supports the notion that distortions in the niobium iodide analogues are electronic in origin. Comparison with the other niobium iodide clusters and their hydrides must await the results of bond calculational and magnetic susceptibility studies presently underway.[19]

Acknowledgment. We thank Dr. C. Rüscher (Institut für Mineralogie, Universität Hannover) for the help with the conductivity measurements, Professor J. Pickardt (Technische Universität, Berlin) for providing the diffractometer for one study, and the Deutsche Forchungsgemeinschaft for financial support of H.-J.M. This research was in part also supported by the National Science Foundation, Solid State Chemistry, via Grants DMR-8318616 and -8902954, and this portion was carried out in facilities of Ames Laboratory, DOE.

Supplementary Material Available: Tables of crystal data and anisotropic displacement parameters for Nb_6I_9S and $Nb_6(H)I_9S$ (2 pages); tables of observed and calculated structure factor data (36 pages). Ordering information is given on any current masthead page.

---

(21) The $Mo_6I_8Se_2$ refinement led to $R/R_w = 0.179/0.158$ for data to $2\theta = 50°$. The positional σ's were 0.03-0.05 Å, and the thermal parameters could not be refined.

Contribution from the Department of Chemistry,
The University, Southampton, SO9 5NH, England

Coordination Chemistry of Higher Oxidation States. 37.[1] Tellurato Complexes of Palladium(IV) and Platinum(IV). Crystal Structures of $Na_8K_2H_4[Pd_2Te_4O_{24}H_2]\cdot 20H_2O$ and $K_6Na_2[Pt(OH)_2(HTeO_6)_2]\cdot 12H_2O$

William Levason,* Mark D. Spicer, and Michael Webster

Received July 3, 1990

The reactions between $[MCl_6]^{2-}$ (M = Pd, Pt) and telluric acid in aqueous sodium or potassium hydroxide have been shown to give Pd(IV) or Pt(IV) tellurate complexes, which have been isolated as their hydrated salts. The compounds have been studied by ^{125}Te and ^{195}Pt NMR spectroscopy, EDX, EXAFS, and single-crystal X-ray diffraction. The structure of $Na_8K_2H_4[Pd_2Te_4O_{24}H_2]\cdot 20H_2O$ has been determined. It crystallizes in the triclinic space group $P\bar{1}$, with $a = 7.403$ (1) Å, $b = 11.929$ (2) Å, $c = 12.429$ (2) Å, $\alpha = 100.28$ (1)°, $\beta = 104.92$ (1)°, $\gamma = 92.23$ (1)°, $V = 1039.4$ Å^3, and $Z = 1$. The structure was refined to $R = 0.042$ from 2146 data ($F > 2\sigma(F)$). Discrete anions that contain octahedral "TeO_6" and "PdO_6" units linked via edge sharing are present in the solid. The structure of the platinum complex $K_6Na_2[Pt(OH)_2(HTeO_6)_2]\cdot 12H_2O$ has been determined. Crystals were found to be monoclinic, space group $C2/m$, with $a = 21.099$ (11) Å, $b = 6.778$ (3) Å, $c = 9.041$ (4) Å, $\beta = 92.10$ (4)°, $V = 1292.1$ Å^3, and $Z = 2$. The structure was refined to $R = 0.041$ from 1170 data ($F > 3\sigma(F)$) and contains discrete anions. Each anion has two bidentate chelate $[HTeO_6]^{5-}$ units bonded to an octahedrally coordinated Pt atom. No H atoms were located. ^{125}Te and ^{195}Pt NMR and EXAFS data are used to identify other species present in solution.

Introduction

Tellurates ($H_{6-n}TeO_6^{n-}$) and periodates ($H_{5-n}IO_6^{n-}$) are known for their ability to stabilize transition-metal centers in high oxidation states. In addition to their inherent interest as examples of rare oxidation states, such materials are often strong multielectron oxidants and have considerable synthetic potential in this role.[2] The known complexes[2] range from extended lattices to discrete anions, and their correct formulation in the absence of structural data is far from easy. A number of predicted structures have subsequently been shown to be erroneous in the light of crystallographic studies. Several structures of periodato complexes have been determined in recent years including those of V(V),[3] Ru(VI),[4] Co(III),[5] Cu(III),[6] and Ag(III),[6] but by contrast we believe that the only discrete transition-metal tellurate anion to be characterized by X-ray diffraction is $Na_5[Cu(H_2TeO_6)_2]\cdot 10H_2O$.[7] We have recently reported a reinvestigation of the periodato complexes of palladium(IV) and platinum(IV)[1] including the crystal structure of $K_4Na_2[Pt(OH)_2(HIO_6)_2]\cdot 10H_2O$. The corresponding tellurate systems have previously been the subject of two brief and inconclusive studies,[8,9] but we are now able to present the results of a detailed structural and spectroscopic investigation of these materials.

Experimental Section

Multinuclear NMR spectra were obtained on a Bruker AM360 spectrometer from aqueous solutions containing a small quantity of D_2O to provide the lock signal and with 10-mm o.d. tubes. Tellurium-125 (113.6 MHz) and platinum-195 (77.6 MHz) were referenced to neat Me_2Te and aqueous K_2PtCl_6, respectively. Raman spectra and analytical (EDX and TGA) data were obtained as described previously.[1] The EXAFS data were obtained at the Synchrotron Radiation Source, Daresbury, England, operating at 2 GeV with an average ring current of 130 mA. Pd K-edge data were recorded on station 9.2 using a double-crystal silicon(220) monochromator, and Pt L_{III}-edge data, on station 7.1 using an order-sorting silicon(111) monochromator. Data were collected in transmission mode from 4 mm path length glass solution cells with Mylar windows. Data analysis utilized standard procedures that have been previously described.[1]

Preparation of $Na_{12}H_2[Pd_2Te_4O_{24}H_2]\cdot 20H_2O$. $PdCl_2$ (0.2 g, 1.13 mmol) was dissolved in H_2O (20 mL) containing a few drops of concentrated HCl. Chlorine gas was bubbled through this solution until no further color change occurred followed by nitrogen to purge the solution of excess chlorine. Telluric acid (0.53 g, 2.3 mmol) and NaOH (to ca.

