

Structure of the Solid Solution $[\text{N}(\text{CH}_3)_4]_2\text{ZnCl}_{1.8}\text{Br}_{2.2}$ in the High- and in a New Low-Temperature Phase

BY E. COLLA

Laboratory of Solid State Physics, Swiss Federal Institute of Technology, CH-8093 Zürich, Switzerland

AND V. GRAMLICH AND W. PETER

Institute of Crystallography, Swiss Federal Institute of Technology, CH-8092 Zürich, Switzerland

(Received 18 August 1986; accepted 8 January 1987)

Abstract. $[\text{N}(\text{CH}_3)_4]_2\text{ZnCl}_{1.8}\text{Br}_{2.2}$, $M_r = 453.3$, hereafter $[\text{TMA}]_2\text{ZnHal}_4$. At 293 K, orthorhombic, $Pnma$, $a = 12.53$ (1), $b = 9.14$ (3), $c = 15.83$ (4) Å, $V = 1812.9$ (7) Å³, $Z = 4$, $D_x = 1.66$ Mg m⁻³, $\mu = 6.76$ mm⁻¹, $F(000) = 894.4$, $R = 0.066$ ($wR = 0.072$) for 1147 observed reflexions on a four-circle diffractometer, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å. The TMA groups exhibit large oscillations. At 198 K, monoclinic, $P12_1/a1$, $a = 24.84$ (5), $b = 9.09$ (6), $c = 15.64$ (5) Å, $\beta = 89.43$ (4)°, $V = 3531.3$ (4) Å³, $Z = 8$, $D_x = 1.70$ Mg m⁻³, $\mu = 6.89$ mm⁻¹, $F(000) = 1788.8$, $R = 0.074$ ($wR = 0.088$) for 1169 observed reflexions. Domains were encountered in the crystal and a large decrease of the temperature factor was observed. The phases studied are separated by two other phases: an incommensurate one and a monoclinic one with a threefold unit cell ($Z = 12$). The ZnHal_4 tetrahedra drive the transitions, rotating principally around the a axis (11°) and shifting their centre along the b axis (0.42 Å). Their small distortion is probably due to the crystal field effect (Hal-Zn-Hal angles range from 108.7 to 112.2°). The mean bond length Zn-Hal is 2.352 Å for $Pnma$ and 2.360 Å for $P12_1/a1$. Tetrahedra in the same bc plane rotate in the same sense.

Introduction. Recently the (x,T) phase diagram of the solid solution $[\text{TMA}]_2\text{ZnCl}_{4-x}\text{Br}_x$ was determined by means of DSC and X-ray measurements (Colla, Muralt, Arend, Ehrensperger, Perret, Godefroy & Dumas, 1984). The system shows complete miscibility over the whole concentration range with common high-temperature symmetry $Pnma$. The phases found are I ($Pnma$, $a = a_0$, $Z = 4$), II and II' (incommensurate, $2/5 + \delta$ and $1/3 + \delta$, along x), III ($Pn2_1a$, ferroelectric, $a = 5a_0$), IV ($P2_1/n11$, $a = 3a_0$), V ($P112_1/a$, $a = a_0$) in two different regions, VI ($P2_12_12_1$, $a = 3a_0$), and VII ($P12_1/a1$, $a = 2a_0$). In order to clarify the mechanism of the successive phase transitions of this system, details of the structure at each phase are desired. The structures of $[\text{TMA}]_2\text{ZnBr}_4$ at room temperature (phase I) and in the low-temperature

configuration (phase IV) have already been determined by Trouélan, Lefebvre & Derollez (1984).

Phases IV, V and VII undergo proper or improper ferroelastic phase transitions and are usually twinned. We report the structure of a solid-solution system ($x = 2.2$) in phase I (293 K) and in the new phase VII (198 K) which does not occur in the pure compounds. It is stable down to $T = 20$ K and exists for x ranging from 0.4 up to 3.0. An efficient method of coping with ferroelastic domain problems is shown.

Experimental. Homogeneous solid-solution crystals were obtained by a growth procedure based on a temperature-difference growth technique with thermally enforced convection and the use of equilibrated solid and aqueous solutions (Arend, Perret, Wüest & Kerkoc, 1986). The composition was determined chemically. A specimen of nearly spherical shape (0.4 mm diameter) was fixed on a capillary tube and coated with epoxy-type resin (Araldite). The temperature of the specimen was controlled at 293.0 (5) K and 198.0 (5) K by a regulated stream of nitrogen gas. Data were collected on an automatic Syntex $P2_1$ four-circle diffractometer with graphite-monochromated $\text{Mo } K\alpha$ radiation. The orientation matrix and the cell parameters were refined by least-squares calculations based on 25 reflexions in the range $6 < \theta < 12^\circ$. For the data collection of phase I the $\theta:2\theta$ scanning mode was used with $2 < \theta < 22^\circ$ [$0.05 < (\sin\theta)/\lambda < 0.54$ Å⁻¹] and for phase VII the ω scanning mode with $1.3 < \theta < 15^\circ$ [$0.03 < (\sin\theta)/\lambda < 0.36$ Å⁻¹]. Systematic absences previously found by precession photographs were confirmed by these measurements. For the low-temperature phase a theoretical space-group analysis (Colla, 1987) and the occurrence of a monoclinic angle $\Delta\beta$ indicated $P12_1/a1$ as the probable space group for phase VII. The space group $Pnma$ for phase I was also confirmed. Three standard reflexions monitored every hour (400, 040, 004) did not exhibit any significant change in intensities. For phase I we measured 7460 reflexions corresponding to 1147

