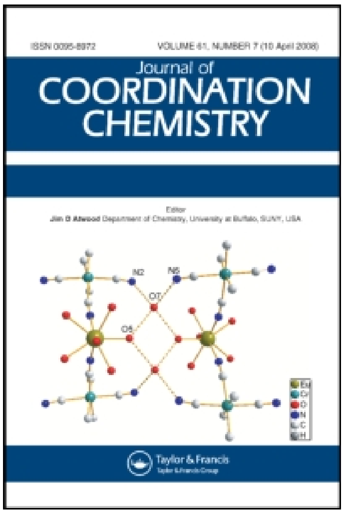
This article was downloaded by:
On: *23 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, infrared spectra and thermal investigation of gold(III) and zinc(II) urea complexes. A new procedure for the synthesis of basic zinc carbonate

Sadeek A. Sadeek[a]; Moamen S. Refat[b]
[a] Faculty of Science, Department of Chemistry, Zagazig University, Zagazig, Egypt [b] Faculty of Education, Department of Chemistry, Port-Said, Suez Canal University, Egypt

To cite this Article Sadeek, Sadeek A. and Refat, Moamen S.(2005) 'Synthesis, infrared spectra and thermal investigation of gold(III) and zinc(II) urea complexes. A new procedure for the synthesis of basic zinc carbonate', Journal of Coordination Chemistry, 58: 18, 1727 — 1734

To link to this Article: DOI: 10.1080/00958970500262254

URL: http://dx.doi.org/10.1080/00958970500262254

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Journal of Coordination Chemistry
Vol. 58, No. 18, December 2005, 1727–1734

Synthesis, infrared spectra and thermal investigation of gold(III) and zinc(II) urea complexes. A new procedure for the synthesis of basic zinc carbonate

SADEEK A. SADEEK*† and MOAMEN S. REFAT‡

†Faculty of Science, Department of Chemistry,
Zagazig University, Zagazig, Egypt
‡Faculty of Education, Department of Chemistry,
Port-Said, Suez Canal University, Egypt

(*Received 10 December 2004; revised 31 January 2005; in final form 3 July 2005*)

Reaction of urea with sodium tetrachloroaurate(III) dihydrate and zinc(II) chloride has been investigated at room and elevated temperature (~90°C) producing three new compounds: $[Au(urea)_4]Cl_3 \cdot 2H_2O$, $[Au_2(NH_2)_2Cl_2(NCO)(OH)] \cdot H_2O$ and $2ZnCO_3 \cdot 3Zn(OH)_2$. The infrared spectra were recorded and the observed bands were assigned. The binuclear gold complex and basic zinc carbonate basic were also investigated by thermal analysis, and general mechanisms describing their decompositions are suggested.

Keywords: Zinc carbonate basic; IR spectra; Sodium tetrachloroaurate; Thermal analysis; Urea

1. Introduction

Stable complexes, formed by the reaction of various metal salts with urea at room temperature in aqueous media, are known [1–5]. However, the inner structures of these complex salts indicate that coordination of urea with the metal ion occurs via formation of oxygen or nitrogen metal bonds, depending on the type of metal salt [6]. Free urea is known to decompose to CO_2 and NH_3 in aqueous media, and the rate of decomposition increases with temperature. The rate of decomposition of coordinated urea, and the nature of the reaction products, were found to be strongly dependent on the type of metal ions and the metal salts used in the reaction [7–12].

The present study was undertaken to investigate the nature of the reaction products of urea with sodium tetrachloroaurate(III) dihydrate and zinc chloride in aqueous solutions at room temperature and at ~90°C. The aim of this work was

---

*Corresponding author. Email: sadeek59@yahoo.com

Journal of Coordination Chemistry
ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/00958970500262254

to discern the role of the metal ion in the decomposition of coordinated urea at high temperatures.

2. Experimental

2.1. *Preparation of the compounds*

2.1.1. [Au(urea)$_4$]Cl$_3$·2H$_2$O (1). The solid complex was prepared by adding diethyl ether solution (50 mL) of $Na(AuCl_4)\cdot 2H_2O$ (0.994 g; 2.5 mmole) to a suspension of urea (0.9 g; 15 mmole) in diethyl ether (50 mL). The reaction mixture was left at room temperature for two days with continuous stirring. The orange precipitate formed was filtered, washed several times with a minimum amount (2 mL) of diethyl ether and then dried under vacuum over phosphorus pentoxide. Anal. Calcd for $C_4H_{20}Cl_3N_8O_6Au$ (FW 579.46): C, 8.28; H, 3.45; N, 19.32; Cl, 18.37; Au, 33.99. Found: C, 8.23; H, 3.49; N, 19.51; Cl, 18.73; Au, 34.11%. Yield, 1.23 g (85%).

