Thermochimica Acta, 178 (1991) 231–239
Elsevier Science Publishers B.V., Amsterdam

COORDINATION COMPOUNDS AS RAW MATERIALS FOR MIXED OXIDES

Part IX. Thermal decomposition of some copper–lanthanide mandelate complexes

P. SPACU, MARIA BREZEANU

Department of Inorganic Chemistry, University of Bucharest, Str. Dumbrava Roşie 23, Bucharest (Romania)

LUMINIŢA PATRON, ADRIANA CONŢESCU and D. CRIŞAN

Institute of Physical Chemistry, Spl. Independenţei 202, Bucharest (Romania)

E. SEGAL

Department of Physical Chemistry, University of Bucharest, Bulevardul Republicii 13, Bucharest (Romania)

(Received 25 June 1990)

ABSTRACT

Copper(II)–lanthanide(III) mandelate complexes, $CuLn_2(C_8H_7O_3)_6(OH)_2 \cdot nH_2O$ (Ln = La, Sm, $n = 1$; Ln = Pr, Nd, Eu, Gd, $n = 3$), were prepared and characterized by elemental analysis, electrical conductance and magnetic susceptibility measurements, and IR and electronic spectra.

The thermal decomposition of these complexes has been studied using TG and DTG techniques in air and argon. The TG curves show three main steps of decomposition. The intermediate oxycarbonate and the final decomposition product were characterized by X-ray diffraction, IR spectroscopy and magnetic susceptibility measurements. The final product is the corresponding $CuLn_2O_4$ (Ln = La–Gd), which can be obtained at temperatures even lower than 800 °C by isothermal decomposition of the coordination compounds.

INTRODUCTION

Although research on rare earth compounds has increased markedly during recent years, there are only a few papers concerning heterometal complexes comprising copper and a lanthanide ion [1–5].

In our laboratory, mixed coordination complex formation of the lanthanide and d-block elements has been widely studied [6–8]. We have studied the thermal behaviour of this new class of mixed coordination compounds in order to understand the mechanisms of decomposition and the nature of the decomposition products [9,10]. The aim of our most recent

0040-6031/91/$03.50 © 1991 – Elsevier Science Publishers B.V.

investigation is to obtain the mixed oxides by unconventional methods: decomposition of polynuclear coordination compounds.

A characteristic of the coordination chemistry of lanthanides is their pronounced tendency to form stable complex compounds with ligands containing oxygen as a donor atom [11]. In tests of their complex formation properties with several organic ligands, the best results were obtained with hydroxyphenylacetic (mandelic) acid. Following our research, we now report data obtained concerning the thermal decomposition of $CuLn_2(C_8H_7O_3)_6(OH)_2 \cdot nH_2O$ (Ln = La–Gd) complexes.

EXPERIMENTAL

Reagents

The oxides Ln_2O_3 (Ln = La, Nd–Gd) and Pr_2O_{11}, of 99.9% purity, were obtained from Fluka. The mandelic acid ($C_6H_5CHOHCOOH$) was extra-pure grade (Merck) and $Cu(NO_3)_2 \cdot 3H_2O$ was purum grade (Reactivul, Bucharest).

Synthesis of the lanthanide compounds

For the synthesis, the lanthanide oxides were transformed into nitrates. The $CuLn_2(C_8H_7O_3)_6(OH)_2 \cdot nH_2O$ complexes were prepared by adding $Ln(NO_3)_3 \cdot 3H_2O$ (Ln = La–Gd) solution to an ammonium mandelate solution in the molar ratio 1:8 to 1:16. The pH of the solution was adjusted from 4.0 to 6.5–7 using dilute NH_4OH solution. Light blue $CuLn_2(C_8H_7O_3)_6(OH)_2 \cdot nH_2O$ (Ln = La, Sm, $n = 1$; Ln = Pr, Nd, Eu, Gd, $n = 3$) crystals were precipitated from the solutions at room temperature over a period of 4 h. After collection by filtration the crystals were washed with water. Thereafter the products were dried in a vacuum desiccator at room temperature. Analytical data for the complexes are given in Table 1.

Instrumentation

The crystalline state of the solid compounds was investigated with a Philips PW 1400 X-ray diffractometer using chromium K_α radiation. The heating curves were recorded with a Paulik–Paulik–Erdey type MOM derivatograph (Q 1500) and on a DuPont TG 951 thermobalance. Visible spectra were recorded with a VSU 1 Zeiss Jena spectrophotometer. IR spectra were measured in a KBr matrix on a UR 10 Zeiss Jena spectrophotometer. Magnetic susceptibilities were measured by the Faraday method at room temperature. Electrical conductance measurements were carried out with a Radelkis conductometer Model OK-102/1 in dimethyl sulphoxide (DMSO) at 25 °C.

