

## COMPLEXES OF 1,4-DIAMINOBENZENE TETRACETIC ACID WITH SOME OF THE TRANSITION METALS

Saeed-ur-Rehman\*, Farhat-un-Nisa and Masood Ahmed

Department of Chemistry, University of Peshawar, Peshawar, Pakistan

(Received 27 April 1995; accepted 21 October 1997)

The chemistry of the novel hexadentate amino carboxylic acid ligand 1,4-diaminobenzene tetracetic acid is reported. The title compound (BDTA) can be compared with ethylene diamino tetracetic acid (EDTA) in its structural and characteristics on coordination to several metal ions. The complexes of (BDTA) with Cobalt (II), Nickel (II), Copper (II), Manganese (II) and Zinc (II) are prepared. The structural properties of the ligand and its complexes are proposed based on elemental analysis, UV-visible, Infra-red, NMR and thermogravimetric analysis and magnetic moments.

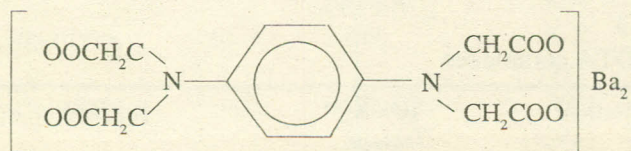
**Key words :** 1,4-diaminobenzene tetracetic acid, Coordination compounds, EDTA.

### Introduction

Multidentate chelating agents can assume a variety of orientations in complexes and form more stable complexes than mono-dentate and bi-dentate chelating agents (Dwyer and Mellor 1964).

Acylic diamine like ethylenediamine and its derivatives are among the well characterized chelating agents for transition metal ions (Hendra and Powell 1960). Similarly aromatic heterocyclic diamines are also the good complexing agents (Schwarzenbach and Ackermann 1949; Mann and Watson 1958; Musker and Hussain 1966; Braun 1985; Khawar and Bozdar 1991; Jolley *et al* 1992).

The present report is concerned with the synthesis and coordination chemistry of ligand 1,4-diaminobenzene tetracetic acid (BDTA), which is derived from 1,4 benzenediamine by replacing hydrogen of amino group with acetate group. The ligand is obtained as the barium salt.



Barium salt of 1,4-Diaminobenzene tetracetic acid [BDTA].

### Materials and Methods

1,4-Diaminobenzene and sulphate salts of nickel (II), cobalt (II), copper (II), manganese (II) and zinc (II) were obtained from standard source suppliers. They were of analytical grade

\*Author for correspondence.

and were used without further purification. The solvents used in the synthetic work were distilled twice.

**Ligand.** The ligand BDTA was prepared according to the procedure described by Leg and Cook (1965).

A cold solution of 41 g (1.02 mol) of sodium hydroxide in 125 ml of water was added to a cold stirred solution of 47.5g (0.5 mol) of monochloro-acetic acid in 35 ml of water at such a rate that the temperature did not rise above 10°C. To this stirred solution, 27g (0.5 mol) of 1,4-diaminobenzene solution was added dropwise over a period of 90min. After waiting for 22 h, 65 g (0.26 mol) of BaCl<sub>2</sub> · 2H<sub>2</sub>O dissolved in 125 ml of boiling water was rapidly added. The heavy cloudy suspension of barium benzene diamine-tetracetic acid formed which was heated at 160°C for 30 min. The precipitate was filtered from the hot solution, thoroughly washed with water and then by acetone. The compound was dried for 2 h in vacuum oven at 50°C. (m.p/Dec 300°C).

**Preparation of the Complexes.** The preparation of Ni(II), Cu(II), Co (II), Mn (II) and Zn (II) complexes was of the same procedure. The reaction was carried out in three necked flask using deoxygenated water.

To the stirred slurry of ligand (BDTA) in boiling water was added dropwise a hot aqueous solution of the metal sulphate. The mixture was heated at 100°C and stirred for 15 min. The precipitated BaSO<sub>4</sub> was removed by filtration.

Evaporation of the filtrate to near dryness under vacuum produced precipitate of the complexes. The precipitate was washed with water then with acetone and dried in an oven under vacuum at 50°C.