---

(1) Part 36: Levason, W.; Spicer, M. D.; Webster, M. *J. Coord. Chem.*, in press.

(2) Downs, A. J.; Adams, C. J. In *Comprehensive Inorganic Chemistry*; Bailar, J. C., Emeleus, H. J., Nyholm, R. S.; Trotman-Dickenson, A. F., Eds.; Pergamon: Oxford, England, 1982; Vol. 2, pp 1452-1456.

(3) Michiue, Y.; Ichida, H.; Sasaki, Y. *Acta Crystallogr., Sect. C* **1982**, *C43*, 175.

(4) El-Hendawy, A. M.; Griffith, W. P.; Piggott, B.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1988**, 1983.

(5) Lebioda, L.; Ciechanowicz-Rutkowska, M.; Baker, L. C. W.; Grochowski, J. *Acta Crystallogr., Sect. B* **1980**, *B36*, 2530.

(6) Adelskold, V.; Eriksson, L.; Wang, P.-L.; Werner, P.-E. *Acta Crystallogr., Sect. C* **1988**, *C44*, 597. Masse, R.; Simon, A. *J. Solid State Chem.* **1982**, *44*, 201.

(7) Levason, W.; Spicer, M. D.; Webster, M. *J. Chem. Soc., Dalton Trans.* **1988**, 1377.

(8) Siebert, H.; Mader, W. *Z. Anorg. Allg. Chem.* **1967**, *351*, 146.

(9) Lister, M. W.; McLeod, P. *Can. J. Chem.* **1965**, *43*, 1720.

0020-1669/91/1330-0967$02.50/0

4 M in hydroxide) were added, and the mixture was boiled to give a bright orange solution. If any undissolved solid remained, the hot solution was filtered before reduction in volume and cooling. An orange crystalline solid formed, which was collected, washed with cold water, ethanol, and diethyl ether, and air-dried. Yield: 65%. Analysis (EDX): Na:Pd:Te = 5.89:0.98:2.00. Analysis (TGA) for H_2O: found, 20.2; calcd, 20.6.

Preparation of $K_6H_2[Pt(OH)_2(HTeO_6)_2]\cdot10H_2O$. K_2PtCl_6 (0.18 g, 0.37 mmol) in H_2O (8 mL) was added dropwise to KOH (0.26 g) in H_2O (1 mL) and the resulting suspension treated with telluric acid (0.17 g, 0.74 mmol) and KOH (1.1 g). After the mixture was boiled for 3–4 h, a yellow-green solution was formed. This was concentrated, cooled, and placed in the freezer (−18 °C) overnight. A pale yellow precipitate was obtained, which was collected, washed with a small quantity of cold water, ethanol, and diethyl ether, and air-dried. Yield: 50%. Analysis (EDX): K:Pt:Te = 5.60:1.03:2.00. Analysis (TGA) for H_2O: found, 16.1; calcd, 16.4.

Preparation of $K_6Na_2[Pt(OH)_2(HTeO_6)_2]\cdot12H_2O$. H_2PtCl_6 (0.73 g, 1.78 mmol) dissolved in H_2O (8 mL) was added to an aqueous KOH solution (0.83 g in 4 mL). Telluric acid (0.84 g, 3.65 mmol) and KOH (4.0 g) were added, and the mixture was boiled until a clear solution resulted. This was then sealed in a Carius tube and heated to approximately 140 °C for 6–8 h. The solution was recovered, and after it was left standing in a closed flask at 8 °C for 2 weeks, a pale yellow crystalline solid was formed. This was filtered out and air-dried. Yield: 60%. Analysis (EDX): K:Na:Pt:Te = 5.86:1.61:1.01:2.00. Analysis (TGA) for H_2O: found, 18.2; calcd, 18.4.

X-ray Structure Determinations

$Na_8K_2H_4[Pd_2Te_4O_{24}H_2]\cdot20H_2O$. Yellow needle crystals of the compound were obtained by treatment of a reaction mixture containing $PdCl_2$, NaOH, H_6TeO_6, and $K_2S_2O_8$ with a small amount of $Ba(OH)_2$ solution and allowing it to stand for 2 weeks. These were mounted in thin-wall glass capillaries. Preliminary photographic examination was used to determine approximate cell dimensions and establish the crystal quality. Many crystals were found to be twinned. With an Enraf-Nonius CAD4 diffractometer fitted with Mo Kα radiation and graphite monochromator, data were measured from a room-temperature crystal (0.45 × 0.2 × 0.15 mm). The cell dimensions were determined from 25 centered reflections, and 3012 reflection intensities were measured ($1.5 < \theta < 23°$; h = 0 to 8, k = −13 to 13, l = −13 to 13). No decay was noted in the three check reflections, and in addition to the usual Lorentz and polarization corrections, an empirical ψ-scan absorption correction (based on three reflections) was applied to the data (transmission (%): minimum, 79.1; maximum 99.7). After the data reduction there remained 2874 unique reflections ($R_{int} = 0.086$).

