

EFFECT OF TYPE AND POSITION OF THE ANIONS ON THE THERMAL DECOMPOSITION OF SOME COPPER(II) COMPLEXES

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A number of copper(II) complexes of some aromatic diamines have been prepared and characterized. The thermal stabilities of the complexes were studied and discussed in terms of covalent bond character, chelate ring size and angle strain. On the other hand, the effective role of the anions on the decomposition pathways was also considered. Moreover, the nature of interaction of the solvent of crystallization has also been investigated.

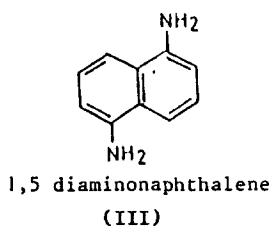
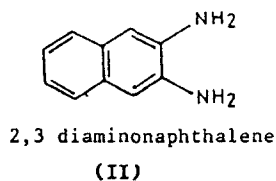
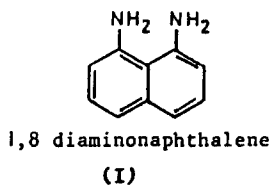
Keywords: copper(II) complexes, thermal decomposition

Introduction

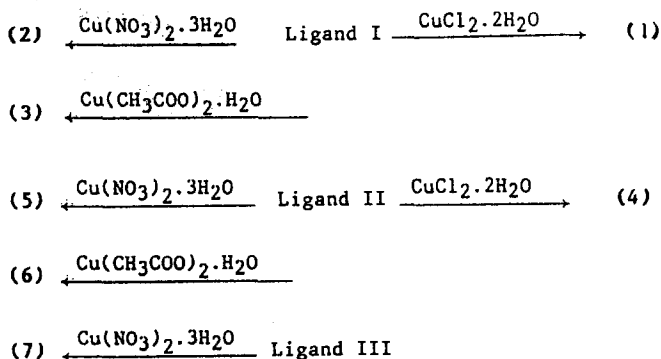
Thermal analysis has been used for investigating a number of solid state phenomena (that are related to coordination compounds)[1-7], as well as for studying the thermal stabilities of some metal complexes. The stabilities were discussed in terms of structural and conformational factors [8], metal-ligand covalent character [9], chelate ring size and localized electron model [10]. A correlation was also found between the stabilities and the electronegativities of the axial donor atoms in some square pyramidal Mn(III) complexes [9]. In virtue of their importance in the field of chemotherapy [11], a number of Cu(II) diamine complexes were prepared and characterized and their thermal stabilities were also studied.

Experimental

Three diamininaphthalene ligands labelled I(L¹), II(L²) and III(L³) were pure laboratory grade from Aldrich, and have the following structure .



Preparation of the complexes:



Scheme 1

The complexes of ligand I (1–3) and those of ligand II (4–6) were prepared by the addition of the stoichiometric amounts of the copper salt in methanol to a hot solution of the ligand I in chloroform or the ligand II in ethanol, (1M :2L) molar ratio. A precipitate was formed after 3 h reflux. The precipitate was filtered off, washed with methanol several times and dried over (CaCl₂/P₄O₁₀). The nitrate complex (7) was prepared by the same method, except the metal salt and the ligand were dissolved in ethanol and chloroform respectively, and the molar ratio used is (1M :1L). The elemental analyses [C, H, N] were performed at N.R.C.,

Dokki Cairo, Egypt. The copper content was estimated iodometrically. IR spectra were measured in KBr discs a Perkin-Elmer 598 spectrophotometer. Electronic spectra were recorded in both DMF and nujol mulls using a Pye-Unicam SP100 spectrophotometer. The molar conductance was measured in DMF using a TACUSSEL conductimetre type (CD6N). The differential thermal analyses (DTA) were measured in air with a heating rate of $10 \text{ deg} \cdot \text{min}^{-1}$ using a Shimadzu XD-30 thermal analyzer. Thermogravimetric analyses (T.G.) were carried out in air with a rate of heating of $10 \text{ deg} \cdot \text{min}^{-1}$ using a Shimadzu XD-30 Thermal Analyzer. X-ray diffraction patterns were recorded using a Shimadzu XD-3 diffractometer with Cu K_{α} radiation.