**Elemental Analysis.** The elemental analysis of ligand (BDTA) and its complexes were carried out on Carbon Analyzer CTA 5C, whereas the anions were determined by the usual conventional methods (Vogel 1962) and C, H, and N elemental analysis were performed through the courtesy of H E J Research Institute of Chemistry in Karachi.

**Magnetic Susceptibility Measurements.** The magnetic moments of the complexes at room temperature were determined by the Gouy method. A double ended Gouy tube was calibrated using  $\text{Hg}[\text{Co}(\text{SCN})_4]$  as standard. Pascal's Constants were used to the observed molar susceptibilities of crystalline complexes for the diamagnetism of the ligand and

**Table 1**  
Elemental analysis of  $\text{Ba}_2\text{BDTA}$

Ligand	Colour	M.P.	C%	N%	H%	O%	Ba%
$\text{Ba}_2$	Greenish	300°C	26.80	4.40	1.82	22.00	44.58
BDTA	white		(27.51)	(4.59)	(1.96)	(0.96)	(44.98)

Theoretical percentages are given in parenthesis.

the anions involved (Figgis and Lewis 1960).

**Infrared Spectra.** The Infra-red absorption spectra of the solid complexes were obtained with I.R Spectrometer Model SP-3-100 PYE Unicam A.M. The I.R spectra were obtained in a nujol mull supported on NaCl and KBr plates.

**UV-Visible Spectra.** The solid state absorption spectra were measured by placing filter paper (Whatman No.1) soaked in nujol mull of the complexes, into the beam of JASCO UNIDEC-I recording spectrophotometer in place of cell.

**Nuclear Magnetic Resonance Spectra.** The H NMR data for the ligand were obtained by NMR spectrophotometer Model JNM-PMX60. Spectra for proton NMR were measured relative to tetramethylsilane (TMS) as an external standard.

**Thermogravimetric Analysis.** Thermogravimetric analysis of the complexes was done on a recording stanton (England) thermogravimetric balance Model HT.SM. Analytically pure anhydrous complexes were used and the thermal measurements were made in triplicate for each complex.

**Table 2**  
Analytical data for BDTA complexes

Complex	Colour	M.P °C	Metal ion%	C%	N%	H%
$\text{H}_2[\text{Ni}(\text{BDTA})]$	Dark	352	14.79	41.80	7.15	3.79
	Green		(14.93)	(42.42)	(7.06)	(3.52)
$\text{H}_2[\text{Cu}(\text{BDTA})]$	Green	340	15.00	42.80	7.25	3.85
			(15.69)	(41.89)	(6.98)	(3.49)
$\text{H}_2[\text{Co}(\text{BDTA})]$	Dark	320	15.00	42.20	7.42	3.65
	Brown		(14.72)	(42.30)	(7.05)	(3.53)
$\text{H}_2[\text{Mn}(\text{BDTA})]$	Dark	330	13.56	43.08	7.45	3.76
	Brown		(14.04)	(42.75)	(7.12)	(3.56)
$\text{H}_2[\text{Zn}(\text{BDTA})]$	White	336	15.89	42.38	7.34	3.52
			(16.2)	(41.65)	(6.49)	(3.34)

Theoretical percentages are given in parenthesis.

**Table 3**  
Magnetic data for BDTA complexes

Compound	Temperature K°	Diamagnetic Correction (cgsu)	$10^6 \times \chi_m^{\text{cor}}$ (cgsu)	$\mu_{\text{eff}}$ (B.M)
$\text{H}_2[\text{Ni}(\text{BDTA})]$	303	170.84	1514.88	4.08
$\text{H}_2[\text{Cu}(\text{BDTA})]$	303	170.84	1342.24	1.71
$\text{H}_2[\text{Co}(\text{BDTA})]$	303	170.84	15969.25	5.87
$\text{H}_2[\text{Mn}(\text{BDTA})]$	303	170.84	96366.00	5.45
$\text{H}_2[\text{Zn}(\text{BDTA})]$	303	170.84	242.00	Dia-mag

$$\mu_{\text{eff}} = 2.84 \chi_m T$$



## Results and Discussion

Analytical data of BDTA and its complexes show that BDTA behaves as hexadentate chelating agent and bears resemblance to EDTA in terms of chelating effects. Analytical data also show that BDTA form mono complexes of the general formula  $H_2 [M(BDTA)]$ . Where M represents Cu, Ni, Co, Zn and Mn metal ions. All the complexes are partially soluble in water and are completely insoluble in most organic solvents, indicating that these complexes may be of polymeric in nature (Huhee 1978).

