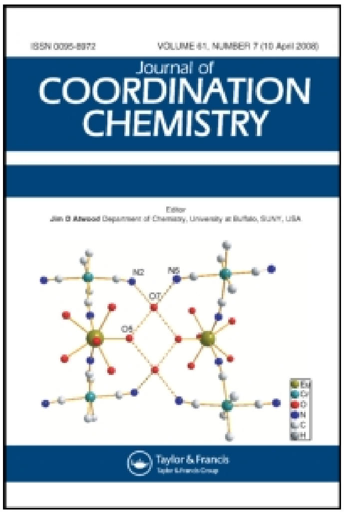

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

A NOVEL ORGANIC-INORGANIC COMPLEX WITH A ONE-DIMENSIONAL HELICAL ANION CHAIN: CRYSTAL STRUCTURE AND THERMAL STUDY OF TRIS(4-BROMO-BENZENAMMONIUM) PENTACHLOROCADMATE [(Br-$C_6H_4NH_3)_3CdCl_5$]

Da-Guang Li[a]; Cai-Ming Liu[a]; Xiao-Zeng You[a]; Wei-Qin Fu[b]; Wei Chen[c]; Kong Mun Lo[c]
[a] Centre for Advanced Studies in Science and Technology of Microstructure, Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing, P.R. China [b] Department of Chemical Engineering, Guangdong University of Technology, Guangzhou, P.R. China [c] Department of Chemistry, University of Malaya, Kuala Lumpur, Malaysia

To cite this Article Li, Da-Guang , Liu, Cai-Ming , You, Xiao-Zeng , Fu, Wei-Qin , Chen, Wei and Lo, Kong Mun(1998) 'A NOVEL ORGANIC-INORGANIC COMPLEX WITH A ONE-DIMENSIONAL HELICAL ANION CHAIN: CRYSTAL STRUCTURE AND THERMAL STUDY OF TRIS(4-BROMO-BENZENAMMONIUM) PENTACHLOROCADMATE [(Br-$C_6H_4NH_3)_3CdCl_5$]', Journal of Coordination Chemistry, 46: 1, 33 — 41
To link to this Article: DOI: 10.1080/00958979808047192
URL: http://dx.doi.org/10.1080/00958979808047192

J. Coord. Chem., 1998, Vol. 46, pp. 33–41
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under
the Gordon and Breach Science
Publishers imprint.
Printed in Malaysia.

A NOVEL ORGANIC–INORGANIC COMPLEX WITH A ONE-DIMENSIONAL HELICAL ANION CHAIN: CRYSTAL STRUCTURE AND THERMAL STUDY OF TRIS(4-BROMO-BENZENAMMONIUM) PENTACHLOROCADMATE [(Br–$C_6H_4NH_3)_3CdCl_5$]

DA-GUANG LI[a], CAI-MING LIU[a], XIAO-ZENG YOU[a,*],
WEI-QIN FU[b], WEI CHEN[c] and KONG MUN LO[c]

[a] *Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Nanjing University, Centre for Advanced Studies in Science and Technology of Microstructure, Nanjing 210093, P.R. China;* [b] *Department of Chemical Engineering, Guangdong University of Technology, Guangzhou 510090, P.R. China;* [c] *Department of Chemistry, University of Malaya, Kuala Lumpur 59100, Malaysia*

(Received 26 March 1997)

The complex (Br–$C_6H_4NH_3)_3CdCl_5$ was prepared. Single-crystal X-ray analysis revealed a novel structure, in which inorganic $(CdCl_5)_n$ helical anion chains are formed by $CdCl_6$ octahedra sharing bridging chlorine atoms, while the organic ammoium cations are bonded along the chains through hydrogen bonds. The complex is stable up to 140°C; phase transition characteristics were investigated by DTA-TGA.

