Popovich, Dimitrova, Kiosse, Burshtein, Malinovskii & Shchedrin, 1976). The ring distances are comparable.

The structure consists of polymeric sheets in the *xy* directions, linked by Cu—O, O—C and C—C bonds. The crystals are made up of stacks of these sheets joined by the bridging Br atoms (which hydrogen bond to the terminal hydroxy groups of the ligand) and water molecules located on the other twofold axis which hydrogen bond to the axial O atoms of the tetragonally distorted octahedral coordination polyhedron of the Cu atom located on a twofold axis. The stacking of these sheets gives rise to cylindrical channels of disordered solvent along the crystallographic *z* axis approximately 15 Å in diameter. The issue of charge neutrality and the nature of the disordered solvent have been discussed previously for the chlorine structure (Norman, Rose & Stenkamp, 1987), and as in that case, we presume that charge neutrality in the present structure is maintained by protons or unidentified cations from the reaction mixture.

The bond distances and angles for this compound are indistinguishable from those reported earlier for the chlorine compound with the exceptions of the interactions holding the layers together. The Cu—Br distance is 0·13 Å longer than the analogous distance in the chlorine derivative, comparable to the differences in ionic radii of chloride and bromide. The situation is similar for the terminal O—Br distance. The hydrogen-bonding distances of the water molecule bridging between the polymeric layers in the crystal are also longer, reflecting the slight increase in the *c* axis.

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Tetraammineplatinum(II) Bis[pertechnetate(VII)]

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Abstract. $[Pt(NH_3)_4][TcO_4]_2$, $M_r = 589{\cdot}21$, triclinic, $P\bar{1}$, $a = 5{\cdot}178\,(2)$, $b = 7{\cdot}725\,(3)$, $c = 7{\cdot}935\,(3)$ Å, $\alpha = 69{\cdot}33\,(3)$, $\beta = 79{\cdot}74\,(3)$, $\gamma = 77{\cdot}41\,(3)°$, $V = 288{\cdot}0\,(2)$ Å^3, $Z = 1$, $D_x = 3{\cdot}396$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu(\text{Mo } K\alpha) = 14{\cdot}58$ mm^{-1}, $F(000) = 268$, room temperature. The structure was refined by full-matrix least-squares calculations to $R = 0{\cdot}026$ and $wR = 0{\cdot}032$ for 1309 unique observed reflections. Pt has square-planar coordination with Pt—N = 2·055 (5) and 2·051 (5) Å. The pertechnetate ions are tetrahedral with Tc—O distances ranging from 1·698 (5) to 1·715 (5) Å. The structure is stabilized by hydrogen bonding between the NH_3 ligands and the O atoms.

Introduction. The chemistry of technetium compounds is of considerable interest in radiopharmacy because of the extensive use of ^{99m}Tc compounds as imaging agents. We have recently started a new program on the synthesis of novel complexes of Tc. We have synthesized $[Pt(NH_3)_4][TcO_4]_2$ and determined its crystal structure. Several pertechnetate salts have been studied by X-ray diffraction. These have been summarized in a recent review by Melnik & Van Lier (1987). The crystal structure of $NH_4[TcO_4]$ has been studied at 295, 208 and 141 K (Faggiani, Lock & Pocé, 1980). The authors found only very minor changes in the structure as a function of temperature. $[Pt(NH_3)_4]^{2+}$ is a large cation which is able to form hydrogen bonds. The results obtained in our study of the structure of $[Pt(NH_3)_4][TcO_4]_2$ are reported below.

Experimental. The title compound was synthesized as follows. $NH_4[TcO_4]$ (0·25 mmol) dissolved in a few ml of water was added to 10 ml of an aqueous

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solution of $[Pt(NH_3)_4]Cl_2$ (0·125 mmol) in a slightly covered beaker. The mixture was allowed to stand at room temperature and crystals adequate for X-ray diffraction started to crystallize after 2–4 days.

Colorless platelet, dimensions (mm) and faces: 0·77 ($1\bar{1}0$ $\bar{1}10$), 0·048 (111 $\bar{1}\bar{1}\bar{1}$) and 0·182 ($10\bar{1}$ $\bar{1}01$); Syntex $P\bar{1}$ diffractometer; graphite-monochromatized Mo $K\alpha$ radiation; cell parameters from refined angles of 15 centered reflections; 1479 independent reflections measured up to $2\theta \le 55°$ by θ–2θ scan technique; range of hkl: $h = 0 \rightarrow 6$, $k = -9 \rightarrow 10$, $l = -10 \rightarrow 10$; standard reflections 400, $0\bar{4}0$ and 006, variations $\le$ 2·0%; scan speed 1·0–24·0° $\min^{-1}$; reflections with $I_{net} \le 2{\cdot}5\sigma(I)$ unobserved, $\sigma(I)$ calculated as in Melanson & Rochon (1975); absorption correction based on equations of crystal faces, transmission factors from 0·122 to 0·327; data corrected for Lorentz and polarization effects; 1309 unique observed reflections; atomic scattering factors of Cromer & Waber (1965) for Pt, Tc, O and N; anomalous-dispersion terms of Pt and Tc from Cromer (1965); isotropic secondary-extinction corrections from Coppens & Hamilton (1970).

