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Thermal investigation of some mixed-ligand copper(II) chelates containing 1,2-diamines and β-ketoenols

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Abstract

Thermal studies by TG/DTA and/or TG/DTG techniques of some mixed-ligand copper(II) chelates were carried out to determine their stabilities and modes of decomposition. The chelates have the formula [Cu(β-dione)(enR)]X, where β-dione is the anion of a β-ketoenol, enR is *N*,*N*′-substituted aryl or alkyl ethylenediamine and X is NO_3^- or ClO_4^-, while the geometry of the ensuing chromophore CuN_2O_2 is square-planar. The degradation processes depend on the anions and the substituents of the ligands. The nitrate compounds are decomposed until the stable oxide, CuO, is formed at ~560°C in both air and nitrogen. The perchlorate compounds, however, are strong explosives in air and vigorously loose almost all their weight in one step. In nitrogen, the thermal profile changes dramatically and instead of explosion a decomposition process takes place affording a metallic residue at ~800°C. Mass spectrometry (MS) was also used to give possible fragmentation patterns. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Copper(II) chelates; β-Ketoenols; *N*,*N*′-substituted ethylenediamines; TG/DTG; TG/DTA; Mass spectra

1. Introduction

The contemporaneous reaction of copper(II) salts with β-ketoenols (β-diones) and certain *N*,*N*′-substituted 1,2-diamines (enR) have revealed bonding interactions and ternary chelate formation [1,2]. These mixed-ligand copper(II) compounds $[Cu(\beta\text{-dione})(enR)]^+$ are more stable than the corresponding $Cu(\beta\text{-dionato})_2$ chelates and the $[Cu(enR)_2]^+$ species. The resulting CuN_2O_2 chromophore attains a virtually square-planar geometry, while the nature of its interactions with the counteranion varies [3]. Electrostatic interactions prevail when bulky polyatomic anions such as NO_3^- or ClO_4^- groups counterbalance the positive charge, while covalent axial interactions arise in the case of the halide ions, increasing the coordination number of copper(II). A structural representation with possible geometries of the studied copper(II) compounds is depicted in Fig. 1.

Interesting possibilities arise when the steric restrictions emanating from the *N*-alkyl groups are eased and the substituents within the β-dionato moiety are altered so that the effects, steric and electronic induced by the groups present compete for bond formation. However, substitution of 1,3-diones in the 2-position is subjected to limitations because of the spatial requirements of the approaching group. Preliminary X-ray structure determinations for the $[Cu(CN\text{-}acac)(dmeen)]^+$ entity, where dmeen is dimethyl–ethyl–ethylenediamine, confirmed the presence of

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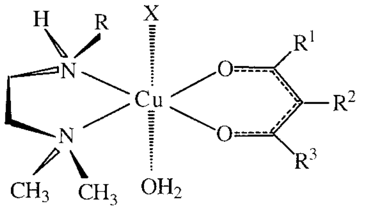

Fig. 1. Structural representation of [Cu(β-dione)(enR)]X chelates.

co-ordinated water in an apical position perpendicular to the basal plane [4,5].

The thermal studies of some ethylenediamine metal complexes revealed conformational changes of individual chelate rings [6], while an increased interest arised in the last decade for volatile β-diketonates for use as precursors of superconducting films with the MOCVD technique (metal–organic chemical vapour deposition) [7]. The significant applications of these materials in electronics industry (as in magnetic and microwave sensors and in circuity junctions) suggest further investigations on the co-ordination chemistry of mixed-ligand complexes containing β-ketoenols and particularly on the factors controlling their thermal stability and volatility. In this respect, we report here the results concerning mass spectral and thermogravimetric studies for some mixed-ligand copper(II) complexes of the type $[Cu(\beta\text{-dione})(enR)]^{+}X$, where X is NO_3^- or ClO_4^-, in order to explore the effects of substituents of the co-ordinated ligands, as well as that of the anions, on the thermal behaviour of these potential precursor compounds.