Keywords: Cadmium; crystal structures; thermal analyses

Low-dimensional solid-state chain or layer complexes have received much attention. For example, perovskite-type layer compounds with general formula $(C_nH_{2n+1}NH_3)_2MX_4$ and $(NH_3C_nH_{2n}NH_3)MX_4$ ($M = Mn$, Cd, Cu; and $X = Cl$, Br) have been extensively investigated due to their interesting

---

[*] Corresponding author.

thermal and magnetic properties.[1–13] However, to the best of our knowledge, no helical chain compounds derived from MX_2 and ammonium ions has been reported. A novel complex salt of 4-bromobenzamine and cadmium chloride, $(Br{-}C_6H_4NH_3)_3CdCl_5$, has been prepared. It belongs to a new kind of compound formulated as $(RNH_3)_3MX_5$, and single-crystal X-ray studies indicated that its novel structure is quite different from those of perovskite-type layer compounds.

EXPERIMENTAL

Synthesis of $(Br{-}C_6H_4NH_3)_3CdCl_5$

The hydrochloride of 4-bromobenzenamine was used after recrystallization from 1 molar hydrochloride acid. The title complex was prepared by refluxing 4-bromobenzenamine hydrochloride (3 mmol) and $CdCl_2 \cdot 2.5H_2O$ (1 mmol) in ethanol (30 cm^3) in the presence of glycine for 1 h; excess concentrated hydrochloride was added dropwise during reflux. After being cooled to room temperature, the solution was left to evaporate for several weeks to give colourless crystals of the title complex. The crystals for elemental analyses were dried *in vacuo*. Yield 68.8%, *Anal.* Calc. for $(Br{-}C_6H_4NH_3)_3CdCl_5$ (%): C, 26.7; H, 2.6; N, 5.2. Found: C, 26.6; H, 2.5; N, 5.1.

Physical Measurements

Elemental analyses were performed on a Perkin-Elmer 240 instrument; IR spectra were recorded in KBr pellets in the 4000–400 cm^{-1} using a Nicolet 170SXFTIR spectrophotometer. Thermogravimetric and difference thermal analyses were performed on a DTA-TGA 2960 instrument under flowing N_2 with a heating rate of 10°C/min.

X-ray Crystallography

A colourless plate of approximate dimensions $0.20 \times 0.20 \times 0.30$ mm was used for X-ray analysis. Reflection data were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated MoK_α radiation ($\lambda = 0.71073$ Å) using the ω-2θ scan technique. Crystal data collection parameters are listed in Table I. Unit cell parameters were

TABLE I Crystal data and data collection parameters for $(Br{-}C_6H_4NH_3)_3CdCl_5$

Formula	$C_{18}H_{21}Br_3Cl_5N_3Cd$
Formula weight	808.76
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	15.6210(10)
b (Å)	7.7443(7)
c (Å)	22.2190(10)
β (°)	98.666(6)
V (Å$_3$)	2657.2(3)
Z	4
T (K)	293(2)
D_{calc} (g cm^{-3})	2.022
$F(000)$	1552
μ (MoKα) (cm^{-1})	58.48
Collection range (°)	$1.32 < \theta < 24.98$
Index ranges	$-18 \leq h \leq 18, 0 \leq k \leq 9, 0 \leq l \leq 26$
No. of observations	4849
No. of independent reflections	4666 [$R(int) = 0.086$]
Data/restraints/parameters	4666/0/274
R ($I > 2\sigma(I)$)	0.068
R_w ($I > 2\sigma(I)$)	0.130
R (all data)	0.130
R_w (all data)	0.149

obtained by a least-squares method based on the setting angles of 25 reflections in the range $10 < \theta < 12°$. A total of 4849 reflections was collected in the range $2.64° \leq 2\theta \leq 49.96°$, of which 4666 were independent ($R_{int} = 0.086$), and 2491 were observed with $I > 2\sigma(I)$ and used in the structure solution and refinement. Intensity data were corrected for Lorentz-polarization effects and absorption (Psi-scan technique).

