1·345 (25) and 1·375 (23), and 1·375 (29) and 1·441 (28) Å respectively and compare well with the corresponding bond lengths, 1·38 (2), 1·36 (2) and 1·42 (2) Å, measured in the Au^I_3 trimer. The nonbonding Au···Au distances in $Au^I_2Au^{III}$ range between 3·348 (1) and 3·383 (1) Å and on the average are equal in length to the 3·368 (1) Å distance observed for Au^I_3.

The complex reported here, $Au^I_2Au^{III}$, is the two-electron oxidation product of the previously reported Au^I_3 (Murray, Raptis & Fackler, 1988) complex. The oxidation of one of the three Au atoms from the I to the III state does not alter significantly the geometry of the nine-membered metallocycle or the bridging pyrazolate rings. However, the high symmetry, D_{3h} (ignoring the phenyl groups), observed for the Au^I_3 complex which crystallized in the crystallographic space group $R\bar{3}c$, is reduced to C_{2v} in the $Au^I_2Au^{III}$ complex which crystallizes in the space group $P2_1/c$. The yet unknown analogous complexes $Au^IAu^{III}_2$ and Au^{III}_3 will have C_{2v} and D_{3h} symmetries respectively. Work towards the characterization of these species is under way.

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The Structure of the Tetraphenylarsonium Salt of the Trichloro(pentane-2,4-dionato)nitrosyltechnetium(II) Anion

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Abstract. Tetraphenylarsonium trichloro(pentane-2,4-dionato)nitrosyltechnetate(II), $[As(C_6H_5)_4][Tc(NO)Cl_3(C_5H_7O_2)]$, $M_r = 717·4$, triclinic, $P\bar{1}$, $a = 10·261$ (4), $b = 11·261$ (10), $c = 13·686$ (10) Å, $\alpha = 101·7$ (5), $\beta = 91·9$ (5), $\gamma = 97·3$ (5)°, $U = 1532·93$ Å^3, $Z = 2$, D_m not measured, $D_x = 1·554$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 18·15$ cm^{-1}, $F(000) = 718$, $T = 293$ K, $R = 0·076$ for 2008 observed reflexions with $I > 3\sigma(I)$. The anion $[Tc(NO)Cl_3(C_5H_7O_2)]^-$ has a distorted octahedral geometry with three Cl atoms, a bidentate pentane-2,4-dione ligand and the nitrosyl *trans* to either of the equivalent oxygens. The other *trans* position is occupied by a Cl atom resulting in a disordered structure.

Introduction. The use of technetium-99m ($t_{1/2} = 6·02$ h) in the field of nuclear medicine is well established, while technetium-99 ($t_{1/2} = 2·1 \times 10^5$ a) enables extensive research into the coordination chemistry of the element. We are interested, in particular, in the synthesis of Tc complexes as possible radiopharmaceuticals in which the Tc atom is in a low oxidation state. Stabilization of low oxidation state requires the presence of a π-acid ligand, which in the complexes we have studied is the NO group. Recently we reported the structure of the complex $[TcNOCl_4(CH_3OH)]^-$ (Brown, Newman, Thornback & Davison, 1987) and its synthesis on a no-carrier added (^{99m}Tc) scale (Cheah, Newman, Nowotnik & Thornback, 1987). This complex is an

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ideal starting material for a range of substitution reactions to prepare novel complexes whose possible application as radiopharmaceuticals may be investigated. In this work we report the structure of the first of these, $[TcNOCl_3(C_5H_7O_2)]^-$, which has been isolated as its tetraphenylarsonium salt.