2. Experimental

2.1. Preparation

The [Cu(β-dione)(enR)]X compounds, where X is the anion NO_3^- or ClO_4^-, were prepared by known methods [8]. The β-diones (β-ketoenols) used are: 2,4-pentanedione (acetylacetone, acacH), 3-methyl-2,4-pentanedione (3-methyl-acetylacetone, CH_3-acacH), 3-cyano-2,4-pentanedione (3-cyano-acetylacetone, CN-acacH), 1-phenyl-1,3-butanedione (benzoylacetone, bzacH), 1,3-diphenyl-1,3-propanedione (dibenzoylmethane, dbmH), 1-phenyl-4,4,4-trifluoro-1,3-butanedione (benzoyltrifluoroacetone, bztfH) and 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (hexafluoroacetylacetone, hfacH).

The *N*,*N'*-alkyl or aryl derivatives (enR) of ethylenediamine (1,2-diamino-ethane, en) used are: *N*,*N*-dimethyl-*N'*-methyl-ethylenediamine (Me_3en), *N*,*N*-dimethyl-*N*,*N'*-dimethyl-ethylenediamine (Me_4en), *N*,*N*-dimethyl-*N'*-benzyl-ethylenediamine (ben) and *N*,*N*-dimethyl *N'*-ethyl-ethylenediamine (dmeen).

2.2. Instrumental

Mass spectra were measured on a RMU-6L Hitachi Perkin-Elmer double focusing mass spectrometer, model TS 250 Fision, using direct probe insertion for the samples, operating at 70 eV. The TG/DTA curves were obtained on a Rigaku–Denki model 8076 D1 thermal analyser. Samples were heated in platinum crucibles using α-Al_2O_3 as a reference compound, in a satatic air atmosphere within the temperature range 25–800°C. The heating rate was 10°C min^{-1} and the sample sizes ranged in mass from 15 to 20 mg. X-ray powder diffraction analyses of the final residues were made with a Philips PW 1130/00 X-ray diffractometer, using Cu Kα radiation. The TG/DTG analyses were performed in dynamic nitrogen atmosphere on a TGS-2 Perkin-Elmer thermobalance at a heating rate of 5°C min^{-1} and/or 10°C min^{-1} in the temperature range 50–850°C, with a sample mass of ~6 mg.

3. Results and discussion

3.1. Mass spectral studies

The most prominent mass spectral peaks of the studied compounds are given in Table 1 and a general schematic representation including the main fragmentation process for the copper chelates is given in bargraph in Fig. 2. In the mass spectra recorded, the molecular ions are not detected, as it was expected, and the highest mass-number ions found correspond to the fragments (a) $[Cu(\beta\text{-dione})_2]^{]+}$, and (b) $Cu(\beta\text{-dione})^{]+}$. It seems that a rearrangement of the ligands in the mixed-ligand copper(II) compounds take place in the ionisation champer and gives the fragment (a), which observed with quite high relative intensity

Table 1
The most relevant mass spectral peaks of the chelates [Cu(β-dione)(enR)]X.

Compound	*m/e* (RI)[a]
[Cu(acac)(dmeen)]NO$_3$	42(83), 43(54), 58(34), 63(20), 65(13), 85(100), 100(52), 116(10), 147(52), 149(28), 162(45), 164(15), 230(19), 245(47), 246(36), 260(45), 262(20), 278(12), 280(5)
[Cu(bzac)(dmeen)]NO$_3$	45(89), 46(100), 55(90), 63(70), 65(30), 79(77), 86(64), 113(80), 116(40), 160(26), 213(68), 224(47), 226(20), 230(54), 238(41), 303(56), 326(54), 339(41), 345(27), 356(44), 357(42), 374(41), 385(28), 387(12), 454(32), 490(68), 492(54), 565(15), 567(10)
[Cu(bztf)(dmeen)]NO$_3$	50(36), 52(33), 56(57), 57(35), 63(73), 65(28), 69(25), 72(39), 78(30), 89(43), 91(68), 104(25), 116(34), 139(22), 146(27), 148(25), 209(32), 210(16), 214(26), 217(32), 277(9), 279(10), 356(17), 423(35), 425(13), 494(100)
[Cu(acac)(dmeen)]ClO$_4$	41(41), 42(100), 43(41), 63(19), 65(9), 85(96), 100(61), 116(10), 147(72), 149(46), 162(66), 219(37), 230(18), 231(26), 233(19), 246(39), 260(45), 262(17), 278(12), 280(5)
[Cu(CN-acac)(dmeen)(H$_2$O)]ClO$_4$	43(50), 58(100), 63(12), 65(5), 83(60), 110(20), 116(10), 125(30), 134(20), 149(20), 194(15), 277(25), 279(10), 303(10), 305(4)
[Cu(Me-acac)(Me$_4$en)]ClO$_4$	41(100), 44(79), 57(78), 72(43), 99(39), 100(38), 114(30), 116(21), 175(6), 176(8), 178(3), 290(40)
[Cu(acac)(Me$_3$en)]ClO$_4$	41(70), 55(100), 63(50), 65(30), 99(72), 102(24), 146(84), 169(80), 231(30), 245(70), 247(30), 264(88), 266(35), 322(6), 324(3)
[Cu(hfac)(ben)]ClO$_4$	28(100), 58(68), 69(22), 91(50), 139(10), 178(14), 190(27), 208(12), 209(14), 317(10), 315(8), 448(4), 450(2)

