Thermochemical studies on copper(II) and nickel(II) complexes of the Schiff base derived from 2-(2-aminophenyl)benzimidazole and salicylaldehyde

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(Received 27 February 1991)

Abstract

Microcalorimetric measurements were made on copper(II) and nickel(II) complexes of the Schiff base (L) derived from 2-(2-aminophenyl)benzimidazole and salicylaldehyde. The complexes were of the general type MX_2L_2 with M = Cu or Ni, and X = Cl, Br, NO_3 or ClO_4. The enthalpies of decomposition of the solid complexes to solid products, MX_2 and L, were derived. Despite showing some variation depending on the anion, the average binding enthalpy of the ligand to nickel was 47.5 ± 7.3 kJ mol^{-1}, greater than that to copper, 16.8 ± 3.5 kJ mol^{-1}, by 30.7 ± 8.1 kJ mol^{-1}

INTRODUCTION

Complexes of metal salts with Schiff bases are well known and have played an important role in developing ideas in coordination chemistry. However, they seem to have largely escaped thermochemical investigation. Copper(II) and nickel(II) complexes with the Schiff base (L) derived from 2-(2-aminophenyl)benzimidazole and salicylaldehyde have been synthesized and characterized [1]. The complexes were of general formula MX_2L_2, with
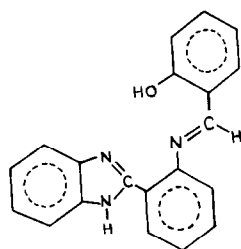
Schiff base L.

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M = Cu or Ni, and X = Cl, Br, NO_3 or ClO_4; they were characterized by elemental analyses, magnetic measurements, ESR, and electronic and IR spectral studies. From the latter it was concluded that the molecule was coordinated as a bidentate ligand to the metal through the phenolic oxygen and the tertiary nitrogen atom of the imidazole ring.

The decomposition of these complexes in an acidic solvent provided a method for deriving the enthalpy of their dissociation reactions according to the equation

$$MX_2L_2(cr) \rightarrow MX_2(cr) + 2L(cr)$$

The enthalpy of this thermochemical reaction was determined by measuring the enthalpy of dissolution of the complex, and separately that of the salt and the ligand so that the solution resulting from the dissolution of the complex was of the same composition as that resulting from the dissolution of the products of dissociation.

To derive the binding enthalpy of the ligand to the metal, the enthalpy of decomposition in the gaseous state is required, but clearly for these complexes, measurement of the enthalpies of sublimation is not feasible. It is, however, often reasonably assumed that the difference between the enthalpies of sublimation of reactants and products is small and constant; hence the enthalpies of decomposition in the solid state will parallel those in the gaseous state [2].

EXPERIMENTAL

The Schiff base was prepared by the condensation of the amine (33 mmol) with salicylaldehyde (33 mmol) in benzene (50 cm^3) by refluxing for several hours in the presence of a small amount of piperidine until the theoretical amount of water was collected in a Dean–Stark trap. The product was filtered, washed with benzene and dried (Found: C, 77.1%; H, 4.6%; N, 13.2%. Expected: C, 76.7%; H, 4.8%; N, 13.4%). The complexes were prepared by adding a solution of the Schiff base (4.8 mmol) in ethanol (30 cm^3) to a hot solution of the metal salt (2.5 mmol) in ethanol (25 cm^3) and refluxing for several hours. On cooling, the precipitated complex was filtered, washed with anhydrous ethanol and dried in vacuo at room temperature. Where possible, the salts used were of analytical grade quality. The calorimetric solvent (S) consisted of dimethylformamide–concentrated hydrochloric acid (36% w/w) in the volume ratio 7 : 3.

