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Thermal decomposition of triethanolamine and monoethanolethylenediamine complexes of some transition metal saccharinates

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Abstract

The thermal decomposition behaviour of triethanolamine (TEA) and monoethanolethylenediamine (me-en) complexes of Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) saccharinates was studied under non-isothermal conditions by TG, DTA and DTG in dynamic nitrogen atmosphere. The decomposition of the TEA complexes proceeds via three main stages. The first stage involves exothermic removal of two CH_2OH groups, due to degradation of uncoordinated ethanol groups of the TEA molecules, and the second and third stages correspond to formation of metal saccharinates and metals as the end products, respectively. All the me-en complexes show similar decomposition behaviour and, after evolution of two CH_2OH groups, they progressively decompose through saccharinate intermediates and subsequently yield metals or metal oxides as the final residue. Tea complexes showed much higher thermal stability than their me-en analogues. A thermal decomposition mechanism for the metal complexes was suggested.

Keywords: Triethanolamine complexes; Monoethanolethylenediamine complexes; Saccharin complexes; Transition metal saccharinates; TG; DTA

1. Introduction

Saccharin (*o*-sulphobenzimide) is not very soluble, but its alkali metal salts are very soluble and widely used as non-caloric artificial sweeteners and food additives [1]. Research on the synthesis and structural analysis of metal–saccharin complexes has been active in the last two decades, because of their potential effectiveness in biological systems and the suspected carcinogenic nature of saccharin [2,3]. Saccharin in its deprotonated form (sac) interacts with trace elements in the human body and readily forms stable compounds in which sac acts as a N-donor monodentate ligand or a counter-ion, depending on the presence of other ligands [4–9]. Nowadays it is generally recognized as safe in the United States [10] and it has also been suggested that the importance of sac lies in its potential use as an antidote for metal poisoning [11].

Naumov et al. [12] studied the thermal decomposition of alkali metal saccharinates, while the decomposition behaviours of aqua complexes of the metal(II) saccharinates were studied by Magri et al. [13] and Icbudak et al. [14]. A thermally induced intramolecular electron transfer process was reported in the thermal decomposition of the aqua complex of the

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Fe(II) saccharinate [15]. Reports on thermal behaviour of hydrazine, ethylenediamine [16] and 1,10-phenanthroline [17] complexes of some transition metal saccharinates have appeared in the literature. As part of our research on the synthesis, spectral and thermal analysis of transition metal complexes of sac with N-donor ligands, we report the thermal decomposition characteristics of some novel triethanolamine (TEA) (also named tris(2-hydroxyethyl)amine) and monoethanolethylenediamine (me-en) (alternatively named *N*-(2-hydroxyethyl)-ethylenediamine) complexes of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) saccharinates.

2. Experimental

2.1. Preparation of the complexes

The TEA, $[N(CH_2CH_2OH)_3]$, and me-en, $(NH_2CH_2CH_2NHCH_2CH_2OH)$, complexes of the metal saccharinates were prepared by the methods reported earlier [18,19].

2.2. Measurements

Simultaneous TG, DTG and DTA curves were obtained using a Rigaku TG8110 thermal analyser combined with a TAS100 thermogravimetric analyser. The experiments were carried out in a dynamic nitrogen atmosphere with a flow rate of 80 ml min^{-1} in the temperature range 20–1100 °C, using platinum crucibles. Sample masses of 5–10 mg and a heating rate of 10 °C min^{-1} were used. Sintered α-alumina was used as the reference material. A small amount of the volatile product lost around 200 °C was obtained by using about 5 g of complex and analysed by ^{1}H NMR and IR spectroscopy. The solid residues were identified by IR spectroscopy.