**Magnetic Studies.** The magnetic moments of the Ni (II), Co (II), Cu (II) and Mn (II) complexes have values within the range of 4.05-6 B.M., showing paramagnetic character of the complexes (Table 3). These values indicate that there is no metal to metal interaction. The magnetic moment of Cu(II) complex is 1.71 B.M., which is very close to spin value for the unpaired electron (Hussain and Saeed-ur-Rehman 1978).

**U.V-Visible Spectra of BDTA Complexes.** Reflectance spectra were observed for various complexes (Table 4).  $H_2[Cu(BDTA)]$  has a single broad peak in the range of 12400 - 12600  $cm^{-1}$  which may contain more than one transition favouring octahedral configuration (Schwarzenbach and Flaschka 1969). The spectrum of  $H_2[Ni(BDTA)]$  shows bands in the region of 13500 - 26500  $cm^{-1}$ . These transition are assigned to  ${}^3T_{1g} \rightarrow {}^3A_{2g}(F)$  and  ${}^3T_{1g} \rightarrow {}^3A_{2g}(P)$  excitation, showing distorted octahedral geometry.  $H_2[Co(BDTA)]$  complex shows a broad peak with a maxima at 10,000  $cm^{-1}$ , which represent  $[t_{2g}{}^6e_g{}^1 \rightarrow t_{2g}{}^5e_g{}^2]$  excitation. Mn (BDTA) complex has a very low  $\Lambda_{max}$  excitations in the rang of 18000 -

**Table 4**

Electronic absorption data of BDTA complexes

Complex	$\Lambda_{max}$	Comments
$H_2[Ni(BDTA)]$	410	${}^3T_{1g} \rightarrow {}^3A_{2g}(F)$
" " "	615	${}^3T_{1g} \rightarrow {}^3A_{2g}(P)$
$H_2[Co(BDTA)]$	560	$t_{2g}{}^6e_g{}^1 \rightarrow t_{2g}{}^5e_g{}^2$
$H_2[Cu(BDTA)]$	610	d-d

**Table 5**

Significant bands in the I.R spectra of BDTA complexes

Compound	O	Phenyl	C-N
$H_2BDTA$	1380m	1580s	820s
$H_2[Ni(BDTA)]$	1400b	1600b	920s
$H_2[Cu(BDTA)]$	1380b	1580b	840s
$H_2[Co(BDTA)]$	1400m	1600b	820s
$H_2[Mn(BDTA)]$	1380b	1600b	840s
$H_2[Zn(BDTA)]$	1380m	1600b	920b

Where b = broad      m = medium      s = sharp

**Table 6**

Proton N.M.R. data for 1,4-diamino benzene and BDTA

Compound	$H_a$ [4H]	$H_b$ [4H]	$H_c$ [8H]
1,4-Diaminobenzene	6.74	7.24	--
BDTA	6.54	--	1.40

