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Correlation between ionic radius and thermal decomposition of Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) diethanoldithiocarbamates

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Abstract

Diethanoldithiocarbamate complexes with Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) were prepared and characterised by elemental analysis, infrared spectroscopy and flame atomic absorption spectroscopy. Their thermal decomposition was investigated by TG/DTG and DSC techniques under dynamic air and nitrogen atmospheres. These studies showed that the smaller the metallic ionic radius the higher was their thermal stability and that the bidentate complex decomposed in a direct way, with no evidence of thyocyanate intermediates. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Dithiocarbamates (DTC) are the products of the reaction between an primary or secondary amine with carbon disulphide in basic media. Such compounds have been widely used in analytical chemistry as complexing agents [1–3], fungicides, pesticides and insecticides in agriculture [4–6], and presents a widespread application in industry. It is important to know the thermal properties of the DTC for these applications where they are submitted to severe temperature changes.

An other important branch of the use of DTC is in medicine as anti-alcoholic drug [7,8], tuberculostatic [9] and more recently as co-adjuvant in AIDS treatment [10].

The diethanoldithiocarbamate (bis-2-hydroxyethyldithiocarbamate, DEDC) is one of the most interesting compound due to the presence of two –OH groups in its structure, which allows the obtain more water soluble complexes. However, few thermoanalytical data are available on DEDC metallic complexes [11,12].

In the present work, structural and thermoanalytical studies of the complexes with general formula ML_2 (M=Fe, Co, Ni, Cu and Zn) with DEDC were performed. These studies showed that there is a relationship between ionic radius of the metal and the thermal stability of the complex.

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2. Experimental

2.1. Preparation of ligand

All the reagents were of analytical grade and used as received. DEDC $[S_2CN(CH_3CH_2OH)_2]^- NH_4^+$ was prepared by dissolution of diethanolamine (0.1 mol) and NH_4OH (0.1 mol) in 50.0 cm^3 of ethanol in an Erlenmeyer. The solution was cooled in an ice bath and carbon disulphide (0.1 mol) slowly added under constant agitation. The resulting white solid was filtered and washed several times with cold ethanol.

2.2. Preparation of complexes

The complexes were prepared by direct reaction of DEDC and $(NH_4)_2Fe(SO_4)_2$, $CoCl_2{\cdot}6H_2O$, $NiCl_2{\cdot}6H_2O$, $CuCl_2{\cdot}2H_2O$ or $Zn(OOCCH_3)_2$, in the molar ratio 1:2 (ligand to metal). The characteristic solids formed in each case were filtered, washed with cooled ethanol several times. The compounds were purified by recrystallisation in ethanol and dried under vacuum for 8 h at 60°C. Finally, the complexes were stored in a refrigerator in dark containers.

2.3. Instrumentation

The compounds were characterised by FTIR spectroscopy in KBr pellets, on a Nicolet 5SXC spectrophotometer. Metals were assigned by flame atomic absorption spectroscopy using an Intralab AA12/1475 (Gemini) spectrophotometer. C, H, N contents were determined by elemental analysis using a Fisons EA 1108 CNHS-O instrument.

TG curves were recorded on a DuPont 9900 thermoanalyser coupled to a TGA 951 thermogravimetric module under a gas flow of 100 cm^3 min^{-1} (N_2 or air), in a Pt crucible, at 10°C min^{-1} heating rate and using samples of about 7 mg of each compound at atmospheric pressure. DSC curves were recorded on a DuPont 9900 thermoanalyser coupled with a DSC 910 calorimetric module under a gas flow of 100 ml min^{-1} (N_2 or air), in aluminium covered pans

Table 1
Results of the characterisation of the complexes: colours, FTIR bands, and analytical data

