Table 4. *Distances less than* 3·2 Å *in the environment of ammonium ions* (Å)

Symmetry code: (i) x,y,z; (ii) $\frac{1}{2} - y, \frac{3}{2} + x - y, \frac{2}{3} + z$; (iii) $\bar{y}, x - y, z$; (iv) $\frac{2}{3} - y, \frac{1}{3} + x - y, \frac{1}{3} + z$; (v) $y - x, \bar{x}, z$; (vi) $\frac{1}{3} + y - x, \frac{2}{3} - x, \frac{2}{3} + z$.

N(1)–O(8^i)	2·740 (27)	N(2)–O(7^{iv})	2·793 (34)
N(1)–O(1^i)	2·778 (24)	N(2)–O(1^v)	2·942 (30)
N(1)–O(8^{ii})	2·956 (27)	N(2)–O(7^{vi})	2·942 (35)
N(1)–O(5^{iii})	3·019 (28)	N(2)–O(4^{ii})	2·948 (36)
N(1)–O(7^{iv})	3·181 (30)	N(2)–O(4^v)	2·967 (36)
N(1)–O(1^{ii})	3·196 (28)	N(2)–O(2^{vi})	3·096 (29)

(1977) have recently reported large distortions in the bidentate SeO$_4$ group when it is acting as a chelating group. In the present structure the selenate group is a bridging one and the angles involved [O(2)–Se(1)–O(3) and O(5)–Se(2)–O(5)] appear normal. Thus, the distortions observed are probably due to hydrogen bonding and also partly to data inaccuracy.

In the environment of each of the two ammonium ions there are six possible hydrogen-bond contacts to selenate O atoms, ranging from 2·74 to 3·20 Å and from 2·79 to 3·10 Å for N(1) and N(2) respectively (Table 4). After our failure to locate H atoms from Fourier maps, an attempt was made to elucidate a possible hydrogen-bonding scheme from geometrical considerations. It too proved unsuccessful.

According to a survey by Khan & Bauer (1972), the ammonium ions are in static or dynamic disorder or no hydrogen bonding is present when the coordination number of ammonium is higher than four. Recently it

was shown, however, that the ammonium ion, at higher coordination numbers, is capable of acting simultaneously as a hydrogen-bond donor and as a strongly electropositive large cation, thus having a dual character (Catti & Franchini-Angela, 1976). In the case of (NH$_4$)$_3$Sc(SeO$_4$)$_3$ the presence of disordered hydrogen bonds around N atoms, possibly together with some purely electrostatic interactions, seems likely.

References

BENELLI, C., DI VAIRA, M., NOCCIOLI, G. & SACCONI, L. (1977). *Inorg. Chem.* **16**, 182–187.

CATTI, M. & FRANCHINI-ANGELA, M. (1976). *Acta Cryst.* **B32**, 2842–2848.

ERÄMETSÄ, O. & HAUKKA, M. (1966). *Suom. Kemistil. B*, **39**, 242–247.

KARLE, J. & KARLE, I. L. (1966). *Acta Cryst.* **21**, 849–859.

KHAN, A. A. & BAUER, W. H. (1972). *Acta Cryst.* **B28**, 683–693.

MELSON, G. A. & STOTZ, R. W. (1971). *Coord. Chem. Rev.* **7**, 133–160.

SIZOVA, R. G., VORONKOV, A. A. & BELOV, N. V. (1974). *Dokl. Akad. Nauk. SSSR*, **217**, 1073–1076; *Sov. Phys. Dokl.* **19**, 472–474.

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

TEZU, H,. IVANOV-EMIN, B. N., KOROTAEVA, L. G. & ZAITZEV, B. E. (1970). *Zh. Neorg. Khim.* **15**, 2060–2063; *Russ. J. Inorg. Chem.* **15**, 1062–1064.

VALKONEN, J., NIINISTÖ, L., ERIKSSON, B., LARSSON, L. O. & SKOGLUND, U. (1975). *Acta Chem. Scand. Ser. A*, **29**, 866–872.