Results and discussion

Vibrational spectra

As shown in Table 2, the spectra of the complexes display bands at $3360\text{--}3100$, $1600\text{--}1580$ and $1280\text{--}1250 \text{ cm}^{-1}$ considered assigned to νNH_2 , $\nu\text{C}=\text{C}$ of the naphthyl ring and $\nu\text{C}-\text{N}$ respectively [12]. The observed shift to lower frequencies in both νNH_2 and $\nu\text{C}-\text{N}$ in the spectra of the complexes (1–6) relative to those observed for the non-coordinated ligands confirms the coordination through the amino group. For complex (7) the spectrum shows a broad/splitted band at $3415\text{--}3200 \text{ cm}^{-1}$, which is assigned to the stretching vibration of free NH_2 group. This assignment leads to the conclusion that ligand III is coordinated from one side. The acetato complexes (3, 6) show two bands near 1560 and $1380\text{--}1345 \text{ cm}^{-1}$ (Table 2) that are assigned to asymmetric and symmetric stretching vibrations of monodentate acetate respectively [13]. In spite of the lot of information about the spectra of nitrate in the literature, there are no sharp differences between the free and the bonded nitrate. Therefore, the spectra of the investigated complexes were compared with that of nickel nitrate (free nitrate). The spectrum of the nitrate complex (5) shows two bands at 1385 (strong/splitted) and 835 cm^{-1} (Table 2) that are quite similar in the shape and position to those of nickel nitrate, indicating the presence of free nitrate [13, 14]. Whilst the spectra of complexes (2) and (7) show bands at 1550 , 1385 (broad) and $1335\text{--}1310 \text{ cm}^{-1}$, indicating monodentate nitrate [13, 14]. The spectra of the complexes exhibit also a medium band in the $500\text{--}450 \text{ cm}^{-1}$ region which is assigned to $\nu\text{M}-\text{N}$ [13]. The observed weak bands within $320\text{--}310 \text{ cm}^{-1}$ in the spectra of some nitrate and acetate complexes are assigned to $\nu\text{M}-\text{O}$ [13]. The chloride complexes show a splitted band near $330\text{--}310 \text{ cm}^{-1}$ which is assigned to *cis* $\nu\text{M}-\text{Cl}$ [13].

Table 1 Analytical and conductance data for complexes

Compound	Colour	Elemental analyses /%				$\Lambda_m/\Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ (DMF)	Initial temperatures of decomposition /°C (DTA)
		C	H	N	Cu		
1 $[\text{CuL}^1\text{Cl}_2]$	dark brown	41.0 (41.6)	3.4 (3.3)	9.6 (9.9)	21.7 (21.2)	slightly soluble	130
2 $[\text{Cu}(\text{L}^1)_2(\text{NO}_3)_2]$	black	47.7 (48.4)	4.0 (4.0)	16.7 (16.7)	12.6 (12.4)	slightly soluble	110
3 $[\text{CuL}^1(\text{OAc})_2] \cdot \text{H}_2\text{O}$	dark brown	47.0 (47.5)	5.0 (4.9)	7.8 (7.4)	17.8 (18.0)	slightly soluble	150
4 $[\text{CuL}^2\text{Cl}_2]$	dark brown	41.0 (41.6)	3.4 (3.4)	9.6 (10.0)	21.7 (21.3)	27*	150
5 $[\text{Cu}(\text{L}^2)_2(\text{NO}_3)_2]$	greenish brown	47.7 (48.2)	4.0 (4.0)	17.0 (16.4)	12.6 (12.5)	110.8	200
6 $[\text{CuL}^2(\text{OAc})_2] \cdot \text{H}_2\text{O}$	dark brown	47.0 (47.5)	5.0 (4.8)	7.8 (8.0)	17.8 (18.3)	28*	150
7 $[\text{Cu}(\text{L}^3)_2(\text{NO}_3)_2] \cdot 2\text{H}_2\text{O}$	black	44.5 (44.0)	4.8 (5.1)	15.6 (15.2)	11.8 (12.0)	106.9	120

* Non-conducting solutions.
Found analyses in parentheses.