The structure was solved in the space group $P\bar{1}$ by using SHELXS-86.[10] Two solutions emerged from the direct methods calculation (TREF) that had a low CFOM (0.037), and one of these gave an *E* map showing three major peaks, one of which was rather smaller, and this was associated with the Pd atom. Repeated structure factor and electron density syntheses located oxygen atoms (22), found five peaks thought to be sodium ions, and left no features unaccounted for in the maps. The distance from the sodium ions to the adjacent oxygen atoms was in agreement with typical Na···O distances for four of the atoms but for the fifth was too large (2.8 Å), and on isotropic refinement the thermal parameter was observed to become negative. The most likely explanation for these observations was that one "sodium" was either potassium or barium, as both of these had been present during the synthesis. The observed distances and the behavior of the models on least-squares refinement supported the presence of a potassium ion in the structure, and subsequent EDX experiments on the same batch of material confirmed this to be the case. (Atom ratios Pd:Te:Na:K = 1.06:2.00:3.94:1.04; Ba = 0%). Mixed cations have been observed before in a number of highly charged large oxoanions.[4,6] The possibility that the original identification of Te and Pd had been incorrect was tested by refining models with other arrangements, but all were markedly worse and supported the original assignment. Toward the end of the structure solution about 10 peaks (0.6–0.9 e $Å^{-3}$) in the difference electron density synthesis were identified as possible H atoms, but these were not included in the model. Full-matrix least-squares refinement (266 parameters, anisotropic (Pd, Te, Na, K, O (not O(6)) and isotropic (O(6)), $w = 1/[\sigma^2(F) + 0.0007F^2]$, maximum shift/error = 0.06, residual electron density 1.28 to −1.24 e $Å^{-3}$) converged to $R = 0.042$. The reason for the failure of O(6) to refine anisotropically is not clear, and it was refined isotropically. Charge balance in the formula is maintained for Pd(IV) and Te(VI) by the inclusion of six H atoms in the molecular formula.

Table I. Crystallographic Data

$Na_8K_2H_4[Pd_2Te_4O_{24}H_2]\cdot20H_2O$	
$H_{46}K_2Na_8O_{44}Pd_2Te_4$	fw = 1735.68
a = 7.403 (1) Å	space group $P\bar{1}$ (No. 2)
b = 11.929 (2) Å	λ = 0.710 69 Å (Mo Kα)
c = 12.429 (2) Å	ρ_{calcd} = 2.772 g cm^{-3}
α = 100.28 (1)°	ρ_{obsd} = 2.64 (2) g cm^{-3}
β = 104.92 (1)°	μ = 39.9 cm^{-1}
γ = 92.23 (1)°	$R(F_o)$ = 0.042
V = 1039.4 $Å^3$	$R_w(F_o)$ = 0.047
Z = 1	
$K_6Na_2[Pt(OH)_2(HTeO_6)_2]\cdot12H_2O$	
$H_{28}K_6Na_2O_{26}PtTe_2$	fw = 1175.09
a = 21.099 (11) Å	space group $C2/m$ (No. 12)
b = 6.778 (3) Å	λ = 0.710 69 Å (Mo Kα)
c = 9.041 (4) Å	ρ_{calcd} = 3.019 g cm^{-3}
$\alpha = \gamma$ = 90°	ρ_{obsd} = 2.89 (2) g cm^{-3}
β = 92.10 (4)°	μ = 87.8 cm^{-1}
V = 1292.1 $Å^3$	$R(F_o)$ = 0.041
Z = 2	$R_w(F_o)$ = 0.051

$K_6Na_2[Pt(OH)_2(HTeO_6)_2]\cdot12H_2O$. Pale yellow slightly hygroscopic prisms separated from the reaction mixture on cooling and were mounted in thin-wall glass capillaries. Photographic X-ray methods were used to obtain approximate cell dimensions and to assess crystal quality. Data were measured from a room-temperature crystal (0.27 × 0.22 × 0.25 mm) as above, and 1279 diffracted intensities were recorded in $\theta/2\theta$ mode ($1 < \theta < 25°$; h = 0–25, k = 0–8, l = −10 to 10). No absorption correction was performed at this stage, and after data reduction there remained 1242 unique reflections. The space group was established on the basis of systematic absences and the structure solution to be $C2/m$ (No. 12). Pt and Te atomic positions were obtained by inspection of the Patterson synthesis, and repeated structure factor and electron density syntheses located the remaining atoms. One of the cations behaved anomalously under refinement and on the basis of peak height data and bond lengths was assigned as a sodium ion. Since Na^+ is not present in the reaction mixture, it was presumed that the caustic solution at the elevated temperature had abstracted sodium from the glass of the Carius tube, which appeared etched after the reaction. This model was refined with all atoms anisotropic to $R = 0.068$ ($R_w = 0.081$). An absorption correction was applied to the fully isotropic model ($R = 0.098$) by using the program DIFABS,[11] and four reflections thought to suffer from extinction were removed at this point. Full-matrix least-squares refinement using the absorption-corrected data converged to $R = 0.041$ ($R_w = 0.051$) (101 parameters, 1170 reflections, anisotropic (Pt, Te, K, Na, O) atoms, $w = 1/[\sigma^2(F) + 0.00005F^2]$, maximum shift/error = 0.06). Although there was some evidence for hydrogen atoms in the difference electron density map, no H atoms were included in the model. The residual electron density was in the range +2.21 to −1.99 e $Å^{-3}$ with the largest peaks at the heavy–atom sites.

Tables I–III give the crystallographic details and final atomic coordinates for the two structures, respectively. Atomic scattering factors for neutral atoms and anomalous dispersion corrections were taken from SHELX-76[12] (O) and ref 13 (Pd, Pt, Te, K, Na). All calculations were performed by using the programs SHELXS-86,[10] SHELX-76,[12] ORTEP-II,[14] PLUTO,[15] STRUPLO-84,[16] DIFABS,[11] and XANADU[17] on an IBM 3090 computer.

Results and Discussion

Complexes of palladium(IV) and platinum(IV) with tellurate ligands were readily prepared by boiling $[MCl_6]^{2-}$ with telluric

---

(10) Sheldrick, G. M. SHELXS-86 Program for Crystal Structure Determination. University of Goettingen, Goettingen, FRG, 1986.

(11) Walker, N.; Stuart, D. DIFABS Empirical Absorption Correction Program. University of London, 1982; *Acta Crystallogr., Sect. A* **1983**, *A39*, 158.

(12) Sheldrick, G. M. SHELX-76 Program for Crystal Structure Determination. University Chemical Laboratory, Cambridge, England, 1976.

(13) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

(14) Johnson, C. K. *Oak Ridge Natl. Lab.* [*Rep.*] *ORNL* (*U.S.*) **1985**, *ORNL-5138*.

(15) Motherwell, W. D. S.; Clegg, W. PLUTO Program for Plotting Molecular and Crystal Structures. Universities of Cambridge and Goettingen, 1978.

(16) Fischer, R. X. *J. Appl. Crystallogr.* **1985**, *18*, 258.