2.1.2. [Au$_2$(NH$_2$)$_2$Cl$_2$(NCO)(OH)]·H$_2$O (2). The brown complex $[Au_2(NH_2)_2Cl_2(NCO)(OH)]\cdot H_2O$ was prepared by mixing equal volumes (50 mL) of aqueous solutions of sodium tetrachloroaurate(III) dihydrate (1.97 g, 5 mmol) and urea (1.8 g, 30 mmol). The mixture was heated with stirring at ~90°C for 10 h. The precipitated complex was filtered, washed several times with hot water and then dried under vacuum over P_2O_5. The same product was obtained upon heating an aqueous solution of the complex $[Au(urea)_4]Cl_3\cdot 2H_2O$ at ~90°C. Anal. Calcd for $CH_7Cl_2N_3O_3Au_2$ (FW 573.92): C, 2.09; H, 1.21; N, 7.31; Cl, 12.36; Au, 68.64. Found: C, 2.10; H, 1.22; N, 7.40; Cl, 12.30; Au, 68.33%. Yield, 1.2 g (86%); m.p. above 300°C.

2.1.3. 2ZnCO$_3$·3Zn(OH)$_2$ (3). This white compound was prepared by mixing equal volumes (100 mL) of aqueous solutions of $ZnCl_2$ (1.36 g, 10 mmol) and urea (3.60 g, 60 mmol). The mixture was heated with stirring for 10 h at ~90°C. The precipitated compound was filtered, washed and dried in a similar manner as the gold complex. Anal. Calcd for $C_2H_6O_{12}Zn_5$ (FW 548.85): C, 4.37; H, 1.09; Zn, 59.55. Found: C, 4.35; H, 1.08; Zn, 59.42%. Yield, 0.75 g (72%); m.p. above 300°C.

2.2. *Analysis of the compounds*

Zinc content was determined gravimetrically as metal oxide and also determined by using atomic absorption. A PYE-UNICAN SP 1900 fitted with the corresponding lamp was used for this purpose. The infrared spectra were recorded in potassium bromide discs using a Gensis II FTIR spectrophotometer or a Perkin-Elmer 1430 ratio-recording, infrared spectrophotometer. Thermogravimetric (TG) and differential thermogravimetric (DTG) analyses were carried out under N_2-atmosphere using a Shimadzu TG-50 H thermal analyzer.

3. Results and discussion

3.1. *[Au(urea)$_4$]Cl$_3$ · 2H$_2$O complex (1)*

At room temperature, urea reacts with sodium tetrachloroaurate(III) dihydrate in diethyl ether to form [Au(urea)$_4$]Cl$_3$ · 2H$_2$O. The infrared spectra of urea and its coordination complex are shown in figure 1 and their bond assignments are given in table 1.

The spectrum of [Au(urea)$_4$]Cl$_3$ · 2H$_2$O, exhibits an absorption band at 1665 cm^{-1} due to the carbonyl vibration, while the corresponding vibration in the spectrum of free urea is observed at 1680 cm^{-1} [6, 13]. The shift of ν(C=O) to a lower wavenumber in the urea complex indicates the formation of a bond between the oxygen of urea and the central gold(III) atom, and that nitrogen is not the donor atom. As a result of such coordination, the ν(C–N) band is expected to shift to higher wavenumber (1495 cm^{-1}) since the nitrogen to carbon bond acquires more double bond character. The infrared bands observed at 3386, 3342 and 3190 cm^{-1} in the spectrum of free urea and assigned to N–H stretching vibrations are observed at almost the same frequencies in the spectrum of the Au(III) urea complex.

3.2. *[Au$_2$(NH$_2$)$_2$Cl$_2$(NCO)(OH)] · H$_2$O complex (2) and 2ZnCO$_3$ · 3Zn(OH)$_2$ compound (3)*

The reactions of aqueous solutions of urea with Na[AuCl$_4$] · 2H$_2$O or ZnCl$_2$ at ~90°C produce [Au$_2$(NH$_2$)$_2$Cl$_2$(NCO)(OH)] · H$_2$O or 2ZnCO$_3$ · 3Zn(OH)$_2$, respectively.

