Glycine Complexation with Uranyl Ion: Absorptiometric, Luminescence, and *X*-Ray Structural Studies of Tetrakis(glycine)dioxouranium(VI) Nitrate†

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Addition of glycine to uranyl nitrate in aqueous acidic solution induces shifts in both the highly structured absorption and emission bands in the visible region. An analysis by Job's method indicates the formation of a complex of stoicheiometry uranyl ion : glycine of 1 : 4. The structure determination of a single crystal of the complex $[UO_2(O_2CCH_2NH_3)_4][NO_3]_2$ by *X*-ray diffraction methods confirms this formulation. The structure has been refined to an *R* factor of 0.026 using 2 281 'observed' measured intensities. The complex is triclinic, space group $P\bar{1}$, with hexagonal bipyramidal co-ordination about the uranium atom. All the glycine ligands are in the zwitterionic form, $NH_3^+CH_2CO_2^-$ and act as *O*-donors; two are bidentate [U–O = 2.562(5)—2.489(6) Å], and two unidentate [mean U–O = 2.437(4) Å]. The uranyl U=O distance is 1.771(5) Å (mean).

Complexation of the dioxouranium(VI) (or uranyl) ion, $[UO_2]^{2+}$, by carboxylic acids has been widely studied and has been thoroughly reviewed recently.[1] Of particular interest has been the site and extent of co-ordination by ambidentate ligands, especially with *N*-donor atoms.[1,2] The simplest amino-acid, glycine, has attracted over 20 investigations of which the most recent[3] provides a reasonably unified picture of the situation prevailing in fairly dilute solution, namely that ligation proceeds through the carboxylate group with no involvement of the amino-group. This potentiometric study[3] indicates that 1:1 and 1:2 complexes are formed with log $\beta_2 = 2.20$ which agrees well with a value of 2.14 obtained polarographically.[4] No complexes higher than 1:2 were detected which contrasts with the situation both for Rh^{IV}[3] and, according to one report,[5] for complexation of glycine with dioxo(sulphato)uranium(VI), for which tris-glycine formulations are given. While the bulk of the evidence clearly favours co-ordination *via* the carboxylate group, Sergeev and Korshunov[6] suggest participation of the amino-group both in the glycinato(1−)uranyl complex[6] and in glycinato(1−)-thorium(IV) complexes,[7] on the basis both of the observed stability constants and of the NH frequency in the i.r. spectra. Such *N*-co-ordination is established[8a] for the bis(glycinato)complex of Cu^{II}, which is bis-chelated in a single plane with glycine as the monoanion, while reaction of glycine with *cis*-$[Pt(NH_3)_2(H_2O)_2]^{2+}$ in water gives initially *cis*-$[Pt^{II}(NH_3)_2(gly)(H_2O)]^{2+}$ [gly = *O*-co-ordinated zwitterion of glycine] which converts slowly into the (*N*,*O*)-chelate complex.[8b]

Accordingly, we have undertaken a study of the interaction of glycine with uranyl ion utilising absorptiometric and luminescence methods in solution and, in the solid state, a structure determination by *X*-ray crystallography.

Experimental

Absorption spectra were recorded on Perkin-Elmer model 552 and Shimadzu model UV-365 instruments. Luminescence spectra were recorded on a Perkin-Elmer model MPF-3 spectrofluorimeter. Luminescence lifetimes were determined with our laser flash kinetic spectrophotometer (Applied Photophysics, London, model K347) as described previously.[9]

Isolation of the Complex $[UO_2(O_2CCH_2NH_3)_4][NO_3]_2$.—Since solution studies (see later) indicated the presence of a 1:4 complex, a solution made up to this formulation was allowed to evaporate slowly to leave a bright yellow amorphous solid. This was redissolved in the minimum amount of water and a quantity placed in an n.m.r. tube (diameter 5 mm); acetonitrile was layered on top and the tube left for 2—3 d whereupon small crystals grew at the interface. The liquid layers were withdrawn carefully to leave a few yellow lath-shaped crystals which were washed with acetonitrile and allowed to dry in a desiccator.

