returned to 1·0 for final refinement].

A weighting scheme of the type $w = 1/[\sigma^2(F) + g(F^2)]$ was applied, and shown to be satisfactory by weight analysis. Final refinement was on F. The weighting constants and the final R factors are given in Table 1. The calculations were carried out with the *SHELXTL* system (Sheldrick, 1981) on a Data General Nova 3 minicomputer. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Final atomic coordinates are given in Table 2,* bond lengths and angles in Tables 3 and 4.

Discussion. Complex (1) (Fig. 1) has the pentagonal bipyramidal geometry expected for a compound with one monodentate and two bidentate ligands. There is some variation in the U—O(ligand) bond lengths

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43991 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

[2·34–2·49 (7) Å], with the bond to the water molecule being significantly longer than the others. Alternate O atoms of the 2,4-pentanedionato groups are above and below the equatorial plane, leading to substantial dihedral angles between the individual groups and the mean plane. The dioxouranium(VI) group has an O—U—O angle of 179·0 (3)° and makes an angle of 88·0 (2)° with the equatorial plane. The packing diagram of this complex (Fig. 2) shows that the neutral molecules have only weak interactions between them.

Complex (2) is composed of dinitratodioxo(2,4-pentanedionato)uranium(VI) anions and 2,4,6-trimethylpyridinium cations. The view of the anion (Fig. 3) and the numbering scheme shows the coordination about the U atom to be hexagonal bipyramidal, with one 2,4-pentanedionate ion and two nitrate ions coordinated in the equatorial plane. In this case, the nitrate groups form the longer U—O bonds. The ions are packed in layers perpendicular to the *a* axis, with the ions alternating in each layer and with a comparatively short approach between the N atom of the cation and the uranyl O atoms (Fig. 4).

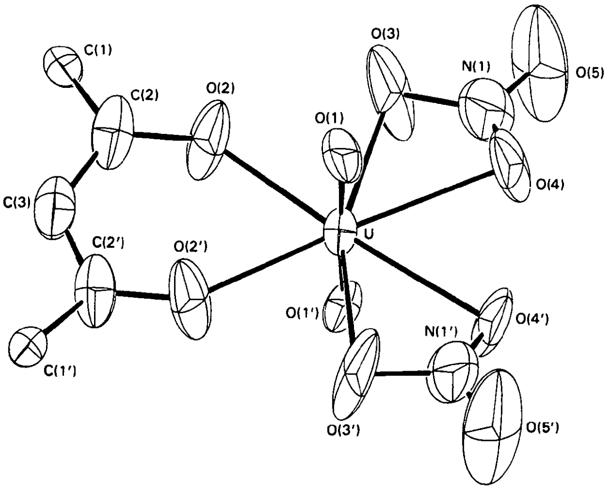

Fig. 3. View of complex (2), showing the atomic numbering. Primed atoms are related to unprimed ones by the twofold axis.

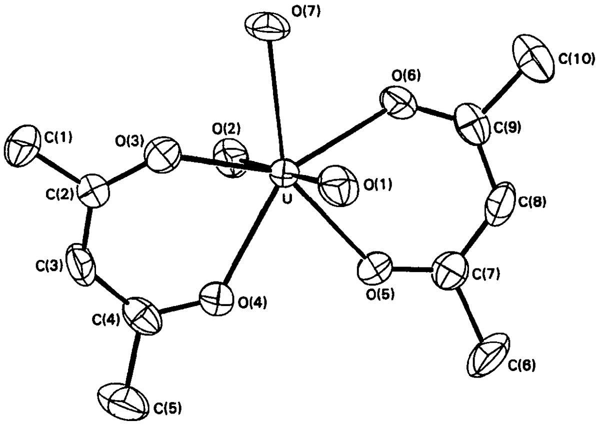

Fig. 1. View of complex (1), showing the atomic numbering.

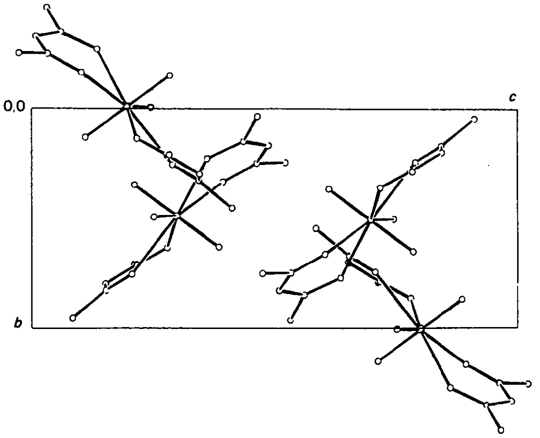

Fig. 2. Packing diagram for complex (1), viewed down **a**.

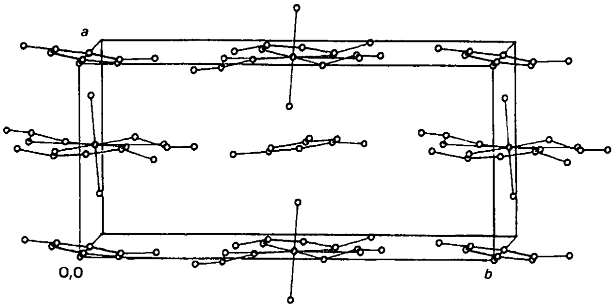

Fig. 4. Packing diagram for complex (2), viewed almost down **c**.

We thank the SERC for support under the CASE scheme (DJF).

References

Alcock, N. W. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, pp. 274–278. Munksgaard: Copenhagen.

Alcock, N. W., Flanders, D. J. & Brown, D. (1984). *J. Chem. Soc. Dalton Trans.* pp. 679–681.

Alcock, N. W., Flanders, D. J., Pennington, M. & Brown, D. (1987). *Acta Cryst.* C**43**, 1476–1480.

Comyns, A. E., Gatehouse, B. M. & Wait, E. (1958). *J. Chem. Soc.* pp. 4655–4665.

Frasson, E., Bombieri, G. & Panattoni, C. (1966). *Coord. Chem. Rev.* **1**, 145–150.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Riedel, Dordrecht, The Netherlands.)

Sheldrick, G. M. (1981). *SHELXTL Users Manual*, revision 4. Nicolet XRD Corporation, Madison, Wisconsin, USA.