Experimental. Preparation by the method of Brown, Newman, Thornback & Pearlstein, (1988); red crystals grown from methanol/water; kite-shaped plates; crystal (0·31 × 0·19 × 0·08 mm) mounted about **a**; Stoe Weissenberg diffractometer; lattice parameters by maximizing fit of axial row reflexions in range $(\sin\theta)/\lambda$ 0·1 to 0·4 Å^{-1}; 3958 reflexions measured, $(\sin\theta)/\lambda < 0·6$ Å^{-1}, 2008 with $I > 3\sigma(I)$; h 0→8, k −12→+12, l −15→+15; standard check reflexions on each layer with no significant changes; absorption correction applied, $T_{\min} = 0·717$, $T_{\max} = 0·866$; Tc and As positions found by Patterson and other atoms by successive difference-Fourier methods, refined by full-matrix least squares on F to $R = 0·076$, $wR = 0·079$; overall scale factor and interlayer scale factors refined, all atoms anisotropic except disordered and H, unit weighting (based on weight analysis and rapid convergence of refinement), 20 H atoms in calculated positions; remaining H atoms omitted; max. $\Delta/\sigma = 0·378$, $\Delta\rho$ excursions +0·9 to −1·0 e Å^{-3}; scattering factors from *International Tables for X-ray Crystallography* (1974); geometry calculations carried out using the *XRAY72* system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) as implemented on the CDC7600 computer at the University of Manchester Regional Computer Centre and all others with *SHELX76* (Sheldrick, 1976) as implemented on the Honeywell Multics computer at Loughborough University of Technology. The relatively high R factor reflects imperfect modelling of the disorder.

Discussion. Final atomic coordinates are given in Table 1,* bond lengths and angles in Table 2, and the numbering scheme of the atoms in Fig. 1. N(3), O(3) and N(4), O(4) refer to the disordered nitrosyls and Cl(3) and Cl(4) to their respective chlorines.

The X-ray data of the triclinic crystal show that the anion has a distorted octahedral geometry with two chlorides mutually *trans* and the other chloride and the nitrosyl occupying disordered positions *trans* to the chemically equivalent oxygens of the pentane-2,4-dionato ligand.

The analysis of the data proved a non-routine problem because of the disorder. The two positions *trans* to the oxygens of the pentane-2,4-dionato ligand have random occupancy of Cl and NO. As Cl and NO have a similar number of electrons differentiation was not possible from a Fourier map. However, the positions of the individual atoms were eventually determined through careful analysis of difference maps and the atoms refined isotropically with occupancy factors of 0·5.

Table 1. *Final positional parameters* (× 10^4) *and isotropic thermal parameters* (Å^2)