Compound	Colour	FTIR bands (cm^{-1})		Found (calcd.) (%)			
		C=S	C–N	Metal	C	N	H
$Fe(DEDC)_2$	Black	987[a]	1482	12.71 (13.41)	28.08 (28.82)	6.49 (6.72)	4.58 (4.80)
$Co(DEDC)_2$	Pale green	988[a]	1489	13.24 (14.05)	27.91 (28.61)	6.33 (6.68)	4.56 (4.77)
$Ni(DEDC)_2$	Light green	985.1023[b]	1514	13.68 (14.00)	28.65 (28.62)	6.72 (6.68)	4.36 (4.77)
$Cu(DEDC)_2$	Dark green	982.998[b]	1493	15.86 (16.54)	28.41 (28.30)	6.48 (6.60)	4.27 (4.72)
$Zn(DEDC)_2$	White	989[a]	1490	15.28 (15.35)	28.18 (28.18)	6.70 (6.57)	4.48 (4.70)

[a] Singlet.

[b] Doublet.

Table 2
TG (mass losses, residues and temperature range) and DSC data corresponding to the composition of the Pyr compounds under nitrogen

Process	Temperature range (°C)	Mass loss or residue (%)		DSC data[a] peak temperature (°C)
		TG	Calcd.	
$Fe(\ DEDC)_2 \rightarrow FeS$	134–530	22.04	21.11	143(endo), 168(endo), 226(endo), 173(exo)
$Co(DEDC)_2 \rightarrow CoS$	175–603	21.14	21.69	195(exo), 209(endo), 231(endo), 306(endo)[b], 418(endo)[b]
$Ni(DEDC)_2 \rightarrow NiS$	190–531	21.66	21.65	208(exo), 303(endo)
$Cu(DEDC)_2 \rightarrow CuS$	171–304	22.55	22.54	144(endo), 184(endo), 188(exo), 226(endo)
$Zn(DEDC)_2 \rightarrow ZnS+C$	166–374	24.57	22.88	178(endo), 309(endo)

[a] Exo: exothermic process; endo: endothermic process.

[b] Shoulder.

with a role at the centre of the lid (ca. 1 mm), at 10°C min^{-1} heating rate and using samples of about 5 mg of each compound at atmospheric pressure. The DSC cell was calibrated using In metal (≥99.9%) as standard for temperature and energy. X-ray diffraction patterns were obtained on VEB-Karl Zeiss Jena URD6 diffractometer. Melting points were recorded using a dry furnace electrothermal digital melting point apparatus.

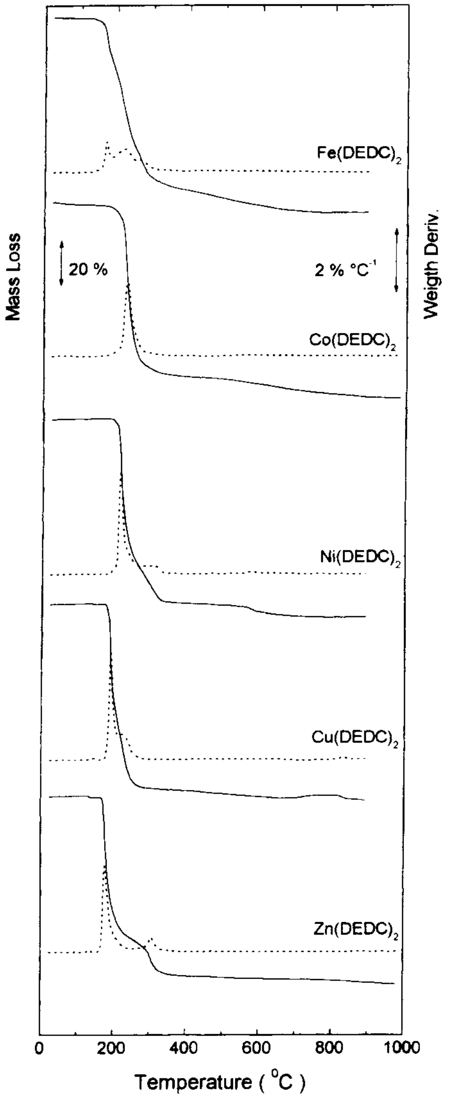


Fig. 1. TG/DTG curves of the complexes in *nitrogen* atmosphere (sample mass ca. 7 mg, 10°C min^{-1}, Pt crucible, N_2 flow 100 ml min^{-1}).

