Thermochimica Acta, 194 (1992) 155–163
Elsevier Science Publishers B.V., Amsterdam

Thermal behaviour of some aromatic diamine complexes

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(Received 12 April 1991)

Abstract

The Co(II) and Ni(II) complexes of some aromatic diamines were prepared and characterised by different analytical and spectral methods. The thermal behaviour of the investigated complexes was also studied. The thermal stabilities of the complexes were discussed in terms of chelate ring size and localised electron model.

INTRODUCTION

Both the structure and thermal behaviour of aliphatic diamine complexes have been extensively studied [1–8]. Nowadays, the metal complexes of aromatic diamines have different applications, especially in the field of chemotherapy [9]. In spite of this importance, little work has been done on this type of diamine metal complex [9,10]. In the present work, a number of aromatic diamine metal complexes were prepared and characterised. The thermal behaviour of the complexes was also studied.

EXPERIMENTAL

Materials

All the aromatic diamines were pure laboratory grade from Aldrich and were used without further purification; they have the structures shown in Scheme 1.

Preparation of the complexes

Complexes 1, 6, 9 and 3–5 (Scheme 2) were prepared by addition of an alcoholic solution of the metal salt to a hot solution of the ligand in

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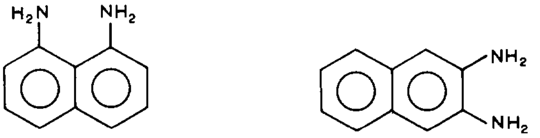


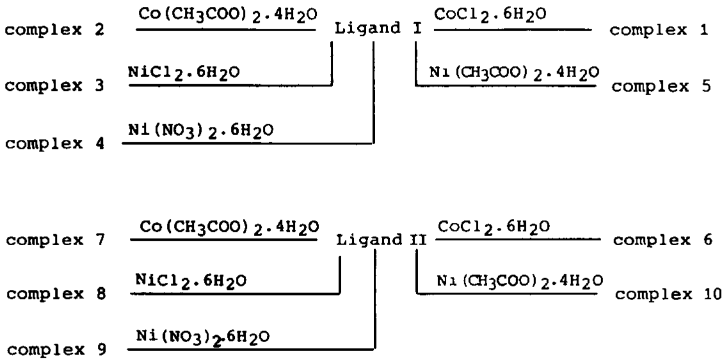
1,8 diaminonaphthalene
Ligand I (L^1)

2,3 diaminonaphthalene
Ligand II (L^2)

Scheme 1.

chloroform in 1M : 2L molar ratio. The mixture was refluxed for 6 hours for complexes 1, 6 and 9 and for 2 hours for complexes 3–5. On cooling to room temperature, the solid complexes were precipitated, filtered off, washed with chloroform and dried in vacuo over $CaCl_2/P_2O_5$.

Complexes 2, 7, 8 and 10 (Scheme 2) were prepared by the same method, except that both the metal salt and the ligand were dissolved in alcohol. The refluxing time for the preparation was 4 hours for complexes 2 and 7 and 8 hours for complexes 8 and 10. Elemental analyses (C, H and N) were performed at the National Research Centre, Dokki, Cairo, Egypt. The cobalt content in the complexes was determined compleximetrically [11]. The nickel content was determined gravimetrically using dimethylglyoxime [11]. IR spectra were measured in KBr discs using a Perkin–Elmer 598 spectrophotometer. Electronic absorption spectra were recorded in both DMF or methanol and nujol mulls using a Pye–Unicam Sp 100 spectrophotometer. Solution electrical conductances were measured in DMF for cobalt and in methanol for nickel using a Tacussel conductimeter, type D6N. The differential thermal analysis (DTA) was recorded in air with a heating rate of 10 °C min^{-1} using a Shimadzu XD-30 thermal analyser. The thermogravimetric analysis (TG) was carried out in air with a heating rate of 10 °C min^{-1} using a Shimadzu DT-30 B thermal analyser.