Tetraethylammonium Trichloro(ethyl vinyl ether)platinum(II)

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Abstract. [(C$_2$H$_5$)$_4$N][PtCl$_3$(C$_4$H$_8$O)], $P2_1/n$, $a = 7\cdot728$ (4), $b = 17\cdot763$ (6), $c = 13\cdot418$ (9) Å, $\beta = 103\cdot71$ (1)°, $U = 1789\cdot4$ Å^3, $Z = 4$, $D_x = 1\cdot87$ g cm^{-3}, $\mu = 86\cdot9$ cm^{-1} (Mo $K\alpha$). The structure contains undistorted tetraethylammonium cations and complex anions of Pt^{II} ligated by three chloride ions and the double bond of the vinyl ether in a square-planar coordination arrangement. The mid-point of the double bond is 0·19 Å off the plane determined by the Pt and three Cl atoms. The C atom of the double bond which bears the ether O atom is 0·08 Å further from the Pt atom than the unsubstituted C atom. There appears to be no significant interaction between the ether O atom and the Pt atom in the solid state. The structure was refined to an R of 0·022 for 1602 independent observed reflections.

Introduction. The structure of [(C$_2$H$_5$)$_4$N][PtCl$_3$-(C$_4$H$_8$O)] has been determined as part of a study of the catalytic activity of Pt^{II} complexes for alkoxide

exchange and cis–trans isomerization of substituted vinyl ethers (Busse, Pesa & Orchin, 1977). We particularly wished to determine whether the unusual behavior of these complexes results from an interaction between the O atom of the vinyl ether and the Pt atom.

Needle-shaped pale-yellow crystals of the title compound were grown from chloroform/hexane solution by an extension of the procedures of Spaulding, Reinhardt & Orchin (1972). Intensities were measured using a Syntex $P1$ diffractometer equipped with a graphite monochromator using Mo $K\alpha$ radiation. The crystal was of approximate dimensions $0.1 \times 0.2 \times 0.3$ mm. The non-standard space group

$P2_1/n$ was chosen to give a β angle close to 90°. 2008 reflections were measured in the range $3° < 2\theta < 41°$; of these, 1608 unique reflections with $F > 3\sigma(F)$ were used in the structure determination. Lp and numerical absorption corrections were made; calculated transmission coefficients varied from 0.38 to 0.63.

The non-hydrogen atoms were located from Patterson and difference syntheses, methylene H atoms were placed in calculated positions (C–H 0.95 Å, tetrahedral geometry), and the remaining H atoms were located in a subsequent difference synthesis. Refinement of non-hydrogen positional and anisotropic thermal parameters and H positional and isotropic thermal parameters converged with $R = 0.022$ and $R' = \Sigma w^{1/2}\Delta/\Sigma w^{1/2}|F_o| = 0.018$, where the weighting scheme has been described previously (Elder & Trkula, 1977). Refinement of H positional and thermal parameters resulted in significant (0.005 level) improvement of the model (Hamilton, 1965). Mean values of $w\Delta^2$ varied only slightly with sin θ or $|F_o|$. A final difference synthesis was essentially featureless. Aside from peaks of 0.6 and 0.5 e Å^{-3} near Pt and Cl(3), all peaks were below 0.25 e Å^{-3}. Complex neutral-atom scattering factors were used. Final atomic coordinates are given in Table 1, with non-hydrogen bond lengths and angles in Tables 2 and 3.*

* Lists of structure factors, thermal parameters, bond lengths and angles involving H and selected non-bonded distances have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32960 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Atomic coordinates ($\times 10^4$, for H $\times 10^3$)

