1974) distorted TlO_6 octahedra are also observed with distances ranging from 2.16 to 2.4 Å, besides distorted TlO_4 tetrahedra characterized by Tl—O distances of 2.13–2.21 Å. The single-crystal X-ray study of $Sr_4Tl_2O_7$ (Schenk & Müller-Buschbaum, 1973) shows a curious 2 + 2 coordination of Tl with two Tl—O distances of 2.08 Å and two others of 2.50 Å. The recent results obtained for the high T_c superconductor $Tl_2Ba_2CuO_{6+\delta}$ (Shimakawa, Kubo, Manako, Igarashi, Izumi & Asano, 1990) from neutron diffraction data suggest a very different behaviour of Tl^{III} in the superconductors, since the TlO_6 octahedra are characterized in that case by two abnormally short apical Tl—O distances (1.98–2.03 Å) orthogonal to the $[TlO]_\infty$ layers, two intermediate Tl—O distances of 2.526 Å and two abnormally long distances of 2.968 Å in the basal plane. It is also worth pointing out that for this oxide the intermediate Tl—O distances are even superior to the larger Tl—O distances encountered not only in $SrTl_2O_4$ but in the three other thallium oxides.

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Redetermination of the Structure of Potassium Tetranitropalladate(II)

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Abstract. $K_2Pd(NO_2)_4$, $M_r = 368.58$, monoclinic, $P2_1/c$, $a = 9.254$ (5), $b = 12.747$ (3), $c = 7.805$ (2) Å, $\beta = 96.43$ (2)°, $V = 914.9$ Å^3 [from setting angles for 14 $0kl$ and 12 $h0l$ data, $2\theta = 18$–34°, λ(Mo $K\alpha$) = 0.71073 Å], $Z = 4$, $D_x = 2.676$ Mg m^{-3}, $\mu = 2.95$ mm^{-1}, $F(000) = 704$, $T = 295$ K, $R = 0.031$ for 2327 unique observed reflections. There are two crystallographically independent $Pd(NO_2)_4^{2-}$ ions, each square planar with symmetry $\bar{1}$ (C_i); Pd—N distances are in the range 2.018 (2)–2.047 (2) Å.

Introduction. As part of a broad investigation of the O-transfer chemistry of coordinated O-rich anions such as NO_2^- and NO_3^-, in both solution and the solid state, we have undertaken a detailed analysis of the crystal and molecular structures of a wide range of nitro and nitrato complexes of the transition metals. We have been directly concerned with those complexes of metals with an established catalytic activity.

The structure of the title compound was originally determined by Poraj-Košic (1947). Since the structure was not refined, and various constraints were used, including the unlikely value of 136° for the O—N—O angles, we have redetermined this structure. The fact that the Pd atoms contribute to only one quarter of the data makes it possible to determine the geometry of the nitro groups particularly precisely.

Experimental. The commercial product (Johnson Matthey plc) was recrystallized from water. A yellow tablet, 0.25 × 0.3 × 0.35 mm, was mounted about [100] on a STADI-2 two-circle diffractometer. Data collection used graphite-monochromated Mo $K\alpha$ radiation, at $T = 295$ K, with ω scans with ω range $(1.0 + 0.5 \sin\mu/\tan\theta)°$. 2616 unique reflections were collected ($2\theta_{max}$ 60°, h 0→12, k 0→17, l −10→10) and 2327 with $F \geq 4\sigma(F)$ were used in all calculations. No significant crystal decay or movement was

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Table 1. *Fractional coordinates and equivalent isotropic thermal parameters* ($Å^2$)

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

	x	y	z	U_{eq}
Pd(1)	0	½	½	0.0164 (2)
Pd(2)	½	0	0	0.0155 (2)
K(1)	0.18055 (6)	0.15773 (4)	0.41954 (6)	0.0303 (3)
K(2)	0.65430 (6)	0.31845 (4)	0.14652 (6)	0.0278 (3)
N(1)	0.11282 (20)	0.62713 (15)	0.43517 (25)	0.0233 (9)
N(2)	0.01236 (19)	0.43292 (14)	0.26788 (24)	0.0229 (9)
N(3)	0.58120 (19)	0.02375 (15)	0.25182 (24)	0.0207 (8)
N(4)	0.39118 (21)	0.13607 (15)	0.01153 (25)	0.0227 (9)
O(1)	0.07483 (23)	0.67760 (17)	0.3036 (3)	0.0466 (12)
O(2)	0.22326 (22)	0.65355 (16)	0.52795 (25)	0.0377 (10)
O(3)	−0.08209 (22)	0.44892 (17)	0.14641 (25)	0.0384 (11)
O(4)	0.11175 (22)	0.37168 (18)	0.2483 (3)	0.0468 (12)
O(5)	0.58731 (22)	−0.04879 (16)	0.35760 (24)	0.0363 (11)
O(6)	0.62381 (23)	0.11117 (15)	0.29930 (23)	0.0397 (10)
O(7)	0.42920 (20)	0.21302 (14)	−0.0695 (3)	0.0367 (10)
O(8)	0.29047 (21)	0.14430 (17)	0.10117 (25)	0.0398 (11)