3. Results and discussion

All the TEA and me-en complexes exhibit an exotherm in the 150–300 °C range with a mass loss after or before melting. The mass loss corresponds to removal of a group with a molar mass of about 60 g. The mass spectra of the TEA and me-en ligands show several fragments [20]. The base peaks appear at *m*/*z* values of 118 and 74 for TEA and me-en, respectively. The loss of 31 mass units in the transition from 149 to 118 suggests the presence of a CH_2OH radical from TEA. The exotherms in the DTA curves of the metal complexes are expected to be due to the degradation of uncoordinated ethanolic groups of the two TEA or me-en molecules and it would be a good guess to attribute them to the formation of an ethylene glycol $(OHCH_2CH_2OH)$ molecule. Although the calculated values for the removal of the two CH_2OH groups are consistent with the experimental values, ^{1}H NMR and IR spectral analyses of the isolated product obtained in the corresponding temperature range do not confirm the proposed assignment for ethylene glycol. Instead, these results suggest the formation of CH_3-O-CO-H by a rearrangement of the two CH_2OH radicals in the gas phase at high temperatures. Identification of the volatile product needs more and detailed research. Therefore, the mass calculations for the corresponding stage are based on the formation of the CH_2OH group.

3.1. Triethanolamine (TEA) complexes

Spectral and structural studies of the TEA complexes of the metal saccharinates show that the TEA ligand behaves as a N,O,O′-donor tridentate ligand in all the metal complexes, while the sac is present as a counter-ion [18,21,22]. However, the dimeric Cu(II) complex crystallizes as a dimethanol solvate and contains two TEA ligands in a monoanionic form, acting as a bridge between the two copper atoms and two sac ligands [18].

Thermoanalytical data for the TEA complexes of metal saccharinates are given in Table 1, while Fig. 1 presents the TG, DTG and DTA of the $[Cd(TEA)_2](sac)_2$ complex.

The $[Mn(TEA)_2](sac)_2$ complex melts at 188 °C and begins to decompose after melting. The elimination of two CH_2OH groups during the degradation of the TEA ligands occurs in the first stage with an exotherm at 229 °C in the DTA curve and a corresponding peak in the DTG curve. The experimental mass loss of 9.64% for the stage agrees well with the calculated value of 8.65%. A sharp colour change from yellow-brown to orange was observed during the elimination of the two CH_2OH groups. In the second stage, the rest of the TEA ligand decomposes to form

Table 1
Thermoanalytical results (TG, DTG, DTA) for the TEA complexes of metal saccharinates

Complexes	Stage	Temperature range (°C)	$DTG_{max.}$[a] (°C)	Removed group	Mass loss in percentage		Solid residue
					Found	Calculated	
$[Mn(TEA)_2](sac)_2$	1	190–248	229(−)	$2CH_2OH$	9.64	8.65	
	2	248–415	360(+), 406(+)		31.48	32.93	$Mn(sac)_2$
	3	415–773	564(+), 729(+)	2Sac	49.39	50.78	Mn
$[Co(TEA)_2](sac)_2$	1	183–271	233(−)	$2CH_2OH$	9.21	8.60	
	2	271–385	343(+), 381(+)		31.75	32.75	$Co(sac)_2$
	3	385–1000	434(+), 891(+)	2Sac-O	45.33	48.28	CoO
$[Ni(TEA)_2](sac)_2$	1	223–256	240(−)	$2CH_2OH$	9.34	8.60	
	2	256–346	343(+)		31.45	32.76	$Ni(sac)_2$
	3	346–1000	403(+)	2Sac-O	47.97	48.29	NiO
$[Cu_2(m\text{-}TEA)_2(sac)_2]\cdot 2CH_3OH$	1	26–120	55(+), 69(+)	$2CH_3OH$	7.31	7.52	$[Cu_2(sac)_2(TEA)_2]$
	2	138–262	190(−), 232(−)	$2CH_2OH$	13.44	14.57	
	3	262–348	334(+)		22.44	20.46	$Cu_2(sac)_2$
	4	348–773	384(+), 434(+)	2Sac	43.51	42.78	2Cu
$[Zn(TEA)_2](sac)_2$	1	188–256	224(−)	$2CH_2OH$	9.76	8.52	
	2	256–374	322(+), 352(+), 369(+)		31.62	32.46	$Zn(sac)_2$
	3	374–856	401(+), 457(+)	2Sac	50.37	50.05	Zn
$[Cd(TEA)_2](sac)_2$	1	210–277	219(−)	$2CH_2OH$	8.60	8.01	
	2	277–442	383(+), 431(+)		29.84	30.49	$Cd(sac)_2$
	3	442–947	685(+)	2Sac	46.21	46.89	Cd
$[Hg(TEA)_2](sac)_2$	1	114–184	225(−)	$2CH_2OH$	6.06	7.19	
	2	184–321	309(+)		28.21	27.37	$Hg(sac)_2$
	3	321–440	335(+), 376(+)	2Sac	42.64	42.20	Hg

