Thermochimica Acta, 182 (1991) 21–27
Elsevier Science Publishers B.V., Amsterdam

Thermal properties of nickel(II) and copper(II) complexes with *N*-methyl-substituted salicylideneaminates

Kikuo Miyokawa

Laboratory of Environmental Science, Hitotsubashi University, Kunitachi, Tokyo, 186 (Japan)

Hisanobu Wakita

Department of Chemistry, Faculty of Science, Fukuoka University, Fukuoka, 814-01 (Japan)

(Received 21 September 1990)

Abstract

The thermal properties of the complexes M(*N*-Me-5-X-salam)$_2$, where M = Cu(II) or Ni(II), X = OCH_3, CH_3, H, Cl, or Br, and salam = salicylideneaminate anion, have been studied by DSC and heat-of-reaction measurements. Polymorphic transitions accompanied by the association reactions of the complex molecules are observed in Ni(*N*-Me-salam)$_2$, Ni(*N*-Me-5-Cl-salam)$_2$ and Cu(*N*-Me-salam)$_2$. The heats of transition, ΔH_{tr}, of these complexes determined from DSC peak measurements are -4.8 kJ mol^{-1}, 4.6 kJ mol^{-1} and 2.2 kJ mol^{-1} respectively. The ΔH_{tr} values calculated from the heats of reaction of these complexes with 6 mol dm^{-3} HCl agree well with those obtained from the DSC measurements. The effect of the ring substituent X on the solid state association reaction is discussed.

INTRODUCTION

Nickel(II) complexes with Schiff-base ligands composed of salicylaldehydes and aryl or alkyl amines are known to have various types of coordination geometry, including tetrahedral, square planar, binuclear square pyramidal and oligomeric octahedral forms [1]. Special interest has been focused on the isolation of a pair of modifications with different molecular structures in order to understand the relation between the nature of the ligand and the molecular structure of these complexes [2–5]. Since, in some cases, one modification can only be prepared from the other modification on heating, it seems of interest to study their thermoanalytical properties [6–8]. This paper describes the thermal properties of the nickel(II) and copper(II) complexes with *N*-methyl-substituted salicyclideneaminates; the influence of various ring substituents on the thermal properties is discussed on the basis of DSC and the heat-of-reaction data.

0040-6031/91/$03.50

EXPERIMENTAL

The complexes M(*N*-Me-5-X-salam)$_2$ where M = Cu(II) and Ni(II), X = OCH_3, CH_3, H, Cl and Br, and salam = salicyclideneaminate anion (Fig. 1), were prepared by the published procedure [5]. Monomeric modifications of nickel(II) and copper(II) complexes were isolated from the solution. Oligomeric modifications of Ni(*N*-Me-salam)$_2$ and Ni(*N*-Me-5-Cl-salam)$_2$ were prepared from the respective monomeric modifications on heating at an appropriate temperature. The dimeric modification of Cu(*N*-Me-salam)$_2$ was prepared by the recrystallization of the monomeric modification from ether solution. Differential scanning calorimetry (DSC) curves were recorded on a Rigaku Denki thermal analyser 8002 at a heating rate of 10 K min^{-1} in an atmosphere of flowing nitrogen, α-Al_2O_3 being used as a reference material. The heat of transition was determined from DSC peak-area measurements. The instrument was calibrated against the heat of transition of potassium nitrate, giving a linear correlation between the peak area S (cm^2) and the heat of transition ΔH (J): $S = (3.76 \pm 0.01)\ \Delta H + (0.00 \pm 0.04)$ under the present experimental conditions. The heat of reaction of each complex (0.02 mol) with 6 mol dm^{-3} HCl (200 ml) at 293 K was determined by the standard method [9]. Thermomagnetic analysis was employed to measure the change in the magnetic properties of the nickel(II) complexes on heating [8].

RESULTS AND DISCUSSION

Thermoanalytical data, heats of transition and the corresponding DSC peak temperatures are given in Table 1, and the DSC curves of the complexes of interest are reproduced in Figs. 2 and 3. The nickel(II) complexes with X = OMe and Me gave a single DSC peak corresponding to melting at around 530 K. As shown in Fig. 2, the monomeric modifications of Ni(*N*-Me-5-Cl-salam)$_2$ and Ni(*N*-Me-5-Br-salam)$_2$ have two separated endothermic peaks: the peaks observed at the lower temperatures correspond to a phase transition and those at higher temperatures correspond to melting accompanied by partial decomposition of the complex. The DSC curve of the monomeric modification of Ni(*N*-Me-salam)$_2$ is somewhat

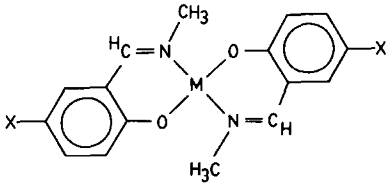

Fig. 1. Molecular structure of M(*N*-Me-5-X-salam)$_2$.