Crystal Data.—$[UO_2(O_2CCH_2NH_3)_4][NO_3]_2$, $C_8H_{20}N_6O_{16}U$, $M = 686.25$, space group $P\bar{1}$, $a = 5.875(1)$, $b = 13.095(3)$, $c = 13.285(2)$ Å, $\alpha = 72.76(1)$, $\beta = 88.36(1)$, $\gamma = 88.27(2)°$, $U = 975.4(3)$ Å^3, $Z = 2$, $D_c = 2.34$ g cm^{-3}, $F(000) = 660$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 79.78 cm^{-1}.

Data were collected using a Syntex $P2_1$ four-circle diffractometer. Maximum 2θ was 50°, with scan range −1.0/+1.05°(2θ) around the $K_{\alpha1} - K_{\alpha2}$ angles, scan speed 2.0—29° min^{-1}, depending on the intensity of a 2-s pre-scan; backgrounds were measured at each end of the scan for 0.25 of the scan time. Three standard reflections were monitored every 200 reflections, and showed slight decay during data collection; the data were thus rescaled. The density could not be determined because the crystals dissolved in the flotation reagents available. Unit-cell dimensions and standard deviations were obtained by least-squares fit to 15 high-angle reflections. Of the 3 447 reflections collected, 2 281 were deemed to be observed [$I/\sigma(I) > 3.0$] and were used in refinement, after being corrected for Lorentz, polarisation, and absorption effects, the last by the analytical method with ABSCOR;[10] maximum and minimum transmission factors were 0.58 and 0.19. The crystal dimensions were 0.82 × 0.20 × 0.24 mm.

A centred, apparently monoclinic cell was initially found with dimensions $a = 5.874(1)$, $b = 15.652(3)$, $c = 23.883(4)$ Å, $\alpha = 89.17(2)$, $\beta = 117.30(1)$, $\gamma = 90.08(2)°$. The deviation of α from 90° was disturbing and a careful check of an oscillation photograph about *b* showed that although many intensities corresponded fairly closely to *m* symmetry, a number departed significantly. It was concluded that the correct symmetry was triclinic; $P\bar{1}$ was chosen arbitrarily, and shown to be correct by the successful refinement. The pseudo-symmetry is explicable with hindsight, because the uranium atoms virtually conform to monoclinic symmetry. Averaging the reflection data using monoclinic symmetry gave an overall internal agreement of 8.1% (*i.e.* considerably worse than the final agreement

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† *Supplementary data available* (No. SUP 56187, 2 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii–xix. Structure factors are available from the editorial office.

