ELSEVIER

Thermochimica Acta 260 (1995) 235–241

thermochimica
acta

Thermal decomposition and stability in a series of tetrafluorborate copper(I) complexes

V.A. de Lucca Neto, A.E. Mauro *, V. Sargentelli, M. Ionashiro

Instituto de Química de Araraquara-UNESP, Araraquara, São Paulo, C.P. 355, CEP. 14800-900 Brazil

Received 22 June 1994; accepted 2 January 1995

Abstract

Tetrafluorborate copper(I) complexes containing acetonitrile, triphenylphosphine, 1,10-phenanthroline, 2,2′-bipyridine and 2-quinolinethiol have been prepared in order to study their thermal stabilities as a function of the ligands present. The characterization of the above compounds was carried out by elemental analysis and IR spectroscopy. Their thermal behaviour has been investigated and the final products were identified by X-ray powder diagrams.

Keywords: Copper; Infrared spectroscopy; Tetrafluorborate; Thermal analysis

1. Introduction

One of our research interests relates to the synthesis, reactivity and solid-state structural characterization of copper compounds with nitrogen- and phosphorus-based ligands [1–4]. Copper(I) complexes stabilized by organic ligands are of great theoretical and practical interest. They are successfully used in organic synthesis and catalysis [5] and their properties depend to a large extent on the nature of the stabilizing ligands. The acetonitrile molecules present in the complex $[Cu(MeCN)_4]BF_4$ may easily be substituted by other ligands, affording new compounds. In the present paper we report the preparation and thermal stability of tetrafluorborate copper(I) complexes containing acetonitrile, triphenylphosphine, 1,10-phenanthroline, 2,2′-bipyridine and 2-quinolinethiol. These compounds were

---

* Corresponding author.

SSDI 0040-6031(95)02253-8

characterized and studied by thermogravimetry (TG), infrared spectroscopy (IR) and X-ray diffraction powder patterns.

2. Experimental

The complex [Cu(MeCN)$_4$]BF$_4$ (**I**) was prepared as previously described [6]. The compounds [Cu(qnSH)(MeCN)$_2$]BF$_4$ (**II**) and [Cu(phen)(MeCN)]BF$_4$ (**III**) were synthesized by reaction of [Cu(MeCN)$_4$]BF$_4$ with an equimolar amount of 2-quinolinethiol (qnSH, C_9H_7NS) and 1,10-phenanthroline (phen, $C_{12}H_8N_2$) in diethyl ether at room temperature.

[Cu(PPh$_3$)$_4$]BF$_4$ (**IV**) was prepared by the reaction of copper(II) tetrafluorborate and triphenylphosphine (PPh$_3$, $C_{18}H_{15}P$) under refluxing conditions in ethanol. The complex [Cu(bipy)(PPh$_3$)$_2$]BF$_4$ (**V**) was obtained by direct reaction of [Cu(PPh$_3$)$_4$]BF$_4$ with 2,2′-bipyridine (bipy,$C_{10}H_8N_2$) in diethyl ether. All syntheses were carried out in dry solvents under nitrogen.

Copper(I) content was estimated by complexometric titration with standard EDTA solution, using PAN 0.05% in ethanol as indicator [7] and by TG curves.

Thermal analysis was carried out using a Perkin-Elmer TGS-2 thermobalance. Samples of approximately 0.7 mg were used, heated at a rate of 20°C min^{-1} in synthetic air. The IR spectra were recorded on a Nicolet 730 SX-FT spectrophotometer as KBr discs and nujol mulls between KBr plates. An X-ray diffractometer, Veb Freiberger Prazisionsmechanik, model HGZ 4/B, with Cu K_α radiation was employed to analyse the residual materials produced by thermal decomposition.

3. Results and discussion

The analytical and thermogravimetry (TG) results for the synthesized compounds are reported in Table 1. The formulae reported in the table are calculated

Table 1
Analytical and thermoanalytical data

Compound	Cu(%)			H(%)	N(%)	P(%)
					Found	
	Calc.	EDTA	TG		(calc.)	
[Cu(MeCN)$_4$]BF$_4$	20.02	20.17	20.20	3.74	17.25	
(white)				(3.85)	(17.81)	
[Cu(qnSH)(MeCN)$_2$]BF$_4$	16.18	16.16	16.30	3.40	9.96	
(orange)				(3.08)	(10.70)	
[Cu(phen)(MeCN)]BF$_4$	17.10	16.15	18.25	3.14	12.12	
(purple)				(2.98)	(10.70)	
[Cu(PPh$_3$)$_4$]BF$_4$	5.31	5.47	6.69			10.30
(white)						(10.33)
[Cu(bipy)(PPh$_3$)$_2$]BF$_4$	7.65	7.35	7.54	4.58	2.91	
(yellow)				(4.61)	(3.37)	

