important bond lengths and angles in Table 2. A stereo-drawing of the unit cell is shown in Fig. 1.*

Discussion. As expected, the crystallographically non-equivalent Pt—C(1), Pt—C(2), and C(1)—N(1), C(2)—N(2) distances, are equal to within one e.s.d. These distances are in close agreement with those reported previously (e.g. Washecheck, Peterson, Reis & Williams, 1976; Williams, Keefer, Washecheck & Enright, 1976; Needham, Johnson, Cornish & Williams, 1977). The cyanides form a planar arrangement around the central Pt atom, although they do not form a square.

The anilinium ion interacts with the platinocyanide group mainly through N—H$\cdots$ $^-$N≡C hydrogen bonds. The dihedral angle between the planes of these two groups is 78°. It appears two bonds in the ring of the anilinium ion [C(4)—C(5), C(8)—C(7)] are longer by four times the standard deviation of the other C—C bonds. The distance between nearest-neighbor anilinium groups is 4·25 Å. The anilinium ion stacking is such that the benzene rings are eclipsed and the nitrogens point toward opposite ends of the unit cell (see Fig. 1).

No Pt—Pt bonds exist in this compound, probably

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* Lists of structure factors, anisotropic thermal parameters and r.m.s. thermal displacements have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32408 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

because of the steric hindrance imposed by the anilinium ions. This interaction is probably the reason why attempts to synthesize partially oxidized anilinium tetracyanoplatinate have as yet been unsuccessful. This cation hindrance has been previously observed in Ba[Pt(CN)₄].4H₂O (Maffly, Johnson & Williams, 1977). However, in that case a Pt—Pt chain was formed, probably because of the smaller cation. It appears that partially oxidized anilinium tetracyanoplatinate did not form in this case because the steric interactions between the anilinium ions favor larger (>5 Å) Pt—Pt separations.

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Calcium Nitrate Tetraurea

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Abstract. Ca(NO₃)₂.4CO(NH₂)₂ is monoclinic, space group $P2_1/c$, $a = 9\cdot246$ (1), $b = 12\cdot668$ (1), $c = 7\cdot684$ (1) Å, $\beta = 113\cdot51$ (1)°, $Z = 2$, $D_m = 1\cdot63$, $D_c = 1\cdot63$ g cm^{-3}. The Ca^{2+} ions are octahedrally coordinated by O atoms from two NO₃$^-$ ions and four urea molecules. The discrete, neutral complexes are linked with hydrogen bonds.

Introduction. Crystals of the title compound were grown by slow evaporation of an aqueous solution of CaNO₃ and urea in a molar ratio 1:4. A crystal ground to the shape of a sphere of diameter 0·20 mm was used

to collect intensity data on an Enraf–Nonius CAD-4 diffractometer. The lattice constants were obtained by least-squares refinement from the setting angles of the reflexions used in the auto-indexing procedure. They agreed with those previously reported (Chojnacki, Lebioda & Weber, 1969).

Three-dimensional diffraction data out to $\theta = 30°$ were recorded with graphite-monochromated Mo $K\alpha$ radiation and a $\theta/2\theta$ scan mode. The scan range over the peak was $0\cdot60° + 0\cdot42°$ tan θ. Background was measured at both sides of each reflexion over one fourth of the scan range. A standard reflexion was

monitored after each group of 23 measurements; the greatest deviation was 3·3%. The measurements were corrected for long-term instabilities. Lorentz and polarization corrections were applied to the intensity data set. Absorption corrections were negligible (μR = 0·045). Of the 2394 measured independent reflexions, 2226 values with $F_o^2 > 0$ were used in subsequent calculations.

The structure was solved by the vector superposition method and repeated Fourier synthesis. Full-matrix refinement of positional and anisotropic thermal parameters of non-hydrogen atoms gave $R = 0·066$. A difference synthesis computed after this step revealed all eight H atoms of the urea molecule, with peak heights ranging from 0·65 to 0·80 e Å^{-3}. The peaks were on preassumed N–H bonds but distances from N atoms ranged from 0·73 to 0·90 Å. These values are too small when compared with 0·99 Å found with a neutron study of the urea structure (Worsham, Levy & Peterson, 1957). A reason for this systematic error could be, apart from asphericity shifts, an anisotropic thermal motion of the H atoms (Hamilton, 1968). Such motion is expected because the N atoms vibrate very anisotropically. The distances and planarity of the

heavy atoms of the urea molecules do not show distortion, so in the subsequent refinement positions of H atoms were calculated from the known geometry of the urea molecule and kept fixed.