(17) Roberts, P.; Sheldrick, G. M. XANADU Program for Crystallographic Calculations. University Chemical Laboratory, Cambridge, England, 1979.

Table II. Atomic Coordinates and Isotropic Temperature Factors[a] ($\times10^3$) for $Na_8K_2H_4[Pd_2Te_4O_{24}H_2]\cdot20H_2O$

atom	*x*	*y*	*z*	*U*, Å^2
Pd(1)	0.01961 (13)	0.11064 (7)	0.08237 (8)	11.0 (4)
Te(1)	0.05925 (11)	0.32295 (6)	0.26336 (6)	11.6 (4)
Te(2)	0.19590 (11)	0.10148 (6)	−0.12016 (6)	10.6 (3)
Na(1)	−0.1636 (7)	0.2722 (4)	0.4637 (5)	30.8 (25)
Na(2)	0.2573 (7)	0.3608 (4)	0.0561 (4)	25.8 (23)
Na(3)	0.5465 (7)	0.1711 (4)	0.1555 (5)	30.2 (25)
Na(4)	0.5917 (7)	0.2202 (4)	0.6368 (5)	29.4 (25)
K(1)	0.7011 (4)	0.2907 (3)	0.9359 (3)	32.1 (15)
O(1)	0.0560 (12)	0.4250 (7)	0.1693 (7)	21.0 (39)
O(2)	−0.1144 (12)	0.3871 (7)	0.3281 (7)	22.3 (41)
O(3)	0.2675 (13)	0.3931 (7)	0.3704 (7)	27.5 (42)
O(4)	0.0609 (12)	0.2038 (7)	0.3569 (7)	21.6 (39)
O(5)	−0.1362 (12)	0.2193 (6)	0.1485 (7)	19.0 (37)
O(6)	0.2128 (11)	0.2247 (6)	0.1879 (7)	16.3 (18)[b]
O(7)	0.0235 (11)	0.1879 (6)	−0.0475 (7)	14.6 (36)
O(8)	0.1871 (10)	0.0123 (6)	0.0096 (6)	11.0 (34)
O(9)	−0.0202 (11)	−0.0124 (6)	−0.1962 (6)	12.8 (35)
O(10)	0.3867 (11)	0.2007 (7)	−0.0262 (7)	18.7 (38)
O(11)	0.1352 (12)	0.1763 (7)	−0.2379 (7)	22.8 (40)
O(12)	0.3487 (12)	0.0032 (7)	−0.1711 (7)	22.0 (41)
O(13)	−0.1654 (14)	0.1219 (8)	0.5669 (8)	31.5 (45)
O(14)	−0.3945 (13)	0.3749 (7)	0.5355 (8)	30.6 (44)
O(15)	0.1338 (14)	0.3929 (8)	0.5761 (8)	34.5 (47)
O(16)	−0.4693 (15)	0.1593 (8)	0.3547 (9)	48.9 (53)
O(17)	0.5235 (13)	0.3913 (9)	0.2176 (9)	43.8 (53)
O(18)	0.2648 (13)	0.4903 (8)	−0.0635 (8)	31.1 (46)
O(19)	0.6291 (13)	0.0867 (8)	0.7584 (8)	31.3 (45)
O(20)	0.4119 (13)	0.3364 (7)	0.7622 (8)	30.9 (45)
O(21)	0.2793 (15)	0.1165 (8)	0.5497 (9)	47.4 (55)
O(22)	0.8554 (13)	0.3377 (8)	0.7662 (8)	34.8 (47)

[a] Equivalent isotropic temperature factor from anisotropic atom $U_{eq} = {}^1/_3 \times$ trace of orthogonalized *U*. [b] Isotropic atom (see text).

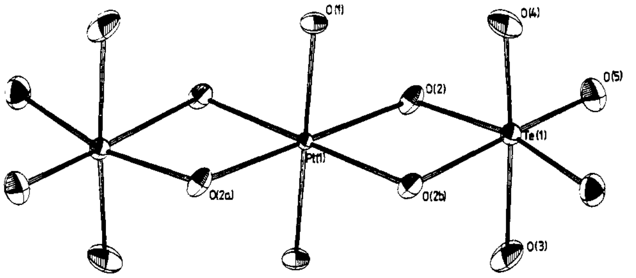

Figure 1. Structure of the anion $[Pt(OH)_2(HTeO_6)_2]^{8-}$ in $K_6Na_2[Pt(OH)_2(HTeO_6)_2]\cdot12H_2O$, showing the atom-labeling scheme. Thermal ellipsoids are drawn to represent 50% probability surfaces. Symmetry codes are (a) -*x*, -*y*, -*z* and (b) *x*, -*y*, *z*. No H atoms are included.

Table III. Atomic Coordinates and Isotropic Temperature Factors[a] ($\times10^3$) for $K_6Na_2[Pt(OH)_2(HTeO_6)_2]\cdot12H_2O$

atom	*x*	*y*	*z*	*U*, Å^2
Pt(1)	0.0000	0.0000	0.0000	6.7 (4)
Te(1)	0.12646 (4)	0.0000	−0.1565 (1)	10.7 (5)
K(1)	0.0400 (2)	0.5000	0.7071 (4)	30.3 (20)
K(2)	0.1908 (2)	0.0000	0.4856 (5)	35.2 (22)
K(3)	0.1949 (2)	0.5000	0.9749 (4)	31.1 (21)
Na(1)	0.1330 (3)	0.5000	0.3319 (7)	18.6 (30)
O(1)	0.0553 (4)	0.0000	0.1861 (11)	14.5 (51)
O(2)	0.0624 (3)	0.1867 (9)	−0.0892 (7)	13.9 (32)
O(3)	0.0725 (5)	0.0000	−0.3532 (12)	28.9 (64)
O(4)	0.1695 (5)	0.0000	0.0283 (13)	26.8 (61)
O(5)	0.1723 (3)	0.2064 (11)	−0.2376 (8)	20.9 (37)
O(6)	0.0618 (4)	0.2578 (11)	0.4076 (9)	30.0 (42)
O(7)	0.2026 (3)	0.2574 (11)	0.2418 (9)	27.2 (41)
O(8)	0.1757 (6)	0.5000	0.5753 (12)	35.0 (71)
O(9)	0.0711 (5)	0.5000	0.1056 (12)	25.2 (61)

[a] Equivalent isotropic temperature factor from anisotropic atom $U_{eq} = {}^1/_3 \times$ trace of orthogonalized *U*.