Scheme 2.

RESULTS AND DISCUSSION

The elemental analyses, molar conductances and the values for the initial temperature of the decomposition of the complexes are listed in Table 1.

IR spectra

The more characteristic bands and their assignments are listed in Table 2. The spectra display bands near 3340–3100, 1635–1610, 1605–1560 and 1280–1255 cm^{-1}. These bands are assigned to $\nu(NH_2)$, $\delta(NH_2)$, $\nu(C{=}C)$ of the naphthyl ring and $\nu(C{-}N)$, respectively. The shift observed in both $\nu(NH_2)$ and $\nu(C{-}N)$ to lower frequencies in the spectra of the complexes relative to those of the ligands confirms the coordination through the amino group. The spectra of acetato complexes show two bands at 1560 and 1410 cm^{-1} that can be assigned to asymmetric and symmetric stretching vibrations of free acetate [12], except for the cobalt acetato complex (complex 2) which shows two bands at 1560 and 1325 cm^{-1}, indicating monodentate acetate [12]. The nitrato complexes show bands at 1385, 1305 and 1010 cm^{-1} that are assigned to monodentate nitrate [12,13]. The spectra of the complexes also show bands near 300–325 and 465–490 cm^{-1} that are assigned to $\nu(M{-}Cl)$ [12,14] and $\nu(M{-}N)$ [12], respectively. The splitting observed for $\nu(Co{-}Cl)$ in complex 1 indicates that the two chlorides are cis [14].

Electronic spectra

As shown in Table 3, the spectra of the complexes show a number of absorption bands in the range 770–320 nm. For cobalt complexes, the spectra in both DMF and nujol mulls are the same, indicating that the DMF does not alter the geometry of the complexes. Therefore, the bands observed near 770–740, 680–600 and 550–510 nm suggest a six-coordinate octahedral geometry [15,16]. The spectra of nickel complexes show a series of bands within the range 730–340 nm, indicating a six-coordinate octahedral geometry [16–18]. The above spectral data, in addition to the elemental analyses and molar electrical conductance data given in Table 1 suggest the structures shown in Scheme 3.

Thermal studies

The DTA curves of the investigated complexes (Fig. 1) show an exothermic peak within the temperature range 260–460 °C (for cobalt) and 215–335 °C (for nickel). This peak is assigned to material decomposition as indicated from the IR spectra of the complexes and their thermoproducts

TABLE 1

Elemental analysis, molar conductance and initial temperature of decomposition of the complexes

Complex	Colour	Analyses, calc. (found) (%)				Λ_m ($S\ cm^2\ mol^{-1}$)	Initial temperature of decomposition (° C)
		C	H	N	M		
1 $Co(L^1)_2Cl_2$	Dark brown	53.82 (53.70)	4.48 (4.65)	12.55 (12.64)	13.22 (13.49)	Partially soluble (DMF)	300
2 $[Co(L^1)_2(OAc)_2]\cdot 2H_2O$	Brown	54.44 (54.45)	5.67 (5.59)	10.59 (10.31)	11.14 (11.22)	Partially soluble (DMF)	150
3 $[Ni(L^1)_3]Cl_2$	Black	59.70 (59.89)	4.97 (5.00)	13.91 (13.82)	9.72 (9.62)	165 (methanol)	270
4 $Ni(L^1)_2(NO_3)_2$	Black	48.13 (48.85)	4.01 (4.05)	16.84 (15.80)	11.77 (11.98)	Partially soluble (methanol)	225
5 $[Ni(L^1)_3]OAc_2$	Black	62.70 (62.60)	5.53 (5.41)	12.90 (13.61)	9.02 (9.12)	Partially soluble (methanol)	240
6 $Co(L^2)_2Cl_2$	Black	53.82 (53.65)	4.48 (5.00)	12.55 (12.41)	13.22 (13.24)	36.6 (DMF)	340
7 $[Co(L^2)_3]OAc_2$	Reddish brown	62.67 (62.50)	5.53 (5.42)	12.90 (12.66)	9.05 (9.48)	Partially soluble (DMF)	370
8 $Ni(L^2)_2Cl_2$	Pale green	53.84 (53.95)	4.48 (5.30)	12.56 (12.64)	13.17 (12.98)	31 (methanol)	315
9 $Ni(L^2)_2(NO_3)_2$	Pale violet	48.13 (48.30)	4.01 (4.05)	16.84 (16.16)	11.77 (11.69)	30 (methanol)	290
10 $[Ni(L^2)_3]OAc_2$	Dirty green	62.70 (62.53)	5.53 (5.80)	12.90 (12.70)	9.02 (9.01)		220