[a] RI: relative intensity.

(RI). The expected fragment [Cu(β-dione)(enR)]$^{]+}$ (c), observed only in some compounds, with low RI, while in one case the detected fragment [Cu(bzac)$_2$(dmeen)]$^{]+}$ (d) gives evidence for the formation of the adduct compound (d) from which, upon elimination of the nitrogenous base enR, the fragment (a) is derived. The most intense peaks of each spectrum are those corresponding to the released β-dione and its daughter fragments following well-known pathways [9].

3.2. Thermal behaviour

The temperature ranges, determined percentage weight losses and thermal effects accompanying the decomposition reactions, derived from the thermoanalytical curves TG/DTA in air atmosphere, for 10 copper(II) chelates are given in Table 2. The DTA curve shape indicates that melting takes place before decomposition, which is accompanied by exothetmic effects. Generally, the degradation processes are

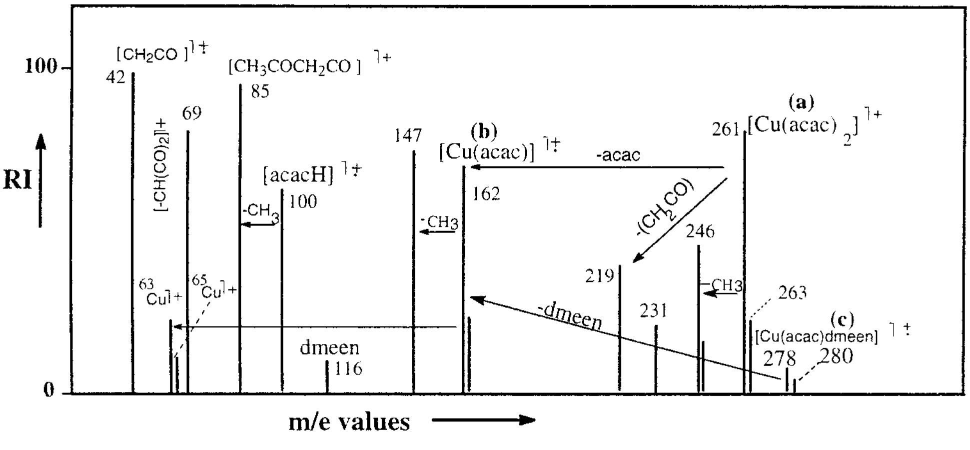

Fig. 2. Schematic representation of the general fragmentation pattern of some copper(II) chelates.