TABLE 1

Analytical, magnetic and molar conductance data of complexes

	Content (%) Found (Calculated)			μ_{eff} exp. (BM)	μ_{eff} calc. (BM)	Λ_M[a] (Ω^{-1} cm^2 mol^{-1})
	Ln	C	H			
$CuLa_2(C_8H_7O_3)_6(OH)_2 \cdot H_2O$	20.9 (21.4)	43.7 (44.3)	3.4 (3.5)	2.18	2.20	28.3
$CuPr_2(C_8H_7O_3)_6(OH)_2 \cdot 3H_2O$	20.6 (20.8)	42.0 (43.0)	4.0 (3.7)	4.33	5.41	30.1
$CuNd_2(C_8H_7O_3)_6(OH)_2 \cdot 3H_2O$	21.7 (21.4)	44.0 (42.8)	3.9 (3.7)	5.01	5.54	17.8
$CuEu_2(C_8H_7O_3)_6(OH)_2 \cdot 3H_2O$	21.8 (22.3)	42.5 (42.3)	4.1 (3.8)	–	–	–
$CuSm_2(C_8H_7O_3)_6(OH)_2 \cdot H_2O$	22.1 (22.5)	44.5 (43.6)	3.6 (3.5)	4.67	5.29	–
$CuGd_2(C_8H_7O_3)_6(OH)_2 \cdot 3H_2O$	23.1 (22.9)	40.4 (41.9)	3.8 (3.6)	10.04	12.36	20.3

[a] For 1×10^{-3} M solutions.

RESULTS AND DISCUSSION

Analytical results showed the stoichiometry of the complexes obtained to be $CuLn_2(C_8H_7O_3)_6(OH)_2 \cdot nH_2O$ (Table 1).

Electrical conductance measurements, on the other hand, revealed that the coordination of the ligands is maintained even in DMSO. For 1 : 1 electrolytes, the molar conductances in DMSO are reported to be 37–43 Ω^{-1} cm^2 mol^{-1} [12]. Molar conductances for $CuLn_2(C_8H_7O_3)_6(OH)_2 \cdot nH_2O$ clearly indicate that they behave as non-electrolytes in DMSO. Obviously the ligands are not displaced by the solvent molecules.

Magnetic moments of the complexes at room temperature are not similar to the tervalent lanthanide ions (Table 1) [13]. Some magnetic interaction between the metal ions was inferred as the magnetic moment of the complex is lower than the calculated value.

Because of the low solubility of the complexes in most solvents, the electronic spectra were measured by reflection on a solid sample. The electronic spectra are given in Fig. 1. In the cases of $CuLn_2(C_8H_7O_3)_6(OH)_2 \cdot nH_2O$ (Ln = La, Sm, Gd) no absorption was found at wavenumbers higher than 16000 cm^{-1}. This is natural, since La(III), Sm(III) and Gd(III) ions have no ligand field band and the broad band in the 18000–10000 cm^{-1} range has been assigned to the d–d transition of Cu(II) [14]. On the other hand, the spectra of Pr and Nd complexes (curve c) exhibit some sharp, yet weak, bands due to f–f transitions in the 25000–15000 cm^{-1} range. Characteristic bands of Nd^{3+} ion in the visible spectrum of

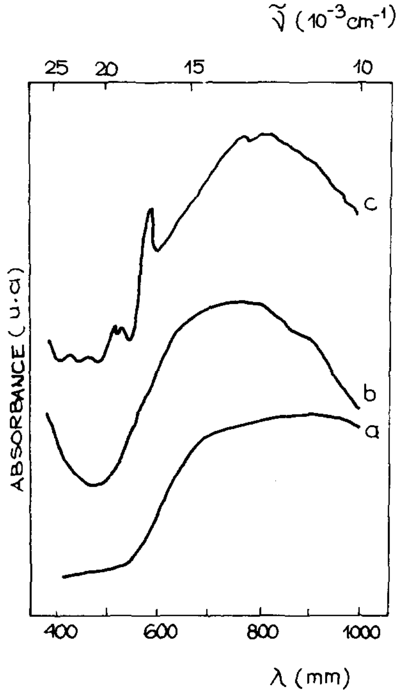

Fig. 1. Diffuse reflectance electronic spectra of (a) $Cu(C_8H_7O_3)_2 \cdot 2H_2O$; (b) $CuGd_2(C_8H_7O_3)_6(OH)_2 \cdot 3H_2O$; (c) $CuNd_2(C_8H_7O_3)_6(OH)_2 \cdot 3H_2O$.