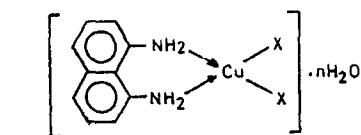
Table 2 IR and electronic spectral data for ligands and their complexes

Com- pound	IR / cm ⁻¹										Electronic spectra / nm		
	vNH ₂	vC=C of naphthyl ring	vC-N	VOAc ⁻	vNO ₃ ⁻	vM-N	vM-O	vM-Cl	<i>d-d</i>	DMF	other bands	nujol	mulls
L ¹	3440-3300 ^a	1590 (s)	1300 (s)										
L ²	3380-3310 ^a	{ 1616(sh) 1510(s)	1275 (s)										
L ³	3415-3220 ^a	1585 (s)	1290 (s)										
1	3300-3200 ^a	1585 (s)	1280 (m)			480 (m)		330-315 ^a	620-480 (sh)	470 (m), 430 (m)	560 (br)		
2	3300-3100 ^a	1590 (s)	1275 (s)	1550 (m) 1385 (s) 1310 (sh)		480 (m)	320 (m)		740-520 (br/sh)	500 (m), 460 (m)	740-480 (br)		
3	3280-3180 ^a	1585 (s)	1280 (s)	1560 ^b 1380 ^c		480 (m)	315 (m)		560-420 (br/sh)		600 (br)		
4	3300-3100 ^a	1600 (m)	1255 (m)					330-315 ^a	660 (sh)	350 (sh)	600 (br)		
5	3300-3200 ^a	1600 (s)	1255 (s)	1385 ^a 835 (m)		500 (m)	310 (m)		650 (sh)	430 (sh), 350 (sh)	600 (sh)		
6	3360-3100 ^a	1590 (m)	1260 (s)	1560 ^b 1380- 1345 ^c						400 (sh), 340 (sh)	600 (br)		
7	3415-3200 ^a	1600-1580 ^a	1250 (m)	1550 (m) 1385 (s) 1335 (sh)		450 (m)			736 (s), 675 (s)	520 (br), 450 (m)	600 (br)		

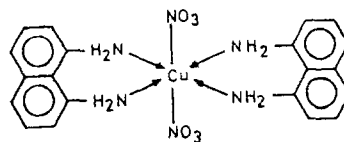
s = strong; sh = shoulder; m = medium; br = broad; ^a = splitted; ^b = asymm.; ^c = symm.

Electronic spectra

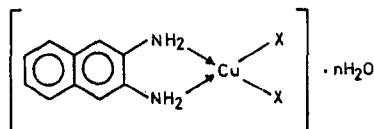
The electronic spectral data of the complexes in both DMF and nujol mulls are listed in Table 2. The observed bands within 650–560 nm for the complexes (1, 3–7) can be assigned to square planar geometry [15–18], whilst the band obtained within 740–520 nm for the nitrate complex (2), suggests a distorted octahedral geometry [15, 16]. The spectra of the complexes (except 7) in both DMF and nujol mulls are nearly the same, indicating that the complexes do not alter their geometry in DMF. The appearance of two new strong bands at 736 and 675 nm in the DMF spectrum of complex (7) indicates that the complex changes its geometry from square planar to octahedral [15, 16]. The higher value of molar conductance ($106.9 \Omega^{-1} \text{cm}^2 \cdot \text{mol}^{-1}$) of this complex can be explained in terms of the substitution of the nitrate by DMF together with the change of geometry. This explanation is also supported by the closer of the above value with that of complex (5) ($110.8 \Omega^{-1} \text{cm}^2 \cdot \text{mol}^{-1}$), which has two free nitrate groups. The above arguments together with the analytical data (Table 1) indicated that the contribution of the following structures became more significant.



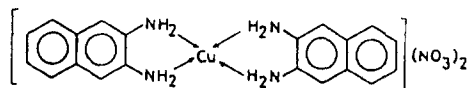
$X = \text{Cl}^-$, $n = 0$, Complex, 1
 $X = \text{OAc}^-$, $n = 1$, Complex, 3



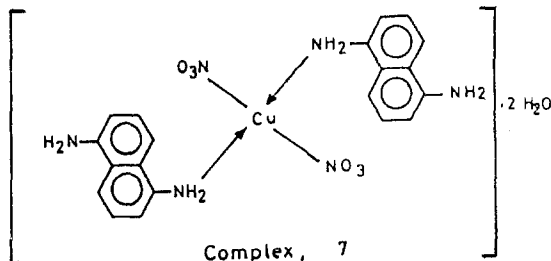
Complex, 2



$X = \text{Cl}^-$, $n = 0$, Complex, 4
 $X = \text{OAc}^-$, $n = 1$ Complex, 6



Complex, 5



Complex, 7

Thermal studies

The complexes show exothermic DTA peaks in the 110°–250°C temperature range (Fig. 1). These peaks are assigned to material decomposition as evident from the IR spectra of the complexes before and after heating up to that range (Fig. 2). The TG curves (Fig. 1) of the acetato complexes (3, 6) and the nitrate complex (7) display weight losses (5%) and (6.6%) respectively in the 40°–110°C temperature range. These weight losses correspond to one molecule of water (5.03%) for (3, 6) and two molecules (6.5%) for (7). The X-ray diffraction patterns of complex (3) before and after heating up to 110°C (Fig. 3) are mainly the same, and characterized by a multitude of reflections. This, in addition to the lower temperature of desolvation (40°–110°C), indicate that water molecules are trapped in the crystal voids and make no contribution in the lattice forces [7, 8]. The weak interaction of water together with its random distribution in the voids