Structure Solution and Refinement

The structure was solved by using the direct methods in the SHELXS86 program,[14] and refined by full-matrix least-squares on F_o^2, where $w = 1/[\sigma^2(F_o^2) + (0.0684P)^2 + 0.0000P]$ and $P = (F_o^2 + 2F_c^2)/3$, converging to $R = 0.068$, $R_w = 0.130$ ($I > 2\sigma(I)$ observed data); $R = 0.130$, $R_w = 0.149$ (all data). All H atoms were generated geometrically and were allowed to ride on their respective parent atoms. One hydrogen atom on each nitrogen atom was located from a difference map and was used to generate the other two hydrogen atoms of the NH_3^+ group. The NH_3^+ groups were treated as idealised rigid rotating groups to fit the maximum sum of the electron density. SHELXL 93[15] was used for refinement. H atom coordinates, thermal parameters and observed and calculated structure factors are available from the authors upon request.

RESULTS AND DISCUSSION

Structure of (Br–$C_6H_4NH_3)_3CdCl_5$

Figure 1 shows the atom numbering scheme and Figure 2 the packing of the ions in the unit cell. Atomic coordinates for non-hydrogen atoms are given in Table II. Selected bond distances and angles are listed in Table III. The anion consists of $(CdCl_5)_n$ helical chains along the *b* axis, which is unique for this kind of Cd derivative. The cadmium atom is coordinated by six chlorine atoms to form a slightly distorted octahedron, as previously suggested in perovskite-type layer compounds.[16,17] In the $CdCl_6$ octahedron of (Br–$C_6H_4NH_3)_3CdCl_5$, there are only two bridging chlorine atoms. In contrast, the mineral layer is quite often made of corner-sharing octahedra forming a perovskite-type structure, where $CdCl_6$ involves four bridging and two non-bridging chlorine atoms. This difference makes the anion in (Br–$C_6H_4NH_3)_3CdCl_5$ form $(CdCl_5)_n$ helical chains rather than the layer structure $(CdCl_4)_n$ in perovskite-type compounds. Another complex, (HOOC–CH=CH–(C_6H_4)–$NH_3)_2CdCl_4$, contains anion chains too,[18] but

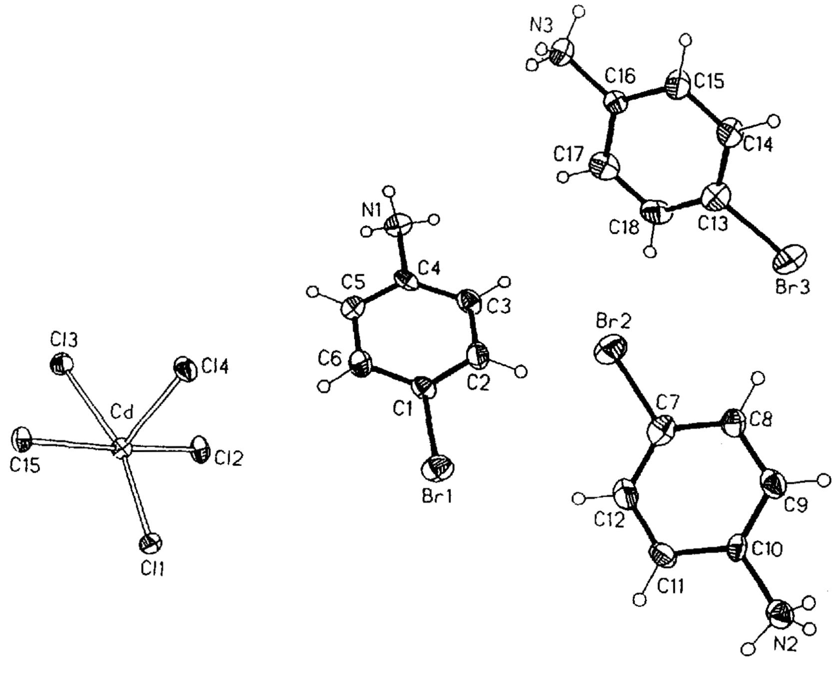

FIGURE 1 The numbering scheme for the atoms of (Br–$C_6H_4NH_3)_3CdCl_5$.