$CuNd_2(C_8H_7O_3)_6(OH)_2 \cdot 3H_2O$ and their assignment are given in Table 2 [13].

The d–d band of $Cu(C_8H_7O_3)_2 \cdot 2H_2O$ (curve a), which can be ascribed to the CuO_4 chromophore, was observed at 11 500 cm^{-1} [15]. The d–d band due to the copper(II) ion in $CuLn(C_8H_7O_3)_6(OH)_2 \cdot nH_2O$ (Ln = La–Gd) falls in the range 15 000–17 000 cm^{-1} (curves b and c). Such a blue shift of the d–d band may be due to the increased planarity of the CuO_4 chromophore on forming a heterometal complex [15].

TABLE 2

Observed absorption peaks of Nd^{3+} ion in electronic spectra of $CuNd_2(C_8H_7O_3)_6(OH)_2 \cdot 3H_2O$

Wavenumber (cm^{-1})		Transition
Observed	From Ref. 13	
17241	17320	$^4G_{5/2} \rightarrow {}^4I_{9/2}$
18868	19182	$^4G_{7/2} \rightarrow {}^4I_{9/2}$
19608	19686	$^2G_{9/2} \rightarrow {}^4I_{9/2}$
21276	21400	$^4G_{11/2} \rightarrow {}^4I_{9/2}$
23256	23214	$^2P_{1/2} \rightarrow {}^4I_{9/2}$

TABLE 3

Infrared spectral data of $CuLn_2(C_8H_7O_3)_6(OH)_2 \cdot 3H_2O$ (Ln = La, Gd) [a]

Mandelic acid	Mandelate complex		$CuLn_2(C_8H_7O_3)_6(OH)_2 \cdot 3H_2O$		Assignment
	Cu	Gd	La	Gd	
3420	–	–	–	–	ν_{OH} alcohol
–	3100	3230	3200	3200	ν_{OH} alcohol, water
1720	–	–	–	–	$\nu_{C=O}$
–	1590	1580	1575	1595	$\nu_{(OCO)}$ asym.
1495	1495	1495	1495	1495	$\nu_{C=C}$
–	1430	–	1425	1440	$\nu_{(OCO)}$ sym.
–	–	1380	1370	1385	
1075	1056	1020	1050	1020	ν_{C-OH} alcohol
930	950	950	950	950	
740	750	750	750	750	$\nu_{=C-H}$
690	690	690	690	690	
650	590	600	610	600	ν_{-C-OH} alcohol
–	660	–	660	650	ν_{Cu-O}

[a] Wavenumbers.

Infrared spectra of the different complexes are essentially similar. The formation of the metal complexes can be diagnosed by the presence of two strong bands at ca. 1575–1595 cm^{-1} ($\nu_{(OCO)}$ asym.) and ca. 1370–1440 cm^{-1} ($\nu_{(OCO)}$ sym.) which can be assigned to the coordinated carboxylate group, while mandelic acid exhibits a band at 1720 cm^{-1} due to the free carboxyl group.

It has been pointed out [16] that the splitting of combination bands in the 1370–1450 cm^{-1} range has often been used in diagnosis of the bonding mode of the carboxylate group. The separation for the La and Gd compounds, for example, falls in the range 50 cm^{-1} (Table 3) and suggests that each of these complexes contains two types of carboxylate ions, namely bidentate and unidentate ions.

For the La–Gd complexes, the bands assignable to the ν_{C-OH} vibrations are observed in the 1050–1020 cm^{-1} region, whereas the corresponding band for the free ligand is observed at 1075 cm^{-1}. The shift of the ν_{C-OH} band towards lower wavenumbers on complexation indicates that all the α-hydroxy groups coordinate to the metal [17].

Selected IR bands of the complexes $CuLn_2(C_8H_7O_3)_6(OH)_2 \cdot nH_2O$ and the ligand and the assignments of some bands are given in Table 3.

The X-ray diffractograms of all the coordination compounds showed an amorphous structure at ambient temperature.