[a] Endothermic (+); exothermic (−).

Mn(II) saccharinate at about 415 °C and this intermediate undergoes endothermic decomposition in the range 415–773 °C to form metallic Mn.

The $[Co(TEA)_2](sac)_2$ complex undergoes complete endothermic decomposition in three stages, after melting at 181 °C. The first stage between 183–271 °C is accompanied by a mass loss of 9.21% (calculated 8.60%) and corresponds to exothermic removal of two CH_2OH radicals. The decomposition of the remaining part of TEA ligand and subsequent formation of the $Co(sac)_2$ intermediate occur in the second stage. In the last stage, in the temperature range 385–1000 °C, decomposition of $Co(sac)_2$ to CoO occurs.

In the case of the $[Ni(TEA)_2](sac)_2$ complex, the exothermic formation of two CH_2OH groups takes place between 223–256 °C accompanied by 9.34% mass loss. The second stage with a mass loss 31.45% (calculated 32.76%) is attributed to the decomposition of the partly degraded TEA ligand and, in the third stage, $Ni(sac)_2$ decomposes to produce NiO.

The $[Cu_2(m\text{-}TEA)_2(sac)_2]\cdot 2CH_3OH$ complex exhibits three distinct decomposition stages. In the first stage, endothermic removal of two methanol solvate molecules occurs at 55 and 69 °C with a mass loss of 7.31% (calculated 7.52%). The complex melts at 125 °C. The degradation of the triethanolaminate ions to form methanol occurs in the second stage in the temperature range 138–262 °C, and results in the formation of the $Cu(sac)_2$ intermediate at 334 °C. A 35.88% mass loss observed in the stage is in good agreement with the calculated mass loss of 35.03%. Over the 348–773 °C range, the DTA curve displays two endotherms at 384 and 434 °C, attributed to the complete decomposition of the $Cu(sac)_2$ intermediate to metallic Cu.

The $[Zn(TEA)_2](sac)_2$ complex melts at a relatively low temperature (90 °C), compared to the other TEA

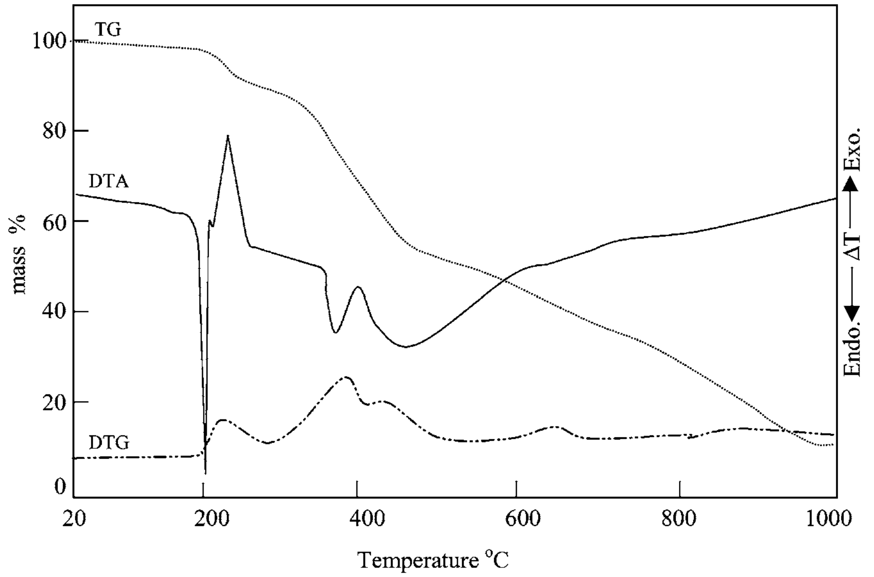

Fig. 1. TG, DTG and DTA curves for $[Cd(TEA)_2](sac)_2$ heated at 10°C min^{-1} in N_2.