Table IV. Interatomic Distances (Å) and Angles (deg) for $K_6Na_2[Pt(OH)_2(HTeO_6)_2]\cdot12H_2O$[a]

Distances			
Te(1)–O(2)	1.964 (6)	Pt(1)–O(1)	2.012 (9)
Te(1)–O(3)	2.076 (11)	Pt(1)–O(2)	2.016 (6)
Te(1)–O(4)	1.872 (11)		
Te(1)–O(5)	1.867 (7)	Pt(1)···Te(1)	3.065 (1)
K(1)···O(min)	2.839 (7)	K(1)···O(max)	3.214 (9)
K(2)···O(min)	2.830 (8)	K(2)···O(max)	3.288 (8)
K(3)···O(min)	2.795 (8)	K(3)···O(max)	2.920 (9)
Na(1)···O(min)	2.343 (9)	Na(1)···O(max)	2.385 (12)
Angles			
O(2)–Te(1)–O(2b)	80.2 (4)	O(4)–Te(1)–O(5)	96.3 (3)
O(2)–Te(1)–O(3)	84.4 (3)	O(5)–Te(1)–O(5b)	97.1 (4)
O(2)–Te(1)–O(4)	92.3 (3)	O(1)–Pt(1)–O(2)	88.1 (3)
O(2)–Te(1)–O(5)	90.6 (3)	O(1)–Pt(1)–O(2a)	91.9 (3)
O(2)–Te(1)–O(5b)	167.7 (3)	O(2)–Pt(1)–O(2b)	77.8 (4)
O(3)–Te(1)–O(4)	175.8 (4)		
O(3)–Te(1)–O(5)	86.5 (3)	Te(1)–O(2)–Pt(1)	100.7 (3)

[a] Symmetry codes: (a) −*x*, −*y*, −*z*; (b) *x*, −*y*, *z*.

acid in ca. 4 M M′OH (M′ = Na, K). Platinum complexes were isolated more cleanly if the reaction mixtures were heated in Carius tubes at 140 °C. Analytical data from different preparative routes always had Pd(Pt):Te ratios of 1:2, but the alkali-metal content and degree of hydration were somewhat variable in keeping with previous studies of this type of complex,[1,7] and while materials with only one type of alkali-metal counterion could be isolated, crystalline samples invariably had mixed cations (Na^+, K^+). The palladium complex was isolated as orange needles by concentration of the reaction mixture, while cooling of the solution obtained from the Carius tube reaction resulted in small pale yellow prisms of the platinum tellurate. The palladium complexes were also made from $PdCl_2$, M′OH, $K_2S_2O_8$, and telluric acid.

X-ray Structural Studies. The discrete $[Pt(OH)_2(HTeO_6)_2]^{8-}$ anion is found in $K_6Na_2[Pt(OH)_2(HTeO_6)_2]\cdot12H_2O$, and the structure is shown in Figure 1. In Table IV are listed pertinent bond lengths and angles. The anion has crystallographic C_{2h} point group symmetry with the two $[HTeO_6]^{5-}$ residues acting as bidentate chelating ligands to trans edges of the "PtO_6" group. This arrangement is very similar to that found[1,4] in $[Pt(OH)_2(HIO_6)_2]^{6-}$ and $[RuO_2(HIO_6)_2]^{6-}$. The H atoms were not located in the X-ray analysis, but from previous periodate and tellurate species such as $[H_2I_2O_{10}]^{4-}$ and $[H_4Te_2O_{10}]^{4-}$ where H atoms were found,[18,19]

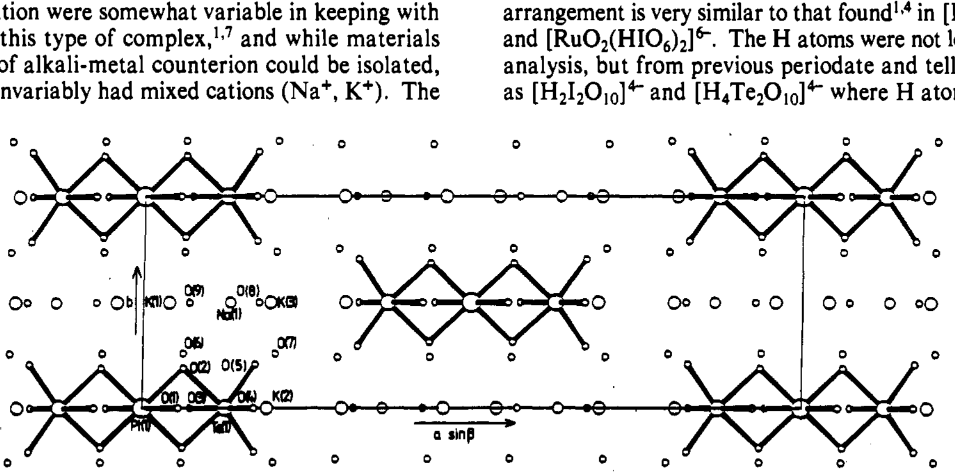

Figure 2. Unit cell diagram for $K_6Na_2[Pt(OH)_2(HTeO_6)_2]\cdot12H_2O$ viewed from the *z* direction.