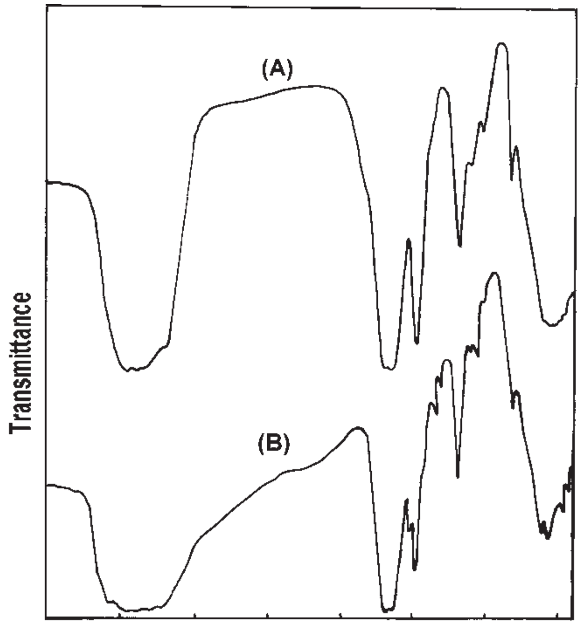


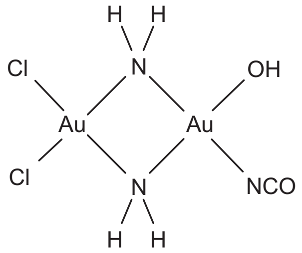
Figure 1. Infrared spectra of (A) urea; (B) [Au(urea)$_4$]Cl$_3$ · 2H$_2$O complex.

Table 1. Infrared frequencies[a] (cm^{-1}) and their assignments for $[Au(urea)_4]Cl_3 \cdot 2H_2O$ and urea.

$[Au(urea)_4]Cl_3 \cdot 2H_2O$	Urea	Assignments[b]
3450 br		ν(O–H); H_2O
3382 w	3386 w	ν_{as}(N–H); NH_2
3340 w	3342 w	
3190 w	3180 w	ν_s(N–H); NH_2
1665 vs	1680 vs	ν(C=O)
1620 vs	1630 vs	$\delta_b(NH_2)$
1495 m	1450 s	ν_{as}(CN)
1460 ms		
1325 m		
1290 w	1164 s	$\delta_r(NH_2)$
1160 s		
1040 w	1070 m	ν_s(CN)
995 m	1000 m	$\delta_t(NH_2)$
944 w		
845 sh		
785 m	790 m	$\delta_w(NH_2)$
760 sh		
590 m	590 w	δ(NCO)
540 m	540 w	δ(NCN)
440 w		ν(Au–O)
415 m		

[a] br, broad; m, medium; s, strong; sh, shoulder; w, weak.

[b] ν, stretching; δ_b, bending; δ_r, rocking; δ_t, twisting; δ_w, wagging.



Formula 1.

The formation of these two compounds upon heating indicates that Au(III) and Zn(II) ions decompose the coordinated urea at the higher temperature.

3.3. *Gold complex*

For $[Au_2(NH_2)_2Cl_2(NCO)(OH)] \cdot H_2O$, the most probable structure is shown in formula 1, where the complex is planar and may have C_s symmetry.

The infrared spectrum (figure 2 and table 2) of this complex shows no bands characteristic of coordinated urea but, instead, bands characteristic of terminal isocyanate [13, 14] at 2180 cm^{-1} and of a coordinated amide group [1, 10, 13] in the 3350–3040 cm^{-1} region. The band at 580 cm^{-1} is attributed to ν(Au–N) (N of $-NH_2$),