complexes, being stable up to 181 °C, at which temperature it begins to decompose. The DTA curve shows a small endotherm at 124 °C, without a mass loss, and it may be attributed to some kind of changes in the melted complex. The reason of the effect is not known. The exotherm at 224 °C is due to the release of two CH_2OH groups with a mass loss of 9.76% (calculated 8.52%). The partly decomposed TEA yields zinc saccharinate at 374 °C and decomposes to give metallic zinc at 856 °C. A continuous weight loss occurs up to 1000 °C, due to the evaporation of the melted zinc.

The $[Cd(TEA)_2](sac)_2$ and $[Hg(TEA)_2](sac)_2$ complexes show similar decomposition characteristics. The first stage corresponds to the loss of two CH_2OH groups and the second stage results in the formation of the metal saccharinates. The last endothermic stage is related to decomposition of the sac ions to produce the metals. However, in the case of the Hg(II) complex, the metallic Hg evaporates at higher temperatures without leaving any residue.

3.2. Monoethanolethylenediamine (me-en) complexes

The me-en complexes of the metal saccharinates contain both the me-en molecules and the sac ions as ligands [19]. The me-en ligand acts as a bidentate N-donor ligand and its ethanol group is not involved in coordination. The sac ions coordinate the metal (through the deprotonated N) as a monodentate ligand. Consequently, the metal ions are octahedrally coordinated by these ligands. Table 2 lists the thermoanalytical data for the me-en complexes of the metal saccharinates and the TG, DTG and DTA curves of the $[Cd(sac)_2(me\text{-}en)_2]$ complex are shown in Fig. 2.

The $[Mn(sac)_2(me\text{-}en)_2]$ complex has a very high thermal stability. Its decomposition begins at about 315 °C after melting at 154 °C, and proceeds in three stages. The mass loss between 163 and 263 °C corresponds to the release of two CH_2OH groups. This process is due to the partial decomposition of the me-en ligand and is represented by an endotherm at 237 °C on the DTA curve and a corresponding peak on the DTG curve. The decomposition of the me-en ligand is completed at 308 °C to give the manganese saccharinate, which also follow a complicated decomposition process to produce metallic Mn at ca. 860 °C.

The TG, DTG and DTA curves for the dimeric $[Co_2(sac)_2(me\text{-}en)_2]\cdot 2H_2O$ complex reveal that the decomposition process proceeds via four main stages. The first stage is attributed to dehydration of the complex at 93 °C, with a mass loss of 4.33% (calculated 4.97%). The complex melts at 162 °C. The degradation of the ligand me-en takes place in the

Table 2
Thermoanalytical results (TG, DTG, DTA) for the me-en complexes of metal saccharinates