Patterson map showed position of Pt; other non-H atoms located by structure factors and Fourier-map calculations; refinement by full-matrix least-squares calculations minimizing $\sum w(F_o - F_c)^2$; individual weights = $1/\sigma^2(F)$; standard deviation (unit weight) = 1·96; $(\Delta/\sigma)_{max}$ = 0·15, ρ(max.) = 0·7 e Å^{-3} (close to Pt) in final Fourier synthesis; R = 0·026 and wR = 0·032. Calculations on a Cyber 830 with programs of Melanson & Rochon (1975).*

Discussion. The refined atomic parameters are listed in Table 1. The Pt atom is located on a center of symmetry at the origin. As expected, the coordination around the Pt^{II} atom is square planar. The bond distances and angles are listed in Table 2. The Pt—N distances [2·055 (5) and 2·051 (5) Å] are normal (Milburn & Truter, 1966; Rochon & Melanson, 1980; Melanson & Rochon, 1978).

The coordination around the Tc atom is tetrahedral with O—Tc—O angles ranging from 108·3 (3) to 110·6 (3)°. The Tc—O bonds are 1·710 (5), 1·715 (5), 1·711 (5) and 1·698 (5) Å. These values agree well with data found in $NH_4[TcO_4]$ (Faggiani, Lock & Pocé, 1980) and in other pertechnetate salts (for a review, see Melnik & Van Lier, 1987). These latter authors observed that the value of the axial ratio c/a decreased when the ionic radius of the cation was reduced. In our case this ratio is small (1·53) for the large cation $[Pt(NH_3)_4]^{2+}$. But this ratio has no significance (except for tetragonal crystals), since compounds crystallize in different crystal systems, have different cation charges, some crystallize with molecules of water and some like $[Pt(NH_3)_4]^{2+}$ form hydrogen bonds with the pertechnetate ions. The presence of a large cation like $[Pt(NH_3)_4]^{2+}$ and of hydrogen bonding does not affect the structure of the pertechnetate ions.

Table 1. *Positional parameters with their e.s.d.'s and equivalent isotropic temperature factors* (× 10^4)

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}(Å^2)
Pt	0	0	0	166
Tc	5002 (1)	3306 (1)	3360 (1)	204
O(1)	3844 (11)	3094 (7)	5569 (6)	377
O(2)	4346 (10)	1468 (6)	2862 (7)	358
O(3)	3544 (10)	5389 (6)	1937 (7)	407
O(4)	8351 (10)	3220 (7)	3064 (7)	350
N(1)	1469 (11)	2412 (7)	−454 (7)	280
N(2)	578 (11)	−894 (7)	2686 (6)	273

Table 2. *Bond distances* (Å) *and angles* (°)

Pt—N(1)	2·055 (5)	N(1)—Pt—N(2)	90·8 (2)
Pt—N(2)	2·051 (5)	N(1)—Pt—N(2′)	89·2 (2)
Tc—O(1)	1·710 (5)	O(1)—Tc—O(2)	109·5 (3)
Tc—O(2)	1·715 (5)	O(1)—Tc—O(3)	110·6 (3)
Tc—O(3)	1·711 (5)	O(1)—Tc—O(4)	109·2 (3)
Tc—O(4)	1·698 (5)	O(2)—Tc—O(3)	110·0 (3)
		O(2)—Tc—O(4)	108·3 (3)
		O(3)—Tc—O(4)	109·2 (3)

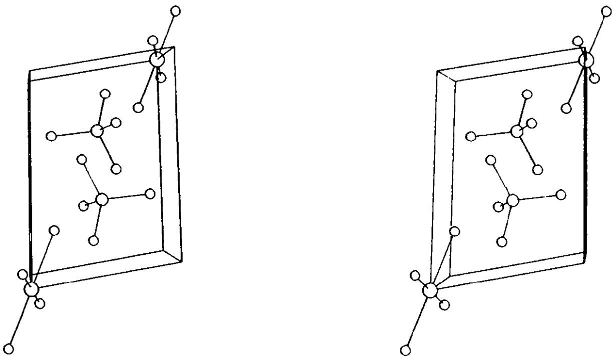

Fig. 1. Stereoscopic drawing of the packing in the crystal $[Pt(NH_3)_4][TcO_4]_2$ (b axis vertical, down c axis).