Table 2
IR spectral data for complexes studied (cm^{-1})

Compound	ν(N–H)	$\delta_s(CH_3)$ + ν_s(C–C)	ν(C$\equiv$N)	ν(CC)	ν(C=N)	ν(C=S)	ν(P–C)	ν_{as}(B–F)	δ_{as}(F–B–F)
$[Cu(MeCN)_4]BF_4$		2303	2274					1026	521
$[Cu(qnSH)(MeCN)_2]BF_4$	3135	2304	2274	1621	1584	1144		1057	521
[Cu(phen)MeCN)]BF_4		2304	2274	1621	1586			1060	520
$[Cu(PPh_3)_4]BF_4$				1583			1160	1090	541
$[Cu(PPh_3)_4]BF_4$				1435			693		
$[Cu(bipy)(PPh_3)_2]BF_4$				1592	1569		1164	1095	513
				1476			750		
				1434					

on these analytical results. The theoretical values for the formulae are also presented.

As shown in Table 2, the spectra of the complexes display a large number of bands assigned to vibrational modes of the organic ligands coordinated to the copper [8] and also exhibit a strong broad band at 1026–1095 cm^{-1} and a sharp one at 513–541 cm^{-1}, which are assignable to the asymmetric B–F stretching and F–B–F bending modes of uncoordinated tetrafluorborate, respectively [8, 9].

For complexes containing acetonitrile, the observed shift to higher frequencies relative to free ligand of the bands assigned to $\delta_s(CH_3) + \nu(CC)$ and $\nu(C \equiv N)$ vibrational modes confirms the coordination to the copper metal through the nitrogen atom [10]. For the compound $[Cu(MeCN)_4]BF_4$, the copper atom is tetrahedrally coordinated by nitrogen atoms belonging to the four acetonitrile ligands. The acetonitrile molecules are arranged around the copper atom so that the whole copper(I) tetra-acetonitrile complex may be described as having an almost ideal tetrahedral symmetry [11].

The presence of a band at 3135 cm^{-1}, assigned to ν(NH), and the absence of ν(SH) (approx. 2500 cm^{-1}) in the spectrum of $[Cu(qnSH)(MeCN)_2]BF_4$ indicate a preferred coordination for the thione form, for the 2-quinolinethiol ligand [12]. The observed bands at 1144 and 385 cm^{-1}, assigned to ν(C=S) and ν(Cu–S), suggest S-donation to the copper by qnSH.

The spectrum of the complex [Cu(phen)(MeCN)]BF_4 shows two bands at 1621 and 1586 cm^{-1} assigned to ν(CC) and ν(C=N), respectively, which are present at higher frequencies when compared with those of the free ligand [13]. This indicates that a chelate ring is being formed through the nitrogen atoms. For compounds containing 2-quinolinethiol and 1,10-phenanthroline, the results suggest a trigonal planar geometry.

The bands at 1583 and 1435 cm^{-1}, characteristic of ν(CC) modes of the phenyl rings, and at 1160 and 693 cm^{-1} assigned to the stretching vibration ν(P–C) in the spectrum of $[Cu(PPh_3)_4]BF_4$, confirm the coordination of the triphenylphosphine to the copper by phosphorus atoms. For complex $[Cu(bipy)(PPh_3)_2]BF_4$, the spectrum shows the characteristic bands of triphenylphosphine ligand and displays a band at 1569 cm^{-1}

assigned to ν(C=N). Thus we may conclude that 2,2′-bipyridine forms a chelate ring through the nitrogen atoms. For these two compounds the data suggest a distorted tetrahedral geometry.

The thermal decomposition of the series of copper(I) complexes studied in this work, as well as their stability, depends on the nature of the ligands, as can be observed from the TG curves in Fig. 1. The initial and final temperatures of the decomposition processes are given in Table 3. Thus, taking into account the initial temperature, it was possible to establish the following relative thermal stability order: **IV** > **V** > **III** > **II** > **I**.