Table 1. Atomic co-ordinates (× 10^4) for $[UO_2(O_2CCH_2NH_3)_4][NO_3]_2$

Atom	*x*	*y*	*z*
U(1)	0	0	0
U(2)	5 000	5 000	5 000
O(11)	2 591(8)	−668(4)	−141(4)
O(12)	1 962(9)	1 780(4)	−242(4)
O(13)	1 902(10)	622(4)	1 355(4)
C(11)	2 499(12)	1 506(7)	727(6)
C(13)	4 001(14)	2 210(6)	1 147(6)
N(11)	4 307(12)	3 259(5)	373(5)
O(14)	369(7)	1 144(4)	−1 812(4)
O(15)	1 697(9)	1 807(4)	−3 454(4)
C(12)	1 976(11)	1 370(5)	−2 513(5)
C(14)	4 359(12)	1 126(6)	−2 102(5)
N(12)	6 084(10)	1 304(5)	−2 955(5)
N(10)	−901(13)	4 139(6)	1 108(5)
O(101)	−833(12)	3 246(5)	951(7)
O(102)	−2 751(11)	4 640(5)	1 065(5)
O(103)	862(11)	4 504(6)	1 340(6)
O(21)	2 513(8)	4 324(4)	4 849(4)
O(22)	7 199(9)	4 333(4)	3 671(4)
O(23)	7 126(8)	3 207(4)	5 255(4)
C(21)	7 794(12)	3 448(6)	4 309(6)
C(23)	9 409(13)	2 730(6)	3 927(6)
N(21)	9 698(11)	1 667(5)	4 715(5)
O(24)	4 722(8)	6 110(4)	3 173(4)
O(25)	3 537(9)	6 756(4)	1 538(4)
C(22)	3 186(12)	6 334(5)	2 484(5)
C(24)	794(11)	6 105(6)	2 876(7)
N(22)	−853(10)	6 299(5)	2 019(5)
N(20)	−4 685(12)	−850(6)	−3 877(5)
O(201)	−6 443(11)	−545(6)	−3 494(6)
O(202)	−2 848(10)	−385(5)	−3 895(5)
O(203)	−4 740(11)	−1 618(6)	−4 245(7)
H(131)	5 461	1 857	1 305
H(132)	3 316	2 305	1 779
H(111)	5 320	3 600	659
H(112)	3 000	3 661	225
H(113)	4 916	3 164	−231
H(141)	4 460	390	−1 684
H(142)	4 665	1 577	−1 670
H(121)	5 730	1 942	−3 434
H(122)	6 039	773	−3 267
H(123)	7 508	1 327	−2 711
H(231)	10 867	3 060	3 781
H(232)	8 833	2 635	3 293
H(211)	8 468	1 237	4 850
H(212)	9 988	1 874	5 294
H(213)	10 931	1 302	4 556
H(241)	375	6 555	3 308
H(242)	720	5 368	3 291
H(221)	−2 338	6 217	2 235
H(222)	−473	5 830	1 652
H(223)	−648	6 979	1 599

achieved), after rejection of 70 pairs of reflections with large differences between corresponding pairs. Thus the intensity symmetry only conforms very approximately to the monoclinic case.

A Patterson synthesis showed near perfect *I*-centring, and indicated that the structure contained two cations each with $\bar{1}$ symmetry rather than one unconstrained cation. With two uranium atoms placed at 0,0,0 and $\frac{1}{2},\frac{1}{2},\frac{1}{2}$, the light atoms were located by successive Fourier syntheses. The false *I*-centring caused some difficulty, particularly in the later stages when the correct peaks had to be selected on chemical grounds. Difference syntheses showed the positions of all the H atoms, including those of the four NH_3^+ groups; H atoms were included with fixed thermal parameter, $U = 0.07$ Å^2, and were refined as rigid CH_2 (C–H = 0.96 Å) or NH_3^+ groups (N–H = 0.91 Å). Final refinement was by cascaded least squares, and the largest peak on a final difference synthesis was of height 3.27 e Å^{-3} near a uranium atom.

A weighting scheme of the form $w = 1/[\sigma^2(F) + gF^2]$ with $g = 0.000\,26$ was applied, and this was shown to be satisfactory by a weight analysis. The final *R* value was 0.026. Computing was with the SHELXTL system on a Data General NOVA3 computer.[11] Scattering factors in the analytical form and anomalous dispersion factors were taken from ref. 12. Final atomic co-ordinates are given in Table 1, and bond lengths and angles in Table 2.

Results and Discussion

Spectroscopy.—Addition of glycine to aqueous acidic uranyl nitrate induces a marked bathochromic–hyperchromic effect on the visible absorption bands (Table 3), and both a red shift in the luminescence bands (Table 4) and an increase in luminescence intensity. It was possible to carry out a Job plot on the absorption data for the uranyl–glycine system (Figure 1) which indicates a co-ordination number approximating to four. The effect of addition of glycine to aqueous acidic uranyl