Table 2
Thermoanalytical results (TG/DTA) for some [Cu(β-dione)(enR)]X chelates in air

Compound	Stage	Temperature range (°C)	DTA		Mass loss (%)	Evolved moiety formula	Mass calculated (%)
			Endo(−)	Exo(+)			
[Cu(acac)(dmeen)]NO_3	1	220–270	180	270	63.3	acac + dmeen	63.1
	2	290–500		360, 380, 480	13.1	NO_2	13.5
	Residue	>500			23.6	CuO	23.4
[Cu(bztf)(dmeen)]NO_3	1	285–300	280	300	47.0	bztf	47.1
	2	300–410		410	24.8	dmeen	25.4
	3	410–560		515	10.6	NO_2	10.1
	Residue	>560			17.6	CuO	17.4
[Cu(bzac)(dmeen)]NO_3	1	280–300	275	300	42.8	bzac	40.0
	2	300–480		410	27.2	dmeen	28.8
	3	480–600		545	10.4	NO_2	11.4
	Residue	>600			19.6	CuO	19.8
[Cu(dbm)(dmeen)]NO_3	1	325–380	320	340	49.2	dbm	48.1
	2	380–470		430	23.5	dmeen	24.9
	3	470–600		530, 545	9.5	NO_2	9.9
	Residue	>600			17.8	CuO	17.1
[Cu(CN-acac)(dmeen)(H_2O)]NO_3	1	120–220	160		4.5	H_2O	4.7
	2	220–320	240	260	61.2	CN-acac + dmeen	62.6
	3	320–500		400, 425, 460	13.1	NO_2	12.0
	Residue	>500			21.2	CuO	20.7
[Cu(acac)(dmeen)]ClO_4	1	245–270	180	270	93.0	Explosion	100.0
		245–500			97.0		
	Residue	>500			–	Empty crucible	–
[Cu(hfac)(ben)]ClO_4	1	220–260	190	260	98.0	Explosion	100
	Residue	>500			–	Empty crucible	–
[Cu(CN-acac)(dmeen)(H_2O)]ClO_4	1	100–220	140, 200		4.3	H_2O	4.3
	2	220–270		270	22.0	acac	23.3
	3	270–340		310	35.0	CN + dmeen	33.7
	4	340–600			23.5	$\{ClO_4\}$	23.6
	Residue	>600			15.2	Cu	15.1
[Cu(acac)(Me_3en)]ClO_4	1	250–270	195	270	92.0	Explosion	100.0
		250–600			96.0		
	Residue	>600			–	Empty crucible	–
[Cu(CH_3-acac)(Me_4en)]ClO_4	1	260–270	260	270	92.0	Explosion	100.0
		260–500		410	95.0		
	Residue	>500			–	Empty crucible	–

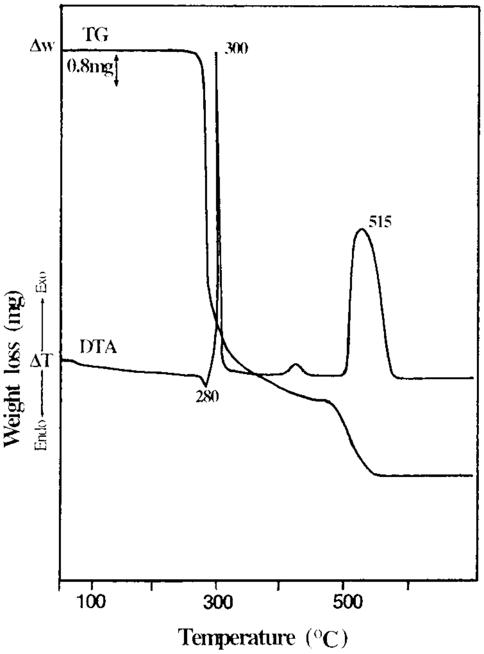

Fig. 3. Thermoanalytical curves (TG/DTA) of [Cu(bztf)(dmeen)]-NO_3 in air.

followed by several thermal effects and depend on the nature of the counteranion and the substituents of the ligands.

In particular, the nitrate compounds are decomposed in two or three stages. Representative TG/DTA curves for the [Cu(bztf)(dmeen)]NO_3 and the [Cu(CN-acac)(dmeen)(H_2O)]NO_3 compounds are depicted in Figs. 3 and 4, respectively. The decomposition proceeds with rupture of the co-ordination bonds, by elimination of the β-dione molecule in the first stage, and the 1,2-diamine ligand in the second stage. Although we expected the 1,2-diamine molecule to be eliminated first, according to our findings in the mass spectra of these compounds mentioned previously, recourse to investigations on the thermodynamics of bond formation in reactions of Cu(β-dione)$_2$ chelates with 1,2-diamines revealed [10] that the Cu–N bonds are stronger than the equatorial Cu–O bonds since they differ in the enthalpy of formation by 38 kJ mol^{-1}. The differences in the decomposition mode of the investigated chelates, derived from mass spectra and thermoanalytical data are probably due to the different conditions in the ionisation champer.