$$B_{eq} = (8\pi^2/3)(\textstyle\sum u_{ii}).$$

	x	y	z	B_{eq}
Tc	10910 (2)	3166 (2)	1944 (1)	5·3 (1)
As	4414 (2)	8117 (2)	2911 (1)	4·9 (1)
Cl(1)	9884 (7)	4871 (5)	1685 (5)	7·4 (4)
Cl(2)	11782 (8)	1329 (6)	2007 (6)	9·8 (5)
Cl(3)	13046 (21)	4221 (16)	2402 (12)	5·6*
Cl(4)	10390 (16)	3426 (14)	3584 (10)	6·8*
O(1)	11335 (15)	2912 (13)	458 (9)	6·2 (7)
O(2)	9089 (13)	2101 (11)	1514 (10)	5·0 (7)
C(1)	11178 (26)	2289 (23)	−1293 (15)	7·3 (11)
C(2)	10600 (22)	2280 (18)	−280 (15)	5·2 (9)
C(3)	9407 (28)	1592 (19)	−222 (16)	6·8 (11)
C(4)	8684 (23)	1520 (18)	633 (16)	5·7 (6)
C(5)	7475 (26)	641 (21)	567 (20)	7·4 (12)
C(6)	15818 (22)	2590 (17)	8487 (13)	4·8 (9)
C(7)	16921 (19)	3403 (19)	8863 (14)	4·7 (9)
C(8)	17053 (28)	3944 (20)	9861 (18)	6·9 (11)
C(9)	16003 (28)	3649 (22)	10447 (16)	6·8 (11)
C(10)	14839 (28)	2829 (22)	10094 (17)	7·1 (12)
C(11)	14771 (23)	2276 (20)	9089 (16)	5·8 (11)
C(12)	12712 (23)	8147 (19)	3459 (14)	5·1 (10)
C(13)	12028 (26)	7085 (20)	3663 (15)	5·8 (11)
C(14)	10790 (25)	7126 (21)	3970 (16)	5·6 (18)
C(15)	10155 (35)	8130 (30)	4095 (18)	9·2 (13)
C(16)	10885 (28)	9202 (22)	3882 (18)	6·8 (12)
C(17)	12172 (28)	9182 (24)	3555 (16)	6·5 (11)
C(18)	15405 (19)	9714 (16)	3064 (13)	4·0 (9)
C(19)	14900 (22)	10588 (20)	2615 (15)	5·8 (10)
C(20)	15544 (26)	11752 (20)	2750 (19)	4·3 (12)
C(21)	16790 (26)	11991 (19)	3231 (19)	6·5 (11)
C(22)	17319 (26)	11094 (23)	3692 (18)	4·6 (11)
C(23)	16618 (25)	9971 (17)	3592 (16)	5·5 (10)
C(24)	14608 (29)	2846 (19)	6431 (14)	6·9 (10)
C(25)	13784 (19)	3637 (20)	7016 (16)	4·7 (10)
C(26)	13046 (30)	4310 (21)	6546 (18)	7·7 (11)
C(27)	13024 (26)	4169 (24)	5530 (20)	7·0 (11)
C(28)	13717 (32)	3409 (27)	4961 (17)	8·3 (12)
C(29)	14510 (26)	2724 (24)	5421 (16)	7·3 (11)
N(3)	12425 (24)	4076 (31)	2282 (27)	5·2*
O(3)	13594 (27)	4332 (37)	2436 (30)	7·3*
N(4)	10442 (54)	3377 (51)	3144 (21)	10·6*
O(4)	9805 (30)	3793 (29)	3780 (22)	6·6*

* Isotropic thermal parameter = $8\pi^2u$ (atoms at half occupancy).

This refinement showed that the Cl and NO ligands opposite the O atoms of the pentane-2,4-dionato group were disordered with random reversal. Attempts to refine the structure in space group $P1$ showed the same disorder. Full-matrix least-squares refinement was carried out with bonds of the disordered nitrosyl fixed at conventional values (Tc—N 1·69 and N—O 1·17 Å).

The bond angles for Tc—N(3)—O(3) and Tc—N(4)—O(4) are 159 (3) and 152 (5)° respectively which differ considerably from that in $[TcNOCl_4(CH_3OH)]^-$ (Brown, Newman, Thornback & Davison, 1987) [175·5 (10)°]. The IR vibration ν(NO) of the former is at 1770 cm^{-1} while that of the latter is 1805 cm^{-1}. Both may be considered as NO^+ instead of NO^-. The disorder and slight axial displacement of the

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and full bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44694 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Principal bond distances* (Å) *and angles* (°)