TABLE 1

Characterisation, and thermoanalytical and heat of reaction data of the complexes

M	X	M (%)		Colour	μ_{eff} [a] (BM)	ΔH_{tr} (T_{max}) [b] (kJ mol^{-1}) (K)	ΔH_{sol} [c] (kJ mol^{-1})
		Found	(Calc.)				
Ni	CH_3	16.39	(16.54)	Green	dia		
	OCH_3	15.17	(15.17)	Green	dia		
	H	17.76	(17.96)	Green	dia	-4.8 ± 0.1 (480)	-124.6
		17.82	(17.96)	Buff	3.37		-121.3
	Cl	14.96	(14.83)	Green	dia	4.6 ± 0.1 (493)	-106.9
		14.87	(14.83)	Green	3.27		-111.9
	Br	12.15	(12.11)	Green	dia	2.3 ± 0.0 (503)	
Cu	CH_3	17.53	(17.67)	Brown	1.83		
	OCH_3	15.97	(16.22)	Green	1.87		
	H	19.16	(19.16)	Green	1.79		-64.7
		19.06	(19.16)	Brown	1.92	2.2 ± 0.0 (375)	-62.0
	Cl	15.71	(15.86)	Green	1.92	2.3 ± 0.0 (393)	
	Br	12.90	(12.98)	Green	1.86	1.7 ± 0.0 (489)	

[a] Determined at room temperature; BM, Bohr magneton.

[b] Heat of transition; DSC peak temperature is given in parentheses.

[c] Heat of reaction with 6 mol dm^{-3} HCl at 293 K.

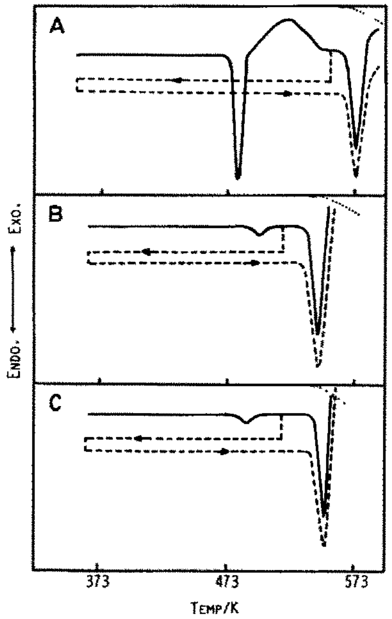

Fig. 2. TG (- - - - - -) and DSC (———) curves of (A) Ni(*N*-Me-salam)$_2$, (B) Ni(*N*-Me-5-Br-salam)$_2$, and (C) Ni(*N*-Me-5-Cl-salam)$_2$.

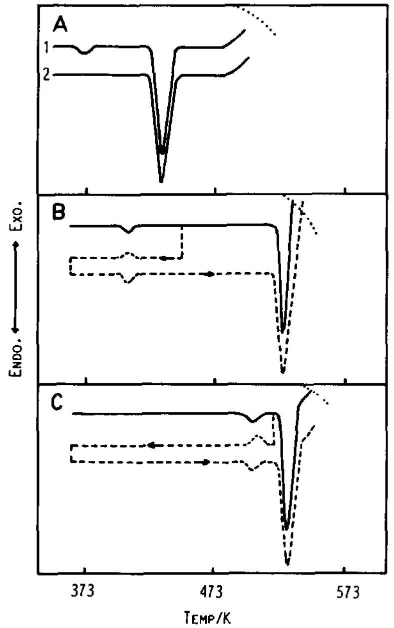

Fig. 3. TG (- - - - - -) and DSC (———) curves of (A) brown modification of Cu(*N*-Me-salam)$_2$ (curve 1) and dimeric modification of Cu(*N*-Me-salam)$_2$ (curve 2) (B) Cu(*N*-Me-5-Br-salam)$_2$, and (C) Cu(*N*-Me-5-Cl-salam)$_2$.