Complexes	Stage	Temperature range (°C)	DTG$_{\mathrm{max.}}$[a] (°C)	Removed group	Mass loss in percentage		Solid residue
					Found	Calculated	
[Mn(sac)$_2$(me-en)$_2$]	1	163–260	237(+)	2CH$_2$OH	9.65	9.88	
	2	263–338	308(+), 321(+)		23.06	23.32	Mn(sac)$_2$
	3	338–857	348(+), 374(+), 426(+), 710(+)	2Sac	57.45	58.08	Mn
[Co$_2$(sac)$_2$(me-en)$_2$]·2H$_2$O	1	25–144	93(+)	2H$_2$O	4.33	4.97	[Co$_2$(sac)$_2$(me-en)$_2$]
	2	170–286	263(+)	2CH$_2$OH	8.71	8.56	
	3	286–354	338(+), 350(+)		20.15	19.92	2Co(sac)$_2$
	4	354–807	370(+), 704(+)	2Sac	50.95	50.31	2Co
[Ni(sac)$_2$(me-en)$_2$]	1	151–204	169(+)	CH$_2$OH	5.12	4.95	
	2	226–320	304(+)		27.85	28.09	Ni(sac)$_2$
	3	320–927	664(+)	2Sac	57.26	57.74	Ni
[Cu(sac)$_2$(me-en)$_2$]	1	190–258	242(+)	2CH$_2$OH	9.87	9.75	
	2	258–347	279(+)		22.58	23.00	Cu(sac)$_2$
	3	347–850	363(+), 379(+), 565(−)	2Sac	56.87	57.30	Cu
[Zn(sac)$_2$(me-en)$_2$]	1	162–261	258(+)	2CH$_2$OH	9.93	9.72	
	2	261–362	349(+)		22.19	22.94	Zn(sac)$_2$
	3	362–977	412(+), 740(+)	2Sac	56.99	57.13	Zn
[Cd(sac)$_2$(me-en)$_2$]	1	227–300	258(+)	2CH$_2$OH	9.26	9.05	
	2	300–371	324(+)		21.36	21.36	Cd(sac)$_2$
	3	371–805	424(+), 705(+)	2Sac	53.09	53.21	Cd
[Hg(sac)$_2$(me-en)$_2$]	1	157–212	158(+), 169(−)	2CH$_2$OH	8.21	8.02	
	2	212–289	218(+), 267(−)		18.66	18.93	Hg(sac)$_2$
	3	289–396	357(+)	2Sac	47.92	47.14	Hg

[a] Endothermic (+); exothermic (−).

second stage in the range 170–286 °C to release two molecules of CH$_2$OH radicals. The decomposition of the me-en ligand is complete at 354 °C to give the corresponding saccharinate. In the last stage, the decomposition of the sac ions occurs to yield Co as the end product.

The first step in the decomposition of [Ni(sac)$_2$(me-en)$_2$] corresponds to the removal of one of the two CH$_2$OH groups at 169 °C due to the partial degradation of the me-en ligand. The experimental mass loss (5.12%) for this stage is in good agreement with the calculated mass loss (4.95%). The remaining part of the ligand decomposes at 304 °C and the decomposition proceeds with a continuous mass loss between 320–27 °C. The final decomposition product is metallic nickel.

The [Cu(sac)$_2$(me-en)$_2$] complex melts at 180 °C and decomposes in three stages. The first stage may be correlated with the evolution of two CH$_2$OH groups at 242 °C, accompanied by a 9.87% mass loss (calculated 9.75%). The decomposition of residue of the me-en ligand results in the production of the saccharinate intermediate at 279 °C and the decomposition of the intermediate occurs in subsequent stages in the temperature range 347–50 °C to metallic copper, with three DTG maxima at 363, 379 and 565 °C.

The [Zn(sac)$_2$(me-en)$_2$] complex exhibits three stages of decomposition. In the first stage, removal of two CH$_2$OH groups takes place in the temperature range 162–261 °C with a mass loss of 9.93% (calculated 9.72%). The following two stages between 261 and 362 °C are attributed to decomposition of the remaining part of the me-en ligand. Decomposition of the zinc saccharinate residue is observed in the last stage between 362 and 977 °C to give metallic zinc.