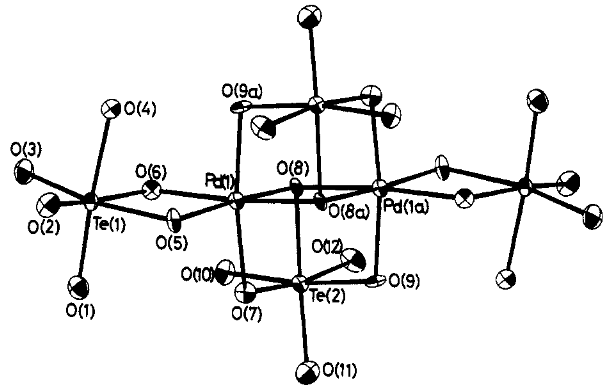

Figure 3. Structure of the anion $[Pd_2Te_4O_{24}H_2]^{14-}$ in $Na_8K_2H_4[Pd_2Te_4O_{24}H_2]\cdot 20H_2O$, showing the atom-labeling scheme. Thermal ellipsoids are drawn to represent 50% probability surfaces. Symmetry code a is -*x*, -*y*, -*z*. No H atoms are included.

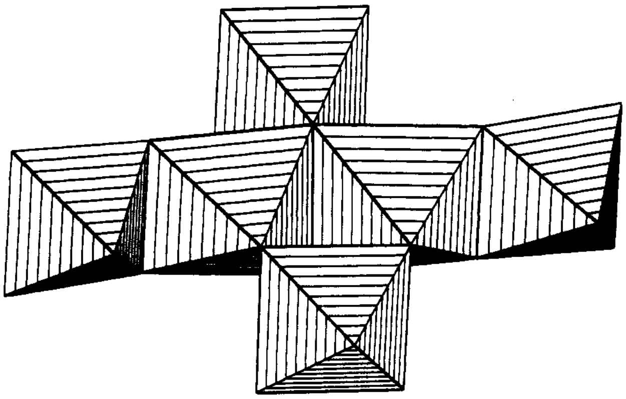

Figure 4. Anion $[Pd_2Te_4O_{24}H_2]^{14-}$ represented as edge-linked octahedra.

we would associate one hydrogen with the long terminal Te(1)–O(3) distance (2.08 (1) Å). As noted before, the bridging oxygen atom (O(2)) forms O–Te–O and O–Pt–O bond angles markedly less than 90° due to Te···Pt repulsion. Like many salts of highly charged oxoanions, the solid contains sodium and potassium ions that form a heavily hydrated network (Figure 2). The sodium ion is in an approximately octahedral six-coordinate environment of water molecules, and the potassium ions (K(1) and K(2)) are surrounded by an irregular polyhedron of eight O atoms. K(3) in six-coordinate, but the angles are further from the idealized octahedral values.

The $[Pd_2Te_4O_{24}H_2]^{14-}$ anion found in the palladium compound has a structure based on edge-linked octahedra and is shown in Figures 3 and 4, and selected bond lengths are given in Table V. The anion has a crystallographic center of symmetry, but in addition there is an approximate 2-fold axis along Pd(1)···Pd(1a) and a consequent mirror plane perpendicular to the 2-fold axis and passing through the center of symmetry, giving approximate C_{2h} point group symmetry. Te(1) has a chemical environment similar to that in the previous structure and forms a bidentate chelating ligand to Pd(1). Again inspection of the Te–O bond lengths (Table V) would favor O(1) being an OH group (Te(1)–O(4) = 1.988 (8) Å). In contrast Te(2) has terminal, doubly bridging (O(7), O(9)), and triply bridging (O(8)) oxygen atoms and sites for H atoms (if any) are not apparent. Charge balance requires the addition of four more hydrogen ions, which are associated with either the water molecules or the anion; if the latter, then the doubly bridging sites are more likely than the triply bridging ones.[20] This $[M_6O_{24}]^{n-}$ geometry does not appear to have been found among other oxoanions of, for example, Mo or W. As with the previous structure, the salt contains extensively hydrated Na and K ions in which the Na ions are approximately octahedral six-coordinate and the K ion is in a seven-coordinate environment.

Table V. Interatomic Distances (Å) and Angles (deg) for $Na_8K_2H_4[Pd_2Te_4O_{24}H_2]\cdot 20H_2O$[a]