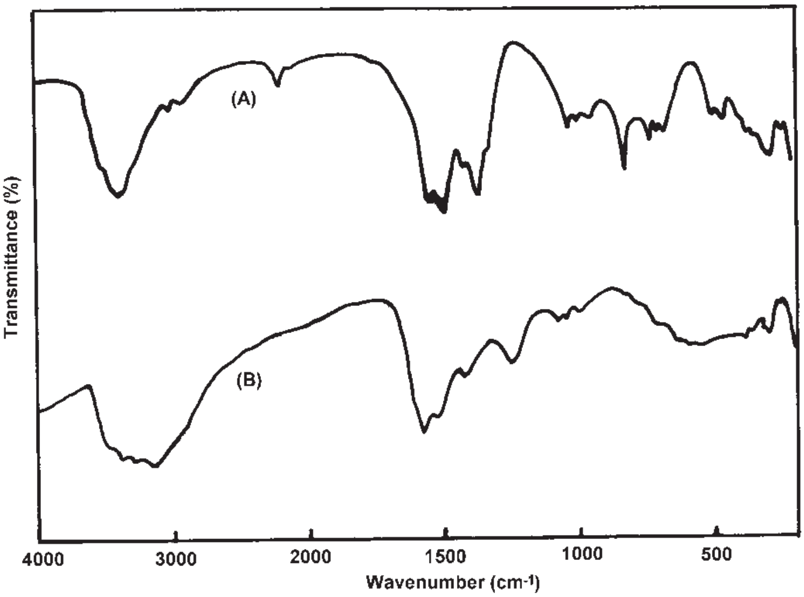


Figure 2. Infrared spectra of (A) $[Au_2(NH_2)_2Cl_2(NCO)(OH)] \cdot H_2O$ complex; (B) $2ZnCO_3 \cdot 3Zn(OH)_2$ compound.

while the two bands at 420 and 400 cm^{-1} are assigned to Au–O stretching vibrations. The weak and medium intensity bands appearing at 365 and 335 cm^{-1} may be considered to the ν(Au–Cl) [13]. In order to verify that the chloride is coordinated and not ionic, the complex solution was tested with an aqueous solution of $AgNO_3$ (no precipitate was formed). The observation of the above bands, together with elemental analysis data, are indicative of the formation of $[Au_2(NH_2)_2Cl_2(NCO)(OH)] \cdot H_2O$. Accordingly, sodium tetrachloroaurate(III) dihydrate reacts with urea at ~90°C according to the equation below.

$$2[Au(urea)_4]Cl_3 \cdot 2H_2O + 7H_2O \xrightarrow{\sim 90^\circ C} [Au_2(NH_2)_2Cl_2(NCO)(OH)] \cdot H_2O + 4HCl + 7CO_2 + 13NH_3$$

The IR vibrations of the complex are distributed between motions of the type A′ and A″; all are monodegenerate and infrared-active. The two bands at 3350 and 3205 cm^{-1} are assigned to ν_{as}(N–H) (A″), while the other bands observed at 3190 and 3040 cm^{-1} are of weak intensity and should be associated with symmetric vibrations of the type ν_s(N–H) (A′). The band at 1560 cm^{-1} may arise from the NH_2 bending vibration, while the group of bands at 1110, 1085 and 1030 cm^{-1} are associated with wagging and twist vibrations of the coordinated NH_2 group; the rocking vibration is assigned at 745 cm^{-1}.

The isocyanate ion (NCO^-) bands are assigned as follows: the N≡C frequency is observed, as expected, at 2180 cm^{-1} while ν(C–O) and δ(NCO^-) are observed at 1455 and 655 cm^{-1}, respectively. This assignment for the bands due to the NCO^-

Table 2. Infrared frequencies[a] (cm^{-1}) and their assignments for $[Au_2(NH_2)_2Cl_2(NCO)(OH)]$ and $2ZnCO_3 \cdot 3Zn(OH)_2$.

$[Au_2(NH_2)_2Cl_2(NCO)(OH)]$	$2ZnCO_3 \cdot 3Zn(OH)_2$	Assignments[b]
3570w	3540 w, 3440 w 3340 mbr, 3320 w	ν(O–H); OH^-
3450 mbr		ν(O–H); H_2O
3350 mbr 3205 w		ν_{as}(N–H)
3190 w 3040 wsh		ν_s(N–H)
2180 m		ν(N≡C); NCO^-
1620 s		$\delta_b(H_2O)$ uncoord. H_2O
1560 m		$\delta_b(NH_2)$
1455 wm	1560 s, 1510 s, 1380 s	ν(C–O); CO_3^{2-} ν(C–O); NCO^-
1280 wm		δ(AuOH)
1110 w 1085 w 1030 w		δ_w and δ_t of (NH_2)
	1040 m 1005 w	δ_b(ZnOH)
	950 m, 830 s, 740 m, 710 vw 690 m	δ(OCO); CO_3^{2-}
745 w		$\delta_r(NH_2)$
655 wbr		$\delta(NCO^-)$
580 wbr		ν(Au–N); NH_2^-
	470 m 425 w, 380 w	ν(Zn–O); (OH^-)
420 w 400 w		ν(Au–O)
365 wsh		ν(Au–Cl)
335 wm		ν(Au–Cl)

[a] br, broad; m, medium; s, strong; sh, shoulder; w, weak.