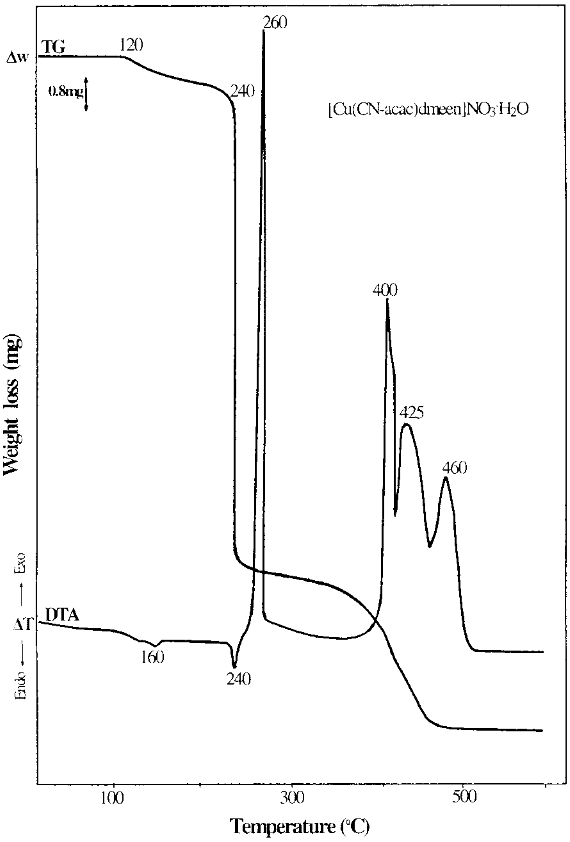

Fig. 4. Thermoanalytical curves (TG/DTA) of [Cu(CN-acac)(dmeen)(H_2O)]NO_3 in air.

In the case of [Cu(acac)(dmeen)]NO_3 and [Cu(CN-acac)(dmeen)(H_2O)]NO_3 chelates, however, it seems that the absence of 1,3-phenyl substituents in the acetylacetone, such as in bzac and dbm, stabilise the Cu–O co-ordination bonds, resulting in the elimination of both ligands β-dione and 1,2-diamine in one stage. In the case of [Cu(CN-acac)(dmeen)(H_2O)]NO_3 chelate, the existence of one co-ordinated water molecule is evidenced from the thermoanalytical curves, Fig. 4, while its decomposition mode is similar with that observed for the chelate [Cu(acac)(dmeen)]NO_3. This means that the 2-substitution of β-dione does not alter significantly the degradation process of these nitrate copper(II) chelates.

Finally, it is concluded that the thermal stability of the studied nitrate chelates with the same 1,2-diamine ligand and different β-diones, based on their initial decomposition temperatures, depends on the substitution of the β-dione and follows the series CN-acac < acac < bzac < bztf < dbm.

The intermediates after the first and second stages are unstable and undergo further decomposition until the stable metal oxide, CuO, is formed at about 560°C, verified from the X-ray powder diffraction data. Where possible the intermediates were deduced by elemental analyses, and mass and IR spectra. It is concluded that the intermediates at ~400°C are consisted from a mixture of $Cu(NO_3)_2$ and Cu, derived from the elimination of two β-dione and two 1,2-diamine molecules from two molecules of the studied copper nitrate chelates. In the third stage, observed in the temperature range 400–560°C, the following reactions take place [11]:

$$Cu(NO_3)_2 \rightarrow CuO + 2NO_2 + \tfrac{1}{2}O_2 \quad \text{and}$$
$$Cu + \tfrac{1}{2}O_2 \rightarrow CuO$$

Evidence for the second reaction gives the broad exothermic peak in the DTA curve, centred at ~515°C [12]. The sum of the two reactions suggests the elimination of the NO_2 moiety calculated from the TG curve and depicted in Table 2.