Table 2. *Bond lengths* (Å), *angles* (°) *and torsion angles* (°)

Pd(1)—N(1)	2.0225 (19)	N(2)—O(3)	1.232 (3)
Pd(1)—N(2)	2.0181 (18)	N(2)—O(4)	1.229 (3)
Pd(2)—N(3)	2.0466 (18)	N(3)—O(5)	1.237 (3)
Pd(2)—N(4)	2.0127 (19)	N(3)—O(6)	1.226 (3)
N(1)—O(1)	1.229 (3)	N(4)—O(7)	1.239 (3)
N(1)—O(2)	1.231 (3)	N(4)—O(8)	1.231 (3)

N(1)—Pd(1)—N(2)	91.84 (7)	O(3)—N(2)—O(4)	119.04 (20)
N(3)—Pd(2)—N(4)	87.78 (8)	Pd(2)—N(3)—O(5)	120.99 (15)
Pd(1)—N(1)—O(1)	121.40 (16)	Pd(2)—N(3)—O(6)	119.74 (15)
Pd(1)—N(1)—O(2)	119.32 (16)	O(5)—N(3)—O(6)	119.27 (20)
O(1)—N(1)—O(2)	119.27 (21)	Pd(2)—N(4)—O(7)	119.16 (15)
Pd(1)—N(2)—O(3)	120.92 (15)	Pd(2)—N(4)—O(8)	120.89 (16)
Pd(1)—N(2)—O(4)	119.97 (15)	O(7)—N(4)—O(8)	119.92 (20)

N(2)—Pd(1)—N(1)—O(1)	53.68 (19)	N(4)—Pd(2)—N(3)—O(5)	136.38 (18)
N(2)—Pd(1)—N(1)—O(2)	−125.11 (18)	N(4)—Pd(2)—N(3)—O(6)	−43.22 (17)
N(1)—Pd(1)—N(2)—O(3)	−89.99 (18)	N(3)—Pd(2)—N(4)—O(7)	109.90 (18)
N(10—Pd(1)—N(2)—O(4)	93.12 (18)	N(3)—Pd(2)—N(4)—O(8)	−68.18 (18)

Coordination of K atoms

K(1)

O atom	Symmetry	O—K(1)
O(1)	$-x, -\frac{1}{2}+y, \frac{1}{2}-z$	2.786 (2)
O(3)	$-x, -\frac{1}{2}+y, \frac{1}{2}-z$	2.842 (2)
O(4)	x, y, z	3.072 (2)
O(4)	$x, \frac{1}{2}-y, \frac{1}{2}+z$	2.738 (2)
O(5)	$1-x, -y, 1-z$	2.955 (2)
O(7)	$x, \frac{1}{2}-y, \frac{1}{2}+z$	2.824 (2)
O(8)	x, y, z	2.794 (2)
O(8)	$x, \frac{1}{2}-y, \frac{1}{2}+z$	3.015 (2)

K(2)

O atom	Symmetry	O—K(2)
O(1)	$1-x, -\frac{1}{2}+y, \frac{1}{2}-z$	3.072 (2)
O(2)	$1-x, 1-y, 1-z$	2.687 (2)
O(2)	$1-x, -\frac{1}{2}+y, \frac{1}{2}-z$	2.811 (2)
O(3)	$1+x, y, z$	2.953 (2)
O(5)	$1-x, \frac{1}{2}+y, \frac{1}{2}-z$	2.801 (2)
O(6)	x, y, z	2.925 (2)
O(6)	$x, \frac{1}{2}-y, -\frac{1}{2}+z$	2.839 (2)
O(7)	x, y, z	2.864 (2)

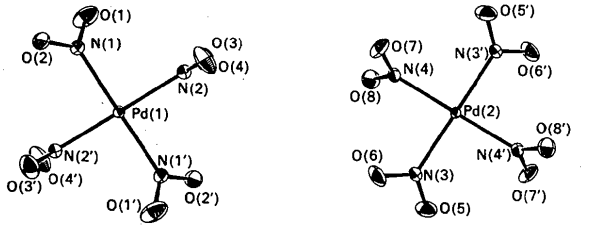

Fig. 1. Perspective views of the two anions projected into the plane. Primed atoms are related to their unprimed equivalents by inversion through the centre of symmetry at the Pd ion.