	x	y	z
Pt	469 (1)	4587 (1)	3098 (1)
Cl(1)	1285 (3)	3336 (1)	3126 (1)
Cl(2)	−366 (3)	5826 (1)	3084 (2)
Cl(3)	−1771 (3)	4389 (1)	1626 (1)
O	3792 (6)	5528 (2)	3897 (3)
N	7347 (9)	1959 (2)	4929 (3)
C(1)	8003 (11)	1164 (3)	4793 (5)
C(2)	8085 (12)	658 (4)	5708 (5)
C(3)	8555 (11)	2347 (4)	5856 (5)
C(4)	10479 (11)	2386 (4)	5843 (5)
C(5)	7417 (13)	2386 (4)	3949 (6)
C(6)	6727 (11)	3174 (3)	3989 (4)
C(7)	5478 (10)	1945 (4)	5121 (5)
C(8)	4071 (11)	1573 (4)	4283 (6)
C(9)	2002 (11)	4711 (4)	4631 (4)
C(10)	3179 (10)	4833 (4)	4017 (5)
C(11)	4540 (11)	5617 (4)	3025 (5)
C(12)	5104 (12)	6420 (4)	2952 (6)
H(1)C(1)	914 (8)	121 (3)	455 (4)
H(2)C(1)	727 (8)	93 (3)	411 (4)
H(3)C(3)	857 (8)	204 (3)	634 (4)
H(4)C(3)	796 (7)	290 (3)	591 (3)
H(5)C(5)	879 (9)	238 (3)	381 (5)
H(6)C(5)	687 (8)	216 (3)	354 (3)
H(7)C(7)	556 (11)	167 (3)	604 (5)
H(8)C(7)	502 (9)	244 (3)	517 (4)
H(9)C(11)	529 (6)	537 (2)	298 (3)
H(10)C(11)	363 (9)	556 (2)	229 (3)
H(11)C(2)	726 (6)	51 (2)	583 (3)
H(12)C(2)	884 (11)	79 (3)	644 (4)
H(13)C(2)	823 (8)	23 (2)	562 (3)
H(14)C(4)	1095 (9)	190 (3)	582 (4)
H(15)C(4)	1112 (7)	262 (2)	638 (3)
H(16)C(4)	1069 (8)	267 (2)	522 (3)
H(17)C(6)	737 (6)	345 (2)	441 (3)
H(18)C(6)	692 (9)	330 (3)	324 (4)
H(19)C(6)	557 (9)	319 (3)	389 (4)
H(20)C(8)	277 (9)	155 (3)	456 (5)
H(21)C(8)	403 (12)	182 (4)	361 (5)
H(22)C(8)	417 (9)	105 (3)	415 (5)
H(23)C(12)	513 (11)	651 (4)	201 (5)
H(24)C(12)	590 (9)	656 (3)	362 (4)
H(25)C(12)	412 (9)	672 (3)	272 (4)
H(26)C(9)	195 (6)	423 (2)	502 (3)
H(27)C(9)	148 (9)	510 (4)	512 (6)
H(28)C(10)	402 (8)	447 (2)	387 (3)

Table 2. Bond lengths (Å)

Pt–C(9)	2.128 (7)	N–C(1)	1.526 (7)
Pt–C(10)	2.208 (7)	N–C(3)	1.531 (8)
Pt–Cl(1)	2.307 (2)	N–C(5)	1.531 (9)
Pt–Cl(2)	2.292 (2)	N–C(7)	1.525 (10)
Pt–Cl(3)	2.324 (2)	C(1)–C(2)	1.511 (9)
C(9)–C(10)	1.382 (12)	C(3)–C(4)	1.492 (12)
C(10)–O	1.345 (8)	C(5)–C(6)	1.494 (9)
C(11)–O	1.431 (9)	C(7)–C(8)	1.519 (10)
C(11)–C(12)	1.501 (10)		

Table 3. Bond angles (°)