The thermal curves (TG/DTG) of the chelate $[Cu(bztf)(dmeen)]NO_3$ recorded in nitrogen atmosphere as a representative example of the nitrate compounds, showed that the chelate is much less stable than in air and abruptly looses ~73% of its weight in one stage (Table 3). The intermediate is gradually decomposed leaving as residue black CuO at 560°C.

The thermoanalytical curves (TG/DTA) in air atmosphere of some perchlorate copper(II) chelates under investigation are depicted in Fig. 5. These chelates are thermally stable until ~240°C, where an explosion takes place, indicated by the strong exothermic in DTA, which accompanies the vigorous loss of mass in one stage (Table 2), leaving an empty crucible. It is known that the simple $Cu(\beta\text{-dione})_2$ complexes are volatile and that their volatility depends on the nature and the position of the substituents in the β-dionato ligand [13]. In the studied mixed-ligand copper(II) chelates, it is noticed that their thermal behaviour depends also on the β-dione and it is not affected by the 1,2-diamine ligand. So, although the substitution of the methyl group (repelling) in 2-position in the case of $[Cu(CH_3\text{-acac})(Me_4en)]ClO_4$, does not alter significantly its thermal stability, when the 2-position

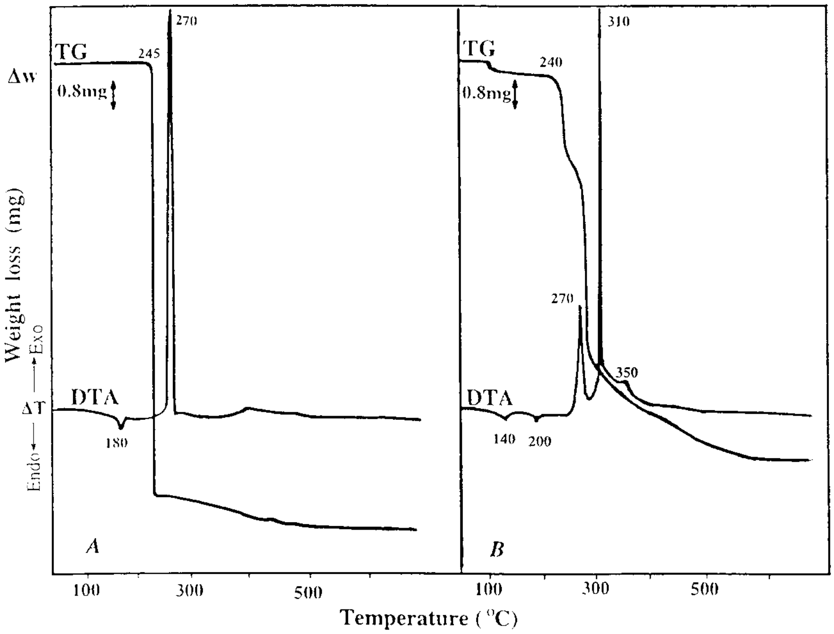

Fig. 5. Thermal curves (TG/DTA) of the compounds: (A) $[Cu(acac)(dmeen)]ClO_4$; and (B) $[Cu(CN\text{-}acac)(dmeen)(H_2O)]ClO_4$ in air.

Table 3
Thermoanalytical results (TG/DTG) for some [Cu(β-dione)(enR)]X chelates in nitrogen

