Short Communication

The Crystal Structure of Potassium Tetraiodoplatinate(II) Dihydrate

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This investigation is part of a study on the effects of different substituents on the geometry of Pt(II) complexes.[1-3] This paper reports the structure of $K_2[PtI_4] \cdot 2H_2O$. Crystals were prepared as described previously.[4] The single crystal used for data collection had an irregular shape, with approximate dimensions 0.035×0.124×0.174 mm. All data were collected on a CAD-4 diffractometer employing monochromated Mo*K*α-radiation (λ = 0.7107 Å). Laue class and systematic extinctions are consistent with the space group *Pbca*. Unit cell dimensions were obtained from 25 θ values determined as $\theta_{hkl} = (\omega_{hkl} - \omega_{\bar{h}\bar{k}\bar{l}})/2$, with the diffractometer in the bisecting mode and measuring $\omega_{\bar{h}\bar{k}\bar{l}}$ at negative θ angle; a = 12.934(3), b = 7.145(2), c = 13.626 (2) Å, V = 1259.2 Å^3 and Z = 4.

The intensities of 1367 reflections in one octant of the reflection sphere ($3 < \theta < 27$) were measured with $\omega - 2\theta$ scan ($\Delta\omega = 0.7 + 0.5\tan\theta$). The ratio $\sigma(I)/I$ required in a scan was 0.028 and the maximum recording time 150 s. The variation in three standard reflections was less than 3 %. I and $\sigma(I)$ were corrected for Lorentz, polarisation and absorption effects, the latter by numerical integration (μ = 111.6 cm^{-1}, transmission factors 0.187–0.520, ϱ_c = 4.31 g cm^{-3}). Only the 1010 reflections with $I > 3\,\sigma(I)$ were used in the calculations. The structure was solved by direct methods,[5] and refined by full-matrix least-squares, minimizing $\Sigma w(|F_o| - |F_c|)^2$ with weights $w^1 = \sigma^2/(4|F_o|^2) + 0.055|F_o|^2 + 10$. Final agreement indices were R = 0.0603 and R_w = 0.0859. A δR plot resulted in a slope of 0.98 and intercept −0.11. Scattering factors with corrections for anomalous dispersion were taken from Ref. 6. Tables of $|F_o|$, $\sigma(|F_o|)$ and $|F_c|$ are available on request from the authors. Final atomic parameters are given in Table 1, and selected distances and angles in Table 2. Computer programs used are those compiled and amended by Lundgren.[7] The PtI_4^{2-} complex with two neighbouring K^+ ions is shown in Fig. 1. The symmetry of this unit is $\bar{1}$, but the coordination around Pt is almost square (Table 2). The Pt···K distance is quite short, viz. 3.44 Å, and two K^+ ions are located in such a way as to form a K_2PtI_4 unit with pseudo-octahedral geometry. The potassium ion coordinates two water molecules (K–O 2.70 – 2.86 Å) and six iodides (K–I 3.64 – 3.93 Å) in four different PtI_4^{2-} complexes, in a somewhat irregular geometry. The water molecule further stabilizes the three-dimensional structure by linking three PtI_4^{2-} complexes through hydrogen bonding (O–I 3.67 – 3.76 Å).

Table 1. Atomic coordinates and isotropic thermal parameters with estimated standard deviations. U_{iso} is calculated from the average of the anisotropic temperature factors.

Atom	*x/a*	*y/b*	*z/c*	U_{iso}/Å^2 [a]
Pt	0.0000	0.0000	0.0000	0.0230(3)
I1	0.0165(1)	0.2137(2)	0.1542(1)	0.0410(5)
I2	0.148501)	−0.2149(2)	0.0657(1)	0.0375(4)
K	0.1348(4)	0.3696(7)	−0.0984(4)	0.0452(15)
O	0.2211(13)	0.4409(27)	0.2981(13)	0.0516(58)

[a] $U_{iso} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \boldsymbol{a}_i \boldsymbol{a}_j$

Table 2. Selected interatomic distances (Å) and angles (°) with estimated standard deviations. (′) = -*x*, -*y*, -*z*.