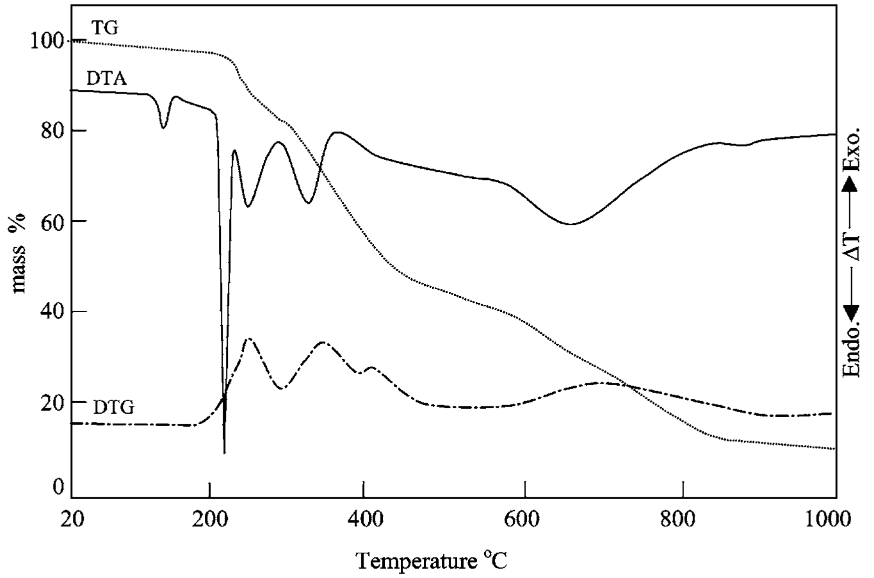

Fig. 2. TG, DTG and DTA curves for [Cd(sac)$_2$(me-en)$_2$] heated at 10 °C min^{-1} in N$_2$.

The [Cd(sac)$_2$(me-en)$_2$] complex shows a small endothermic effect at 147 °C, probably due to a reversible phase transition in the solid state. The complex is stable up to 227 °C and then begins to decompose with melting. The me-en ligand undergoes endothermic decomposition first at 258 by losing two CH$_2$OH groups and then at 324 °C to give Cd(sac)$_2$. The total experimental mass loss (30.62%) for these stages is in good agreement with the calculated mass loss (30.41%). The last stage in the temperature range 300–805 °C is due to decomposition of Cd(sac)$_2$ to produce metallic cadmium.

The [Hg(sac)$_2$(me-en)$_2$] complex decomposes in three stages. The endothermic removal of two CH$_2$OH groups takes place in the temperature range 157–212 °C, after melting at 157 °C. The decomposition of the partly degraded ligand is completed at 289 °C to produce the corresponding saccharinate intermediate, which decomposes between 289 and 396 °C to form metallic Hg, which evaporates at higher temperatures.

4. Conclusions

The solid metal complexes studied are stable at the room temperature and decompose progressively during heating. The thermoanalytical results of the TEA and me-en complexes conclusively prove that the main feature is the evolution of two CH$_2$OH groups in the first stage of decomposition, and the formation of the metal saccharinates as intermediates, which decompose to the respective metals. Our efforts to isolate the intermediates were unsuccessful in most cases due to the overlapping decomposition stage. Hence, we tried to assign the possible intermediates from the TG mass losses, which are reasonably consistent with the calculated values. In some cases, IR spectrometer was used for the identification of the solid intermediates. The presence of the carbonyl and sulfonyl absorption bands in the IR spectra of the intermediates obtained after removal of the amine ligands suggests that the intermediates consist mainly of the corresponding metal saccharinates.

The thermal behaviour of the solid metal complexes indicates that their stability sequence is Ni > Cd > Mn > Zn > Co > Cu >Hg for the TEA complexes and Cu > Co > Cd > Mn > Zn > Hg >Ni for the me-en complexes. This does not conform to the Irving–Williams series, which reflect the stability of divalent metal complexes in solution [23]. For a given metal, the TEA complexes usually show much higher thermal stability than their me-en analogues. The thermal stabilities of the metal complexes are usually determined by the metal–ligand strength, but in the case of the TEA and me-en complexes, the metal–ligand strength seems to be insignificant to determine the thermal stability. The results of the present work show that the thermal stabilities of the metal complexes with the TEA and me-en ligands are largely due to the reactivity of the free ethanolic groups, which initiate the decomposition of the metal complexes. The general decomposition scheme of the metal complexes can be summarized in the following mechanisms.