Thermal decomposition of copper–lanthanide mandelato-complexes

Thermograms in static air and dynamic argon atmospheres are shown in Fig. 2. The decomposition was found to proceed through various steps. At

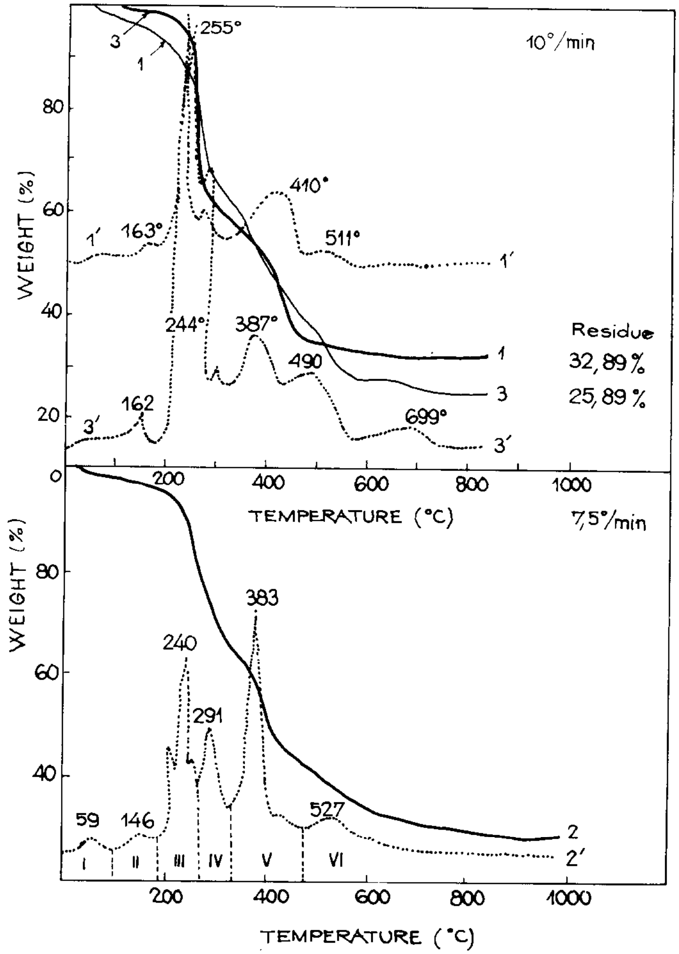

Fig. 2. TG (1, 2, 3) and DTA (1,', 2', 3') curves for: $CuLa_2(C_8H_7O_3)_6(OH)_2 \cdot H_2O$ in static air (1, 1') and in flowing argon (2, 2'); a mechanical mixture of lanthanum mandelate and copper mandelate in static air (3, 3').

least three steps could be identified from the TG curves: (i) dehydration; (ii) decomposition of the anhydrous mandelate complex to produce an oxycarbonate; (iii) decomposition of the oxycarbonate to $CuLn_2O_4$.

Cu–Ln mandelato-complexes were found to undergo dehydration up to 120 °C, then up to 190 °C, with a respective weight loss of around 4% (except for Ln = La and Sm) and 1.5%, compared with the calculated 4.03–3.93% and 1.36–1.38% corresponding to the loss of $3H_2O$ and $1H_2O$ per molecule respectively. This dehydration appears as an endotherm on the DTA curve.

Decomposition of anhydrous mandelate was found to be the most important and at the same time the most complex stage of thermal change. This process was found to be exothermic both in air and in argon, and

TABLE 4

TG data on the decomposition of $CuLn_2(C_8H_7O_3)_6(OH)_2 \cdot nH_2O$

Lanthanide	Weight loss (%)		Residue (%)
	Calc.	Found	
La	68.8	68.8	31.2
Pr	69.4	70.8	29.2
Nd	69.1	70.0	30.0
Sm	67.6	67.5	32.5
Eu	68.3	69.2	30.8
Gd	67.8	68.6	31.4

considerable foaming was observed. Decomposition started at around 200 ° C and was almost complete at around 500 ° C in air. At the end of this step an oxycarbonate, $CuLa_2O_{4-x}(CO_3)_x$, was identified as the product. By isothermal heating of Cu–La mandelato-complexes in air at 400 ° C for 30 min, the isolated oxycarbonate was found to have a value for x of 1. Analysis of a sample of the residue gave La = 43.2%, Cu = 19.8% and CO_2 = 12.1%, which agreed very well with the calculated values for $x = 1$ (La = 44.7%, Cu = 20.4% and CO_2 = 13.2%). The oxycarbonate was further identified by its IR spectrum, which showed absorption maxima at 1400–1500 cm^{-1} $(\nu_{CO_3^{2-}}$