Anion			
Tc–Cl(1)	2·385 (7)	Tc–O(1)	2·06 (1)
Tc–Cl(2)	2·372 (8)	Tc–O(2)	2·08 (1)
Tc–Cl(3)	2·36 (2)	O(1)–C(2)	1·27 (2)
Tc–Cl(4)	2·29 (1)	O(2)–C(4)	1·28 (2)
Tc–N(3)	1·74 (3)	C(1)–C(2)	1·53 (3)
Tc–N(4)	1·71 (3)	C(2)–C(3)	1·38 (3)
N(3)–O(3)	1·20 (4)	C(3)–C(4)	1·42 (3)
N(4)–O(4)	1·16 (5)	C(4)–C(5)	1·47 (3)
Cation			
As–C(6)	1·91 (2)	As–C(24)	1·90 (4)
As–C(12)	1·93 (2)	average C–C	1·39 (3)
As–C(18)	1·92 (2)		
Anion			
Tc–N(3)–O(3)	158·6 (33)	Cl(3)–Tc–O(2)	175·3 (6)
Tc–N(4)–O(4)	152·1 (47)	Cl(3)–Tc–N(4)	93·8 (17)
Cl(1)–Tc–Cl(2)	172·6 (2)	Cl(4)–Tc–O(1)	178·7 (6)
Cl(1)–Tc–Cl(3)	97·5 (5)	Cl(4)–Tc–O(2)	89·7 (5)
Cl(1)–Tc–Cl(4)	93·0 (5)	Cl(4)–Tc–N(3)	91·2 (12)
Cl(1)–Tc–O(1)	86·8 (5)	O(1)–Tc–O(2)	89·0 (5)
Cl(1)–Tc–O(2)	86·9 (4)	O(1)–Tc–N(3)	90·1 (13)
Cl(1)–Tc–N(3)	92·1 (12)	O(1)–Tc–N(4)	175·8 (19)
Cl(1)–Tc–N(4)	90·6 (20)	O(2)–Tc–N(3)	178·6 (14)
Cl(2)–Tc–Cl(3)	87·8 (5)	O(2)–Tc–N(4)	87·6 (17)
Cl(2)–Tc–Cl(4)	92·0 (5)	Tc–O(1)–C(2)	126·3 (14)
Cl(2)–Tc–O(1)	88·1 (5)	Tc–O(2)–C(4)	126·9 (14)
Cl(2)–Tc–O(2)	87·7 (4)	C(1)–C(2)–C(3)	120·3 (18)
Cl(2)–Tc–N(3)	93·3 (12)	C(2)–C(3)–C(4)	128·4 (19)
Cl(2)–Tc–N(4)	94·2 (20)	C(3)–C(4)–C(5)	120·8 (19)
Cl(3)–Tc–O(1)	89·8 (6)		
Cation			
C(12)–As–C(18)	113·1 (8)	C(18)–As–C(24)	108·4 (9)
C(12)–As–C(6)	108·9 (9)	C(6)–As–C(24)	109·9 (9)
C(12)–As–C(24)	108·7 (11)	average C–C–C	120·0 (22)
C(18)–As–C(6)	107·8 (8)		

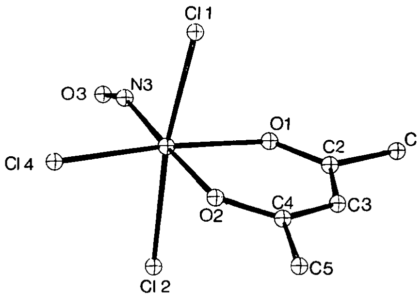

Fig. 1. Molecular structure and atom numbering for the anion showing one of the disordered arrangements where N(3), O(3) and Cl(4) are the disordered atoms.

two ligands result in some loss of accuracy in the bond lengths and angles and detailed discussion of these is therefore not possible.

The pentane-2,4-dionato ligand bond distances and angles are comparable with those reported for other Tc complexes containing this ligand (Bandoli, Clemente, Mazzi & Roncari, 1978) and the non-disordered chlorines have bond distances to the Tc which are unremarkable. There are no significant intermolecular contacts.

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Structure of Dibromo(thiosemicarbazide)cadmium(II) Monohydrate

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Abstract. $[CdBr_2(SCN_3H_5)].H_2O$, $M_r = 381{\cdot}354$, monoclinic, Ia (No. 9), $a = 7{\cdot}063$ (1), $b = 14{\cdot}234$ (4), $c = 8{\cdot}751$ (5) Å, $\beta = 100{\cdot}28$ (2)°, $V = 865{\cdot}7$ (3) Å^3, $Z = 4$, $F(000) = 704$, $D_x = 2{\cdot}926$, Nb-filtered Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å), μ(Mo $K\alpha$) = 118·3 cm^{-1}, $T = 298$ (3) K, $R(F) = 0{\cdot}031$ for 1125 observed reflections. The coordination geometry about Cd is an octahedron formed by three Br, two S and one N atoms. The crystal structure consists of infinite parallel chains of coordinated cadmium atoms linked to each other by a double bridge of Br and S. The water molecule is located between the chains and is connected by hydrogen bonds with the N atoms of the organic ligands.

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