[b] ν, stretching; δ_b, bending; δ_r, rocking; δ_t, twisting; δ_w, wagging.

agrees quite well with those known for corresponding isocyanate complexes [13, 14]. The ν(O–H) frequency of the terminal hydroxo group is assigned to the medium intensity band at 3570 cm^{-1}, while the bending motion, δ_b(AuOH), is assigned at 1280 cm^{-1}.

To confirm the proposed structure of the Au(III) complex, $[Au_2(NH_2)_2Cl_2(NCO)(OH)] \cdot H_2O$, thermogravimetric (TG) and differential thermogravimetric (DTG) analysis were carried out under N_2 flow (figure 3A). The thermal degradation for the complex exhibits two degradation steps. The first step of decomposition occurs in the range 50–105°C, with a maximum temperature at 75°C, and is accompanied by a weight loss of 3.16% corresponding exactly to the loss of a water molecule. Loss of water of crystallization at a relatively low temperature may indicate weak H-bonding involving the H_2O molecule and the complex. The second step of degradation occurs at a maximum temperature of 240°C and is accompanied by a weight loss of 26.57%, corresponding to the loss of $NH_4Cl + HCl + 2NO$. The actual weight loss from these two steps is 29.73%, close to the calculated value 29.26%.

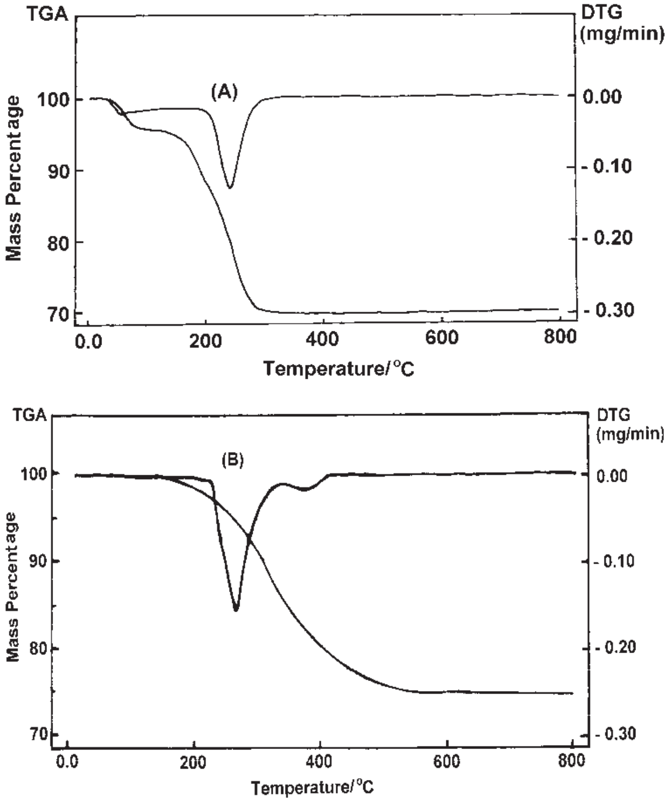


Figure 3. TGA and DTG diagram of (A) $[Au_2(NH_2)_2Cl_2(NCO)(OH)] \cdot H_2O$ complex; (B) $2ZnCO_3 \cdot 3Zn(OH)_2$ compound.

The following mechanism is proposed for the thermal decomposition of $[Au_2(NH_2)_2Cl_2(NCO)(OH)] \cdot H_2O$:

$$[Au_2(NH_2)_2Cl_2(NCO)(OH)] \cdot H_2O \xrightarrow{50-105^{\circ}C} [Au_2(NH_2)_2Cl_2(NCO)(OH)] + H_2O$$

$$[Au_2(NH_2)_2Cl_2(NCO)(OH)] \xrightarrow{240^{\circ}C} 2Au + C + NH_4Cl + HCl + 2NO$$

3.4. *Zinc compound*

In the case of the basic zinc carbonate, $2ZnCO_3 \cdot 3Zn(OH)_2$, the infrared spectrum of the obtained compound (figure 2, table 2) shows no bands due to coordinated urea but, instead, a group of bands characteristic for ionic carbonate [7, 13] are observed (table 2). Characteristic bands for hydroxide ion [15] lying in the 3540–3320 cm^{-1} region are assigned to the O–H stretching vibration motions. The bands at 1040 and 1005 cm^{-1} can be considered to arise from the bending motion, δ_b(ZnOH). The IR spectra and the elemental analysis data indicate that $2ZnCO_3 \cdot 3Zn(OH)_2$ is formed. The formation of basic zinc carbonate is supported by measuring the infrared spectrum of the commercially obtained zinc carbonate hydroxide, $2ZnCO_3 \cdot 3Zn(OH)_2$ [16].