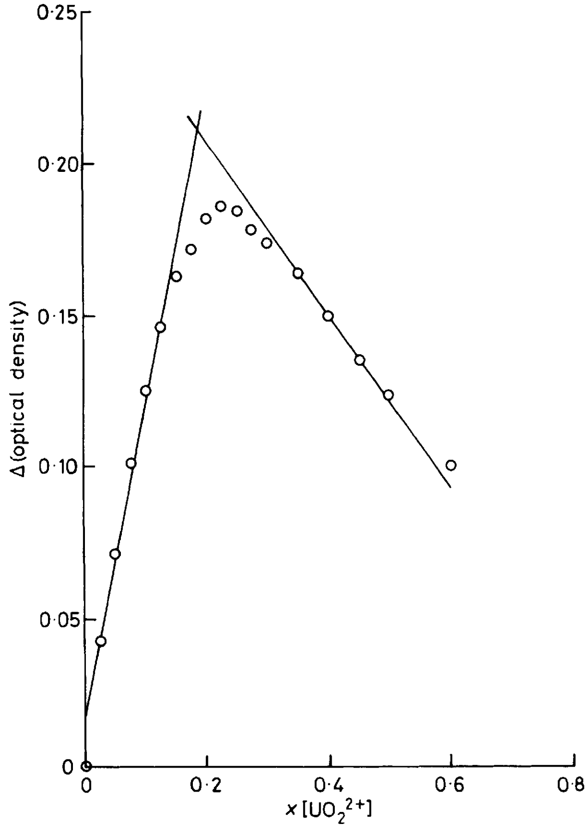

Figure 1. Job plot for the complexation of uranyl ion (*x* = mole fraction) with glycine: $[UO_2^{2+}]$ + [glycine] = 1.00 mol dm^{-3}, $[HClO_4]$ = 0.6 mol dm^{-3}, $[NO_3^-]$ = 2.00 mol dm^{-3} (as Na^+ salt), λ = 468 nm, cell pathlength 0.50 cm. Uranyl salt as the dinitrate hexahydrate

Table 2. Significant bond lengths (Å) and angles (°) with estimated standard deviations in parentheses for $[UO_2(O_2CCH_2NH_3)_4][NO_3]_2$

	Molecule 1 (n = 1)		Molecule 2 (n = 2)	
U–O(n1)	1.765(5)		1.777(2)	
U–O(n2)	2.562(5)		2.502(6)	
U–O(n3)	2.489(6)		2.561(5)	
U–O(n4)	2.436(4)		2.438(4)	
O(n2)–C(n1)	1.275(10)		1.263(8)	
O(n3)–C(n1)	1.263(9)		1.256(9)	
C(n1)–C(n3)	1.524(13)		1.498(11)	
C(n3)–N(n1)	1.464(9)		1.481(8)	
O(n4)–C(n2)	1.285(8)		1.269(8)	
O(n5)–C(n2)	1.224(8)		1.228(8)	
C(n2)–C(n4)	1.509(10)		1.493(9)	
C(n4)–N(n2)	1.469(9)		1.474(9)	
N(n0)–O(n01)	1.246(12)		1.245(10)	
N(n0)–O(n02)	1.246(10)		1.251(10)	
N(n0)–O(n03)	1.238(11)		1.243(12)	
O(n1)–U–O(n1′)	180.0		180.0	
O(n1)–U–O(n2)	92.7(2)		92.3(2)	
O(n1)–U–O(n3)	87.1(2)		86.4(2)	
O(n1)–U–O(n4)	90.4(2)		89.6(2)	
O(n2)–U–O(n3)	51.9(2)	128.1(2) *	51.0(2)	129.0(2) *
O(n2)–U–O(n4)	64.4(2)	115.6(2) *	64.3(2)	115.7(2) *
O(n3)–U–O(n4)	116.0(2)	64.0(2) *	114.9(2)	65.1(2) *
U–O(n2)–C(n1)	91.5(4)		95.7(5)	
U–O(n3)–C(n1)	95.3(5)		93.1(7)	
O(n2)–C(n1)–O(n3)	121.2(8)		120.1(7)	
O(n2)–C(n1)–C(n3)	120.8(6)		118.6(7)	
O(n3)–C(n1)–C(n3)	117.8(7)		121.2(6)	
C(n1)–C(n3)–N(n1)	111.4(6)		112.2(6)	
U–O(n4)–C(n2)	135.7(4)		135.7(4)	
O(n4)–C(n2)–O(n5)	124.8(6)		124.4(6)	
O(n4)–C(n2)–C(n4)	115.5(6)		116.6(6)	
O(n5)–C(n2)–C(n4)	119.6(6)		118.9(6)	
C(n2)–C(n4)–N(n2)	112.3(6)		113.0(6)	
O(n01)–N(n0)–O(n02)	119.9(8)		120.3(8)	
O(n01)–N(n0)–O(n03)	119.5(8)		120.3(8)	
O(n02)–N(n0)–O(n03)	120.5(8)		119.4(7)	