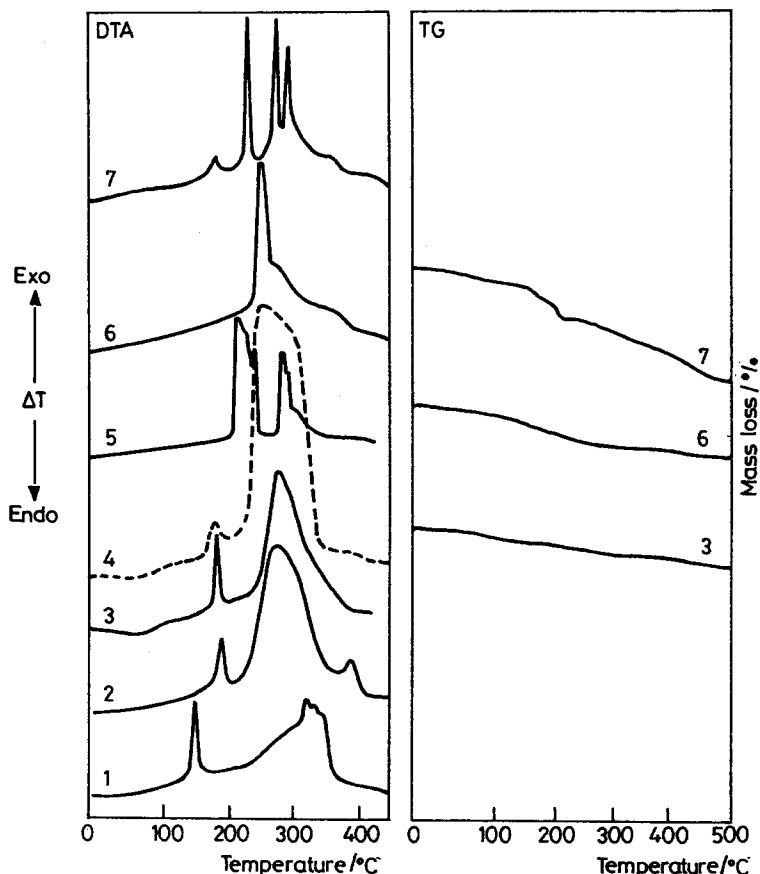


Fig. 1

are being responsible for the very weak and broadening feature of the endothermic desolvation DTA peak in that temperature range.

Again, for the decomposition reactions if the initial temperature of decomposition was taken as a measure of the thermal stability of the complexes, the following remarks can be considered and discussed.

1. For chloro complexes, the complex (4) shows a higher thermal stability than that of (1). This can be explained in terms of chelate ring size and covalent bond character [9]. The lower electronegativity of chloride than that of nitrogen, and the largest nephelauxetic effects (cloud expanding between metal and ligand) of chloride [14] make the covalent character of copper-chloride bond greater than that of copper-nitrogen bond. Therefore, the rupture of the chelate ring is being the initial step of the decomposition reaction [9, 19]. So, the higher thermal