Compound	Stage	Temperature range (°C)	DTG$_{max}$ (°C)	Mass loss (%)	Evolved moiety formula	Mass calculated (%)
[Cu(bztf)(dmeen)]NO$_3$	1	175–250	225	73.0	bztf + dmeen	72.5
	2	250–560		9.0	NO$_2$	10.1
	Residue	>560		18.0	CuO	17.4
[Cu(acac)(dmeen)]ClO$_4$	1	210–240	230	83.0		
		210–500		91.0	Decomposition	
	Residue	>500		9.0	Cu	16.8
[Cu(CN-acac)(dmeen)(H$_2$O)]ClO$_4$	1	60–120	100	4.0	H$_2$O	4.3
	2	180–250	235	22.0	acac	23.3
	3	250–670		32.5	CN + dmeen	33.7
	4	670–800	750	28.5	ClO$_4$	23.6
	Residue	>800		13.0	Cu	15.1
[Cu(CH$_3$-acac)(Me$_4$en)]ClO$_4$	1	190–230	213	28.5	CH$_3$-acac	28.8
	2	230–460	270	29.0	Me$_4$en	29.6
	3	460–620	∼550	28.5	ClO$_4$	25.4
	Residue	>660		14.0	Cu	16.2
[Cu(hfac)(ben)]ClO$_4$	1a + 1b	200–290	232, 260	71.0	hfac + ben	70.3
	2	290–600	∼530	23.0	ClO$_4$	18.1
	Residue	>600		6.0	Cu	11.6
[Cu(acac)(Me$_3$en)]ClO$_4$	1	200–260	230	27.0	acac	27.2
	2	260–540	280	28.5	Me$_3$en	28.0
	3	540–810	750	30.5	ClO$_4$	27.4
	Residue	>810		14.5	Cu	17.4

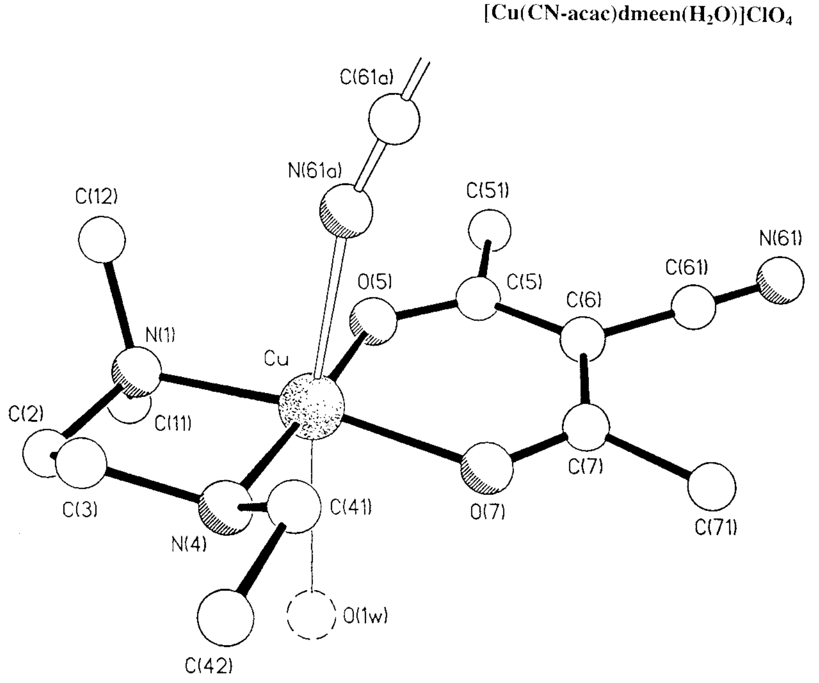

Fig. 6. Molecular structure of the chelate [Cu(CN-acac)(dmeen)(H$_2$O)]ClO$_4$.