The final values of discrepancy indices for all $F_o > 0$ were $R = 0·057$, $R_w = 0·058$, $R_g = 0·068$ where $R = \Sigma \Delta F / \Sigma F$, $R_w = \Sigma w^{1/2} \Delta F / \Sigma w^{1/2} F$ and $R_g = \Sigma w \Delta F^2 / \Sigma w F^2$; shift-to-e.s.d. ratios in the last cycle were less than 0·3. The weights used were

$$w = \frac{1}{(1·94 + F_o + 0·0184F_o^2)}$$
$$\times \frac{I}{A^*(\text{Lp})^{-1}[\sigma^2(I) + 0·0001I^2]}.$$

The calculations were performed with the system of programs written by Sheldrick (1972). The atomic scattering factors of Cromer & Waber (1965) were used.[†]

The final heavy-atom positional parameters and their standard deviations are given in Table 1,[†] those of the H atoms are in Table 2.

Discussion. In the structure, complexes around Ca^{2+} form discrete units linked by hydrogen bonds. The complex is centrosymmetric with the Ca^{2+} ion in the

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Table 1. *Final heavy-atom positional parameters* ($\times 10^4$) *and their standard deviations*

	x	y	z
Ca	0	5000	5000
O(1)	2236 (2)	4510 (1)	4438 (2)
O(2)	3975 (3)	3405 (2)	4460 (3)
O(3)	4245 (3)	4177 (2)	7018 (3)
N(1)	3511 (2)	4039 (1)	5336 (2)
O(4)	571 (2)	3946 (1)	7640 (2)
N(2)	1162 (3)	3092 (2)	10408 (3)
N(3)	2208 (3)	4722 (2)	10369 (3)
C(1)	1295 (2)	3920 (1)	9412 (3)
O(5)	1311 (2)	6422 (1)	6796 (2)
N(4)	2543 (2)	7905 (1)	8263 (3)
N(5)	3963 (2)	6426 (2)	8238 (3)
C(2)	2567 (2)	6907 (2)	7732 (2)

Table 2. *Hydrogen-atom parameters* ($\times 10^3$)

The positional parameters used in the refinement are calculated from the geometry of the urea molecule. All H atoms were assigned a common isotropic temperature factor which refined to 3·78 Å^2.

	x	y	z
H(1)	174	307	1182
H(2)	48	249	967
H(3)	279	470	1178
H(4)	231	535	963
H(5)	354	829	901
H(6)	150	826	788
H(7)	496	681	899
H(8)	398	568	784

Table 3. *Distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Nitrate ion

N(1)–O(1)	1·254 (2)	O(1)–N(1)–O(2)	117·8 (2)
N(1)–O(2)	1·230 (2)	O(1)–N(1)–O(3)	121·5 (2)
N(1)–O(3)	1·209 (2)	O(2)–N(1)–O(3)	120·7 (2)

Urea 1

C(1)–O(4)	1·255 (2)	N(2)–C(1)–N(3)	117·6 (2)
C(1)–N(2)	1·333 (3)	O(4)–C(1)–N(2)	120·8 (2)
C(1)–N(3)	1·337 (3)	O(4)–C(1)–N(3)	121·6 (2)

Urea 2

C(2)–O(5)	1·255 (2)	N(4)–C(2)–N(5)	118·4 (2)
C(2)–N(4)	1·331 (2)	O(5)–C(2)–N(4)	121·0 (2)
C(2)–N(5)	1·337 (3)	O(5)–C(2)–N(5)	120·6 (2)

Calcium shell

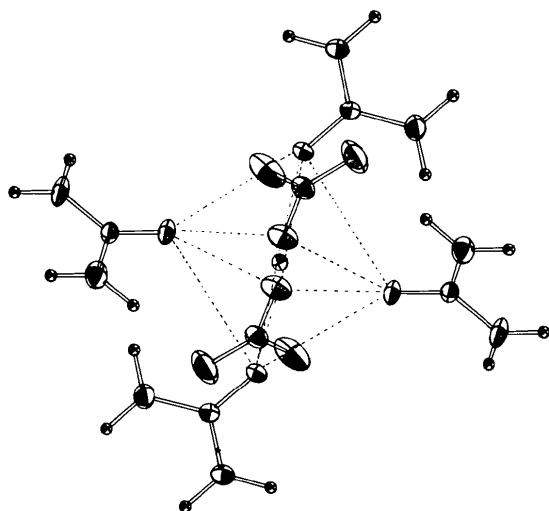| Ca–O(1)	2·358 (1)	O(1)–Ca–O(4)	95·7 (1)
Ca–O(4)	2·307 (1)	O(1)–Ca–O(5)	91·4 (1)
Ca–O(5)	2·299 (1)	O(4)–Ca–O(5)	92·6 (1)
Ca–nitrate ion plane	1·072	Ca–O(1)–N(1)	136·5 (1)
Ca–urea 1 plane	0·133	Ca–O(4)–C(1)	143·5 (1)
Ca–urea 2 plane	0·233	Ca–O(5)–C(2)	150·8 (1)