apparent. Starting parameters for Pd and K were taken from the previous determination (Poraj-Košic, 1947). Refinement was by *SHELX*76 (Sheldrick, 1976) using scattering factors of Cromer & Mann (1968). All O and N atoms were found in the first difference map. After isotropic refinement ($R = 0.081$) empirical absorption corrections were applied (*DIFABS*; Walker & Stuart, 1983) giving maximum correction of 1.20, minimum of 0.91 and $R = 0.066$. All atoms were refined anisotropically. At final convergence, $R = 0.031$, $wR = 0.046$, $S = 0.98$ for 140 refined parameters, and the final difference synthesis showed a peak of 1.0 and a trough of 1.4 e $Å^{-3}$ in the vicinity of the Pd atoms. An empirical extinction parameter refining to $8.8\ (4) \times 10^{-7}$ was applied. The weighting scheme $w^{-1} = \sigma^2(F) + 0.000614|F|^2$ gave satisfactory agreement analyses, and in the final cycle the maximum shift over e.s.d. was 0.04. Molecular geometry calculations used *CALC* (Gould & Taylor, 1985) and Figs. 1 and 2 were produced by the version of *ORTEP* included in the *GX* crystallographic program system (Mallinson & Muir, 1985), and *PLUTO* (Motherwell & Clegg, 1978).

Discussion. Final atomic coordinates and thermal parameters are given in Table 1,* and interatomic distances, angles and torsion angles in Table 2. Thermal ellipsoid plots of the two independent anions are in Fig. 1 and a packing diagram is presented in Fig. 2. All N—O distances are within three standard deviations of the mean value of 1.232 (4) Å and all angles at N are within ten standard deviations of 120°. The tilts of the nitro groups relative to the

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55010 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA0078]

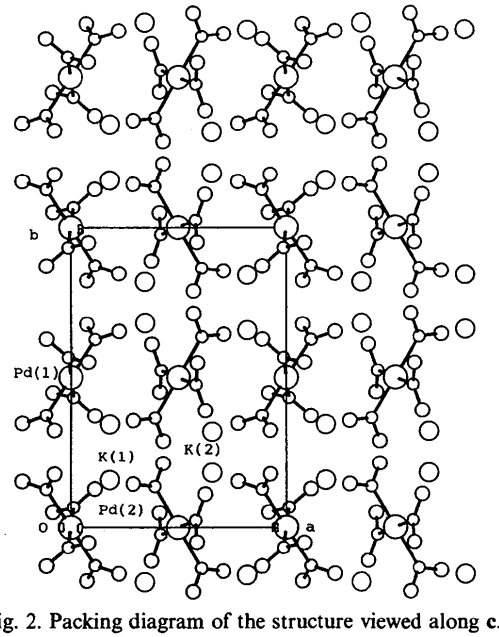

Fig. 2. Packing diagram of the structure viewed along c.

coordination plane are given by the torsion angles in Table 2. The planes defined by the *trans* nitro groups make angles with one another of 87.4° about Pd(1) and 73.3° about Pd(2). The K atoms are coordinated by eight O atoms, forming a distorted square antiprism about each K atom. In each case, one nitro group only is chelated to K. No K···O contacts other than those given are shorter than 3.23 Å. The structure appears to be similar to that of $K_2Pt(NO_2)_4$ (Porai-Koshits, Kukina & Nikolaev, 1978).

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Structure of Bis(thiourea)gold(I) Bromide, $[Au\{SC(NH_2)_2\}_2]Br$

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Abstract. $[Au(CH_4N_2S)_2]Br$, $M_r = 429.20$, monoclinic, $C2/c$, $a = 8.703$ (2), $b = 16.025$ (8), $c = 6.799$ (2) Å, $\beta = 100.83$ (2)°, $V = 931.3$ (6) Å^3, $Z = 4$, $D_x = 3.060$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 20.394$ mm^{-1}, $F(000) = 776$, $T = 298$ K, $R = 0.0632$ and $wR = 0.0929$, obtained for 48 variable parameters and 609 averaged reflections with $F > 0\sigma(F)$. The asymmetric unit consists of one half of a centrosymmetric bis(thiourea)gold(I) molecule with thiourea ligands coordinating in a monodentate fashion through the S atom [Au(1)—S(1) = 2.291 (4) Å]. The thiourea groups are essentially planar but are twisted by an angle of 21.0° about the S—C atoms. The Au atoms in adjacent molecules are separated by a distance of 3.400 Å and the Br^- counterions are located in the cavities formed by the terminal amine groups of the thiourea ligands.

Introduction. The ability of thiourea to form stable adducts with a variety of transition metals is well established and the structures of several of these have been determined [see, for example, Girling, Chatterjee & Amma (1973)]. A number of interesting structural features such as twisting and tilting of the thiourea ligands have been observed, although whether or not this can be attributed to back-bonding interactions between filled metal *d* orbitals and ligand π^* orbitals remains to be established; such observations appear to be largely independent of the transition metal involved.

Crystallographic data concerning the structures of Au–thiourea complexes are scarce, although there is currently much interest in these complexes since thiourea may prove to be important as an alternative to the use of cyanide in the extraction of gold from ores. Raman and solution infrared studies have been carried out and provide evidence for the existence of S-bound species in thiourea complexes of Au^I and Au^{III}, and suggest that the N-bound species may also be formed initially with Au^0 (Freeman, Baglin, Wilkes & MacDougall, 1986; Marcotrigiano, Peyronel & Battistuzzi, 1972). Although linkage

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