As the complexes were available in only small amounts, a microcalorimetric method was used. The Beckman Instruments Inc. Model 190B Microcalorimeter is a twin-differential calorimeter in which the heat produced in the reaction vessels is conducted through two surrounding thermopiles (approx. 10^4 copper–constantan junctions, wired in opposition) to an aluminium heat sink encasing the thermopiles. A detailed description of the
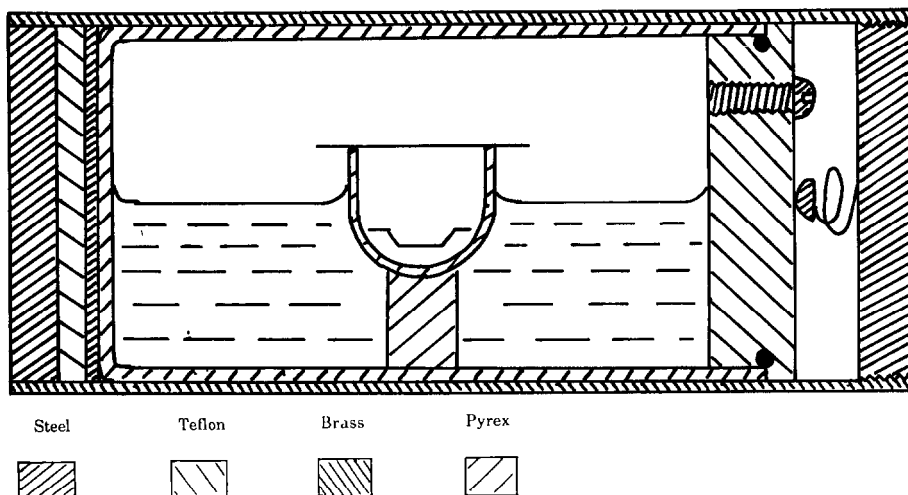
Fig. 1. Microcalorimeter reaction vessel

construction and method of operation has been given [3,4]. The thermopile output after amplification with a Seteram NV724 nanovoltmeter was measured at pre-set time intervals with a Solartron 7065 digital voltmeter and the values were then transferred to a microcomputer for storage and subsequent calculation of the area under the voltage–time curve, which was proportional to the total heat produced. .

The reaction vessel (see Fig. 1) was designed for the reaction of solids with liquids. The solid sample, approx. 3 mg, was weighed in a small platinum crucible which was then placed in the sample holder. The top of the sample holder, which had been ground flat, was covered with a thin microscope slide to protect the solid from the solvent vapour. The solvent was introduced using a hypodermic syringe through a hole in the Teflon stopper; the hole was then closed with a nylon screw. The glass reaction vessel was placed within a thin brass cylinder whose ends were made of Teflon and steel of poor thermal conductivity because the thermopile responds only to heat passing through the cylindrical surface. Reaction, or dissolution, was initiated by axial rotation, when the crucible and its contents fell into the solvent. The reference cell contained solvent with an empty crucible to compensate for the thermal effects of stirring and of absorption onto the glass and Teflon surfaces. The reaction vessel contains a large vapour space but thermal corrections for the change in vapour composition on reaction are small because the resulting solutions are dilute and furthermore will cancel because of the equivalence of the compositions of the solutions resulting from dissolution of the complex and that of its decomposition products. The calorimeter was calibrated electrically by substituting electric heaters in place of the reaction vessels.
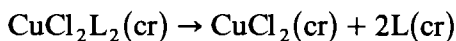
TABLE 1

Molar enthalpies of reaction and solution

	Reactant i	Solvent [a]	Solution	No. of expts	$\Delta_i H$ (kJ mol^{-1})
1	$CuCl_2L_2$	S	F_1	5	55.0 ± 2.3
2	L	S	A_1	3	17.3 ± 0.4
3	$CuCl_2$	A_1	F_1	3	-22.7 ± 0.4
4	$CuBr_2L_2$	S	F_2	4	30.9 ± 2.0
5	$CuBr_2$	A_1	F_2	2	-30.5 ± 1.8
6	H_2O	S	A_2	3	-3.0 ± 0.5
7	$Cu(NO_3)_2L_2$	A_2	F_3	5	10.8 ± 1.5
8	$Cu(NO_3)_2 \cdot 3H_2O$	A_1	F_3	4	-8.9 ± 1.3
9	$NiCl_2L_2$	S	F_4	4	73.1 ± 2.6
10	$NiCl_2$	A_1	F_4	5	-44.7 ± 1.3
11	$NiBr_2L_2$	S	F_5	4	49.3 ± 2.0
12	$NiBr_2$	A_1	F_5	4	-78.2 ± 1.9
13	$Ni(NO_3)_2L_2$	A_2	F_6	3	64.0 ± 0.3
14	$Ni(NO_3)_2 \cdot 6H_2O$	A_1	F_6	4	-26.4 ± 2.0
15	$Ni(ClO_4)_2L_2$	A_2	F_7	4	-14.7 ± 0.7
16	$Ni(ClO_4)_2 \cdot 6H_2O$	A_1	F_7	3	-70.1 ± 0.5