The packing of the molecules is shown in Fig. 1. It consists of alternate layers of $[Pt(NH_3)_4]^{2+}$ ions located at the origin and pertechnetate ions located at $x = \frac{1}{2}$. The structure is stabilized by extensive hydrogen bonding between the ammine ligands and the O atoms of the different layers. The distances and angles between atoms possibly involved in hydrogen bonds are shown in Table 3. The distances N···O are fairly long [2·960 (8) to 3·236 (8) Å] indicating that each of these bonds is not very

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52110 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Distances* (Å) *and angles* (°) *between atoms possibly involved in hydrogen bonding*

N(1)···O(1)	3·078 (7)	Pt—N(1)···O(1)	99·0 (2)
N(1)···O(2)	3·040 (7)	Pt—N(1)···O(2)	102·9 (2)
N(1)···O(3)	2·960 (8)	Pt—N(1)···O(3)	88·7 (2)
N(1)···O(4)	3·158 (7)	Pt—N(1)···O(4)	95·4 (2)
N(2)···O(1)	2·992 (8)	Pt—N(2)···O(1)	101·9 (2)
N(2)···O(2)	2·998 (8)	Pt—N(2)···O(2)	104·4 (2)
N(2)···O(3)	3·149 (7)	Pt—N(2)···O(3)	83·7 (2)
N(2)···O(4)	3·236 (8)	Pt—N(2)···O(4)	93·2 (2)

strong. In $NH_4[TcO_4]$ the hydrogen-bonded distances, N···O, were found to be 2·899 (2) and 2·984 (2) Å at 298 K (Faggiani, Lock & Pocé, 1980).

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Crystal Chemistry of *cyclo*-Hexaphosphates. V. Structure of Cadmium Sodium *cyclo*-Hexaphosphate Tetradecahydrate

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Abstract. $Cd_2Na_2P_6O_{18}.14H_2O$, $M_r = 996{\cdot}816$, triclinic, $P\bar{1}$, $a = 7{\cdot}709\,(1)$, $b = 11{\cdot}028\,(6)$, $c = 9{\cdot}231\,(2)$ Å, $\alpha = 108{\cdot}25\,(5)$, $\beta = 110{\cdot}06\,(5)$, $\gamma = 79{\cdot}77\,(5)$°, $V = 698\,(1)$ Å^3, $Z = 1$, $D_x = 2{\cdot}371$ Mg m^{-3}, $\lambda(\text{Ag}\ K\bar{\alpha}) = 0{\cdot}5608$ Å, $\mu = 1{\cdot}036$ mm^{-1}, $F(000) = 492$, $T = 294$ K, final $R = 0{\cdot}019$ for 3182 reflections. The atomic arrangement can be described as rows of CdO_6 octahedra alternating with the P_6O_{18} anions along the *c* axis. These rows are interconnected by chains of edge-sharing and corner-sharing octahedra parallel to the *a* axis. Cd/Na disorder is observed on a general position while a water molecule belonging to a sodium coordination sphere is statistically distributed on two general positions. The hydrogen-bond scheme is described.

Introduction. During the course of a systematic investigation of *cyclo*-hexaphosphate crystal chemistry we previously reported the chemical preparation and crystal structure of the first example of a hydrated monovalent divalent *cyclo*-hexaphosphate: $Li_2Mn_2P_6O_{18}.10H_2O$ (Averbuch-Pouchot, 1989).

In the present work we describe the chemical preparation and crystal structure for a second compound of this type: $Cd_2Na_2P_6O_{18}.14H_2O$.

This salt exhibits several features rather unusual in the crystal chemistry of condensed phosphates.

Experimental. Crystals of the title compound are prepared by adding an aqueous solution of cadmium chloride to an aqueous solution of sodium *cyclo*-hexaphosphate to obtain a Cd/Na stoichiometry of 1/2 in the final solution. By evaporation at room temperature, diamond-like thick plates of $Cd_2Na_2P_6O_{18}.14H_2O$ appear in the solution.

Crystal size: 0·32 × 0·32 × 0·15 mm. Density not measured. Nonius CAD-4 diffractometer, graphite monochromator. 20 reflections ($10{\cdot}0 < \theta < 11{\cdot}5$°) for refining unit-cell dimensions. ω scan, scan width: 1·20°, scan speed variable between 0·02 and 0·06° s^{-1}, total background measuring time: between 30 and 10 s. 3380 reflections collected, $2 < \theta < 27{\cdot}5$°, $\pm h$, $\pm k$, l, $h_{\max} = 12$, $k_{\max} = 17$, $l_{\max} = 15$. Two orientation (520 and $\bar{5}\bar{2}0$) and two intensity ($\bar{4}30$ and $4\bar{3}0$) control reflections without any significant varia-

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