ELSEVIER

Thermochimica Acta 336 (1999) 61–64

thermochimica acta

www.elsevier.com/locate/tca

Thermal analysis of some cobalt(II) azido complexes of the type $CoL_4(N_3)_2$ for L = pyridine derivative ligands

Mohamed A.S. Goher

Department of Chemistry, Faculty of Science, Kuwait University, P.0. Box 5969, 13060 Safat, Kuwait

Received 3 February 1999; accepted 21 June 1999

Abstract

The thermal dissociation of three cobalt(II) azido complexes of the type $CoL_4(N_3)_2$ where L = 4-benzoyl-, 4-ethyl-, and 3-hydroxypyridine, have been studied by thermogravimetry (TGA and DTA) and IR spectroscopy. The three complexes form an intermediate 1 : 2 complex which explodes in the case of the 4-benzoylpyridine complex. Hydrogen bonding plays a significant role in the stability and decomposition of the 1 : 4 and 1 : 2 complexes in the case of 3-hydroxypyridine ligand.

Keywords: Cobalt(II) azido complexes; Pyridine derivatives; TGA

1. Introduction

The azide ion, N_3^- is a versatile ligand which can bind metal ions in a variable manner giving rise to terminal, end-on bridging and end-to-end bridging modes described elsewhere [1–7]. This versatility of the azide ligand not only enriches the stereochemistry of the transition metal ions but also their spectroscopic and magnetic properties [8–13]. Although much work on metal azido complexes has been undertaken [1–13], their thermal properties have received little attention. This may be due to the explosive nature of metal azides and their extreme sensitivity to shock. Although, shock resistance and thermal stability became apparent for azido complexes that contain large counter ions or a central metal whose oxidation state is stabilized by certain ligands, our trials for studying the thermal decomposition of some copper(II) azido complexes with pyridine ligands not only failed but also damaged the apparatus itself even when we used amounts less than 2 mg. Now we succeeded to follow the thermal behaviour of three cobalt(II) azido complexes of some pyridine derivative ligands by thermogravimetry and IR spectroscopy. The result of this study is the subject of the present paper.

2. Experimental

The complexes were prepared by mixing an aqueous solution (2 mmol) of cobalt(II) nitrate hexahydrate with an ethanolic solution of the pyridine ligand (5 mmol) followed by addition of an aqueous solution of sodium azide (5 mmol). The final mixture was filtered (if needed) and allowed to stand in an open beaker over several days to produce crystalline complexes.

The IR spectra were recorded in KBr pellets on a Brucker IFS-25 model FT-IR spectrophotometer. Electronic spectra of solid complexes mulled in Nujol

PII: S0040-6031(99)00176-8

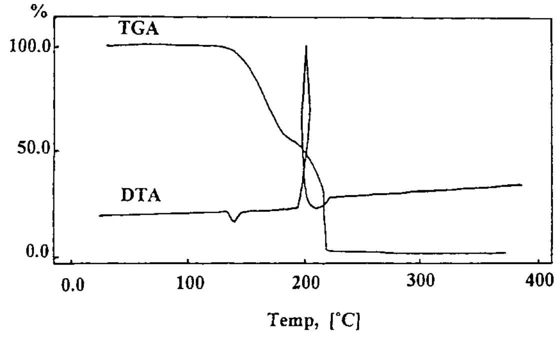


Fig. 1. Thermal analysis of $[\mathrm{Co(4\text{-}Bzpy)_4(N_3)_2}]$.

were measured over the range 200–800 nm using a Pye-Unicam SP 8000 spectrophotometer. Thermal decompositions were carried out using a DTA-50 Shimadzu differential analyzer and TGA-50 Shimadzu thermogravimetric analyzer in aluminum pan. The experimental conditions for the DTA runs were as follows: heating rate: $10^\circ\mathrm{C\ min^{-1}}$, purge gas: dry nitrogen ($30.0\ \mathrm{ml\ min^{-1}}$), sample weights: ca. 1.5 mg. The instruments were calibrated with standards in the conventional way. The experimental procedures and instruments used for other measurements are as described previously [10–12].