* Values for primed atoms, which are related to unprimed ones by an inversion centre.

Table 3. Absorption spectra of uranyl nitrate and $[UO_2(O_2CCH_2NH_3)_4][NO_3]_2$; $[HClO_4]$ = 0.20 mol dm^{-3}, T = 293 K

λ/nm	
$[UO_2]^{2+}$ [a]	$[UO_2(O_2CCH_2NH_3)_4]^{2+}$ [b]
485.0	488.0
467.0	470.0
449.0(sh)	453.0(sh)
436.5(sh)	438.0(sh)
424.5	422.5(sh)
412.5[c]	416.5[c]
401.5	409.0(sh)
392.0(sh)	
381.0(sh)	
368.0	365.0(sh)
358.0	

[a] $[UO_2^{2+}]$ = 0.10 mol dm^{-3}. [b] $[UO_2(O_2CCH_2NH_3)_4{}^{2+}]$ = 0.019 mol dm^{-3}. [c] $\lambda_{max.}$.

Table 4. Emission spectra of uranyl nitrate and $[UO_2(O_2CCH_2NH_3)_4]^{2+}$; $[HClO_4]$ = 0.20 mol dm^{-3}, T = 293 K

	$\lambda_{excitation}$/nm [a]	$\lambda_{emission}$/nm [a]
$[UO_2]^{2+}$ [b]	412.5	490.0, 510.0,[c] 531.5, 557.0
$[UO_2(O_2CCH_2NH_3)_4]^{2+}$ [d]	416.5	495.0,[c] 516.0, 537.5, 561.0

[a] 5-nm Slits. [b] $[UO_2{}^{2+}]$ = 0.10 mol dm^{-3}. [c] λ_{max}. [d] $[UO_2(O_2CCH_2NH_3)_4{}^{2+}]$ = 0.019 mol dm^{-3}.

nitrate, on the luminescence lifetime (τ) shown in Figure 2, indicates that complexation increases as the ligand concentration is increased, giving longer-lived states (similar to the effects with phosphate and fluoride ions[13]), until at the highest glycine concentrations a plateau region is reached.

The i.r. spectrum of the recrystallised complex (KBr disc) showed that $\nu_{asym}(CO_2^-)$ increased from 1 590 (free glycine) to 1 640 cm^{-1}, while $\nu_{sym}(CO_2^-)$ decreased from 1 415 to 1 385 cm^{-1}. The N–H stretching frequencies were unchanged on complexation to $[UO_2]^{2+}$, indicating a lack of involvement in ligation.

The solution data indicate that, at least under the glycine concentrations studied, the co-ordination of glycine involves *four* ligands (rather than the two suggested previously[3]). This was confirmed unequivocally by the *X*-ray structure determination.

Structure Determination.—A view of the cation $[UO_2(O_2CCH_2NH_3)_4]^{2+}$ is shown in Figure 3 together with the atomic numbering. The co-ordination about the uranium atom is seen to be hexagonal bipyramidal with four glycine molecules co-ordinated in the equatorial plane, all *via* their carboxylate oxygen atoms. Two of the glycine molecules are monodentate