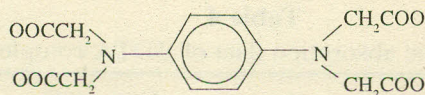
**Table 7**

Thermogravimetric analysis of BDTA complexes

Complexes	Initial Weight (mg)	Evaporating Moiety	Weight Loss (mg)	Evaporating Moiety	Weight Loss (mg)	Residue	Weight of Residue
$H_2[Ba(BDTA)]$	60	BDTA 240-400°	30 (30)	---	--	Bao	30 (30)
$H_2[Ni(BDTA)]$	30	CO <sub>2</sub>	3 (3)	---	--	Ni(BD)	7 (7)
$H_2[Cu(BDTA)]$	100	CO+H <sub>2</sub> O 80-200°	29 (29)	CO+H <sub>2</sub> O 200-400°	30 (31)	Cu(BD)	40 (41)
$H_2[Co(BDTA)]$	90	CO+H <sub>2</sub> O 100-320°	20 (20)	CO+H <sub>2</sub> O 320-600°	44 (47)	CoO	26 (23)
$H_2[Mn(BDTA)]$	100	CO+H <sub>2</sub> O 40-340°	20 (20)	CO+H <sub>2</sub> O 340-560°	47 (47.5)	Mn(BD)	33 (32)
$H_2[Zn(BDTA)]$	60	CO+H <sub>2</sub> O 140-420°C	20 (20.7)	---	---	Zn(BD)	40 (39.29)

BD = Benzene diamine. Theoretical percentages are given in the parenthesis.





1,4-Diaminobenzene tetracetic acid [BDTA]

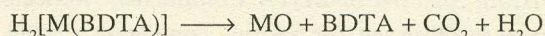
41000  $\text{cm}^{-1}$  and only on the basis of absorption spectra structure can not be assigned (Fig 2-5).

**Infrared Spectra.** A summary of IR bands of the solid complexes in nujol mull in the selected region has been given in the Table 5. The IR spectra of BDTA has sharp bands at 1380, 1580 and 820  $\text{cm}^{-1}$  assigned to C-O,  $\text{C}_6\text{H}_6$  and C-N vibrations, respectively. In the metal complexes these bands either shift to high frequency or become broad or/and split up into two or three bands, suggesting coordination through these groups. In complexes of Ni, Cu, Co, Mn, and Zn three distinct absorptions bands at 1600, 1420, 1380, and 920  $\text{cm}^{-1}$  are observed. The asymmetric stretching mode of acetate group shifts from 1380  $\text{cm}^{-1}$  to 1420  $\text{cm}^{-1}$  in metal complexes, and absorption frequency for N-C stretch at 820  $\text{cm}^{-1}$  in BDTA also shows changes in position in the metal complexes, showing coordination both through nitrogen and acetate groups (Nakamoto 1970).

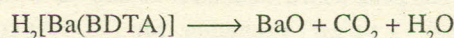
**$^1\text{H.N.M.R}$  Spectral Analysis.** The resonance lines assignment for the ligand (BDTA) and strating material 1,4-diaminobenzene are given in Table 6, a typical spectrum is shown in (Figure 1). Several features are apparent. The proton associated with amino-carboxylate and amino groups are found at lower field i.e. 6.74 ppm. The protons associated with the benzene ring are found at 7.24 ppm. In case of BDTA the resonance lines of protons of amino groups are at upper

field i.e. 1.40 ppm (due to attraction of electron by barium ion). Integration of peaks is well in agreement with that of the formula.

**Thermogravimetric Analysis.** The thermal stabilities of BDTA complexes of copper, cobalt and manganese are same but differ from the nickel complex, indicating a difference in their structures Table 7. (Hussain and Saeed-ur-Rehman 1978). The pyrolysis curves of the copper, cobalt and manganese complexes indicate the removal of two acetate groups from the ligand as carbon dioxide and as water moieties in the temperature range of 100-420°C. It is remarkable that the second acetate group remains attached and vaporizes slowly as compared with other acetate group, leaving behind 1,4-diaminobenzene diacetate and metal oxide as the residue. In  $\text{H}_2$  [(Ni (BDTA))] complex very slow vaporization of unknown moiety take place and the complex shows stability up to 750°C. The thermal behavior of the complexes may be summarized by the following equation.



The difference in thermal behaviour of the complexes of Co, Cu and Mn from Ni at least points towards the difference in the coordination geometry of these complexes. The thermal behaviour of BDTA differs significantly from its complexes. The thermogram of BDTA indicates the detachment and vaporization of all the moieties in the range of 200-400°C and leaving BaO as the residue.



The decomposition pattern is shown in Fig. 6-8.