3. Results and discussion

Crystal structure determination showed that the complex $[\mathrm{Co(4\text{-}benzoylpyridine)_4(N_3)_2}]$, (1) contained discrete *trans* six-coordinated Co(II) polyhedra with terminal azido ligands [14]. The IR spectra of the complexes revealed the existence of terminal asymmetric azides. In the case of $[\mathrm{Co(3\text{-}hydroxypyridine)_4(N_3)_2}]$ complex, the existence of hydrogen bonds of the types O—H–O between two hydroxy groups and O—H–N between a hydroxy group and uncoordinated nitrogen of an azide group is indicated by the appearance of several medium to strong broad bands at 3390, 3160 and 2560 $\mathrm{cm^{-1}}$ in its IR spectrum. The electronic spectra of the solid complexes are typical of *trans* six-coordinate cobalt(II) complexes, suggesting that the three complexes have the same structure. The far IR spectra exhibit a single band for each of ν $\mathrm{Co\text{–}N_3}$ and ν Co–N(L) modes in the ranges 300–280 and 280–210 $\mathrm{cm^{-1}}$, respectively, supporting the *trans* octahedral geometry for all of the three complexes.

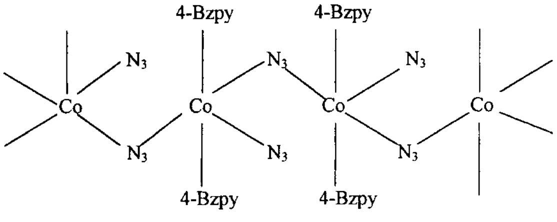
The three complexes are of good purity as indicated by their elemental analyzes confirming the formulation of them as $\mathrm{CoL_4(N_3)_2}$.

3.1. $[\mathrm{Co(4\text{-}benzoylpyridine)_4(N_3)_2}]$ (1)

Fig. 1 shows the TGA and DTA curves for thermal decomposition of complex (1). The complex is stable till ca. 120°C at which it starts decomposition and continued to ca. 120°C with an experimental loss of weight of 42.3%. This amount corresponds to a loss of two 4-Bzpy molecules (calcd.: 42%). This step appears in the DTA curve as a small endotherm with $T_{\max} = 137.6^\circ\mathrm{C}$ and $\Delta H = -57.0$ kJ/mol, and may be represented by the following equation:

$$n[\mathrm{Co(4\text{-}Bzpy)_4(N_3)_2}] \xrightarrow{120\text{–}180^\circ\mathrm{C}} [\mathrm{Co(4\text{-}Bzpy)_2(N_3)_2}]_n + 2n\,\text{4-Bzpy}$$

The IR spectrum of the new complex suggests that one of the two azido groups acts as a bridge as indicated by the appearance of a new ν_{as} $(\mathrm{N_3})$ band at 2068 $\mathrm{cm^{-1}}$ in addition to the original band at 2044 $\mathrm{cm^{-1}}$ assigned for terminal azides in the 1 : 4 complex. This complex may have the following polymeric structure (I), in which the cobalt atoms attain five-coordination geometry. The 1 : 2 complex is not sufficiently stable at that temperature and starts a gradual decomposition until ca. 215°C at which it decomposes almost completely. The observed loss of weight in this step is 55.4%. The weight of the residue of 2.4% at ca. 240°C, which decreases to 1.4% at 380°C, is very small when compared with that (6.7%) if the residue is cobalt metal. The IR spectra in the



(I)

range 250–300°C shows no vibrations due to azide, only weak to very weak bands due to the organic ligand. This result suggests that an explosion of the 1 : 2 complex, rather than decomposition takes place just above 200°C, and appears in the DTA curve as an exotherm with $T_{max} = 206°C$ and $\Delta H = 275.1$ kJ/mol.