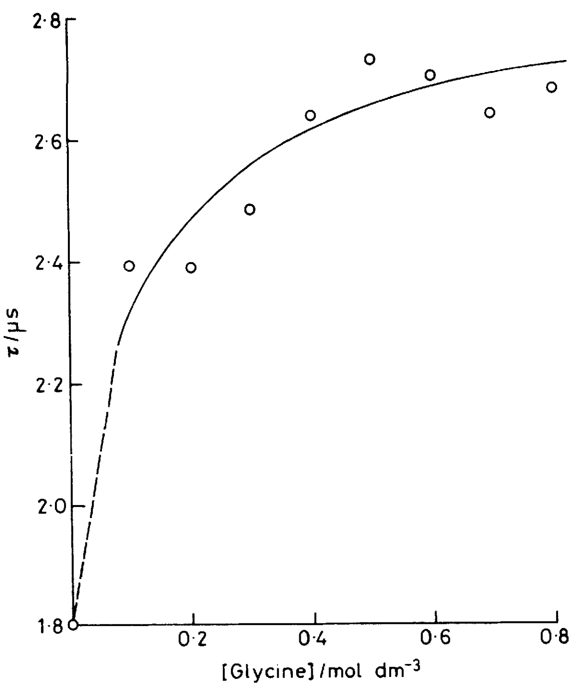

Figure 2. Dependence of lifetime (τ) of excited $[UO_2]^{2+}$ upon glycine concentration; $[UO_2{}^{2+}]$ = 0.1 mol dm^{-3}, $[HClO_4]$ = 0.2 mol dm^{-3}

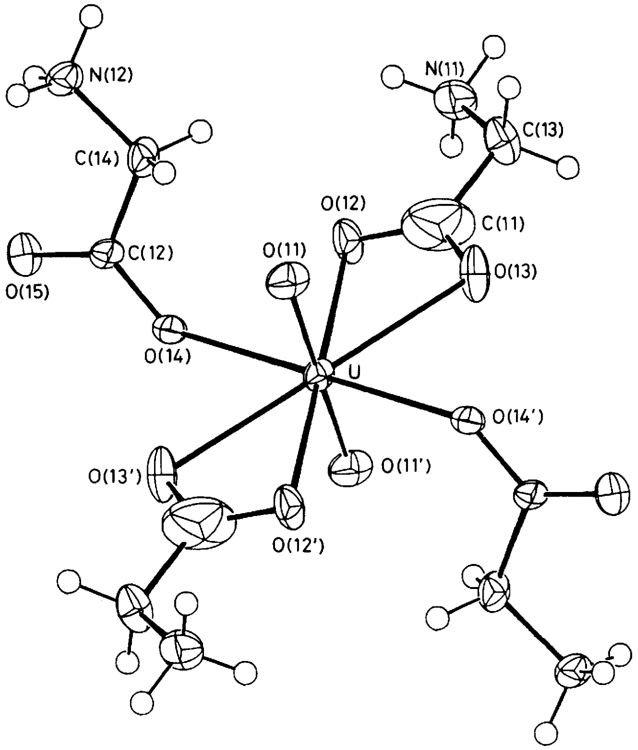

Figure 3. The $[UO_2(O_2CCH_2NH_3)_4]^{2+}$ cation 1, showing the atomic numbering (primed atoms are related to unprimed atoms by a two-fold axis). Cation 2 is virtually identical