3. Results and discussion

The metallic complexes showed different colours as summarised in Table 1. In this table, the analytical data and the main FTIR absorption bands for the compounds are also presented. These were in agreement with the formulae proposed for the complexes confirming that they were all anhydrous.

The dithiocarbamate behaved as either a monodentate or bidentate ligand. FTIR spectroscopy enabled a distinction between these two possibilities from the C=S stretching at 950–1050 cm^{-1}. If the compound

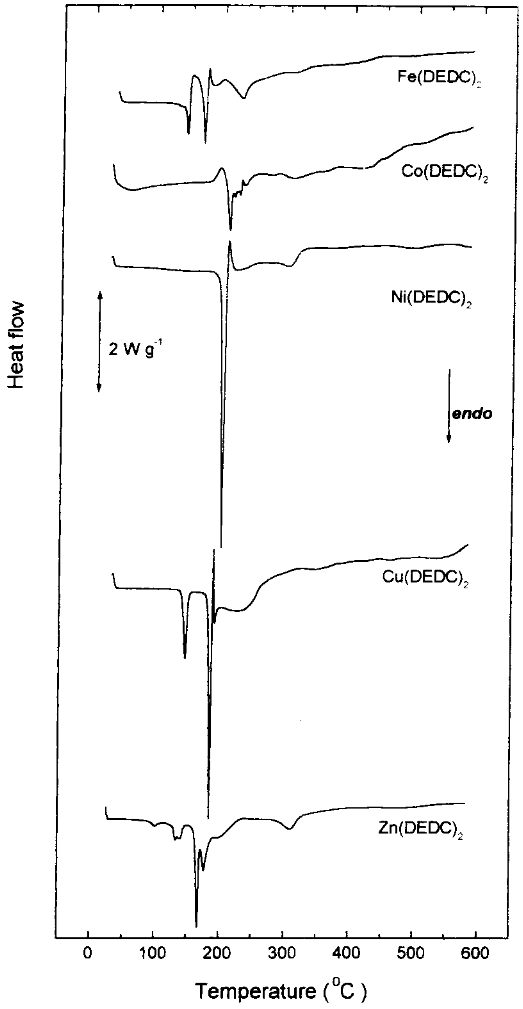


Fig. 2. DSC curves of the complexes in *nitrogen* atmosphere (sample mass ca. 5 mg, 10°C min^{-1}, covered Al crucible, N_2 flow 100 ml min^{-1}).

was monodentate, a doublet was observed in this region while a singlet appeared for a bidentate complex [13–16].

According to this criteria, the Ni(DEDC)$_2$ and Cu(DEDC)$_2$ showed monodentate character. All other compounds in the present series showed a singlet at 950–1050 cm^{-1} region and were bidentate. This is in agreement with earlier studies [17] and are related to the ionic radius of the two cations.

3.1. Thermal decomposition under nitrogen

All transitions, temperature ranges, mass losses and DSC analyses were carried out under nitrogen and are presented in Table 2. The TG/DTG and DSC response are shown in Figs. 1 and 2. Intermediates and final products are assigned in Table 2 as determined by their XRD patterns.

Ni, Cu and Zn complexes showed similar decomposition behaviour in that they decompose in two steps as can be seen for the TG/DTG curves generating the corresponding sulphides as the main decomposition products at characteristic temperature. However, the DSC responses showed that the processes were different. Ni and Cu complexes (monodentate) presented a sharp endotherm followed by an exotherm decomposition process, while Zn(DEDC)$_2$ showed only endothermic processes, in the 200–300°C temperature range.

The Cu(DEDC)$_2$ exhibited an endotherm before 200°C and the Zn(DEDC)$_2$ has three endotherms. Consecutive heating and cooling suggested that decomposition occurred at 144°C for copper 101, 133, 140°C for zinc complexes are related to crystalline changes. Melting was observed at 164°C for Zn(DEDC)$_2$.

