

ENTHALPY OF FORMATION OF Co(cytosine)₂Cl₂

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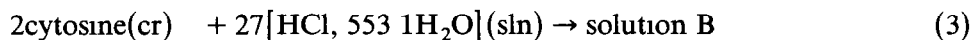
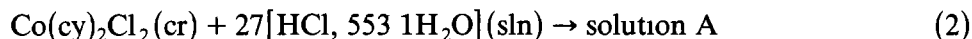
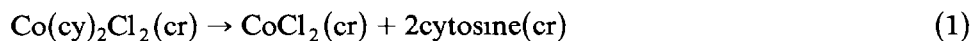
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ABSTRACT

The value $\Delta H_f^\ominus[\text{Co(cytosine)}_2\text{Cl}_2, \text{cr}] = -835.0 \pm 4 \text{ kJ mol}^{-1}$ has been determined from solution calorimetry. The mean bond dissociation $\bar{D}(\text{Co-cytosine}) = 216 \pm 13 \text{ kJ mol}^{-1}$ is calculated.

The enthalpy, $\Delta H(1) = -51.7 \pm 3 \text{ kJ mol}^{-1}$, 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 $\Delta H(2) = -29.7 \pm 1.5 \text{ kJ mol}^{-1}$, $\Delta H(3) = 0.41 \pm 0.08 \text{ kJ mol}^{-1}$ of cytosine and $\Delta H(4) = -82.2 \pm 2.1 \text{ kJ mol}^{-1}$, at 298 K.



Using the ΔH_f^\ominus values cytosine(cr) -235.4 ± 0.9 [1], $\text{CoCl}_2(\text{cr}) = -312.5 \pm 0.5 \text{ kJ mol}^{-1}$ [2], we calculate the value $\Delta H_f^\ominus[\text{Co(cytosine)}_2\text{Cl}_2, \text{cr}] = -835.0 \pm 4 \text{ kJ mol}^{-1}$. Incorporating the enthalpy of sublimation of this complex, $\Delta H_{\text{sub}}^{298} = 162 \pm 14 \text{ kJ mol}^{-1}$ [1,3] leads to the value $\Delta H_f^\ominus[\text{Co(cytosine)}_2\text{Cl}_2, \text{g}] = -673.0 \pm 18 \text{ kJ mol}^{-1}$.

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

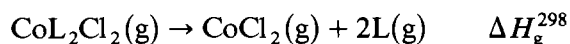
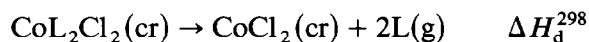


TABLE 1

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

L	$\Delta H_{\text{d}}^{298}$	$\Delta H_{\text{sub}}^{298}$	$\Delta H_{\text{g}}^{298}$	$\overline{D}(\text{M-L})$
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

$\Delta H_{\text{f}}^{\ominus}(\text{CoCl}_2, \text{cr}) = -312.5 \pm 0.5 \text{ kJ mol}^{-1}$ [2], $\Delta H_{\text{sub}}^{298}(\text{cytosine}) = 155 \pm 3 \text{ kJ mol}^{-1}$ [3], and a more recent value $\Delta H_{\text{sub}}^{298}(\text{PPh}_3) = 96.2 \pm 0.2 \text{ kJ mol}^{-1}$ [6] than was used previously [4]. Enthalpies of the gas-phase dissociation reactions $\Delta H_{\text{g}}^{298}$ can be calculated by incorporating the enthalpies of sublimation of the complexes and the value $\Delta H_{\text{sub}}(\text{CoCl}_2) = 234 \pm 2 \text{ kJ mol}^{-1}$ [7].

Also shown in Table 1 are the mean bond dissociation energies of the metal ligand bonds $\overline{D}(\text{M-L}) = \frac{1}{2} \Delta H_{\text{g}}^{298}$.

The structure of gaseous $\text{Co}(\text{cy})_2\text{Cl}_2$ is not known. However, a crystal study of the complex $\text{Cu}(\text{cy})_2\text{Cl}_2$ 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 $\text{Co}(\text{cy})_2\text{Cl}_2$ will be similar. If $\overline{D}(\text{Co-N, pyridine}) = \overline{D}(\text{Co-N, cytosine})$, then $\overline{D}(\text{C-O, cytosine}) = 50 \text{ kJ mol}^{-1}$, a value which is consistent with the likely structure of this complex.

The complex $\text{Co}(\text{cy})_2\text{Cl}_2$ was prepared by the method given in ref. 9. The CHN microanalysis was satisfactory. Enthalpies of solution reactions were measured by use of an LKB 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.

REFERENCES

- 1 R. Sabbah, M. Nabavian and M. Laffitte, *C. R. Acad. Sci.*, 284 (1977) 953
- 2 Technical Note 270 3/4 National Bureau of Standards, Washington DC, (1968) 1969
- 3 P. B. Burkinshaw and C. T. Mortimer, *J. Chem. Soc. Dalton Trans.*, (1984) 75
- 4 S. J. Ashcroft, G. Beech and C. T. Mortimer, *J. Chem. Soc. A*, (1967) 929
- 5 C. Airoidi, A. P. Chagas and O. A. De Oliveira, *J. Chem. Thermodyn.*, 15 (1983) 153

- 6 J B Pedley and J Rylance, CATCH Data, Organic and Organometallic Compounds, University of Sussex, 1977
- 7 M P Kularm and V V Dadape, High Temp Sci, 3 (1979) 277
- 8 M Sundaralingan and J A Carrabine, J Mol Biol, 61 (1971) 287
- 9 M Goodgame and K W Johns, Inorg Chim Acta, 46 (1980) 23