Pt–I1	2.606(2)
Pt–I2	2.616(1)
I1–I2	3.679(2)
I1–I2′	3.708(2)
Pt–K	3.437(5)
I1–Pt–I2	90.45(5)

Table 3 gives observed and "calculated" Pt–X distances in some selected compounds. The average value of the observed Pt–I distance in the title compound as well as in *trans*-$Pt(THT)_2I_2$ (THT = tetrahydrothiophene)[3] is only 0.03 Å shorter than would be expected from covalent radii.[8] For the compounds K_2PtBr_4[9] and K_2PtCl_4[10] (not isostructural with $K_2PtI_4 \cdot 2H_2O$) and the compounds *trans*-PtL_2X_2 with X = Br or Cl the agreement is even better.[11] Two O or two S in *trans* position[1,3] also indicate additivity of the covalent radii, while for P the observed Pt–P distance is 0.10 Å shorter than that calculated.[11]

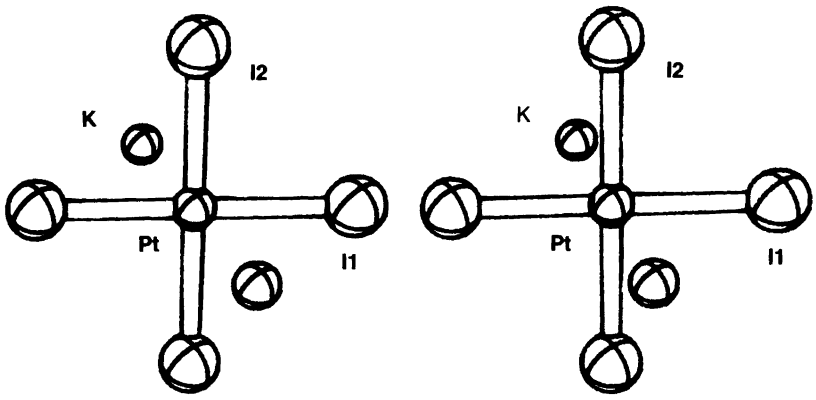

Fig. 1. A stereoscopic view of the coordination around Pt with the two neighbouring K^+ ions.

Table 3. Observed and calculated Pt–X distances in some selected Pt(II) complexes. The calculated distances are the sum of the covalent radii of Pt(II) (1.31 Å) and X according to Pauling.[a]

Complex	Ref.	Donor	Distance/Å	
			Observed	Calculated
PtI_4^{2-}	This work	I	2.61	2.64
$PtBr_4^{2-}$	9	Br	2.45	2.45
$PtCl_4^{2-}$	10	Cl	2.31	2.30
trans-$Pt(THT)_2I_2$[b]	3	I	2.61	2.64
		S	2.31	2.35
$Pt(NO_3)_4^{2-}$	1	O	2.00	1.97
trans-$Pt[P(C_2H_5)_3]_2Br_2$	11	Br	2.43	2.45
		P	2.32	2.41
trans-$Pt[P(C_2H_5)_3]_2$	11	Cl	2.32	2.30
		P	2.30	2.41
cis-$Pt(DMSO)_4^{2+}$[c]	2	O	2.05	1.97
		S	2.21	2.35
cis-$Pt(DMSO)_2Cl_2$	12	Cl	2.32	2.30
		S	2.24	2.35
cis-$Pt[P(CH_3)_3]Cl_2$	13	Cl	2.38	2.30
		P	2.25	2.41

[a] Ref. 8. [b] THT = tetrahydrothiophene. [c] DMSO = dimethyl sulfoxide.

As expected, the agreement between observed and "calculated" distances is poor for *cis* complexes. In this case the bond distances should be affected by differences in ground state *trans* influence of the donor atoms in *trans* position. However, the distance between *trans* donor atoms can also be calculated with reasonable accuracy in *cis* complexes, using the Pt–X distances for the *trans* compounds. The observed O···S, Cl···S and Cl···P distances in the *cis* complexes are 4.26, 4.56 and 4.63 Å, respectively, compared to 4.31, 4.62 and 4.62 Å calculated from the data for the *trans* compounds (Table 3).

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