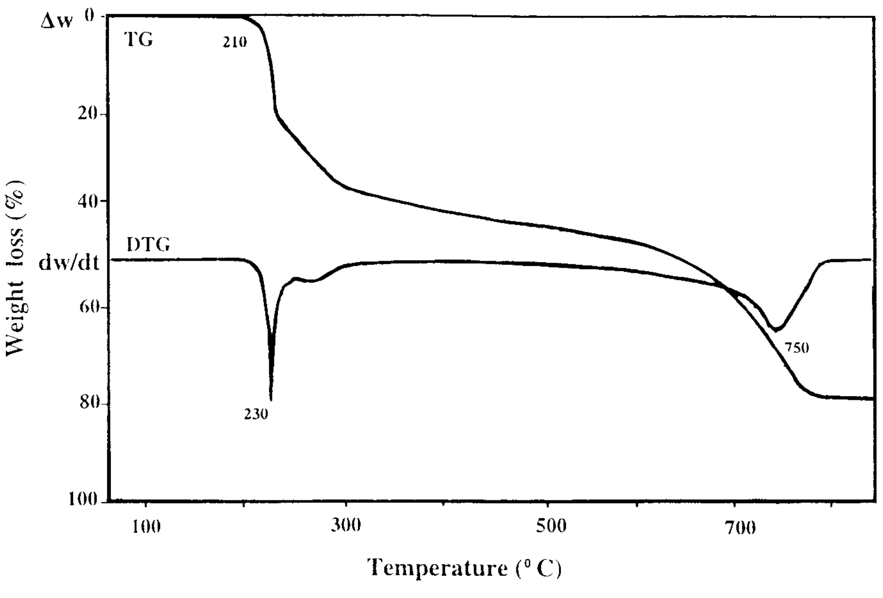

Fig. 7. Thermogravimetric curves (TG/DTG) of [Cu(acac)(Me$_3$en)]ClO$_4$ in nitrogen.

is occupied by a cyano group (electron withdrawing), such as in the [Cu(CN-acac)(dmeen)(H_2O)]ClO_4 chelate, a gradual decomposition takes place instead of explosion. The decomposition begins with the elimination of the water molecule at 100°C, following by the rupture of the co-ordination bonds and bonds inside the β-dionato ligand. This decomposition mode is in agreement with the fragmentation pattern observed in the mass spectrum of this compound. The significant differences in the thermal behaviour of the afore-mentioned copper(II) chelate can be explained, besides the electronic effect induced by the cyano group, with the different molecular and crystal structures of this compound. Although the chromophore CuN_2O_2 attains a square-planar arrangement, the co-ordination of the water molecule and the approach of a second cyano group to the copper(II) ion in the way it is shown in Fig. 6, suggest an octahedral arrangement of the molecule and oligomerization of this compound [5].

Thermogravimetric studies (TG/DTG) over the temperature range 50–850°C were also carried out in nitrogen for five perchlorate copper(II) chelates. Representative thermal curves for [Cu(acac)(Me_3en)]-ClO_4 are given in Fig. 7 and the thermoanalytical data derived from the thermal curves are presented in Table 3. The thermal profile of these compounds changes dramatically in nitrogen and instead of explosion, a decomposition process takes place affording a metallic copper residue at ~800°C.

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References

[1] Ch. Tsiamis, M. Themeli, Inorg. Chim. Acta 206 (1993) 105.

[2] Ch. Tsiamis, L.C. Tzavellas, Inorg. Chim. Acta 207 (1993) 179.

[3] Ch. Tsiamis, L.C. Tzavellas, C.A. Kavounis, J. Cardin, Inorg. Chim. Acta 254 (1997) 411.

[4] [Cu(CN-acac)dmeen]$NO_3 \cdot H_2O$, unpublished results.

[5] Ch. Tsiamis, M. Lalia-Kantouri, D. Williams, [Cu(CN-acac)(dmeen)(H_2O)]ClO_4, unpublished results.

[6] G. De, P.K. Biswas, M.R. Chauhuri, Chem. Soc. Dalton Trans. (1984) 2591.

[7] R.E. Sievers, S. Turnipseed, L. Huang, A.F. Laglante, Coord. Chem. Rev. 128 (1993) 285.

[8] Ch. Tsiamis, Inorg. Chim. Acta 200 (1992) 651, and references therein.

[9] Sh. Sasaki, Y. Itagaki, T. Kurokawa, K. Nakanishi, A. Kasahara, Bull. Chem. Soc. Jpn. 40 (1967) 76.

[10] D.P. Graddon, W.K. Ong, J. Inorg. Nucl. Chem. 37 (1975) 469.

[11] C. Duval, Inorganic Thermogravimetric Analysis, 2nd Edition, Elsevier, Amsterdam, 1963.

[12] M. Lalia-Kantouri, M. Hartophylles, Thermochim. Acta 224 (1993) 203.

[13] K.J. Eisentraut, R.E. Sievers, J. Inorg. Nucl. Chem. 29 (1967) 1931.