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# ENTHALPY OF FORMATION OF SOLID $K_2Pt(CN)_4$

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## ABSTRACT

The enthalpy change of the reaction $K_2Pt(CN)_4(s) + 4KCl(s) \rightarrow K_2PtCl_4(s) + KCN(s)$ has been determined calorimetrically as $\Delta H = +447\ 9 \pm 3\ 5$ kJ $mol^{-1}$ The value $\Delta H_f^{\ominus}[K_2Pt(CN)_4,s] = -218\ 2 \pm 4\ 8$ kJ $mol^{-1}$ is obtained

There is considerable interest because of their use in tumour therapy in complexes of the type $ML_2Cl_2$, where M is Pd or Pt, and L is a ligand containing a Group V or VI donor atom such as N or S There is a need to know the enthalpies of formation of these complexes to provide a better understanding of the energetics of reactions in which they are involved Enthalpies of formation may be determined from measurements of the enthalpies of reactions in which the complex is either formed or converted to a more stable complex Examples [1,2] are shown in reactions (1) and (2)

$$(NH_4)_2PdCl_2 + 2(C_2H_5)_2S \rightarrow trans\text{-}PdCl_2\{(C_2H_5)_2S\}_2 \qquad (1)$$

$$\text{Pt(9-methyladenineH)Cl}_3 + 4\ KCN \rightarrow K_2Pt(CN)_4 + \text{9-methyladenineHCl} + 2KCl \qquad (2)$$

The formation reaction is suitable for a thermochemical study of palladium compounds, because the reactions are fast and one isomer often forms preferentially, but less suitable for platinum compounds, where reactions are slow and a mixture of isomers often forms Here, conversion to the more stable tetracyano complex is preferred Recent kinetic studies have shown that rates of reaction of cyanide with, e g $PtCl_4^{2-}$, are sufficiently rapid [3] to cause no problems when a calorimeter of the LKB 8700 type is used

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Calculation of the enthalpy of formation of the complex depends on a value for $\Delta H_f^{\ominus}[K_2Pt(CN)_2,s]$ As this is not available in the literature, we have determined the enthalpy $\Delta H(3) = +447\ 9 \pm 3\ 7$ kJ $mol^{-1}$, of reaction (3) so that it may be calculated The enthalpies of reactions (4)–(6) where the symbol $H_2O$ refers to $10^4$ mol water, have been measured

$$K_2Pt(CN)_4(s) + 4KCl(s) \rightarrow K_2PtCl_4(s) + 4KCN(s) \qquad (3)$$

$$K_2PtCl_4(s) + [100KCN, H_2O](l) \rightarrow [K_2Pt(CN)_4, 4KCl, 96KCN, H_2O](l) \qquad (4)$$

$$K_2Pt(CN)_4(s) + [4KCl, 96KCN, H_2O](l) \rightarrow [K_2Pt(CN)_4, 4KCl, 96KCN, H_2O](l) \qquad (5)$$

$$4KCl(s) + [96KCN, H_2O](l) \rightarrow [4KCl, 96KCN, H_2O](l) \qquad (6)$$

$$4KCN(s) + [96KCN, H_2O](l) \rightarrow [100KCN, H_2O](l) \qquad (7)$$

The value of $\Delta H(3)$ is calculated by use of the relationship $\Delta H(3) = \Delta H(5) - \Delta H(4) + \Delta H(6) - \Delta H(7)$ from the values $\Delta H(4) = -407\ 2 \pm 1\ 9$ kJ $mol^{-1}$, [2] $\Delta H(5) = +54\ 05 \pm 0\ 6$ kJ $mol^{-1}$, $\Delta H(6) = +33\ 4 \pm 1\ 1$ kJ for 4 mol KCl and $\Delta H(7) + = +46\ 8 \pm 0\ 2$ kJ for 4 mol KCN [6] Using the values [6] $\Delta H_f^{\ominus}(K_2PtCl_4,s) = -1063.6 \pm 0\ 2$ kJ $mol^{-1}$, $\Delta H_f^{\ominus}(KCl,s) = -435\ 87 \pm 0\ 02$ kJ $mol^{-1}$ and $\Delta H_f^{\ominus}(KCN,s) = -112\ 55 \pm 0\ 2$ kJ $mol^{-1}$, we obtain $\Delta H_f^{\ominus}\{K_2Pt(CN)_4,s\} = -218\ 2 \pm 4\ 8$ kJ $mol^{-1}$

The rather small value for the enthalpy of formation of $K_2Pt(CN)_4$, as indeed of KCN, may be attributed to large positive enthalpy changes needed to atomise the carbon and nitrogen that constitute the cyanide ion

We have been unable to find a crystal structure determination for $K_2Pt(CN)_4$, and are thus not able to estimate a value for the single ion hydration enthalpy for the $Pt(CN)_4^{2-}$ anion Given crystal structures for $K_2Pt(CN)_4$ and for another tetracyanoplatinate(II) of different structure type, it would then be possible to get good estimates both of the single ion hydration enthalpy for $Pt(CN)_4^{2-}$ and of the charge distribution within the anion [4] (see, for example, the recent treatment of hexafluoroelementate(IV) anions in this manner [5]

## EXPERIMENTAL

Potassium tetrachloroplatinate(II) and potassium tetracyanoplatinate(II) (Johnson Matthey) were used as supplied Potassium cyanide (BDH) was heated to 100 °C in vacuo for several hours to remove any ammonium acetate formed by hydrolysis Potassium chloride was dried over $P_2O_5$ Enthalpies of reaction were measured by use of the LKB 8700 calorimeter equipped with a 25 ml reaction vessel Calibrations were by the electrical substitution method Uncertainties quoted are twice the standard deviations of the mean values, which refer to 298.15 K

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