Fig. 1. Thermal ellipsoids for the complex drawn with the computer program *ORTEP* (Johnson, 1965).

special position $(0,\frac{1}{4},\frac{1}{4})$. Fig. 1 shows the Ca^{2+} environment. There is no O–O contact shorter than 3·1 Å within the Ca shell. Bond lengths and angles and their e.s.d.'s are listed in Table 3. One O of each NO$_3^-$ ion is directed towards the cations, unlike the structure of a hydrated counterpart, Ca(NO$_3$)$_2$.CO(NH$_2$)$_2$.3H$_2$O (Lebioda, 1972), where two of the nitrate O atoms are coordinated giving a coordination number of eight. The Ca atom is not on the line of the N–O bond, $\angle$ N(1)–O(1)–Ca equals 136·5°, nor in the plane of the nitrate ion. Among Ca–O bonds the distance to the O atom of the NO$_3^-$ ion is the longest.

The O atoms of the urea molecules are coordinated with Ca^{2+} and are acceptors of hydrogen bonds. The angles between the cation, the O and the H atoms are Ca–O(4)–H(6) 102·2°, Ca–O(5)–H(2) 94·0°. The Ca^{2+} ion is approximately in the planes of the urea molecules. The hydrogen-bonding scheme is shown in Fig. 2. It is not discussed in detail because of the low
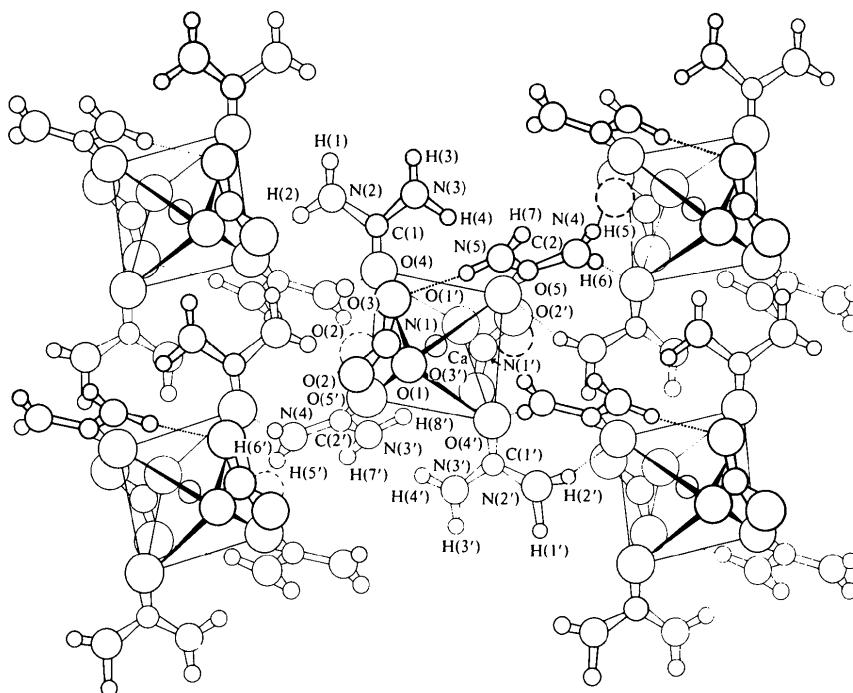

Fig. 2. The hydrogen bonding viewed normal to the crystallographic *bc* plane. Atoms drawn with a broken line are from the neighbouring layers.

Table 4. *Distances* (Å) *and angles* (°) *in the hydrogen-bonding system*

Hydrogen parameters used were calculated from geometrical considerations. H $\cdots$ *A–B* denotes the angle between the hydrogen, and the covalent bond formed by the acceptor. 'H to *A* plane' is the distance from the hydrogen to the plane of the free electron pairs of the acceptor.