TABLE 2

IR spectra of the ligands and their metal complexes

Complex	$\nu(NH_2)$	$\delta(NH_2)$	$\nu(C{=}C)$ naphthyl ring	$\nu(C{-}N)$	$\nu(M{-}N)$	$\nu(M{-}Cl)$
L^1	3420–3300 (split)	1630 (sh)	1590 (s)	1300 (s)		
L^2	3380–3310 (split)	1640 (m)	1610	1275 (s)		
1	3300–3100 (split)	1630 (m)	1590 (s)	1280 (s)	470 (m)	320–300 (split)
2	3300–3100 (br)	1620 (sh)	1560 (br)	1280 (w)		
3	3280–3140 (split)	1615 (s)	1580	1275 (s)	485 (m)	
4	3340–3120 (split)	1610 (s)	1575	1280 (m)		
5	3300–3200 (split)	1620 (sh)	1595 (m)	1275 (m)		
6	3300–3100 (br, split)	1620 (m)	1590 (m)	1265 (s)	465 (s)	300 (m)
7	3340–3200 (br, split)	1620 (sh)	1560 (br)	1260 (w)	465 (m)	
8	3290–3120 (split)	1635 (s)	1605 (s)	1255	490 (m)	325 (m)
9	3340–3140 (split)	1635 (s)	1605 (s)	1255	490 (m)	
10	3360–3100 (split)	1635 (s)	1600 (m)	1265		

Key: s, strong; sh, shoulder; m, medium; w, weak; br, broad.