3.2. [Co(4-ethylpyridine)$_4$(N$_3$)$_2$] (2)

The TGA and DTA curves for complex (2) are presented in Fig. 2. This complex starts decomposition at ca. 50°C and the first step continued till ca. 180°C, with a loss of weight of 37.6% which corresponds to a loss of two 4-Ethpy molecules (calcd.: 37.5%). This step is similar to that in case of the former complex of 4-Bzpy, leading to the formation of an intermediate 1 : 2 complex.

$$n[\mathrm{Co(4\text{-}Etpy)_4(N_3)_2}] \xrightarrow{50\text{–}180°\mathrm{C}} [\mathrm{Co(4\text{-}Etpy)_2(N_3)_2}]_n + 2n\,\text{4-Etpy}$$

This 1 : 2 complex is polymeric and contains bridging azides as indicated by the appearance of the $\nu_{as}(N_3)$ bands at 2074, 2053 and 2043 cm^{-1} instead of the single band at 2041 cm^{-1} for the 1 : 4 complex. This polymeric complex is not stable and decomposed immediately with a loss of weight of 44.3%. This value corresponds to a loss of two 4-Etpy molecules and an azide group (calcd.: 44.8%). This step appears in the DTA as an exotherm with $T_{max} = 199.3°C$ and $\Delta H = 108.5$ kJ/mol. We may assume that cobalt(II) is reduced to cobalt(I) with the formation of polymeric [Co(N$_3$)]$_n$. The IR spectrum of this polymeric compound at 200°C shows the azide bands at 2104, 2073 and 2056 cm^{-1}. At 250°C, the IR spectrum indicates that there is no azide at all.

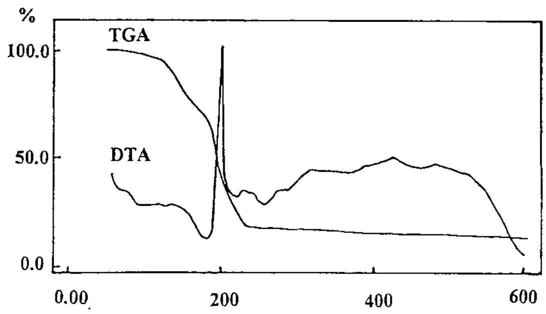


Fig. 2. Thermal analysis of [Co(4-Etpy)$_4$(N3)$_2$].

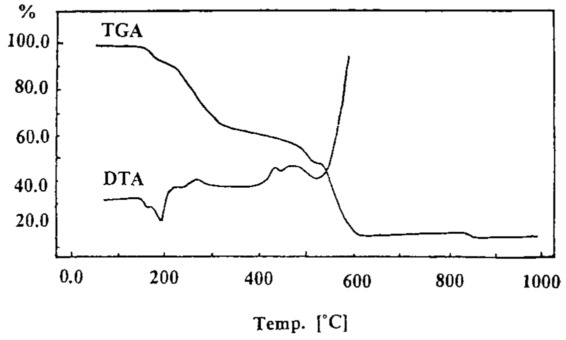


Fig. 3. Thermal analysis of [Co(3-hydpy)$_4$(N$_3$)$_2$].

3.3. [Co(3-hydroxypyridine)$_4$(N$_3$)$_2$] (3)

The TGA and DTA curves for complex (3) are represented in Fig. 3. This complex starts decomposition in the 120–160°C range with a loss of weight of 6.9% which corresponds to a loss of two OH groups (calcd.: 6.4%). This step appears in the DTA curve as two overlapped endotherms with $T_{max} = 152.6°C$ and $\Delta H = -192.0$ kJ/mol. The loss of the OH groups is confirmed by the change in the IR bands in the 3200–2600 cm^{-1} range. This step is followed by a gradual decomposition until ca. 270°C, with a loss of weight of 29.6% which corresponds to the loss of two py moieties with the formation of the 1 : 2 intermediate complex. This complex is stable until 420°C, at which it starts decomposition until ca. 520°C with a loss of weight of 16% which corresponds to a loss of the two azides as confirmed by the IR spectroscopy. The residue decomposed immediately in the 520–580°C range with a loss of weight of 31.6% and a final residue of CoO (exp. = 15.6%, calcd.: = 14.3%).