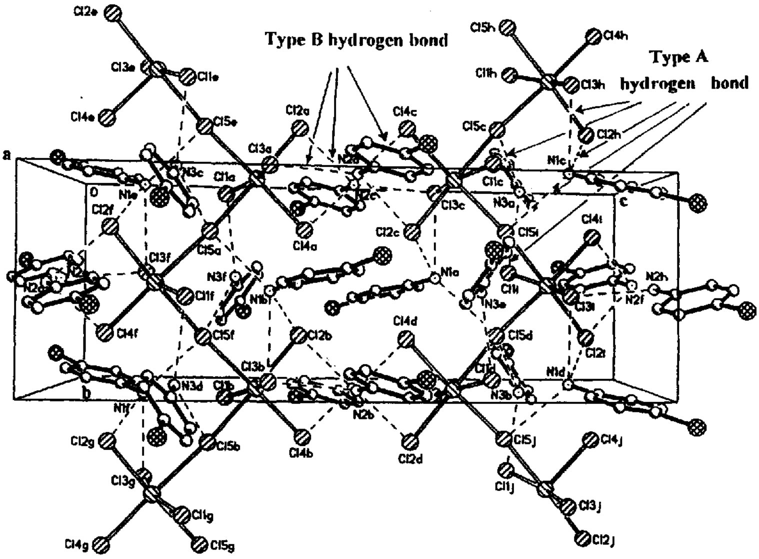

FIGURE 2 A view of the unit cell down the *a* axis.

these are built up from rows of $(CdCl_4)$ tetrahedra, and each $(CdCl_4)$ tetrahedron is on a mirror symmetry plane.

The distances of the Cd atom to the bridging Cl atoms in $(Br{-}C_6H_4NH_3)_3CdCl_5$ (average 2.781(3) Å) are significantly longer than those of the Cd atom to the non-bridging chlorine atoms (average 2.584(3) Å); a similar trend was observed in perovskite-type layer compounds such as $(C_{12}H_{14}N_2O)[CdCl_4]$[16] and $(C_6H_{10}N_2)[CdCl_4]$.[17] The Cd–Cl–Cd bond is not linear but forms an angle of 164.91(10)°, while the Cl–Cd–Cl bond angle formed by Cd and two bridging chloride atoms is 90.20(3)°.

Crystalline cohesion is achieved by means of two types of hydrogen bonds; type A forms the helical chain structure and the type B is for connects chains, as shown in Figure 2. Type A hydrogen bonds occur between the nitrogen atom of 4-bromobenzenammonium (N1 and/or N3) and the chlorine atoms of the $(CdCl_5)_n^{3n-}$ anion ($N{-}H \cdots Cl$ average 2.512 Å). Hydrogen bonds are formed by all three hydrogen atoms in NH_3^+ groups, in which two hydrogen atoms involve two non-bridging chlorine atoms but the third involves a bridging chlorine atom. This hydrogen bond is quite different from those in perovskite-type layer complexes; the latter hydrogen bond often involves only one hydrogen atom of ammonium groups.

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $(\mathrm{Br{-}C_6H_4NH_3})_3\mathrm{CdCl_5}$. *U*(*eq*) is defined as one third of the trace of the orthogonalized *Uij* tensor