TG/DTG-temperature plots for cobalt complex showed that decomposition occurred in a single step while the iron complex showed a complex decomposition in three steps, represented by successive endotherms and exotherms in the DSC response.

Table 3
TG (mass losses, residues and temperature range) and DSC data corresponding to the composition of the Pyr compounds under air. (intermediates and final decomposition products characterised by XRD patterns)

Process	Temperature range (°C)	Mass loss or residue (%)		DSC data[a] peak temperature (°C)
		TG	Caled.	
Fe(DEDC)$_2$→Fe(C$_4$H$_8$ONCS$_2$)$_2$+2H$_2$O	134–192	8.47[b]	8.65	145(exo)
Fe(C$_4$H$_8$ONCS$_2$)$_2$→FeL[c]+[N(C$_4$H$_8$O)$_2$]	192–312	41.50[b]	41.37	286(exo)
FeL[c]→Fe$_2$O$_3$	312–636	19.53[d]	19.20	457(exo)
Co(DEDC)$_2$→CoSO$_4$+C[e]	173–322	36.17[d]	36.95	199(exo), 230(exo), 207(endo), 219(endo)
CoSO$_4$→mixture of oxydes and sulphate	322–562	9.95[b]	–	523(exo)
Mixture→Co$_2$O$_3$	694–774	19.63[d]	19.77	–
Ni(DEDC)$_2$→Ni(SCN)$_2$	186–250	57.03[b]	57.38	200(exo), 207(endo)
Ni(SCN)$_2$→NiS[f]+C[e]	250–527	18.74[b]	–	270(exo)
NiS—NiO+Ni$_3$S$_4$+Ni$_3$S$_2$	527–655	−1.35[g]	–	440(exo)[h], 533(exo)[h]
NiO+Ni$_3$S$_4$+Ni$_3$S$_2$→NiO+aup[i]	655–762	19.95[d]	17.82	–
Cu(DEDC)$_2$→CuS	171–304	77.57[b]	77.46	185(endo), 189(exo), 256(exo), 288(exo)
CuS→Cu$_2$O(SO$_4$)	334–435	3.97[g]	–	377(exo), 429(exo)
Cu$_2$O(SO$_4$)→CuO	594–709	7.29[b]	–	–
Zn(DEDC)$_2$→ZnO+aup[i]	168–728	21.96[d]	19.19	178(endo), 302(endo), 510(exo)

[a] Exo: exothermic process; endo: endothermic process.
[b] Relative to mass loss.
[c] L: partially decomposed ligand.
[d] Relative to residue.
[e] Amorphous carbonaceous residue.
[f] Identified by test with HCl.
[g] Mass gain.
[h] Shoulder.
[i] Aup: amorphous unidentified product.

3.2. Thermal decomposition in air

All the transitions, temperature ranges, mass losses and DSC responses observed in air atmosphere are shown in Table 3, the TG/DTG and DSC responses are presented in Figs. 3 and 4. Intermediates and final products of the decomposition are assigned in Table 3 as characterised from their XRD patterns.