complicated: it shows an endothermic peak at around 480 K, followed by a broad exothermic peak at 510 K and another endothermic peak at 575 K. Thermomagnetic analysis of monomeric Ni(*N*-Me-salam)$_2$ and Ni(*N*-Me-5-Cl-salam)$_2$ indicated that the endothermic reactions taking place at the lower temperatures are associated with a change in their magnetic properties, from diamagnetic to paramagnetic, arising from the oligomerization reaction of these complex molecules [2]. Thus the DSC curve of Ni(*N*-Me-salam)$_2$ can be interpreted as the oligomerization taking place together with the melting of the complex at 480 K; the resulting oligomer solidifies at 510 K and the oligomeric modification then melts at 575 K. The heats of transition, ΔH_{tr}, of Ni(*N*-Me-salam)$_2$ and Ni(*N*-Me-5-Cl-salam)$_2$ are -4.8 kJ mol^{-1} and 4.6 kJ mol^{-1} respectively. Although the oligomeric modification of Ni(*N*-Me-5-Br-salam)$_2$ has been reported to be produced from the monomeric form on heating [4], no DSC peak was observed prior to melting that could be assigned to the phase transition together with oligomerization of the complex molecules. As partial paramagnetism was observed in the melt of the complex, the oligomerization is considered to be coincident with the melting of the complex. The DSC peak observed at 503 K is merely due to a change in the crystal structure. The present results appear to imply that the monomeric nickel salicyclideaminates tend to associate at high temperatures in the solid or molten state; however, it has been reported that the oligomeric modification of Ni(*N*-phenyl-salam)$_2$ undergoes an exothermic transformation into the monomeric modification at 438 K [8].

Some copper(II) salicylideneaminates undergo the dimerization reaction in both the solution [10] and solid state [11,12]; thus it seems of interest to compare the thermal properties of copper(II) complexes with those of the nickel(II) complexes. Interestingly, the thermal behaviour of the copper(II) complexes resembles that of the nickel(II) complexes. The copper(II) complexes with X = OMe and Me gave no DSC peak corresponding to a phase transition, and merely melt at around 490 K. The remaining copper(II) complexes give two DSC peaks, as shown in Fig. 3. The peaks observed at the lower temperatures correspond to the phase transition and those at the higher temperatures to the melting. The green modification of Cu(*N*-Me-salam)$_2$ melts at 433 K whereas its brown modification undergoes an endothermic phase transition at 375 K and then melts at 433 K. As the brown and green modifications are composed of monomeric square-planar [13] and dimeric square-pyramidal molecules [14] respectively, the DSC peak at 375 K is ascribed to the polymorphic transition accompanied by the dimerization reaction of the complex molecules. The heat of transition of this complex was found to be 2.2 kJ mol^{-1}. A similar phase transition has been observed from the brown (monomer) to the green modification (dimer) of Cu(*N*-cyclohexyl-salam)$_2$ [11] and its ΔH_{tr} value has been reported to be 13.3 ± 0.3 kJ mol^{-1} [12]. In the DSC curves of Cu(*N*-Me-5-Cl-salam)$_2$ and Cu(*N*-Me-5-Br-salam)$_2$, endothermic peaks due to phase transitions are observed at 393 K and 489 K respectively. These transitions are reversible and may not be accompanied by the association of the complex molecules, because all such transitions have been found to be irreversible processes (Fig. 1). The isolation of the other modifications and their crystal structural data are required to obtain a definite conclusion.

The heat of reaction ΔH_r of these complexes with hydrochloric acid (6 mol dm^{-3}) was measured to check the heat of transition determined by the DSC method. Although the solution species were not identified, it is not unreasonable to assume that the final state of the solution is identical in both modifications; then the difference between the heats of reaction of the two modifications represents the heat of the transition. The heats of transition calculated from the ΔH_r values given in Table 1 are as follows: -3.3 kJ mol^{-1} for Ni(*N*-Me-salam)$_2$; 5.0 kJ mol^{-1} for Ni(*N*-Me-5-Cl-salam)$_2$; and 2.7 kJ mol^{-1} for Cu(*N*-Me-salam)$_2$. These values agree well with those determined by DSC peak-area measurements. Sacconi et al. [3] have reported the heat of transition of Ni(*N*-Me-salam)$_2$ as -3.4 kJ mol^{-1} which is in good agreement with the present value.