The TEA complexes:

$$[\mathrm{M(tea)_2}](\mathrm{sac})_2 \underset{-2\mathrm{CH_2OH}}{\rightarrow} [\mathrm{M(L^*)_2}](\mathrm{sac})_2$$

$$[\mathrm{M(L^*)_2}](\mathrm{sac})_2 \underset{-2\mathrm{L^*}}{\rightarrow} \mathrm{M(sac)_2}$$

$$\mathrm{M(sac)_2} \underset{-2\mathrm{sac}}{\rightarrow} \mathrm{M(or\,MO)}$$

The me-en complexes:

$$[\mathrm{M(sac)_2(me\text{-}en)_2}] \underset{-2\mathrm{CH_2OH}}{\rightarrow} [\mathrm{M(sac)_2(L^*)_2}]$$

$$[\mathrm{M(sac)_2(L^*)_2}] \underset{-2\mathrm{L^*}}{\rightarrow} \mathrm{M(sac)_2}$$

$$\mathrm{M(sac)_2} \underset{-2\mathrm{sac}}{\rightarrow} \mathrm{M}$$

Here, L^* indicates partly degraded amine ligand.

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References

[1] L.O. Nabors, C.G. Robert, Alternative Sweeteners, 2nd Edition, Marcel Dekker, New York, 1991.
[2] I.C. Munro, C.A. Modie, D. Krewski, H.C. Grice, Toxicol. Appl. Pharmacol. 32 (1957) 513.
[3] M.J. Allen, E. Bayland, C.E. Dukes, E.S. Horning, J.G. Watson, Br. J. Cancer 11 (1957) 212.
[4] B. Kamenar, G. Jovanovski, Cryst. Struct. Commun. 11 (1982) 257.
[5] Z. Haider, K.M.A. Malik, K.J. Ahmed, H. Hess, H. Riffel, M.B. Hursthouse, Inorg. Chim. Acta 72 (1983) 21.
[6] Z. Haider, K.M.A. Malik, K.J. Ahmed, Inorg. Synth. 23 (1985) 47.
[7] F.A. Cotton, G.E. Lewis, C.A. Murillo, W. Schwotzer, G. Valle, Inorg. Chem. 23 (1984) 4038.
[8] F.A. Cotton, E. Libby, C.A. Murillo, G. Valle, Inorg. Synth. 27 (1990) 306.
[9] Y. Zhang, Spectrosc. Lett. 31 (1998) 1609.
[10] J. Anderson, B. Deskins, The Nutrition Bible, William Morrow and Company, 1995.
[11] E.W. Ainscough, E.N. Baker, A.M. Brodie, Inorg. Chim. Acta 172 (1990) 185.
[12] P. Naumov, G. Jovanovski, S. Abbrent, L.E. Tergenius, Thermochim. Acta 359 (2000) 123.
[13] D. Magri, G. Dascenzo, S.N. Cesaro, E. Chiacchieri, Thermochim. Acta 36 (1980) 279.
[14] H. Icbudak, V.T. Yilmaz, H. Olmez, J. Thermal. Anal. 53 (1998) 843.
[15] V.T. Yilmaz, Synth. React. Inorg. Met. Org. Chem. 29 (1999) 62.
[16] H. Icbudak, T.K. Yazicilar, V.T. Yilmaz, Thermochim. Acta 335 (1999) 93.
[17] V.T. Yilmaz, F. Yilmaz, Y. Topcu, O. Andac, K. Guven, J. Mol. Struct. 560 (2001) 9.
[18] Y. Topcu, O. Andac, V.T. Yilmaz, W.T.A. Harrison, J. Coord. Chem., in press.
[19] V.T. Yilmaz, A. Karadag, C. Thoene, J. Coord. Chem., in press.
[20] W.G. Mallard, P.J. Linstrom (Eds.), NIST Chemistry WebBook, NIST Standard Reference Database Number 69, National Institute of Standards and Technology, Gaithersburg, 2000.
[21] Y. Topcu, Ö. Andac, V.T. Yilmaz, W.T.A. Harrison, Acta Crystallogr. E57 (2001) m82.
[22] Ö. Andac, Y. Topcu, V.T. Yilmaz, K. Guven, Acta Crystallogr., submitted for publication.
[23] C.S.G. Philips, R.J.P. Williams, Inorganic Chemistry, Oxford University Press, Oxford, 1966.