	Distances		
Te(1)–O(1)	1.829 (8)	Te(2)–O(7)	1.967 (7)
Te(1)–O(2)	1.810 (8)	Te(2)–O(8)	2.097 (7)
Te(1)–O(3)	1.815 (8)	Te(2)–O(9)	1.973 (8)
Te(1)–O(4)	1.988 (8)	Te(2)–O(10)	1.813 (8)
Te(1)–O(5)	1.956 (8)	Te(2)–O(11)	1.816 (8)
Te(1)–O(6)	1.951 (8)	Te(2)–O(12)	1.806 (8)
Pd(1)–O(5)	1.977 (8)	Pd(1)···Te(1)	3.021 (2)
Pd(1)–O(6)	1.965 (8)	Pd(1)···Te(2)	3.107 (2)
Pd(1)–O(7)	2.002 (8)	Pd(1)···Pd(1a)	2.992 (2)
Pd(1)–O(8)	2.011 (7)	Pd(1)···Te(2a)	3.109 (2)
Pd(1)–O(8a)	2.031 (8)		
Pd(1)–O(9a)	1.991 (8)		
Na(1)···O(min)	2.384 (10)	Na(1)···O(max)	2.514 (11)
Na(2)···O(min)	2.336 (10)	Na(2)···O(max)	2.572 (9)
Na(3)···O(min)	2.270 (10)	Na(3)···O(max)	2.686 (9)
Na(4)···O(min)	2.361 (10)	Na(4)···O(max)	2.562 (11)
K(1)···O(min)	2.703 (8)	K(1)···O(max)	2.907 (10)
	Angles		
O(1)–Te(1)–O(2)	95.4 (4)	O(7)–Te(2)–O(8)	78.6 (3)
O(1)–Te(1)–O(3)	95.0 (4)	O(7)–Te(2)–O(9)	86.5 (3)
O(1)–Te(1)–O(4)	176.3 (3)	O(7)–Te(2)–O(10)	88.0 (4)
O(1)–Te(1)–O(5)	92.0 (4)	O(7)–Te(2)–O(11)	90.3 (4)
O(1)–Te(1)–O(6)	91.9 (3)	O(7)–Te(2)–O(12)	169.4 (3)
O(2)–Te(1)–O(3)	98.0 (4)	O(8)–Te(2)–O(9)	78.6 (3)
O(2)–Te(1)–O(4)	87.0 (4)	O(8)–Te(2)–O(10)	91.4 (3)
O(2)–Te(1)–O(5)	90.9 (4)	O(8)–Te(2)–O(11)	164.4 (3)
O(2)–Te(1)–O(6)	168.1 (3)	O(8)–Te(2)–O(12)	91.0 (3)
O(3)–Te(1)–O(4)	87.5 (4)	O(9)–Te(2)–O(10)	169.4 (3)
O(3)–Te(1)–O(5)	168.1 (4)	O(9)–Te(2)–O(11)	89.9 (3)
O(3)–Te(1)–O(6)	90.7 (4)	O(9)–Te(2)–O(12)	89.5 (4)
O(4)–Te(1)–O(5)	85.1 (3)	O(10)–Te(2)–O(11)	99.2 (4)
O(4)–Te(1)–O(6)	85.3 (3)	O(10)–Te(2)–O(12)	94.3 (4)
O(5)–Te(1)–O(6)	79.5 (3)	O(11)–Te(2)–O(12)	99.5 (4)
O(5)–Pd(1)–O(6)	78.6 (3)	O(6)–Pd(1)–O(9a)	93.8 (3)
O(5)–Pd(1)–O(7)	95.4 (3)	O(7)–Pd(1)–O(8)	79.9 (3)
O(5)–Pd(1)–O(8)	174.6 (3)	O(7)–Pd(1)–O(8a)	95.0 (3)
O(5)–Pd(1)–O(8a)	98.6 (3)	O(7)–Pd(1)–O(9a)	171.4 (3)
O(5)–Pd(1)–O(9a)	92.2 (3)	O(8)–Pd(1)–O(8a)	84.5 (4)
O(6)–Pd(1)–O(7)	91.7 (3)	O(8)–Pd(1)–O(9a)	92.7 (3)
O(6)–Pd(1)–O(8)	98.7 (3)	O(8a)–Pd(1)–O(9a)	79.8 (3)
O(6)–Pd(1)–O(8a)	173.0 (3)		
Te(1)–O(5)–Pd(1)	100.4 (4)	Te(2)–O(9)–Pd(1a)	103.3 (4)
Te(1)–O(6)–Pd(1)	101.0 (4)	Te(2)–O(8)–Pd(1a)	97.7 (4)
Te(2)–O(7)–Pd(1)	103.0 (3)	Pd(1)–O(8)–Pd(1a)	95.5 (4)
Te(2)–O(8)–Pd(1)	98.3 (3)		

[a] Symmetry code: (a) −*x*, −*y*, −*z*.

Spectroscopic Data. Infrared and Raman spectra of these complexes are characteristic of tellurates in an octahedral environment but do not distinguish the different structural types.[3] The UV-visible spectra consist of intense absorptions in the UV region tailing into the visible region, with a shoulder in the palladium complex at 35 100 cm^{-1}. These bands almost certainly arise from charge-transfer transitions and are very similar to those obtained from similar periodate complexes.[1]

Multinuclear (^{125}Te and ^{195}Pt) NMR spectra were obtained from aqueous solutions of these complexes at room temperature. The crystalline palladium tellurate complex in water gave rise to a ^{125}Te spectrum consisting of two resonances of equal intensity at 804 and 856 ppm, consistent with the two tellurium environments in the structure of the dimeric anion; the high-frequency resonance is thought to arise from the bridging site. However, spectra of the crude reaction mixture demonstrate that this dimer is in fact the minor species initially formed in solution, the major species being characterized by a single resonance at 801 ppm. This complex is apparently converted to the dimer on concentration of the solution, and it is the dimer that also crystallizes preferentially. Rapid precipitation from solution by using acetonitrile

---

(18) Tobias, K. M.; Jansen, M. *Z. Anorg. Allg. Chem.* **1986**, *538*, 159.
(19) Fuchs, J.; Loederich, R.; Pickardt, J. *Z. Naturforsch.* **1982**, *37B*, 587.
(20) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; J. Wiley and Sons: New York, 1988; p 463.