Association reactions of complex molecules with concomitant formation of new bonds are generally exothermic processes. Yokoi and Chikira have reported the enthalpy of dimerization of Cu(*N*-R-salam)$_2$ (R = Pr, Bu) in methylcyclohexane to be about -13 kJ mol^{-1} [10]. Nevertheless, all the polymorphic transitions characterized by exothermic association reactions are observed as endothermic processes, except for Ni(*N*-Me-salam)$_2$. This may be attributed to the relatively large difference in crystal packing energy between the two modifications, which predominates over the exothermicity of the association reaction. While the equilibrium study of Ni(*N*-Me-salam)$_2$ has indicated that the oligomeric form is favoured at low temperatures in solution [15], the oligomerization reaction occurs at high temperatures in the solid state. This must be explained in terms of the crystal packing effect.

Crystal structural analyses of Cu(*N*-Me-salam)$_2$ [4] and Cu(*N*-cyclohexyl-salam)$_2$ [11] have demonstrated that the association of the complexes occurs through the coordination of the phenolato oxygen atom in the complex molecule to the metal ion of an adjacent complex molecule. Therefore both the Lewis basicity of the phenolato oxygen and the Lewis acidity of the metal ion are important factors for the occurrence of the present association reaction. The introduction of an electron-releasing group such as OMe or Me on the aryl ring, is expected to decrease the Lewis acidity of the nickel(II) ion and the increase the Lewis basicity of the phenolato oxygen atom. The thermoanalytical study of the pyridine adducts of Ni(*N*-Me-5-X-salam)$_2$ has indicated that the Lewis acidity of the nickel(II) ion decreases when X = OMe and Me [16]. The fact that association reactions in complexes with X = OMe and Me do not occur, suggests that a low Lewis acidity of the metal ion may be disadvantageous for the occurrence of association reactions; that is, as far as the electronic effect is concerned, electron-withdrawing substituents are favourable for association reactions in the solid state. Although 5th-position substituents on the aryl ring seem to cause hardly any intramolecular and intermolecular steric hindrance for the association reaction, a paucity of crystal structural data makes it difficult to assess the steric effect of the substituents on the solid-state association reaction.

ACKNOWLEDGEMENT

Our thanks are expressed to Messrs. M. Naito and K. Takakura for their assistance with the experiments.

REFERENCES

1 R.H. Holm, G.W. Everett and A. Chakarvorty, Progr. Inorg. Chem., 7 (1966) 83.
E.K. Barefield and D.H. Busch, Quart. Rev., 22 (1968) 456.
2 C.M. Harris, S.L. Lenzer and R.L. Martin, Aust. J. Chem., 11 (1958) 331.
3 L. Sacconi, P. Paoletti and R. Cini, J. Am. Chem. Soc., 80 (1958) 3583.
4 H.C. Clark and R.J. O'Brien, Can. J. Chem., 37 (1959) 436.
5 A. Takeuchi and S. Yamada, Rev. Roum. Chim., 22 (1977) 781.
6 N. Arai, N. Sorai and S. Seki, Bull. Chem. Soc. Jpn., 45 (1972) 2398.
7 A. Takeuchi and S. Yamada, Inorg. Chim. Acta, 8 (1974) 225.

8 K. Miyokawa, H. Hirashima and I. Masuda, Bull. Chem. Soc., Jpn., 54 (1981) 3361.
9 J. Sameshima, Butsurikagaku Jikkenho, Shokabou, Tokyo, 1970, pp. 225–230.
10 H. Yokoi and M. Chikira, J. Chem. Soc., Dalton Trans., (1975) 2101.
11 H. Tamura, K. Ogawa, A. Takeuchi and S. Yamada, Bull. Chem. Soc. Jpn., 52 (1979) 3522.
12 K. Miyokawa and I. Masuda, J. Phys. Chem. Solids, 47 (1986) 139.
13 E.C. Lingerfelter, G.L. Simmons, B. Morosin, C. Scheringer and C. Freiberg, Acta Crystallogr., 14 (1961) 1222.
14 D. Hall, S.V. Scheat and T.N. Waters, J. Chem. Soc. A, (1968) 1460.
15 H.C. Clark and A.L. Odell, J. Chem. Soc., (1955) 3431.
16 H. Masuda, T. Kawarada, K. Miyokawa and I. Masuda, Thermochim. Acta, 63 (1983) 307.