Furthermore, some conclusions may be drawn from this order. Firstly, the complexes containing phosphine possess higher stability compared with the corresponding acetonitrile-containing compounds. The most plausible explanation would be that the copper–phosphorus bonds are stronger than the bonds of copper with nitrogen. It is also important that phosphine is a good π-acid which would provide an additional

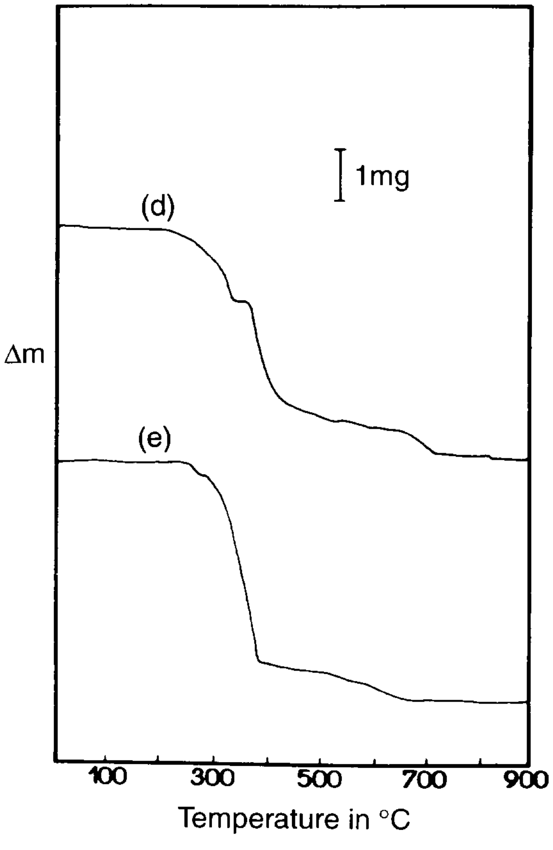

Fig. 1. TG curves: a, $[Cu(MeCN)_4]BF_4$; b, $[Cu(qnSH)(MeCN)_2]BF_4$; c, $[Cu(phen)(MeCN)]BF_4$; d, $[Cu(PPh_3)_4]BF_4$; e, $[Cu(bipy)(PPh_3)_2]BF_4$.

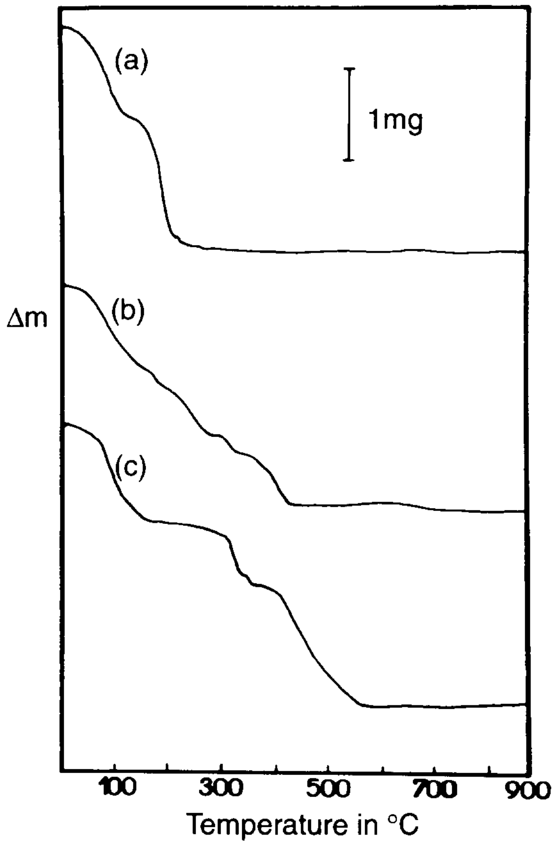

Fig. 1 *(continued)*

Table 3
Initial and final temperatures of the thermodecomposition processes and residues of the tetrafluorborate copper(I) complexes

Complexes	Temperature/°C		Mass/mg		Residue%	
	Initial	Final	Initial	Final	Found	Calc.
$[Cu(MeCN)_4]BF_4$	30	350	3.01	0.71	23.59	23.59[a]
$[Cu(qnSH)(MeCN)_2]BF_4$	35	730	2.94	0.60	20.41	20.20[b]
$[Cu(phen)(MeCN)]BF_4$	40	650	3.65	0.70	19.18	19.12[c]
$[Cu(PPh_3)_4]BF_4$	245	680	5.39	0.54	10.02	9.26[d]
$[Cu(bipy)(PPh_3)_2]BF_4$	50	700	5.60	1.00	17.86	18.11[e]

[a] CuO_2 and CuO. [b] CuO. [c] Cu_2O. [d] Cu_2O and $Cu_2P_2O_7$. [e] $Cu_2P_2O_7$.