	x/a	*y/b*	*z/c*	*U(eq)*
Cd	4701(1)	32(1)	3327(1)	34(1)
Br(1)	805(1)	6261(2)	4577(1)	56(1)
Br(2)	223(1)	8994(2)	6092(1)	65(1)
Br(3)	−271(1)	8478(2)	7900(1)	70(1)
Cl(1)	3211(2)	665(4)	2737(1)	38(1)
Cl(2)	4375(2)	−2502(4)	4041(1)	46(1)
Cl(3)	6343(2)	−450(4)	3600(1)	46(1)
Cl(4)	4609(2)	2432(4)	4133(1)	48(1)
Cl(5)	5228(2)	2587(3)	2565(1)	36(1)
N(1)	4009(5)	4635(11)	6395(4)	43(2)
N(2)	−3574(5)	9892(12)	5037(4)	44(2)
N(3)	3514(5)	10290(11)	7915(4)	40(2)
C(1)	1821(7)	5710(14)	5138(4)	36(3)
C(2)	1727(8)	5432(15)	5733(5)	48(3)
C(3)	2447(7)	5041(16)	6152(5)	46(3)
C(4)	3238(7)	5008(14)	5946(4)	35(2)
C(5)	3337(7)	5291(15)	5368(5)	44(3)
C(6)	2600(7)	5657(15)	4944(5)	47(3)
C(7)	−967(7)	9258(15)	5769(5)	45(3)
C(8)	−1526(7)	9873(16)	6131(5)	46(3)
C(9)	−2397(7)	10113(15)	5884(5)	46(3)
C(10)	−2661(6)	9673(13)	5292(5)	34(3)
C(11)	−2112(7)	9009(15)	4924(5)	44(3)
C(12)	−1247(8)	8776(16)	5171(5)	53(3)
C(13)	911(8)	9052(16)	7886(5)	48(3)
C(14)	1254(8)	10434(14)	8227(5)	47(3)
C(15)	2109(8)	10821(15)	8234(6)	52(3)
C(16)	2592(7)	9837(13)	7910(4)	32(2)
C(17)	2254(8)	8467(15)	7570(5)	51(3)
C(18)	1389(8)	8048(15)	7575(5)	52(3)

TABLE III Selected bond distances (Å) and angles (°) for $(\mathrm{Br{-}C_6H_4NH_3})_3\mathrm{CdCl_5}$

Cd–Cl(1)	2.541(3)	Cd–Cl(5)$^{\#1}$	2.755(3)
Cd–Cl(3)	2.573(3)	Cd–Cl(5)	2.807(3)
Cd–Cl(4)	2.600(3)	Cd$^{\#2}$–Cl(5)	2.755(3)
Cd–Cl(2)	2.622(3)	Br(1)–C(1)	1.912(10)
Br(2)–C(7)	1.900(11)	Br(3)–C(13)	1.903(12)
N(1)–C(4)	1.472(12)	N(2)–C(10)	1.463(12)
N(3)–C(16)	1.481(12)		
Cl(1)–Cd–Cl(3)	162.36(9)	Cl(4)–Cd–Cl(5)$^{\#1}$	177.60(9)
Cl(1)–Cd–Cl(4)	94.35(9)	Cl(2)–Cd–Cl(5)$^{\#1}$	87.32(9)
Cl(3)–Cd–Cl(4)	95.63(10)	Cl(1)–Cd–Cl(5)	83.22(8)
Cl(1)–Cd–Cl(2)	102.13(9)	Cl(3)–Cd–Cl(5)	82.65(8)
Cl(3)–Cd–Cl(2)	91.52(10)	Cl(4)–Cd–Cl(5)	87.92(9)
Cl(4)–Cd–Cl(2)	94.69(9)	Cl(2)–Cd–Cl(5)	173.83(9)
Cl(1)–Cd–Cl(5)$^{\#1}$	83.94(8)	Cl(5)$^{\#1}$–Cd–Cl(5)	90.20(3)
Cl(3)–Cd–Cl(5)$^{\#1}$	85.61(9)	Cd$^{\#2}$–Cl(5)–Cd	164.91(10)

$^{\#1}$ $-X+1, Y-1/2, -Z+1/2$; $^{\#2}$ $-X+1, Y+1/2, -Z+1/2$.