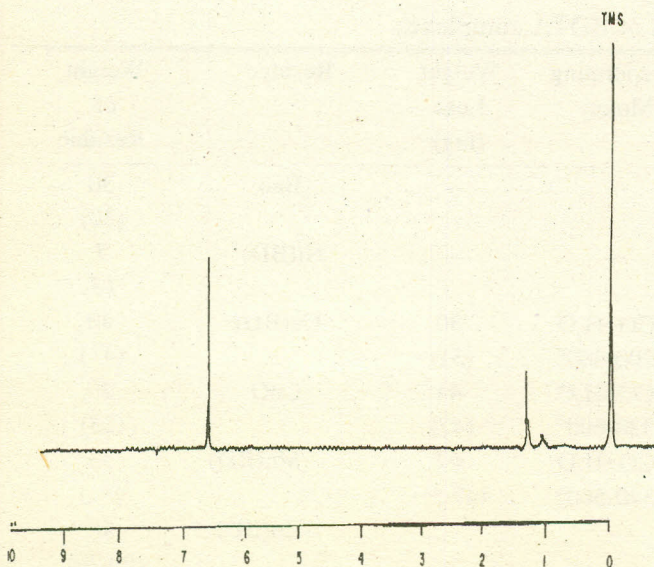
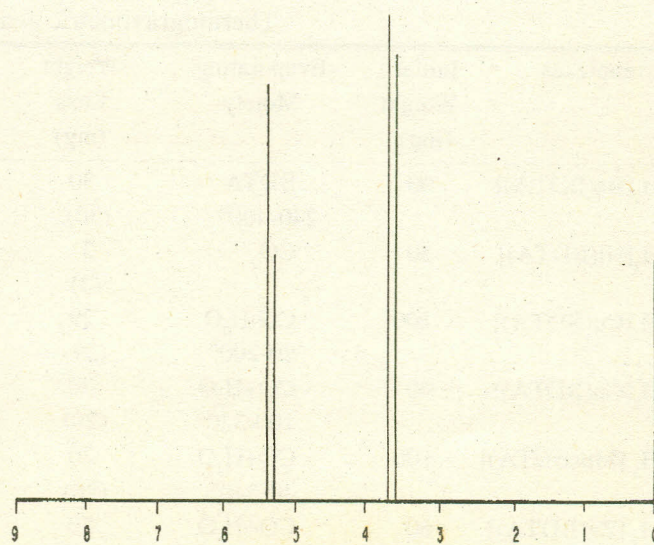


Fig. 1. Proton NMR spectra A of BDTA.

Fig. 2.  $\text{C}^{13}$  spectra A of BDTA.



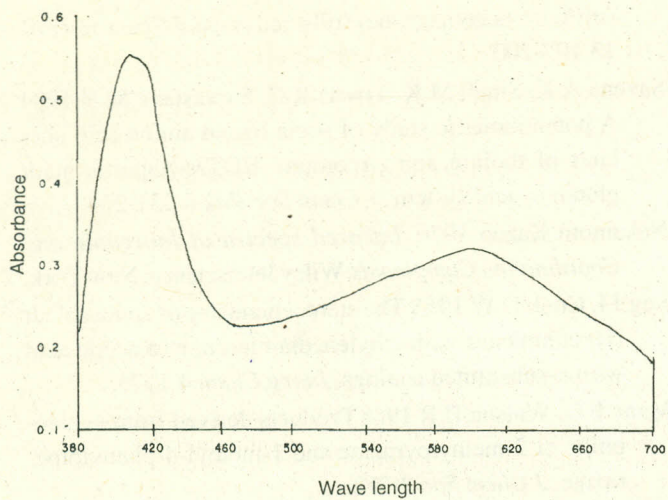


Fig. 3. Absorption spectra of nickel BDTA complex

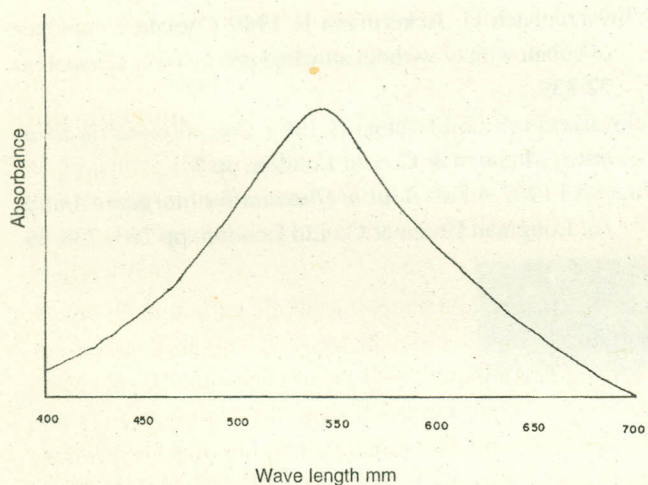


Fig. 4. Absorption spectra of cobalt BDTA complex.