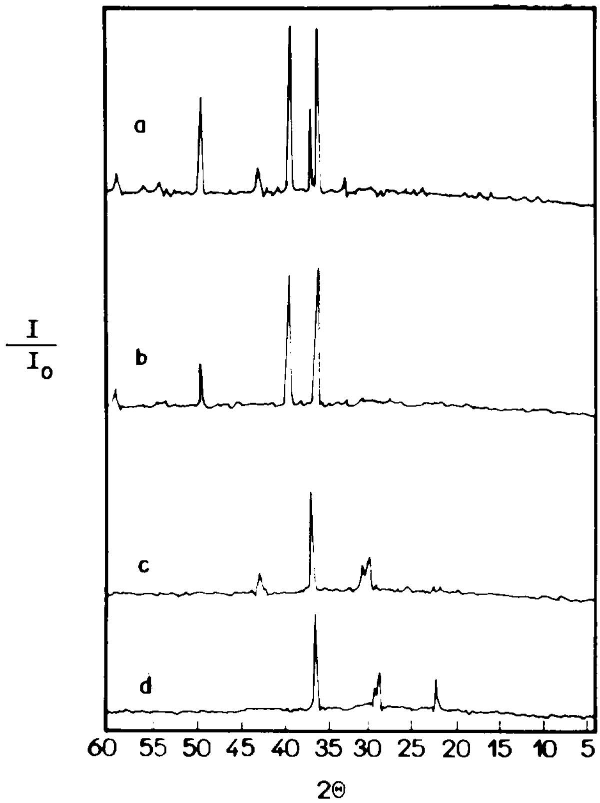

Fig. 2. X-ray powder patterns of the complexes residues: a, $[Cu(MeCN)_4]BF_4$; b, $[Cu(qnSH)(MeCN)_2]BF_4$; c, $[Cu(phen)(MeCN)]BF_4$; d, $[Cu(PPh_3)_4]BF_4$.

stability to copper(I) complexes. A similar argument explains the higher stability of the complex $[Cu(PPh_3)_4]BF_4$ when compared with $[Cu(bipy)(PPh_3)_2]BF_4$.

Secondly, the higher thermal stability of $[Cu(qnSH)(MeCN)_2]BF_4$ and $[Cu(phen)(MeCN)]BF_4$ complexes as compared with $[Cu(MeCN)_4]BF_4$ could be explained by partial substitution of acetonitrile groups by 2-quinolinethiol and 1,10-phenanthroline. The former ligand leads to the formation of a Cu–S bond which is stronger than the corresponding Cu–N bond [14]. In the case of phenanthroline group, the formation of a five-membered chelate ring is observed, thus increasing the stability of the compound.

Finally, the residues are different for each compound and are given in Table 3. As determined from TG curves, the following compounds may be considered as final products: copper(I) oxide; copper(II) oxide; cupric pyrophosphate or a mixture of phases. Fig. 2 shows the X-ray diffraction patterns of these compounds identified by comparison with ASTM files [15].

Acknowledgments

We thank the CNPq, CAPES, FAPESP and FINEP for financial support and Dr. Petr Melnikov for technical assistance.

References

[1] J.Z. Schpector, E.E. Castellano, G. Oliva, A.E. Mauro and M.R. Roveri, Acta Crystallogr. Sect. C, 41 (1985) 204.
[2] J.Z. Schpector, E.E. Castellano, A.E. Mauro and M.R. Roveri, Acta Crystallogr. Sect. C, 42 (1986) 302,
[3] O.L. Casagrande, Jr., S.I. Klein, A.E. Mauro and K. Tomita, Transition. Met. Chem., 14 (1989) 45.
[4] A.E. Mauro, S.I. Klein, J.S. Saldana, C.A. de Simone, J.Z. Schpector and E.E. Castellano, Polyhedron, 24 (1990) 2937.
[5] G.W.J. Fleet and P.J.C. Harding, Tetrahedron Lett., 22 (1981) 675.
G.W. Parshall, Homogeneous Catalysis, John Wiley, New York, 1980.
[6] J. Hathaway, D.G. Holah and J.D. Postlethwaite, J. Chem. Soc., (1961) 3215.
G.J. Kubas, Inorg. Synth., 19 (1979) 90.
[7] H.A. Flaschka, EDTA Titrations, an Introduction to Theory and Practice, Pergamon Press, New York, 1964.
[8] K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, John Wiley, New York, 1970.
N.B. Colthup, L.H. Daly and S.E. Wiberley, Introduction to Infrared and Raman Spectroscopy, Academic Press, London, 1964.
[9] N.N. Greenwood, J. Chem. Soc., (1959) 3811.
[10] B.N. Storhoff and H.C. Lewis, Jr., Coord. Chem. Rev., 23 (1977) 1.
[11] I. Csoregh, P. Kierkegaard and R. Norrestam, Acta Crystallogr. Sect. B, 31 (1975) 314.
[12] E. Spinner, J. Chem. Soc., (1960) 1237.
[13] A.R. Katritzky, Q. Rev., 13 (1959) 353.
[14] R.G. Pearson, Chem. Br., 3 (1967) 103; J. Am. Chem. Soc., 85 (1963) 3533.
[15] Powder Diffraction File, Sets 5–661; 5–667 and 21–880, Joint Committee on Diffraction Standards.