TABLE IV Hydrogen bond distances (Å) and angles (°) for $(Br-C_6H_4NH_3)_3CdCl_5$

N1-H1a···Cl 1	2.588(153.7)	N1-H1b···Cl 5	2.536(137.9)
N1-H1c···Cl 2	2.428(161.4)	N2-H2a···Cl 3	2.300(174.3)
N2-H2b···Cl 2	2.514(141.5)	N2-H2c···Cl 4	2.331(161.0)
N3-H3a···Cl 1	2.511(132.8)	N3-H3b···Cl 5	2.378(167.8)
N3-H3c···Cl 4	2.631(155.4)		

Type B hydrogen bonds occur among the nitrogen atom of 4-bromo-benzenammonium (N2) and the chlorine atoms from two adjacent $(CdCl_5)_n^{3n-}$ anions (N–H···Cl average 2.382 Å). Like type A, all three hydrogen atoms in NH_3^+ groups take part. However, all involving chlorine atoms are not bridged (two non-bridging chlorine atoms come from a $(CdCl_5)_n^{3n-}$ anion, the third non-bridging chlorine atom from an adjacent $(CdCl_5)_n^{3n-}$ anion). These hydrogen bonding distances are shorter than those of type A, suggesting that they are stronger.

IR Spectra and Thermal Analysis

In the IR spectra, there are two broad bands around 3009 and 2948 cm^{-1}, mainly attributed to classical N–H stretching vibrations of $-NH_3^+$, shifted to lower wavenumber due to the extensive hydrogen bonding. The presence of two bands is consistent with the result of the X-ray analysis. Other bands occur at 1617(w), 1568(m), 1484(s), 1600(m), 1070(s), 1015(s), 811(s), 483(s) and on comparable to those of $(Br-C_6H_4NH_3)Cl$ in standard spectra.[19]

$(Br-C_6H_4NH_3)_3CdCl_5$ is stable only up to 140°C. TG showed that it decomposes losing ammoium chloride in three distinct steps (Figure 3), *i.e.*, *via* two intermediate steps (stable phases) corresponding to the tetrachloride $(Br-C_6H_4NH_3)_2CdCl_4$ and trichloride $(Br-C_6H_4NH_3)CdCl_3$, respectively. The latter decomposes at 215°C to $CdCl_2$. On the basis of weight changes (25.4, 25.6 and 26.0% respectively), these processes corresponded to the loss of three $(Br-C_6H_4NH_3)Cl$ molecules (theory 25.8%) step by step. Similar trends were observed in perovskite-type layer compounds $(NH_4)_2CdX_4$ (X = Cl, Br).[20] The DTA curve for $(Br-C_6H_4NH_3)_3CdCl_5$ showed three endothermic peaks at 142, 203 and 238°C, corresponding to three phase transitions. Two $(Br-C_6H_4NH_3)^+$ ions connected with the same $(CdCl_5)_n$ chain probably were lost first, then the $(Br-C_6H_4NH_3)^+$ ammonium connected with different $(CdCl_5)_n$ chains. This would be in good agreement with the structure analysis, which shows that connection by type B hydrogen bonds is slightly stronger than that by Type A hydrogen bonds.