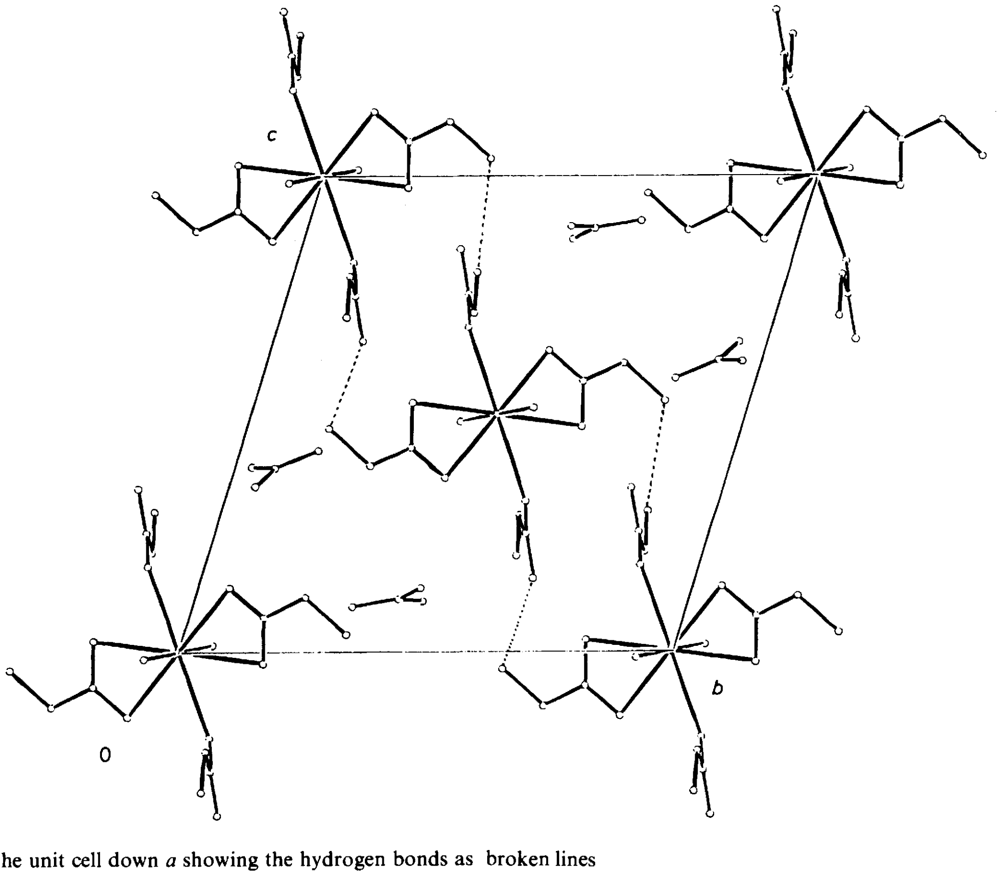

Figure 4. View of the unit cell down *a* showing the hydrogen bonds as broken lines

Table 5. Hydrogen bonds; distances (Å) and angles (°)

(*a*) N(11)–H(113) ··· O(25)	
N(11)–H(113)	0.91 *
H(113) ··· O(25)	1.913(9)
N(11) ··· O(25)	2.810(9)
N(11)–H(113) ··· O(25)	168.2(8)
(*b*) N(21)–H(212) ··· O(15)	
N(21)–H(212)	0.91 *
H(212) ··· O(15)	1.946(9)
N(21) ··· O(15)	2.788(9)
N(21)–H(212) ··· O(15)	153.1(7)

* Bond length fixed; H atoms held in rigid tetrahedral geometry, with freedom for the NH_3 unit to move.

and two are bidentate. The two cations found in the unit cell (cations 1 and 2) (Figure 4) are very similar, each having asymmetric co-ordination to the bidentate glycine molecules with one longer and one shorter distance: U(1)–O(12) and U(1)–O(13) are 2.562(5) and 2.489(6) Å respectively and U(2) is 2.502(6) Å from O(22) and 2.561(5) Å from O(23). The distances to the unidentate glycine are shorter, 2.436(4) and 2.438(4) Å. These small but statistically significant differences are the only obvious variations between the two cations.

There is however a larger difference between the two nitrate groups in their orientation in the cell, which can be seen in Figure 4. One nitrate makes a larger angle to the *b* axis than the other and is also oriented differently in the *a*–*b* plane. Presumably this provides the driving force for the small distortions from monoclinic symmetry. It is presumably possible for the nitrate groups to take up these alternative orientations because they sit in a relatively large cavity without strong interactions. The shortest contact distances they make are O ··· H distances of 1.998(10) Å [O(101) ··· H(111)] and 1.992(10) Å [O(202) ··· H(213)]. The cations are linked into infinite chains by hydrogen bonding (Table 5), N(11)–H(113) ··· O(25) and N(21)–H(212) ··· O(15), which can be seen in the view of the cell down the *a* axis (Figure 4) where the hydrogen bonds are shown as broken lines.

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