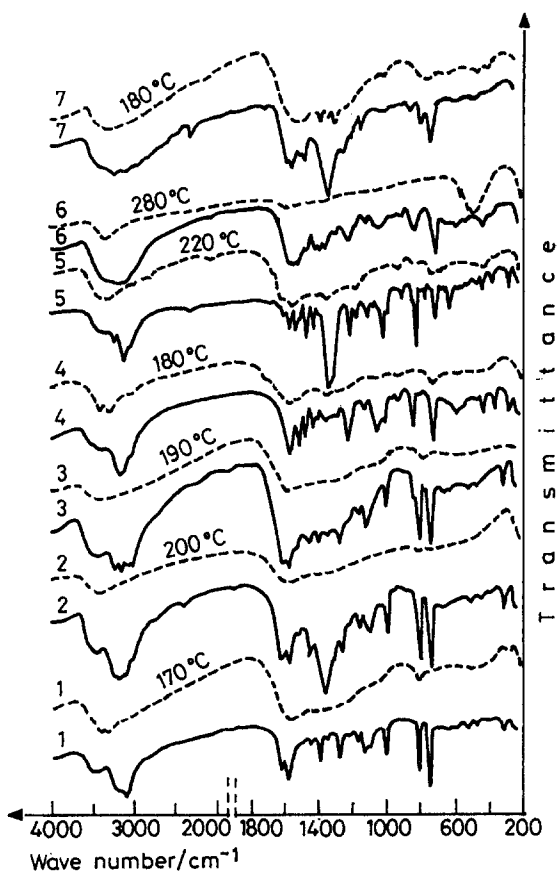


Fig. 2

stability of (4) is attributed to the five membered chelate ring, which shows a higher stability than the six membered one of (1) [20].

2. For the acetato (3, 6) and the nitrate (2, 7) complexes the rupture of chelate ring is not the first step of the decomposition reaction. This can be taken from the similarity of the decomposition temperatures of the acetato complexes (that have a different chelate ring size), and the lower temperature of the nitrate complex (2) than that of (7) (which has no chelate rings). This can be also explained on the basis of covalent bond character. The higher electronegativity of oxygen than that of nitrogen causes the decrease of covalent bond character of copper-oxygen bond (i.e. weak orbital overlap). So, the rupture of the metal-acetate or nitrate is the initial step [9, 19] followed by subsequent decomposition of the complexes.

3. Complex (5) is thermally stable as compared with other complexes, this could be explained in terms of geometry and angle strain. The presence of nitrate in the primary valency leads to an ideal square planar (dsp^2) geometry (N_4 donors), which display a lower extent of repulsion between bonded electrons in the valence shell of copper (lower angle strain with higher stability) [8, 14].

4. The lower thermal stability shown by the octahedral complex (2) can also be explained using the above factors (geometry and angle strain). The octahedral geometry (sp^3d^2) with incomplete 3d orbital of copper(II) complexes shows a lower stability than the square planar (dsp^2) ones [14]. This, in addition to the higher repulsions between bonded-bonded and bonded-nonbonded electrons (of oxygen) in the valence shell of copper (which results in a higher angle strain) are responsible for the lower stability [10, 14].

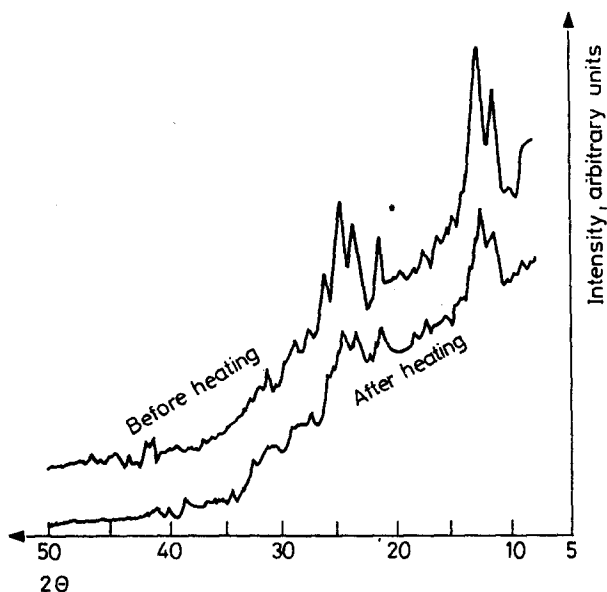


Fig. 3

Conclusion

Based on the above arguments, we can extract the following results.

i) The experimental data obtained seem to meet the suggested structure of the complexes.

ii) The type and position of the anions play an effective role in the thermal stability of the complexes.

iii) The validity of some electronic models to deal with the thermal stability.

iv) The data obtained confirm our previous foundation on other related complexes [10].

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Zusammenfassung — Es wurde eine Anzahl von Kupfer(II)-Komplexen einiger aromatischer Diamine hergestellt und beschrieben. Die thermische Stabilität der Komplexe wurde als Funktion des kovalenten Bindungscharakters, der Chelatringgröße und der Winkelspannung untersucht und diskutiert. Andererseits wurde auch der Einfluß der Anionen auf den Zersetzungsweg in Erwägung gezogen. Außerdem wurde auch die Wechselwirkung zwischen Lösungsmittel und Kristallisierung untersucht.