D–H$\cdots$*A*	Acceptor position	*D*$\cdots$*A*	H$\cdots$*A*	$\angle$*D*–H$\cdots$*A*	$\angle$H$\cdots$*A–B*	H to *A* plane
N(4)–H(6)$\cdots$O(4)	$\bar{x}, \frac{1}{2} + y, \frac{3}{2} - z$	2·986 (2)	1·99	174·5	105·1	1·17
N(5)–H(8)$\cdots$O(3)	x, y, z	3·043 (2)	2·04	173·7	112·3	0·96
N(4)–H(5)$\cdots$O(2)	$\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$	3·055 (2)	2·12	154·0	106·1	0·73
N(2)–H(2)$\cdots$O(5)	$\bar{x}, -\frac{1}{2} + y, \frac{3}{2} - z$	3·079 (2)	2·09	168·6	110·2	0·79
N(3)–H(3)$\cdots$O(1)	$x, y, 1 + z$	3·128 (2)	2·30*	138·7	92·6	2·01
N(2)–H(1)$\cdots$O(2)	$x, y, 1 + z$	3·187 (2)	2·29*	132·1	102·6	0·85

* Probably too long to be designated a hydrogen bond.

accuracy of the H positions, but distances and angles obtained with calculated H positions are in Table 4. The acceptors are O atoms of planar molecules with sp^2 hybridization and two free electron pairs lying in the plane of the molecule, so angles between the H, O and the atom to which the O is bonded are given, as well as distances from the H to the acceptor plane. Four of the eight H atoms are involved in hydrogen bonding. One bond is between atoms of the same complex, three others link Ca complexes in a three-dimensional net.

There are probably no hydrogen bonds but only van der Waals contacts between $N(3)\cdots O(1)$ and $N(2)\cdots O(2)$ as the $H(3)-O(1)$ and $H(1)-O(2)$ distances of $2\cdot 30$ Å are too long.

In the structure, only 50% of the possible hydrogen bonds are formed. This can be explained by the H atoms of urea being all in the plane of the molecule and unable to realize simultaneously the geometrical requirements for hydrogen bonding.

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Biphenyl: Three-Dimensional Data and New Refinement at 293 K*

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Abstract. $C_{12}H_{10}$, monoclinic, $P2_1/a$, $a = 8\cdot 12$ (2), $b = 5\cdot 63$ (1), $c = 9\cdot 51$ (2) Å, $\beta = 95\cdot 1$ (3)°, $Z = 2$. X-ray diffraction shows the molecule to be planar, but libration around the long axis of the molecule presents an unusually large value 109 (°)^2, thus suggesting a statistically centrosymmetric arrangement.

Introduction. Previous X-ray analyses of biphenyl at room temperature have been published (Trotter, 1961; Robertson, 1961; Hargreaves & Rizvi, 1962). The present study was undertaken to compare structural and thermal parameters, and particularly librational tensors at 293 and 110 K (Charbonneau & Delugeard, 1976). Colourless thin needles, elongated along the crystallographic b axis, were grown from a methanol solution by slow evaporation. Unit-cell dimensions used for the refinement were those of Hargreaves & Rizvi (1962). Measurements were made on an Enraf–Nonius three-circle automatic diffractometer with Zr-filtered Mo $K\alpha$

radiation, and the θ–2θ scanning method (scan range $1\cdot 30$°). A control reflexion, monitored every 50 reflexions, fluctuated no more than 2%. 697 independent reflexions were used in the structure determination (absorption effects were neglected).

The refinement started with the coordinates given by the study at low temperature, with the ANHAR program (Baudour, 1972) based on Kay & Behrendt's (1963) formula; this program includes translational and librational tensors of the assumed rigid-body molecule in the structure factor expression, and takes the internal degree of freedom due to the single bond into account. The weight, w, for each reflexion was $w = 1/\sigma^2(|F_o|)$ with $\sigma^2(|F_o|) = (1/N)(F_o^2/4I^2)[CN + (B_1/4) + (B_2/4) + (I^2/400)]$. CN is the total number of counts collected during the scan, B_1 and B_2 are the background counts, I is the net intensity and N is the number of cycles of measurements for the reflexion. Five cycles of refinement led to the following final values of the agreement indices: $R_1 = \Sigma w||F_o| - |F_c||/\Sigma w|F_o| = 0\cdot 063$; $R_2 = |\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o^2)|^{1/2} = 0\cdot 068$.

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* Structural Transition in Polyphenyls. V.