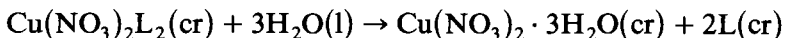[a] S, calorimetric solvent composition (see text)

RESULTS

The individual molar enthalpies of reaction and solution are given in Table 1, where in accord with normal thermochemical practice, the uncertainties given are twice the standard deviation of the mean. The enthalpy of solution of water, when added to the calorimeter solvent, was measured using the solution-reaction calorimeter previously described [5]; the remaining measurements were made by microcalorimetry. The enthalpies of the thermochemical reactions were derived as follows:

$$CuCl_2L_2(cr) \rightarrow CuCl_2(cr) + 2L(cr)$$

$$\Delta_r H_m^{\ominus} = \Delta_1 H - 2\Delta_2 H - \Delta_3 H = 43.1 \pm 2.5 \text{ kJ mol}^{-1}$$

$$CuBr_2L_2(cr) \rightarrow CuBr_2(cr) + 2L(cr)$$

$$\Delta_r H_m^{\ominus} = \Delta_4 H - 2\Delta_2 H - \Delta_5 H = 26.8 \pm 2.8 \text{ kJ mol}^{-1}$$

$$Cu(NO_3)_2L_2(cr) + 3H_2O(l) \rightarrow Cu(NO_3)_2 \cdot 3H_2O(cr) + 2L(cr)$$
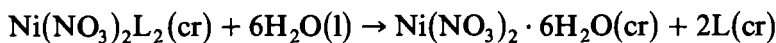
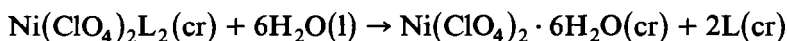$$\Delta_r H_m^{\ominus} = \Delta_7 H + 3\Delta_6 H - 2\Delta_2 H - \Delta_8 H = -23.9 \pm 2.6 \text{ kJ mol}^{-1}$$

$$NiCl_2L_2(cr) \rightarrow NiCl_2(cr) + 2L(cr)$$

$$\Delta_r H_m^{\ominus} = \Delta_9 H - 2\Delta_2 H - \Delta_{10} H = 83.2 \pm 3.0 \text{ kJ mol}^{-1}$$

$$NiBr_2L_2(cr) \rightarrow NiBr_2(cr) + 2L(cr)$$

$$\Delta_r H_m^{\ominus} = \Delta_{11}H - 2\Delta_2 H - \Delta_{12}H = 92.9 \pm 2.9 \text{ kJ mol}^{-1}$$

$$Ni(NO_3)_2L_2(cr) + 6H_2O(l) \rightarrow Ni(NO_3)_2 \cdot 6H_2O(cr) + 2L(cr)$$

$$\Delta_r H_m^{\ominus} = \Delta_{13}H + 6\Delta_6 H - 2\Delta_2 H - \Delta_{14}H = 37.8 \pm 2.2 \text{ kJ mol}^{-1}$$

$$Ni(ClO_4)_2L_2(cr) + 6H_2O(l) \rightarrow Ni(ClO_4)_2 \cdot 6H_2O(cr) + 2L(cr)$$

$$\Delta_r H_m^{\ominus} = \Delta_{15}H + 6\Delta_6 H - 2\Delta_2 H - \Delta_{16}H = 2.8 \pm 3.2 \text{ kJ mol}^{-1}$$