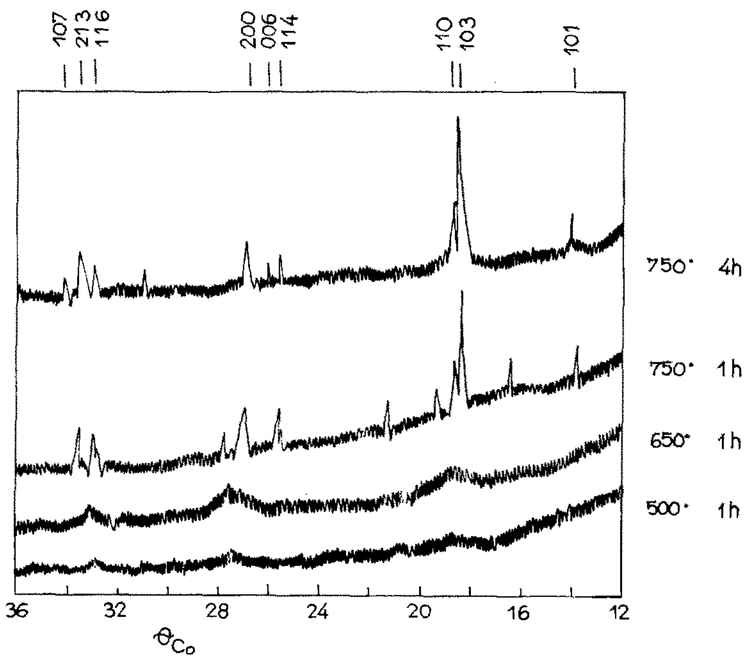

Fig. 3. Diffractograms of the oxide residues from decomposition of $CuPr_2(C_8H_7O_3)_6(OH)_2 \cdot 3H_2O$.

TABLE 5

Lattice parameters at room temperature and magnetic moments of $CuLn_2O_4$ (Ln = La–Gd)

	Experimental values			Literature data		
	Lattice parameters (Å)		μ_{eff} exp. (BM)	Lattice parameters (Å) [19]		μ_{eff} exp. [20] (BM)
	a	*c*		*a*	*c*	
$CuLa_2O_4$ [a]	5.367	13.16	0.86	5.363	13.17	0.00
$CuPr_2O_4$	3.953	12.20	4.79	3.958	12.18	5.15
$CuNd_2O_4$	3.943	12.15	4.77	3.945	12.15	5.04
$CuSm_2O_4$	3.913	12.03	2.37	3.908	12.01	3.04
$CuEu_2O_4$	3.906	11.98	5.09	3.903	11.96	–
$CuGd_2O_4$	3.889	11.89	11.30	3.892	11.90	11.34

[a] For orthorhombic $CuLa_2O_4$ the experimental value of the third lattice parameter is $b = 5.413$ Å, in agreement with $b = 5.406$ Å [19].

asym.) and 860 cm^{-1} ($\nu_{CO_3^{2-}}$ deform.), similarly to rare earth oxycarbonates [18]. Furthermore, in argon the residual product was identified as $CuLa_2O(CO_3)_3$. The oxycarbonate was amorphous on X-ray examination.

The final stage of decomposition was the loss of CO_2 from $CuLa_2O_{4-x}(CO_3)_x$ to produce $CuLa_2O_4$. The observed weight loss was slightly higher than the calculated value but the total weight loss up to this stage (Table 4) compared favourably with the calculated value for the formation of the oxocuprate, $CuLn_2O_4$. The oxide products resulting from the decomposition of the coordination compounds were analysed by X-ray diffraction; up to 750 °C the oxide residue was amorphous (Fig. 3). The formation of a crystalline phase begins at 750 °C. After 4 h thermal treatment at 750 °C, the lines of very well crystallized $CuLn_2O_4$ (Ln = La–Gd) appear (Fig. 3, Table 5). The IR spectra of $CuLa_2O_4$, $CuPr_2O_4$ and $CuGd_2O_4$ (Fig. 4) are similar to those already reported [21]. Here, the temperature of crystalline