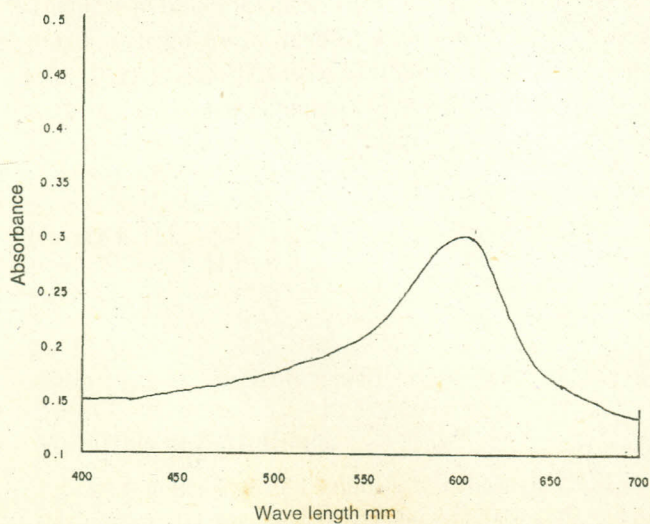


Fig. 5. Absorption spectra of copper BDTA complex.

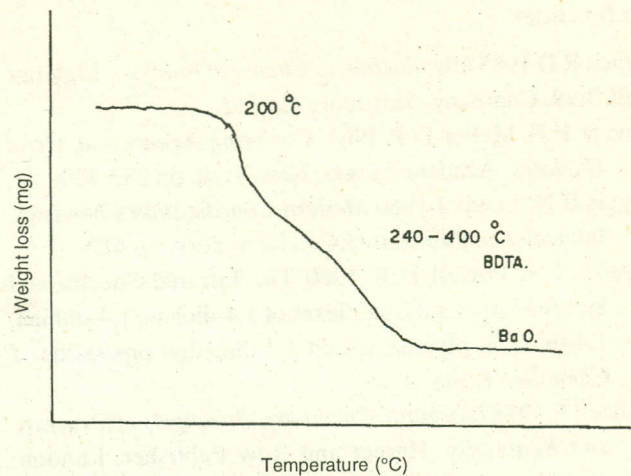


Fig. 6. Thermogram for BDTA.

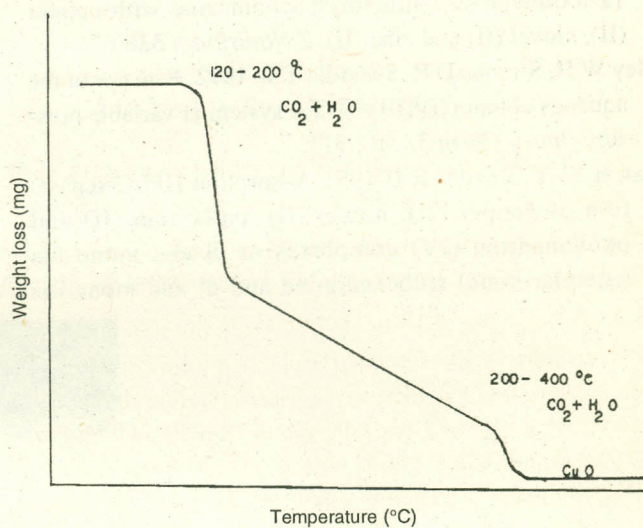


Fig. 7. Thermogram for BDTA.