The decomposition of this complex may be summarized by the following equations:

$$n[\mathrm{Co(py\text{-}OH)_4(N_3)_2}] \xrightarrow{120\text{–}160°\mathrm{C}} n[\mathrm{Co(py\text{-}OH)_2(py)_2(N_3)_2}]_n + 2n\,\mathrm{OH}$$

$$n[\mathrm{Co(py\text{-}OH)_2(py)_2(N_3)_2}] \xrightarrow{120\text{–}270°\mathrm{C}} [\mathrm{Co(py\text{-}OH)_2(N_3)_2}]_n + 2n\,\mathrm{py}$$

$$[\mathrm{Co(py\text{-}OH)_2(N_3)_2}]_n \overset{420–520^\circ\mathrm{C}}{\rightarrow} [\mathrm{Co(py\text{-}OH)_2}]_n + 2n\,\mathrm{N_3}$$

$$[\mathrm{Co(py\text{-}OH)_2}]_n \overset{520–580^\circ\mathrm{C}}{\rightarrow} 2n\,\mathrm{py} + n\,\mathrm{H_2O} + n\,\mathrm{CoO}$$

It is clear that complex (3) thermally decomposed in a manner which is different from those of complexes (1) and (2), although all of them form the intermediate 1 : 2 complex. This difference is due to the existence of hydrogen bonds in complex (3), which plays a significant role in the stability and decomposition behaviour not only of the 1 : 4 but also the intermediate 1 : 2 complex.

The thermal behaviour of the three cobalt(II) azide complexes differ from that of $[\mathrm{Mn(N_3)_2(pyrazole)_4}]$ complex having also *trans*-arrangement six-coordinate manganese(II), terminal azides and hydrogen bonds [15]. The manganese(II) complex loses two pyz molecules and N_3 group, then the third pyz molecule followed by decomposition of the fourth pyz molecule and finally an explosion of the residue.

4. Conclusions

The thermal behaviour of three cobalt(II) azido complexes of the same type $\mathrm{CoL_4(N_3)_2}$ has been studied. The results of this study show that the thermal behaviour of the three complexes is different from one to another although all of them form the 1 : 2 intermediate complex, depending on the nature of the ligand and in turn on the metal–N(N_3) bonds. The existence of hydrogen bonds consolidating the structure of the complex plays an important role in the stabilization and decomposition of the complex and the intermediate. Explosion is not a property associated with all metal–azido complexes but depends on several factors including the nature of the metal ion, its oxidation state and the nature of the complex as a whole. Nevertheless, accumulated data are required before concluding such factors.

Acknowledgements

The financial support from the Kuwait University Research Administration Project SC077 and the Department of Chemistry, General Facility Projects (Analab) are gratefully acknowledged.

References

[1] Z. Dori, R. Ziolo, Chem. Rev. 73 (1973) 247.
[2] M.A.S. Goher, R.-J. Wang, T.C.W. Mak, Polyhedron 11 (1992) 2137.
[3] M.A.S. Goher, T.C.W. Mak, Inorg. Chim. Acta 85 (1984) 117.
[4] M.A.S. Goher, T.C.W. Mak, Inorg. Chim. Acta 89 (1984) 119.
[5] M.A.S. Goher, T.C.W. Mak, Inorg. Chim. Acta 99 (1985) 223.
[6] A. Escuer, R. Vicente, J. Ribas, M.S. El-Fallah, X. Solans, M. Font-Bardia, Inorg. Chem. (1993) 3727.
[7] R. Cortes, L. Lezama, J.L. Pizarro, X. Solans, M.I. Arriortua, T. Rajo, Angew. Chem. Jnt. Ed. Engl. 33 (1994) 2488.
[8] F.A. Mautner, M.A.S. Goher, Polyhedron 11 (1992) 2537.
[9] M.A.M. AbuYoussef, K. Gatterer, H.P. Fritzer, M.A.S. Goher, Spectrochim. Acta 48A (1993) 1633.
[10] M.A.S. Goher, F.A. Mautner, N.A. Al-Salem, Polyhedron 16 (1997) 2239.
[11] M.A.S. Goher, A. Escuer, M.A.M. Abu-Youssef, F.A. Mautner, Polyhedron 17 (1998) 4265.
[12] M.A.S. Goher, F.A. Mautner, Polyhedron 17 (1998) 1516.
[13] A. Escuer, R. Vicente, M.A.S. Goher, F.A. Mautner, Inorg. Chem. 36 (1997) 3440.
[14] M.A.S. Goher, F.A. Mautner, to be published.
[15] M.A.S. Goher, F.A. Mautner, M.A.M. Abu-Youssef, Transition Met. Chem., in press.