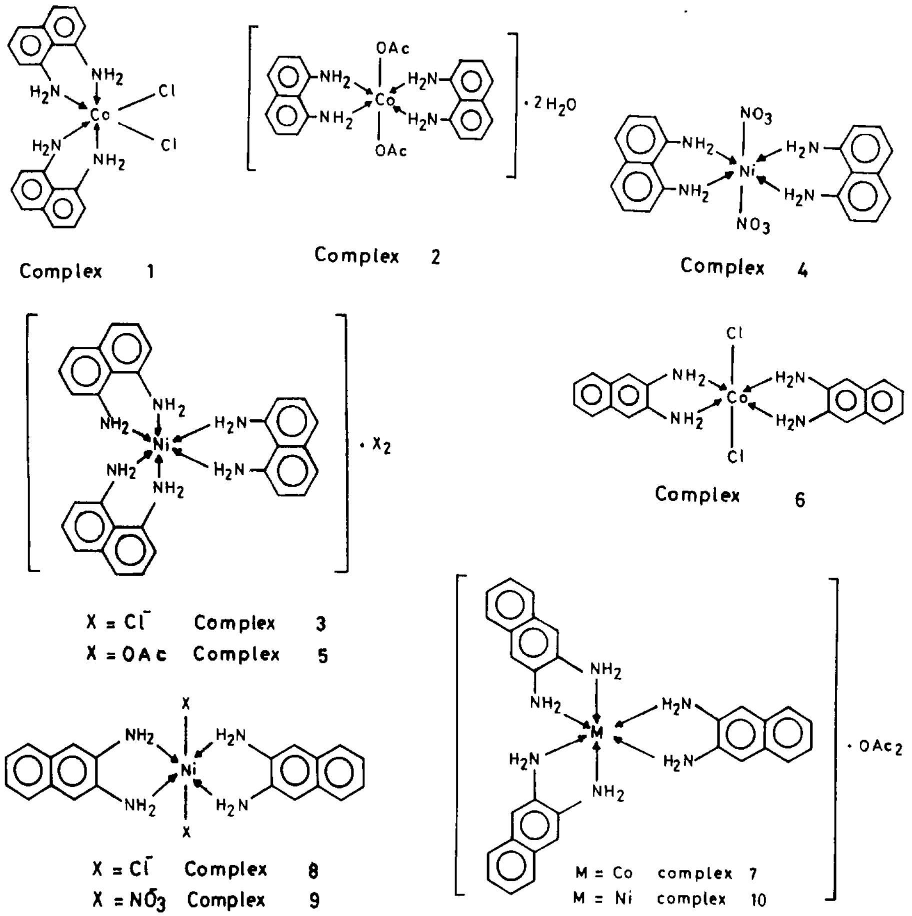
in that temperature range. The DTA curve of the cobalt complex 2 also shows an endothermic peak in the temperature range 40–90 ° C. This peak is assigned to desolvation (loss of water of crystallisation). This assignment was confirmed by the weight loss (6.90%) obtained by the thermogravimetry curve (Fig. 1), which corresponds to two molecules of water (6.81%). The X-ray diffraction patterns of both solvated and desolvated forms are the same and are characterised by a multitude of reflections of low intensity, indicating a low degree of crystallinity [19]. This result, in addi-

TABLE 3

Electronic spectra of the complexes

Complex	Solvent	λ_{max}(nm)	
		d–d transition	Other bands
1	DMF	770 (s)	680 (sh), 510 (br), 340 (sh)
2	DMF	750 (w)	500 (sh), 290 (m)
3	Methanol	660 (sh)	520 (sh), 440 (sh), 340 (s)
4	Methanol	660 (sh)	520 (sh), 420 (sh), 345 (s)
5	Methanol	580–440 (br)	380 (sh)
6	Methanol	660 (sh)	600 (sh), 520 (sh), 460 (sh), 340 (m)
7	Chloroform	740 (sh)	500 (sh), 330 (br)
8	Methanol	700 (w)	400 (sh), 340 (s)
9	Methanol		380 (sh), 340 (s)
10	Methanol	700 (sh)	450 (sh), 425 (s), 350 (s)

Key: sh, shoulder; s, strong; br, broad; m, medium; w, weak.



Complex 1

Complex 2

Complex 4

$X = Cl^-$ Complex 3
$X = OAc$ Complex 5

Complex 6

$X = Cl^-$ Complex 8
$X = NO_3^-$ Complex 9

M = Co complex 7
M = Ni complex 10

Scheme 3.

tion to the ease of desolvation (40–90 ° C) suggests the weak interaction of water, i.e. water plays little or no role in the lattice forces and occupies the crystal voids [20].

On the other hand, if the initial temperature of the decomposition peak (Table 1) is taken as a measure of the thermal stabilities of the complexes, the following comments can be made:

1 The complexes of ligand **II** show a higher thermal stability than those of ligand **I**. This can be attributed to the chelate ring size. Ligand **II** forms a five-membered chelate ring with a higher thermal stability than the six-membered one which can be formed by ligand **I**.