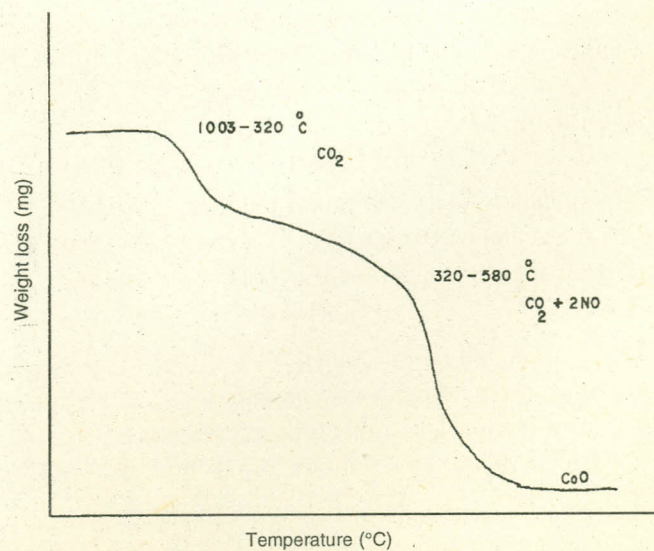


Fig. 8. Thermogram for CO (BDTA) complex.



## References

- Braun R D 1985 *Introduction to Chemical Analysis*. McGraw Hill Book Company, Singapore, pp 112.
- Dwyer P F, Mellor D P 1964 *Chelating Agents and Metal Chelates*. Academic Press, New York, pp 283-329.
- Figgis B N, Lewis J 1960 *Modern Coordination Chemistry*. Interscience Publication Co., New York, pp 412.
- Hendra P J, Powell D B 1960 The Infrared Spectra and Structure of metal Complexes of 1,4-dioxan, 1,4-dithian, 1,4-thioxan, piperazine and 1,4-dimethyl piperazine. *J Chem Soc* **5** 105.
- Huhee J E 1978 *Inorganic Chemistry, Principles of Structure and Reactivity*. Harper and Row Publisher, London, pp 485.
- Hussain M S, Saeed-ur-Rehman 1978 Complexes of 5,6,11,12-tetrahydro-2,8-dimethylphenomazine with copper (II), nickel (II) and zinc (II). *Z Naturforsch* **33b** 67.
- Jolley W H, Stranks D R, Swaddle T W 1992, Kinetics of the aqueous cobalt (II)/(III)/EDTA system at variable pressure. *Inorg Chem* **31** 507-511.
- Khawar M Y, Bozdar R B 1991 Adsorption HPLC separation of copper (II), nickel (II), palladium (II) and oxovanadium (IV) complexes of dl and mono-bis (acetylacetonate)-stilbenedimine and dl and mono-bis (trifluoro-acetylacetonate) stilbenedimine. *J Chem Soc Pak* **13** 197-200.
- Saxena A K, Singh M K, Tiwari R C, Sarvastava M N 1984 A potentiometric study of some ligand amino acid chelates of thium and zirconium: EDTA-Aspartic acid/ glutamic acid system. *J Chem Soc Pak* **6** 231-234.
- Nakamoto Kazuo 1970 *Infrared spectra of Inorganic and Coordination Compounds*. Wiley Interscience, New York.
- Leg J I, Cook D W 1965 The stereochemistry of some cobalt (II) complexes with ethylenediamine-n, n'-diacetic acid with n-substituted analogs. *Inorg Chem* **4** 1576.
- Mann F G, Watson H R 1958 Products derived from nucleophilic of 2-methylpyrazine and 1-methyl-4-phenylpiperazine. *J Chem Soc* **2** 772.
- Musker W K, Hussain M S 1966 Square-planar complexes of nickel (II) and copper (II) with 1,5-diazacyclooctane. *Inorg Chem* **5** 1416.
- Schwarzenbach G, Ackermann H 1949 Chelate complexes of cobalt with or without attached group. *Helv Chim Acta* **32** 839.
- Schwarzenbach G, Flaschka H 1969 *Complexometric titrations*. Methuen & Co Ltd London, pp 8.
- Vogel A I 1962 *A Text Book of Quantitative Inorganic Analysis*. Longman Green & Co Ltd London, pp 263, 738-39.