DISCUSSION

To compare the relative binding enthalpies we require the enthalpies of dissociation

$$MX_2L_2(cr) \rightarrow MX_2(cr) + 2L(cr)$$

For $Cu(NO_3)_2L_2$, $Ni(NO_3)_2L_2$ and $Ni(ClO_4)_2L_2$, however, the hydrated salt was produced in the thermochemical reaction. From the Russian Tables of Thermodynamic Properties [6], the following enthalpies of formation of the crystalline salts were used to derive the enthalpies of decomposition listed in Table 2 from the enthalpies of the thermochemical reactions: $Cu(NO_3)_2$, -305.1 ± 1.4; $Cu(NO_3)_2 \cdot 3H_2O$, -1217.1 ± 1.6; $Ni(NO_3)_2$, -418.7 ± 2.7; and $Ni(NO_3)_2 \cdot 6H_2O$, -2215.1 ± 2.8 kJ mol^{-1}. The enthalpy of hydration of $Ni(ClO_4)_2(cr)$ to form $Ni(ClO_4)_2 \cdot 6H_2O(cr)$ was assumed to equal the corresponding value for the nitrate.

Assuming that the difference between the enthalpy of sublimation of the complex and that of the dissociation products is small and constant, the dissociation enthalpies in the solid state will parallel those in the gaseous state [2]. Although the binding enthalpy of the ligand L in MX_2L_2 varies

TABLE 2

Enthalpies of decomposition at 298.15 K: $MX_2L_2(cr) \rightarrow MX_2(cr) + 2L(cr)$

Complex	$\Delta_{dec}H$ (kJ mol^{-1})
$CuCl_2L_2$	43.1 ± 2.5
$CuBr_2L_2$	26.8 ± 2.8
$Cu(NO_3)_2L_2$	30.6 ± 3.3
$NiCl_2L_2$	83.2 ± 3.0
$NiBr_2L_2$	92.9 ± 2.9
$Ni(NO_3)_2L_2$	114.6 ± 3.3
$Ni(ClO_4)_2L_2$	79.6 ± 3.5

somewhat with the change in X, the average binding enthalpy of L to CuX_2 is 16.8 ± 3.5 kJ mol^{-1}, and to NiX_2, 47.5 ± 7.3 kJ mol^{-1}, an increase of 30.7 ± 8.1 kJ mol^{-1}. It has been observed previously that for complexes in which a ligand is bound to the metal through the oxygen and nitrogen atoms, the corresponding differences in binding enthalpies for copper and nickel are, for oxinates, 111 ± 15 kJ mol^{-1} [5], and for glycinates, 75 ± 10 kJ mol^{-1} [7]. In these latter cases the binding enthalpy refers to dissociation in the gaseous state to the ligand radical, whereas for these Schiff base complexes the dissociation is in the solid state to the molecule.

The Schiff base acts as a bidentate ligand through the phenolic oxygen and the azomethine nitrogen in the non-polar form of the ligand, or to the pyridine-like imine nitrogen of the imidazole ring in the zwitterion form. Some recent spectroscopic studies of copper and nickel complexes of the Schiff base (L^1) from 2-aminobenzimidazole and salicylaldehyde [8] have shown that this Schiff base can be in either the non-polar or zwitterion form in $MX_2L_2^1$ complexes, e.g. in this case with $CuCl_2L_2^1$ and $NiBr_2L_2^1$, the ligand was in the non-polar form, whereas in $CuBr_2L_2^1$ and $NiCl_2L_2^1$, the ligand was in the zwitterion form. A change in the form of the ligand is more likely to produce a change in the binding enthalpy than interaction of the ligand with the anion in MX_2. The binding enthalpies of the Schiff base in these complexes are small and any change in the structure of the ligand can be expected to have a marked, and at present, unquantifiable effect. Because the precise form of the ligands in the complexes studied in this paper has not yet been determined, the average binding enthalpies have greater significance than the individual values.

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