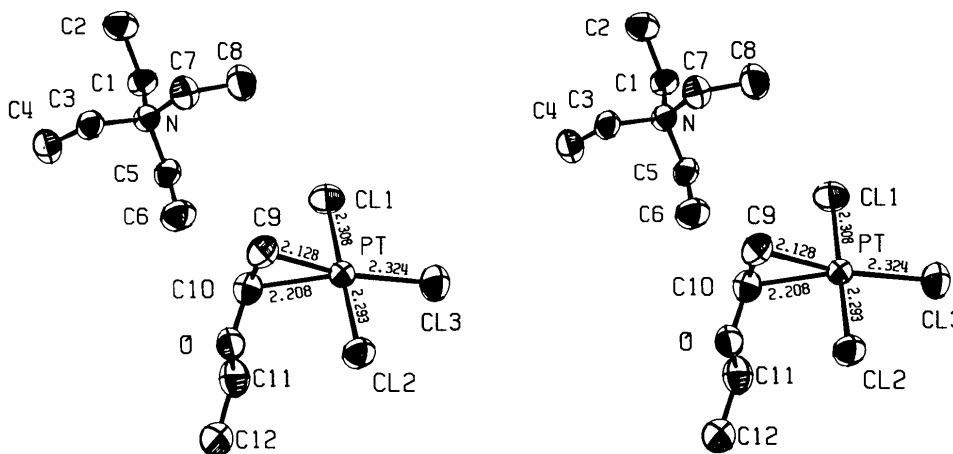| Cl(1)–Pt–Cl(2)	179.2 (9)	C(1)–N–C(7)	111.2 (5)
Cl(1)–Pt–Cl(3)	90.8 (1)	C(1)–N–C(3)	111.0 (5)
Cl(2)–Pt–Cl(3)	89.2 (1)	C(1)–N–C(5)	106.0 (5)
C(9)–Pt–C(10)	37.1 (3)	C(3)–N–C(5)	109.6 (5)
C(9)–Pt–Cl(3)	165.7 (3)	C(3)–N–C(7)	106.8 (5)
C(10)–Pt–Cl(3)	157.2 (2)	C(5)–N–C(7)	112.3 (5)
C(10)–C(9)–Pt	74.6 (4)	N–C(1)–C(2)	113.8 (6)
C(9)–C(10)–Pt	68.3 (4)	N–C(3)–C(4)	115.4 (6)
C(10)–O–C(11)	114.9 (5)	N–C(5)–C(6)	114.8 (6)
C(9)–C(10)–O	121.1 (6)	N–C(7)–C(8)	114.9 (6)
O–C(11)–C(12)	109.8 (6)		

Fig. 1. Stereo pair showing the asymmetric unit containing the title complex with H omitted.

Discussion. The structure as shown in Fig. 1 is formed from tetraethylammonium cations and square-planar Pt^{II} anions. The cations are well ordered and show usual geometry. The average C—N distance is 1·528 (3) Å and the average C—C distance is 1·504 (13) Å. All contacts between cations and anions appear to be of normal lengths.

The Pt atom and three chloride ions all lie in the same plane to within 0·01 Å. The plane defined by Pt and the two olefinic C atoms makes an angle of 86·5° with the Pt coordination plane. The mid-point of the C—C double bond is 0·185 Å from the coordination plane. This distortion is similar to that reported by Sartori & Leoni (1976) in the structure of cis-dichloro-[(R)-α-methylbenzylamine][(S)-1,2,2-trimethylpropyl (R)-vinyl ether]platinum(II), where the mid-point of the C—C bond is 0·38 Å from the coordination plane. The unsubstituted C atom of the double bond, C(9), is 0·08 (1) Å closer to Pt than the C atom, C(10), bearing the ether O atom. In general, analogous bond lengths agree to within 1σ of those reported in the previous, somewhat less precise structure. The major discrepancy is in the C(methylene)—O bond length: 1·431 (9) Å here, 1·51 (3) Å previously. The Pt—Cl bond trans to the ethylene moiety appears to be slightly longer [2·324 (2) Å] than the average Pt—Cl bond length [2·300 (11) Å] for those Cl atoms trans to each other. The difference, 0·024 (11) Å, is in the direction expected but is only marginally significant. The ether O atom is 3·038 (4) Å from the Pt atom. While this is somewhat less than the sum of the van der Waals radii, 3·3 Å, the coordination geometry of the double bond [C(10) is further from Pt than C(9)] indicates little, if any, attractive interaction between O and Pt.

All calculations were performed on an IBM 370/168 computer located at the University of Cincinnati. A locally modified version of XRAY 67 (Elder, 1974) was used for all calculations. We thank Professor M. Orchin for suggesting this problem and for useful discussions.

References

Busse, P., Pesa, F. & Orchin, M. (1977). *J. Organomet. Chem.* In the press.
Elder, R. C. (1974). *Inorg. Chem.* **13**, 1037–1042.
Elder, R. C. & Trkula, M. (1977). *Inorg. Chem.* **16**, 1048–1051.
Hamilton, W. C. (1965). *Acta Cryst.* **18**, 502–510.
Sartori, F. & Leoni, L. (1976). *Acta Cryst.* B**32**, 145–149.
Spaulding, L. A., Reinhardt, B. A. & Orchin, M. (1972). *Inorg. Chem.* **11**, 2092–2094.