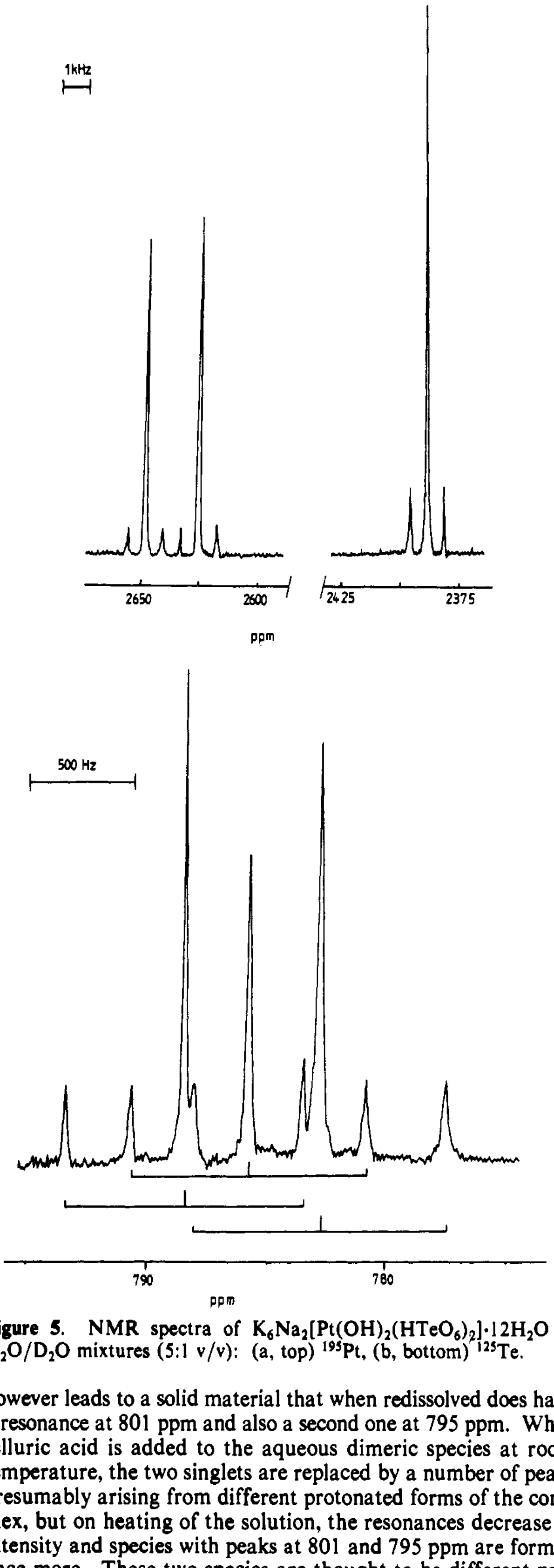

Figure 5. NMR spectra of $K_6Na_2[Pt(OH)_2(HTeO_6)_2]\cdot12H_2O$ in H_2O/D_2O mixtures (5:1 v/v): (a, top) ^{195}Pt, (b, bottom) ^{125}Te.

however leads to a solid material that when redissolved does have a resonance at 801 ppm and also a second one at 795 ppm. When telluric acid is added to the aqueous dimeric species at room temperature, the two singlets are replaced by a number of peaks presumably arising from different protonated forms of the complex, but on heating of the solution, the resonances decrease in intensity and species with peaks at 801 and 795 ppm are formed once more. These two species are thought to be different protonated forms of a monomeric species, possibly $[Pd(OH)_2(HTeO_6)_2]^{8-}$ by analogy with the platinum periodate and tellurate complexes. Aqueous solutions of $[Pt(OH)_2(HTeO_6)_2]^{8-}$ were studied by ^{125}Te and ^{195}Pt NMR spectroscopy and also exhibited complex behavior. Typical spectra are shown in Figure 5. Solutions derived from crystalline samples gave ^{195}Pt spectra with peaks at 2650, 2625, and 2388 ppm each with associated ^{125}Te satellites. Likewise, the ^{125}Te spectra contained three resonances at 788.4, 785.7, and 782.7 ppm exhibiting ^{195}Pt satellites. The coupling constants derived from these satellites enable correlation of these resonances with the three $^{195}Pt/^{125}Te$ pairs being 2388/788.4 (J = 1135 Hz), 2625/785.7 (J = 1200 Hz), and 2650/782.7 (J = 1120 Hz). Addition of a weak acid such as H_6TeO_6 to this solution results in the conversion of the two species at 2650 and 2625 ppm to the species at 2388 ppm, presumably by protonation. It has been noted previously[21] that a chemical shift change of this approximate magnitude accompanies protonation of $[Pt(OH)_nCl_{6-n}]^{2-}$ species.

EXAFS Studies. In an effort to understand the solution behavior of these tellurate complexes, Pt L_{III}-edge and Pd K-edge EXAFS studies were undertaken on specifically prepared solutions. In general EXAFS data from samples containing several species are difficult to interpret with confidence and so the preparation of solutions containing only one component was necessary. The platinum tellurate solution was prepared by dissolving $K_6H_2[Pt(OH)_2(HTeO_6)_2]\cdot10H_2O$ in water and then acidifying (to ca. pH 2) with telluric acid. A single resonance in the ^{195}Pt NMR spectrum at 2388 ppm and in the ^{125}Te NMR spectrum at 788.4 ppm (J = 1135 Hz) confirmed the presence of a single platinum-containing species. Analysis of the data obtained from this solution strongly suggested that the species present was structurally very similar to that determined crystallographically for $[Pt(OH)_2(HTeO_6)_2]^{8-}$. The platinum is surrounded by six atoms at 2.00 (2) Å with two nonbonded tellurium atoms at 3.02 (3) Å (cf. crystallographic distances d(Pt–O) = 2.015 (av) Å; d(Pt⋯Te) = 3.065 Å). Despite the presence of an excess of tellurate in the solution, attempts to fit a model with three tellurate ligands led to significantly poorer fits (20% increase in R factor), precluding the presence of a tris(tellurato) complex. These data are consistent with the assertion that the different resonances seen in the NMR spectra arise from differing degrees of protonation of one basic structural form.

The palladium species studied was prepared from $[PdCl_6]^{2-}$ and 2 equiv of H_6TeO_6. The ^{125}Te NMR spectrum exhibited a single resonance at 801 ppm with traces (<1%) of telluric acid and of the $[Pd_2Te_4O_{24}H_2]^{14-}$ ion. The lack of significant amounts of telluric acid in the spectrum indicates a Pd:Te ratio of 1:2 in this solution species. Having spectroscopically precluded the presence of the $[Pd_2Te_4O_{24}H_2]^{14-}$ anion, we find that few chemically reasonable possibilities remain and despite the indifferent quality of the EXAFS data (resulting from the poor solubility of this complex) our analysis would suggest a monomeric species analogous to the platinum tellurate described above, with d(Pd–O) = 1.98 (2) Å and d(Pd⋯Te) = 2.96 (4) Å.

Acknowledgment. We thank Dr. D. C. Povey of the University of Surrey (Pt) and Prof. M. B. Hursthouse of Queen Mary and Westfield College, London, (Pd) for X-ray data collections (the latter on the SERC/QMWC diffractometer), the Director of the Daresbury Laboratory for the provision of facilities, Dr. T. R. Gilson for collection of the Raman data, and the Science and Engineering Research Council for financial support (M.D.S.).

Supplementary Material Available: Tables SI–SVI, listing crystallographic data, anisotropic thermal parameters, full bond length and angle data, and refined EXAFS parameters, and Figure S1, showing a unit cell diagram for $Na_8K_2H_4[Pd_2Te_4O_{24}H_2]\cdot20H_2O$ (8 pages); Tables SVII and SVIII, listing observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

---

[21] Carr, C.; Goggin, P. L.; Goodfellow, R. J. *Inorg. Chim. Acta* **1984**, *81*, L25.