non-equivalent reflexions ($R_{\text{int}} = 0.055$) with $I > 3\sigma(I)$ in the range $0,0,0 < hkl < 13,9,17$ and for phase VII 5547 reflexions corresponding to 1169 non-equivalent reflexions ($R_{\text{int}} = 0.043$) with $I > 3\sigma(I)$ in the range $0,0,10 < hkl < 13,6,10$. The weights were calculated as $1/\sigma(I)$. The *XRAY72* crystallographic programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) and *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) were used to determine the structure on a CDC computer; H-atom positions not found; scattering factors from Cromer & Mann (1968); anomalous-dispersion terms from Cromer (1965); no absorption or extinction corrections; anisotropic LS refinement based on F values; estimated agreement factors $S = 1.75$ and 2.32 , ratio of max. shift to e.s.d. 1.1 and 0.9 , max. heights in final difference Fourier synthesis smaller than 1.6 and 0.8 e \AA^{-3} for the high- and low-temperature phases respectively.

Discussion. *Phase I (Pnma).* The average structure of $[\text{TMA}]_2\text{ZnBr}_4$ in the high-temperature phase (Trouélan *et al.*, 1984), which is expected to be isostructural with the solid solution, was employed for the initial structure with the centrosymmetric space group *Pnma* in the least-squares calculations. Refinement with anisotropic thermal parameters converged at $R = 0.066$. The population parameters of Hal atoms for the four sites of the tetrahedra did not show any significant anomaly, suggesting a random distribution of the Cl and Br anions for this concentration. A difference Fourier map using the non-hydrogen atomic parameters did not

Table 1. *Positional parameters and equivalent isotropic temperature factors (\AA^2) at $T = 293 \text{ K}$ (phase I) with e.s.d.'s in parentheses*

PP is the population parameter (blank means 1.0). $U_{\text{eq}} = \frac{1}{3} \text{ trace } U$.

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}	PP
Zn(1)	0.2478 (2)	0.2500	0.4083 (1)	0.068 (1)	
Cl(1)	0.0604 (2)	0.2500	0.4043 (2)	0.098 (2)	1.73 (2)
Cl(2)	0.3112 (2)	0.0386 (3)	0.3391 (2)	0.105 (2)	1.67 (1)
Cl(3)	0.3138 (3)	0.2500	0.5462 (2)	0.121 (3)	1.57 (2)
N(1)	0.149 (1)	0.2500	0.097 (1)	0.077 (1)	
N(2)	-0.012 (1)	0.2500	0.6728 (9)	0.08 (1)	
C(11)	0.268 (3)	0.2500	0.099 (2)	0.18 (1)	
C(12)	0.109 (2)	0.124 (3)	0.144 (2)	0.25 (1)	
C(13)	0.103 (3)	0.2500	0.011 (2)	0.19 (1)	
C(21)	-0.057 (2)	0.2500	0.762 (2)	0.15 (1)	
C(22)	0.049 (2)	0.119 (3)	0.659 (2)	0.23 (1)	
C(23)	-0.098 (3)	0.2500	0.611 (3)	0.25 (2)	

show residual maxima larger than 1.6 e \AA^{-3} . Hydrogen atoms were not found around the C atoms in the map and were not used in further calculations. C atoms show high thermal vibrations and the thermal parameters of the Hal atoms are strongly anisotropic (Fig. 1). The final atomic parameters and their standard deviations are listed in Table 1.*

Phase VII (P12₁/a1). In order to collect useful data we tried to solve the domain problem by applying mechanical stress on the crystal at low temperature by means of micropincers mounted on the collimator of the diffractometer. After orientation at the desired temperature it was possible to observe the monoclinic angle by an ω scan around the b axis using the reflections 004 and 004.

The fact that the intensity ratio of the split peaks was proportional to the volume ratio of the domains enabled us to choose a suitable direction for the driving force moving the domain walls. Thus we could successfully switch from the smaller domain to the other one. We obtained an almost-single-domain crystal where the contributions of undesired twins were negligible.

