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ENTHALPY OF FORMATION OF $Co(cytosine)_2Cl_2$

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ABSTRACT

The value $\Delta H_f^{\ominus}[Co(cytosine)_2Cl_2,cr] = -835.0 \pm 4$ kJ mol^{-1} has been determined from solution calorimetry The mean bond dissociation $\bar{D}$(Co-cytosine) = 216 ± 13 kJ mol^{-1} is calculated

The enthalpy, $\Delta H(1) = -51.7 \pm 3$ kJ mol^{-1}, of reaction (1) (below) has been calculated from the relationship $\Delta H(1) = \Delta H(2) - 2\Delta H(3) - \Delta H(4)$, using the measured values $\Delta H(2) = -29.7 \pm 1.5$ kJ mol^{-1}, $\Delta H(3) = 0.41 \pm 0.08$ kJ mol^{-1} of cytosine and $\Delta H(4) = -82.2 \pm 2.1$ kJ mol^{-1}, at 298 K

$$Co(cy)_2Cl_2(cr) \rightarrow CoCl_2(cr) + 2cytosine(cr) \qquad (1)$$

$$Co(cy)_2Cl_2(cr) + 27[HCl, 553.1H_2O](sln) \rightarrow solution\ A \qquad (2)$$

$$2cytosine(cr) + 27[HCl, 553.1H_2O](sln) \rightarrow solution\ B \qquad (3)$$

$$CoCl_2(cr) + solution\ B \rightarrow solution\ A \qquad (4)$$

Using the $\Delta H_f^{\ominus}$ values cytosine(cr) -235.4 ± 0.9 [1], $CoCl_2$(cr) = -312.5 ± 0.5 kJ mol^{-1} [2], we calculate the value $\Delta H_f^{\ominus}[Co(cytosine)_2Cl_2,cr] = -835.0 \pm 4$ kJ mol^{-1} Incorporating the enthalpy of sublimation of this complex, $\Delta H_{sub}^{298} = 162 \pm 14$ kJ mol^{-1} [1,3] leads to the value $\Delta H_f^{\ominus}[Co(cytosine)_2Cl_2,g] = -673.0 \pm 18$ kJ mol^{-1}

The enthalpies ΔH_d^{298} of the dissociation of crystalline complex CoL_2Cl_2, where L is pyridine, 2-methylpyridine, triphenylphosphine [4] and acetonitrile [5] to crystalline $CoCl_2$ and gaseous ligand have been reported previously and values are shown in Table 1. They are based on

$$CoL_2Cl_2(cr) \rightarrow CoCl_2(cr) + 2L(g) \qquad \Delta H_d^{298}$$

$$CoL_2Cl_2(g) \rightarrow CoCl_2(g) + 2L(g) \qquad \Delta H_g^{298}$$

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TABLE 1

Enthalpies of dissociation of CoL_2Cl_2 complexes (kJ mol^{-1})

L	ΔH_d^{298}	ΔH_{sub}^{298}	ΔH_g^{298}	$\bar{D}$(M–L)
pyridine	189	[100] [a]	323	162
2-methylpyridine	172	[100]	306	153
acetonitrile	100 [b]	[100]	312	156
triphenylphosphine	242	[100]	342	171
cytosine	351	162 ± 14 [c]	433	216

[a] Brackets indicate estimated values [b] Ref 5 [c] Ref 3

$\Delta H_f^{\ominus}(CoCl_2,cr) = -312\ 5 \pm 0\ 5$ kJ mol^{-1} [2], ΔH_{sub}^{298}(cytosine) = 155 ± 3 kJ mol^{-1} [3], and a more recent value $\Delta H_{sub}^{298}(PPh_3) = 96\ 2 \pm 0\ 2$ kJ mol^{-1} [6] than was used previously [4] Enthalpies of the gas-phase dissociation reactions ΔH_g^{298} can be calculated by incorporating the enthalpies of sublimation of the complexes and the value $\Delta H_{sub}(CoCl_2) = 234 \pm 2$ kJ mol^{-1} [7]

Also shown in Table 1 are the mean bond dissociation energies of the metal ligand bonds $\bar{D}(M\text{–}L) = \frac{1}{2}\Delta H_g^{298}$

The structure of gaseous $Co(cy)_2Cl_2$ is not known However, a crystal study of the complex $Cu(cy)_2Cl_2$ has been made [8] This species is essentially planar with two strong Cu–N(3) bonds (1 955 Å) and two Cu–Cl bonds Weak intramolecular Cu–O(2) interactions (2 808 Å) above and below the plane complete the octahedral geometry It is possible that the structure of gaseous $Co(cy)_2Cl_2$ will be similar If $\bar{D}$(Co–N, pyridine) = $\bar{D}$(Co–N, cytosine), then $\bar{D}$(C–O, cytosine) = 50 kJ mol^{-1}, a value which is consistent with the likely structure of this complex

The complex $Co(cy)_2Cl_2$ was prepared by the method given in ref 9 The CHN microanalysis was satisfactory Enthalpies of solution reactions were measured by use of an L K B solution calorimeter Temperature changes in the vessel were determined with a platinum resistance sensor which formed one arm of a modified Whetstone bridge The amplified off-balance potential was recorded by a BBC Model B micro-computer Measurement of the enthalpy of solution of THAM in acid gave results to within 0 05% of the anticipated value Uncertainties quoted are twice the standard deviation of the mean value of five determinations in each case

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