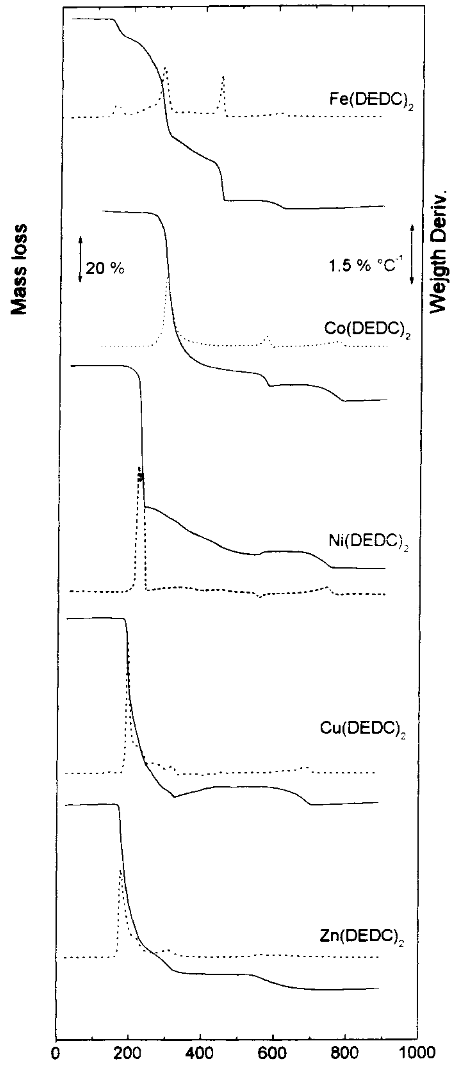


Fig. 3. TG/DTG curves of the complexes in *air* atmosphere (sample mass ca. 7 mg, 10°C min^{-1}, Pt crucible, air flow 100 ml min^{-1}).

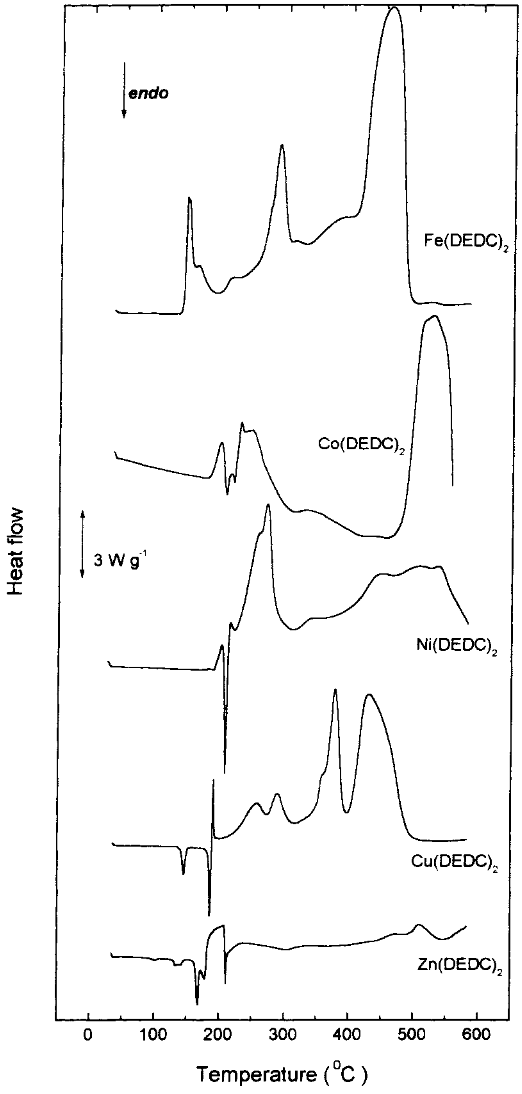
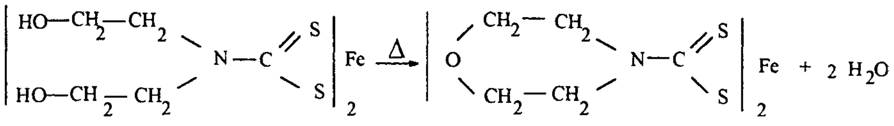


Fig. 4. DSC curves of the complexes in *air* atmosphere (sample mass ca. 5 mg, 10°C min^{-1}, covered Al crucible, air flow 100 ml min^{-1}).

The decomposition of the Co, Cu and Zn complexes were similar to those described under nitrogen, the differences being that they were observed above 400°C and involving the residues formed in the first step.

Iron and nickel complexes decomposed completely differently from that observed under N_2. Ni(DEDC)$_2$ decomposed via a thyocyanate intermediate according in agreement with the DSC response, in which the decomposition is initially exothermic followed by a sharp exothermic process.