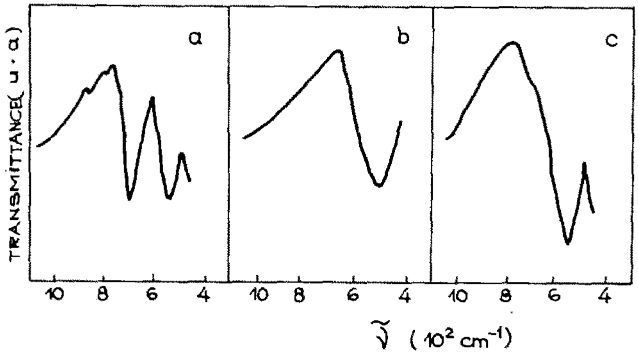

Fig. 4. IR spectra of (a) $CuLa_2O_4$; (b) $CuPr_2O_4$; (c) $CuGd_2O_4$.

phase formation is at least 100° lower than in the systems previously studied [19,22].

Thermal decomposition of a mechanical mixture of lanthanum mandelate and copper mandelate, $Cu(C_8H_7O_3)_3 \cdot 2H_2O$ (1 part)–$La(C_8H_7O_3)_2 \cdot 3H_2O$ (2 parts), was carried out in order to compare the behaviour of the mixture with that of the coordination compound. A comparison of the thermograms (Fig. 2a and 2c) reveals that the mechanical mixture decomposes in a different way to the Cu–La mandelato-complexes. The final residue at 800 °C is a mixture of La_2O_3 and CuO, the latter being identified by X-ray powder diffraction. This further establishes that the Cu–La mandelato-complex is a single phase containing both lanthanum and copper in the complex.

REFERENCES

1 Yu.I. Salinikov and V.V. Ustiak, Koord. Khim., 10 (1984) 1636.
2 D. Harrison and J.C. Buenzli, Inorg. Chim. Acta, 109 (1985) 185.
3 A. Bancini and C. Benetti, J. Am. Chem. Soc., 107 (1985) 8128.
4 M. Sakamoto, M. Takagi and H. Okawa, Bull. Chem. Soc. Jpn., 61 (1988) 1613.
5 M. Sakamoto and H. Okawa, Bull. Chem. Soc. Jpn., 61 (1988) 3319.
6 P. Spacu, S. Ploştinaru, L. Patron, A. Conţescu and N. Stănică, Rev. Roum. Chim., 30 (1985) 837.
7 P. Spacu, S. Ploştinaru, L. Patron, A. Conţescu, D. Crişan and N. Stănică, Rev. Roum. Chim., 32 (1987) 249.
8 P. Spacu, L. Patron, S. Ploştinaru, A. Conţescu and N. Stănică, Rev. Roum. Chim., 34 (1989) 1275.
9 E. Eftimie, E. Segal, L. Patron, S. Ploştinaru and A. Conţescu, Thermochim. Acta, 91 (1985) 369.
10 P.G. Schullerus, S. Ploştinaru, A. Conţescu, L. Patron and E. Segal, Thermochim. Acta, 153 (1989) 263.
11 W.E. Hatfield and R. Whyman, in R.L. Carlin (Ed.), Transition Metal Chemistry, Vol. 5, Marcel Dekker, New York, 1969.
12 W.J. Geary, Coord. Chem. Rev., 7 (1981) 81.
13 S.P. Sinha, Complexes of the Rare Earths, Pergamon, London, 1966.
14 M. Tanaka, M. Kitaoka and S. Kida, Bull. Chem. Soc. Jpn., 50 (1977) 127.
15 W. Kanda, M. Nakamura, H. Okawa and S. Kida, Bull. Chem. Soc. Jpn., 55 (1982) 471.
16 S. Battaglia and G.C. Pellacani, J. Am. Chem. Soc., 102 (1980) 2663.
17 N.B. Colthup, L.H. Daly and S.E. Wiberley, Introduction to Infrared and Raman Spectroscopy, Academic Press, New York, 1975.
18 G.H. Makiskova and S.B. Pirkes, Zh. Neorg. Khim., 29 (1984) 921.
19 I.S. Saplyghin and B.V. Lazarev, Zh. Neorg. Khim., 24 (1979) 1475.
20 T. Arakawa, S. Takeda, G. Adachi and J. Shiokawa, Mater. Res. Bull., 14 (1979) 507.
21 I.S. Saplyghin and N.V. Porotnikov, Zh. Neorg. Khim., 29 (1984) 853.
22 C.S. Ganguly and K.K. Single, Indian J. Chem., Sect. A, 15A (1977) 284.