2 The cobalt complexes (except complex 2) show a higher thermal stability than those of nickel. This can be discussed in terms of repulsions among electron pairs in the valence shell of the central ion. Both nickel and cobalt ions in the investigated complexes have multiple bonding (six bonds) in their valence shells. But due to the higher electronegativity of nickel than

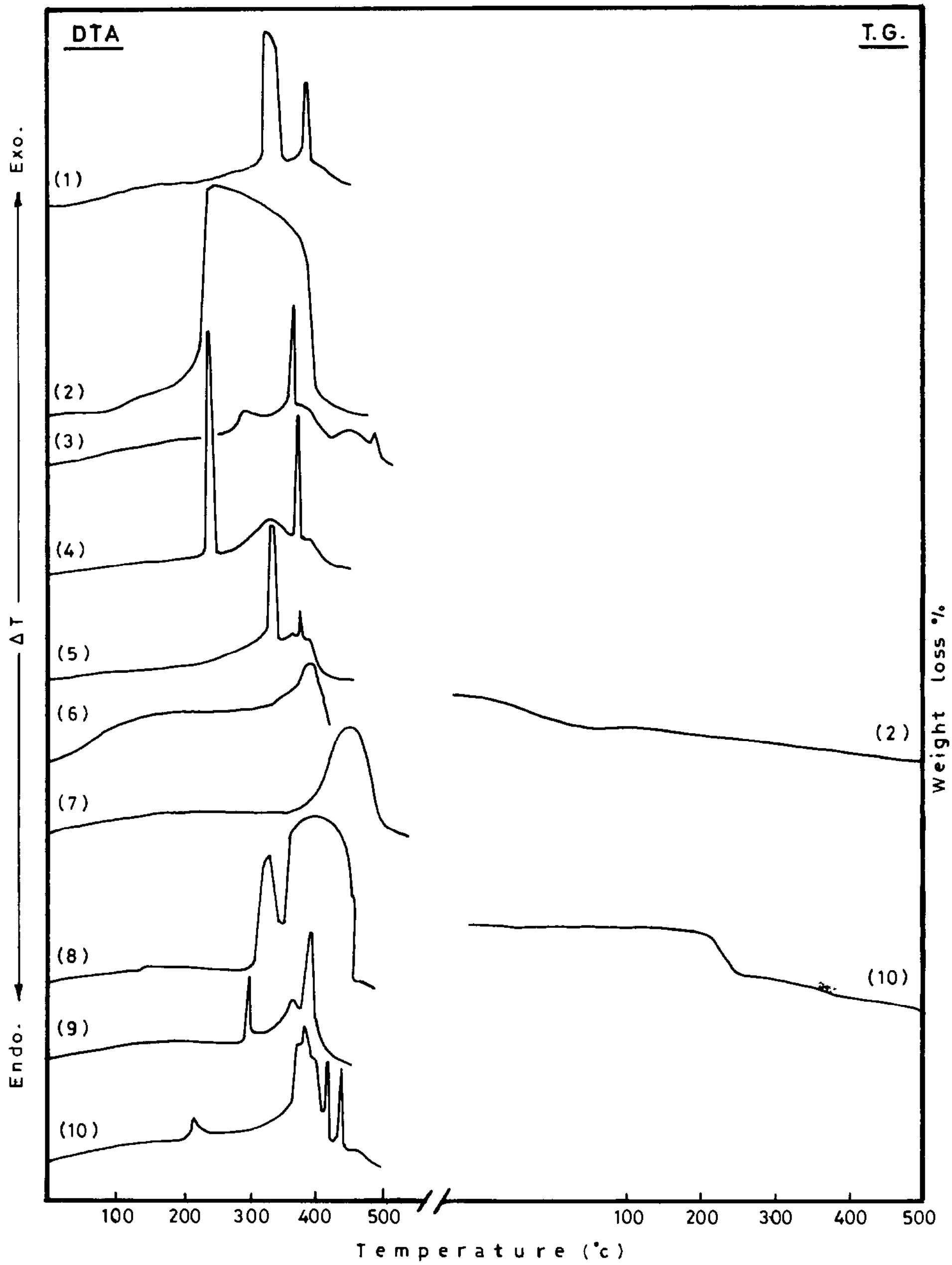


Fig. 1. DTA and TG curves of Co(II) and Ni(II) complexes.

that of cobalt, the space occupied by a bonding pair in the valence shell of nickel is greater than that of cobalt. This leads to a higher repulsion between the bonding pairs in the valence shell of nickel (small ionic size), which in turns alters the bond angles from those of ideal octahedral, giving a lower stability [21]. It is noteworthy that the situation may be inverted with lower coordination numbers, where the repulsion between electron pairs is decreased. Therefore, the electronegativity of the central metal ion becomes the predominant factor in the stability.