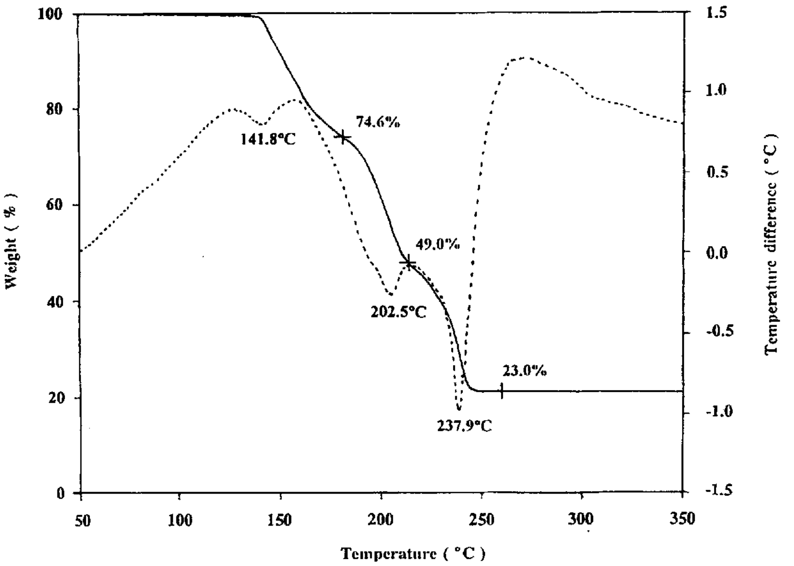

FIGURE 3 Thermogravimetric scan of $(BrC_6H_4NH_3)_3CdCl_5$ under flowing N_2 with a heating rate of 10°C/min.

Acknowledgements

This work was supported by a major project grant from the State Science and Technology Commission, the National Science Foundation of China and the University of Malaya (IRPA Grant No. 09-02-03-0004).

References

[1] L.J. de Jongh and A.R. Miedena, *Adv. Phys.*, **23**, 1 (1974).

[2] R. Kind, *Ferroelectrics*, **24**, 81 (1980).

[3] W. Depmeir, *J. Solid State Chem.*, **29**, 15 (1979).

[4] R. Mokhlisse, M. Couzi, N.B. Chanh, Y. Haget, C. Hauw and A. Meresse, *J. Phys. Chem. Solids*, **46**, 187 (1985).

[5] N.B. Chanh, C. Hauw, A. Meresse, M. Rey-Lafon and L. Ricard, *J. Phys. Chem. Solids*, **46**, 1413 (1985).

[6] M.A. White, *J. Chem. Phys.*, **81**, 6100 (1984).

[7] H. Hagemann and H. Bill, *J. Phys.*, **C18**, 6441 (1985).

[8] M. Couzi, N.B. Chanh, A. Meresse, P. Négrier, R.J. Papoular and R. Millet, *Phase Transition*, **14**, 69 (1989).

[9] P. Négrier, M. Couzi, N.B. Chanh, C. Hauw and A. Meresse, *J. Phys. France*, **50**, 405 (1989).

[10] F. Guillaume, C. Sourisseau, G. Lucazeau and A.J. Dianoux, *J. Phys. Chem. Solids*, **49**, 1079 (1988).

[11] K.J. Schenk and G. Chapuis, *J. Phys. Chem.*, **92**, 7141 (1988).

[12] T. Ishihara, J. Takahashi and T. Goto, *Phys. Rev. B*, **42**, 11099 (1990).

[13] C. Lartigue-Bourdeau, U.B. Chanh, P. Duplessix and B. Gallois, *J. Phys. Chem. Solids*, **54**, 349 (1993).

[14] G. Kopfman and R. Huler, *Acta Crystallogr.*, **B24**, 348 (1968); G.M. Shieldrick, *Acta Crystallogr.*, **A46**, 467 (1990).

[15] G.M. Shieldrick, *SHELX93, Program for crystal structure refinement* (University of Göttingen, Germany, 1993).

[16] X.-Y. Huang, Q. Ye, Q.-J. Meng and X.-Z. You, *Acta Crystallogr.*, **C51**, 2285 (1995).

[17] Q. Ye, Q.-J. Meng, X.-Z. You and X.-Y. Huang, *Acta Crystallogr.*, **C52**, 33 (1996).

[18] N.B. Chanh, C. Courseille, R. Duplessix, A. Meresse, M. Couzi and B. Tieke, *Mol. Cryst. Liq. Cryst.*, **188**, 261 (1990).

[19] *Standard Spectra Collection*, (Sadtler Research Laboratories, Division of Bio-rad. Laboratories, Inc., 1980).

[20] P.N. Namboodiri and V.V. Deshpande, *Thermochim. Acta*, **144**, 183 (1989).