$Fe(DEDC)_2$ decomposed in a three step process which was radically different to that in nitrogen and had no correlation with results obtained for other complexes in the series. In the first step, a dehydration reaction produced the morpholinodithiocarbamate according to stoichiometric calculations:



This reaction is confirmed since dehydration of the diethanolamine is an industrial method for preparing morpholine [18]. The occurrence of such a reaction justifies the differences observed in relation to the other complexes in the series, since a cyclic DTC is being decomposed instead of an aliphatic one.

3.3. Ionic radius/thermal stability

From the data obtained in this work, it was possible to show with the complex form with ions of higher ionic radius, the lower was the initial decomposition temperature of the complex as measured by TG, see Table 4, and so nickel with the smallest ionic radius produces the most stable complex. The manganese(II) complexes studied earlier under the same conditions in the same equipment followed their behaviour [12]

Similar results has been observed recently with cyclic DTC [16,19], in relation to thermal stability. In agreement with that results Ni(DEDC) with a monodentate character decomposed via the thyocyanate intermediate, while the other complexes in which the ligand is bidentate decomposed in a direct way.

Table 4
Dependence of ionic radius of the elements and TG initial decomposition temperature of the complexes

Elements	Ionic radius[a]	Initial decomp. temp. (°C)
Zn(II)	0.74	167
Cu(II)	0.71	171
Ni(II)	0.69	189
Co(II)	0.72	174
Fe(II)	0.77	133
Mn(II)[b]	0.80	125

[a] [20].

[b] [17].

References

[1] D. Coucovanis, Prog. Inorg. Chem. 11 (1970) 233.

[2] R.J. Magee, J.O. Hill, Rev. Anal. Chem. 8 (1985) 5.

[3] G.D. Thorn, R.A. Ludwig, The Dithiocarbamates and Related Compounds, Elsevier, Amsterdam, 1962.

[4] R.J. Magee, Rev. Anal. Chem. 1 (1973) 33.

[5] A. Hulanicki, Talanta 14 (1967) 1371.

[6] A.K. Ramrakhiani, R.S. Shukla, J. Indian Chem. Soc. 8 (1980) 856.

[7] T. Kitson, Ed. Chem. (1985) 43.

[8] G. Vefforazzi, W.F. Almeida, G.J. Burin, R.B. Jaeger, F.R. Puga, A.F. Rahde, F.G. Reyes, S. Schvartsman, Teratog. Carcinog. Mutag. 15 (1995) 313.

[9] A. Weuffen, A. Kewitsch, Arch. Expt. Veterinaermed 21 (1967) 1049.

[10] M.F. Rabbi, A. Finnegan, L. Al-Hartli, S. Stong, K.A. Roebuck, J. Aquired Immune Defic. Syndr. Hum. Retrovirol. 19 (1998) 321.

[11] B. Annuar, J.O. Hill, R.J. Magee, Thermochim. Acta 8 (1974) 439.

[12] G. Marino, G.O. Chierice, C.D. Pinheiro, A.G. Souza, Thermochim. Acta 328 (1999) 209.

[13] A.N. Bhat, R.C. Fay, D.F. Lewis, A.F. Lindmark, S.H. Strauss, Inorg. Chem. 13 (1974) 886.

[14] B.F.G. Jhonson, K.H. Al-Obaidi, J.A. McCleverty, J. Chem. Soc. A (1969) 1668.

[15] T.M. Brow, J.N. Smith, J. Chem. Soc. Dalton Trans. (1972) 1614.

[16] A. Domenicano, A. Vaciago, L. Zambonelli, Chem. Commun. 14 (1966) 476.

[17] E.T.G. Cavaiheiro, M. Ionashiro, G. Marino, S.T. Breviglieri, G.O. Chierice, Trans. Metal Chem. 25 (2000) 69.

[18] The Merck index, 12th Edition, Merck & Co. Inc., Rahway, NJ, USA, 1996.

[19] E.T.G. Cavalheiro, M. Ionashiro, G. Marino, S.T. Breviglieri, G.O. Chierice, J. Braz. Chem. Soc. 10 (1999) 65.

[20] F.A. Cotton, G. Wilkinson, Química Inorgânica, 1st Edition, Livros Técnicos e Científicos, Rio de Janeiro, 1978.