3 The lower thermal stability of the cobalt acetato complex (complex 2) may be attributed to the repulsion between the multiple-bonding electron pairs in the valence shell of cobalt, as well as to the higher repulsion obtained by the non-bonded pairs of electrons on the axial donating oxygen of the acetate group and the bonded electrons. This explanation can be confirmed by the lower thermal stability of the nitrato complexes of nickel that show the same effect (repulsion between bonding and non-bonding electrons).

4 The high thermal stability difference (150 ° C) between the acetato complex of cobalt (7) and that of nickel (10) may be discussed in terms of a steric effect, in addition to the higher repulsion between bonded electron pairs in the valence shell of the nickel ion. The small ionic size of nickel relative to that of cobalt leads to a higher steric hindrance between the individual (not fused) chelates, giving a lower stability. This explanation was confirmed by the thermogravimetric weight loss (24%) of complex 10 (Fig. 1), which corresponds to one amine molecule (24.28%) and relieves the strain in the complex. Additional evidence was provided by the small thermal stability difference (25 ° C) between the chloro-complex of cobalt (6) and that of nickel (8) which show no steric effect because they have only two chelate rings.

From the above discussion, it can be seen that the data obtained are consistent with the suggested structures.

REFERENCES

1 W.W. Wendlandt, J. Inorg. Nucl. Chem., 25 (1963) 833.
2 Y. Fukuda and K. Sone, J. Inorg. Nucl. Chem., 34 (1972) 2315.
3 D.A. Buckingham and D. Jones, Inorg. Chem., 4 (1965) 1387.
4 M. Corbella and J. Ribas, Inorg. Chim. Acta, 132 (1987) 75.
5 W.K. Musker and M.S. Hussain, Inorg. Chem., 8 (1969) 528.
6 L.K. Singh and S. Mitra, Inorg. Chim. Acta, 133 (1987) 147.
7 M.A. Hitchman and G. Jamer, Inorg. Chim. Acta, 88 (1984) 119.
8 A. Ghosh, G. De and N. Ray Chaudhuri, J. Chem. Res., 104 (1987) 1.
9 B.A. Howell and E.W. Walles, Inorg. Chim. Acta, 142 (1988) 185.
10 D.P. Singh and V.B. Rana, Transition Met. Chem., 11 (1986) 23.
11 L. Vogel, Quantitative Inorganic Chemistry, 3rd edn., Longmans, London, 1961.
12 K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 3rd edn., Wiley–Interscience, New York, 1977.
13 B.M. Gatehouse, S.E. Livingstone and R.S. Nyholm, J. Chem. Soc., (1957) 4222.
14 J. Reedijk and J. Verbiest, Transition Met. Chem., 3 (1978) 51.
15 M. Keeton, A.B.P. Lever and B.S. Ramaswamy, Can. J. Chem., 48 (1970) 3185.
16 N. Saha and D. Mukherjee, Polyhedron, 2 (1983) 47.

17 L. Sacconi, Transition Met. Chem., 4 (1968) 199.
18 C.D. Burbridge, D.M.L. Goodgame and M. Goodgame, Inorg. Chim. Acta, 4 (1970) 231.
19 A.M. Donia and M.A. El-Ries, Thermochim. Acta, 174 (1989) 65.
20 S.R. Byran, Solid State Chemistry of Drugs, Academic Press, New York, London, 1982.
21 T. Moeller, Inorganic Chemistry, 1st edn., Wiley, New York, 1982.