Nardelli *et al.* [17] have indicated that $ZnCl_2$ reacts with urea at room temperature to form $[Zn(urea)_2Cl_2]$. The recorded infrared spectrum for this complex reveals the presence of a O → Zn bond and the absence of N → Zn bonds. Accordingly, at higher temperature the following reaction may take place:

$$5[Zn(urea)_2Cl_2] + 18H_2O \xrightarrow{ca.\,90^\circ C} 2ZnCO_3 \cdot 3Zn(OH)_2 + 10NH_4Cl + 8CO_2 + 10NH_3$$

The thermal decomposition of the $2ZnCO_3 \cdot 3Zn(OH)_2$, (figure 3B) exhibits two main degradation steps. The first step of decomposition occurs at a maximum temperature of 270°C and is accompanied by a weight loss of 9.79%, corresponding to the loss of $3H_2O$ in agreement with the theoretical value of 9.83%. The second step of decomposition occurs at 352°C and is accompanied by a weight loss of 15.89%, corresponding to the loss of $2CO_2$ giving ZnO as a final product. The infrared spectrum of the final product shows only the bands associated with the oxide.

Accordingly, the following mechanism is proposed for the thermal decomposition of the $2ZnCO_3 \cdot 3Zn(OH)_2$:

$$2ZnCO_3 \cdot 3Zn(OH)_2 \xrightarrow{270\,^\circ C} 2ZnCO_3 \cdot 3ZnO + 3H_2O$$

$$2ZnCO_3 \cdot 3ZnO \xrightarrow{352\,^\circ C} 5ZnO + 2CO_2$$

References

[1] R.B. Penland, S. Mizushima, C. Curran, J.V. Quagliano. *J. Amer. Chem. Soc.*, **79**, 1575 (1957).
[2] J.P. Barbier, R. Hugel. *Inorg. Chim. Acta*, **18**, 253 (1976).
[3] G. Nabakhtiani, G. Tsintsadze, L. Chachkhiani, M. Chogovadze. *Bull. Georg. Acad. Sci.*, **162**, 252 (2000).
[4] R. Keuleers, J. Janssens, H.O. Desseyn. *Thermochim. Acta*, **354**, 125 (2000).
[5] P.C. Srivastava, C. Aravindaksahn. *Z. Phys. Chem. Leipzig*, **264**, 61 (1983).
[6] A. Yamaguchi, T. Miyazawa, T. Shimanouchi, S. Mizuchima. *Spectrochim. Acta*, **10**, 170 (1957).
[7] M.S. Refat, S.M. Teleb, S.A. Sadeek. *Spectrochim. Acta*, **60**, 2803 (2004).
[8] S.M. Teleb, M.S. Refat, S.A. Sadeek. *Ukrianian Chem. J.*, **70**, 35 (2004).
[9] M.S. Refat, S.A. Sadeek, S.M. Teleb. *J. Argentinian Chem. Soc.*, **92(4/6)**, 23 (2004).
[10] S.M. Teleb. *Thermochim. Acta*, **228**, 131 (1993).
[11] S.A. Sadeek. *J. Phys. Chem. Solids*, **54**, 919 (1993).
[12] S.M. Teleb, S.A. Sadeek, E.M. Nour. *J. Phys. Chem. Solids*, **54**, 85 (1993).
[13] K. Nakamoto. *Infrared Spectra of Inorganic and Coordination Compounds*, Wiley, New York (1969).
[14] S.A. Sadeek, M.S. Refat, S.M. Teleb. *J. Korean. Chem. Soc.*, **48**, 358 (2004).
[15] R.S. Tobias, M.J. Sprague, G.E. Glass. *Inorg. Chem.*, **7**, 1714 (1968).
[16] Susan Budavari, *The Merck Index*, 12th Edn, Merck & Co. Inc., Whitehouse Station, NJ, USA, p. 1733 (1998).
[17] M. Nardelli, A. Braibanti, I. Chierici. *Gazzetta Chimica Italiana*, **87**, 1226 (1957).