Thermochimica Acta, 144 (1989) 369–371
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

THERMAL STABILITY OF SOME NOVEL MIXED-LIGAND COMPLEXES OF COPPER(II)

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(Received 29 September 1988)

INTRODUCTION

Thermal studies have not kept pace with synthetic progress in the case of mixed-ligand complexes of copper(II) containing a dibasic tridentate Schiff base as the primary ligand, and a neutral monodentate donor as the secondary ligand [1–4]. In the present study the effect of diverse monodentate ligands on the thermal stability of one such series of complexes, [Cu(Nap:gly)B], where H_2Nap:gly is *N*-(2-hydroxy-1-naphthylidene)glycine [5], and B is ammonia, a heterocyclic base or an amine, was examined. The complexes were also characterized using the appropriate physico-chemical methods.

EXPERIMENTAL

Preparation of [Cu(Nap:gly)(NH_3)]

Copper(II) sulphate pentahydrate (1.24 g, 0.005 mol) dissolved in water (20 ml) was added to a stirred solution of potassium *N*-(2-hydroxyl-1-naphthylidene)glycinate (1.34 g, 0.005 mol) in liquor ammonia (50 ml). After stirring for 2 h the precipitated complex was filtered, washed three times with 10-ml portions of water, once with ethanol, and dried under vacuum.

Preparation of other [Cu(Nap:gly)B] complexes

All the other mixed-ligand complexes containing heterocyclic base (pyridine, α-, β- or γ-picoline), or amine (ethylamine, diethylamine or triethylamine) were prepared similarly using the respective base (30 ml in case of heterocyclic base, and 75 ml of 25% aqueous solution in the case of amine) in place of liquor ammonia. Crystallization occurred either on concentration

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under reduced pressure or on adding water (20 ml). The crystals were washed successively with alcohol and petroleum spirit and dried under vacuum.

Analysis and measurements

TG curves were recorded on a Stanton Recording Thermobalance (Model TR-1): heating rate (static air) 4 K min^{-1}; chart speed 6 in. h^{-1}. The thermoanalytical curves were redrawn as mass versus temperature. The spectra were recorded on a Pye Unicam SP3-300 IR spectrophotometer and a Pye Unicam SP 1800 UV–visible spectrophotometer.

RESULTS AND DISCUSSION

The stoichiometry complexes were formulated on the basis of their C, H and N elemental analytical data and their non-electrolytic nature in DMF and DMSO. The observed magnetic moments (1.8–1.9 B.M.) and the visible-spectrum bands of the complexes are compatible with a square-planar geometry [6]. The IR spectral data of the complexes are in good agreement with the reported [5] bonding mode of the tridentate ligand moiety through its quinone oxygen, deprotonated amino nitrogen and a carboxylate oxygen. Bands due to the monodentate ligand showed a characteristic shift on coordination.

Thermogravimetric studies

Weak intermolecular hydrogen-bond interaction can be envisaged in the ammine complex. Such an interaction will be obstructed in the amine complexes by the blocking alkyl group(s). In agreement, expulsion of ammonia from [Cu(Nap:gly)(NH_3)] commences at a higher temperature (235 °C) than that of the amine from their complexes. Loss of $C_2H_5NH_2$, $(C_2H_5)_2NH$ and $(C_2H_5)_3N$ occurs at 215 °C, 225 °C and 195 °C, respectively. These results indicate that the metal–amine bond strength varies in the order tertiary amine < primary amine < secondary amine. On the basis of the electron-releasing character of the alkyl group, the order of basicity expected for the amines is $(C_2H_5)_3N > (C_2H_5)_2NH > C_2H_5NH_2$. However, the bond angles of the amines become compressed in the amine complexes. Since the resulting strain increases with increasing substitution of the amine, the tendency to release strain by dissociation from the complex should be in the order $C_2H_5NH_2 < (C_2H_5)_2NH < (C_2H_5)_3N$. Hence, the observed order of thermal stability of the amine complexes appears as a compromise between basic strength and strain.

TABLE 1

Analytical data and other details of mixed-ligand complexes [Cu(Nap:gly)B]: the calculated values are given in parentheses

B	Yield (%)	Analytical data (%)			μ (B.M.)	Decomposition temperature (°C)	Weight loss due to removal of B (%)
		C	H	N			
Ammonia	80	51.20 (50.71)	4.14 (3.93)	8.79 (9.10)	1.83	235	4.91 (5.53)
Ethylamine	70	54.01 (53.62)	4.51 (4.81)	7.89 (8.34)	1.88	215	12.88 (13.42)
Diethylamine	78	55.18 (56.09)	5.69 (5.54)	7.14 (7.70)	1.84	225	19.73 (20.10)
Triethylamine	60	57.69 (58.20)	5.89 (6.18)	6.85 (7.15)	1.88	195	24.29 (25.81)
Pyridine	79	58.00 (58.43)	3.51 (3.81)	7.03 (7.57)	1.99	215	20.18 (21.38)
α-Picoline	62	58.90 (59.42)	3.97 (4.20)	6.98 (7.30)	1.82	200	23.12 (24.25)
β-Picoline	64	58.71 (59.42)	3.90 (4.20)	6.91 (7.30)	1.83	225	23.29 (24.25)
γ-Picoline	68	58.69 (59.42)	3.92 (4.20)	6.88 (7.30)	1.92	230	23.55 (24.25)

These factors were further examined by studies of the thermal decomposition of complexes containing pyridine and picolines. Pyridine is removed from the complexes at 215 °C, whereas α-picoline is removed at a lower temperature (200 °C). Removal of β-, and γ-picoline commences at 225 °C and 230 °C, respectively. Since α-picoline is as basic as γ-picoline, the observed lower thermal stability of the α-picoline complex is fully attributable to the steric factor. In this context, it may be noted that attempts to prepare the analogous quinoline complex were unsuccessful.

In all cases further weight loss occurred continuously, owing to the decomposition of the *N*-(2-hydroxy-1-naphthylidene)glycinato moiety, and the final product obtained was CuO, as ascertained by X-ray diffraction studies. Thermogravimetric studies also supported the formulation of the complexes, because the expected and found weight loss for the removal of the monodentate ligand agreed in all cases (Table 1).

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