Least-squares calculations with starting parameters as in the high-temperature phase were first performed on the small unit cell of phase I but with symmetry $P12_1/m1$ using only $2h,k,l$ reflexions. We obtained an average structure with strong anisotropic thermal factors for the tetrahedra ($R \approx 0.10$), giving a qualitative idea of the shifts and rotations of the molecules which were possibly occurring. We applied different shift and rotation models to the ZnHal_4 tetrahedra, calculated by theoretical space-group analysis and in agreement with the average structure information. However, these trials were not successful.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43710 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

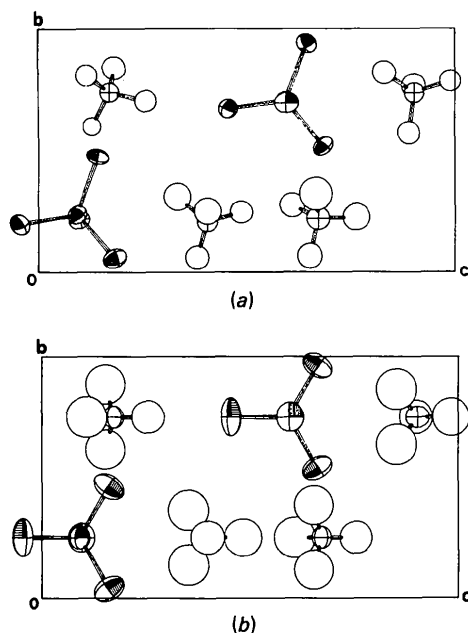


Fig. 1. (a) Asymmetric unit of the structure of phase VII. (b) The corresponding view of phase I.

Since the phase angles of the $2h, k, l$ reflexions were known from the average structure we tried to find the phase angles of the satellites with *MULTAN* (Main *et al.*, 1980), starting from these known phases. After some unsuccessful trials random starting phase angles were used and a good solution was found which showed all ZnHal₄ tetrahedra. The remaining TMA tetrahedra were easily found in a difference Fourier map. Least-squares refinements reached an agreement factor of $R \approx 0.074$. The residual maxima in the difference Fourier map were smaller than $0.8 \text{ e } \text{Å}^{-3}$. In Table 2 the final atomic parameters and their standard deviations are listed. By comparison with the high-temperature structure a large decrease of the thermal parameters in the low-temperature phase is observed. The TMA groups drastically reduce their librational vibrations and may thus play an important role in the phase transition. The most significant shift of these groups occurs along the b axis with values between 0.12 and 0.38 Å .

The ZnHal₄ tetrahedra show similar behaviour. The disorder produced by the librational vibration around the a axis disappears. The translation (t_b) and rotations (θ_a, θ_c) of the two independent tetrahedra are 0.575 and 0.175 Å , $-9, -11$ and $-2.3, 5.5^\circ$ respectively. The tetrahedra lying in planes parallel to the bc plane rotate around the a axis in the same sense, supporting the microscopic model with ferro-rotational interactions inside these planes and competition between different planes.

In some β -K₂SO₄-type structures the environment of one of the cations is unfavourable because the cavity is too large and the valence calculations give values lower than those expected. The quantitative analysis performed on Cs₂CdBr₄ by Altermatt, Arend, Gramlich, Niggl & Petter (1984) could not be applied in our case, the cation being a TMA-molecule ion. Simulations with a large spherical ion did not yield satisfactory results. The explanation may lie in the large variety of conformations of this molecule which can produce a multitude of different hydrogen-Hal contacts.

As in phase I we observed small and probably insignificant deviations of the population parameters from the average values. In contrast to our results, Jannot (1986) found for TMA₂ZnCl_{4-x}Br_x with $x < 0.4$ using Raman spectroscopy a significant preference of the Br anions to occupy the top position in the a direction of the tetrahedra. Such a distribution is consistent with the idea of preferred libration of the tetrahedra around the a axis, leaving the heavy Br anion at the relatively motionless top site. This interpretation is certainly not complete for the whole concentration range since we found a random distribution of the Hal anions but their rotation around the a axis remains the most important one. In the low-temperature phase of the pure Br compound the most important rotation is around the c axis (Trouélan, Lefebvre & Derollez,

Table 2. *Positional parameters and equivalent isotropic thermal factors* (Å^2) at $T = 198 \text{ K}$ (phase VII) with *e.s.d.'s in parentheses*

PP is the population parameter (blank means 1.0). $U_{\text{eq}} = \frac{1}{3} \text{ trace } U$.

	x	y	z	U_{eq}	PP
Zn(1)	0.3725 (2)	0.2958 (5)	0.4073 (3)	0.049 (7)	
Hal(11)	0.2777 (3)	0.3048 (7)	0.4040 (4)	0.063 (1)	0.99 (2)
Hal(12)	0.4052 (3)	0.4834 (7)	0.3170 (4)	0.056 (9)	0.99 (2)
Hal(13)	0.4027 (2)	0.0612 (6)	0.3560 (3)	0.050 (8)	1.14 (8)
Hal(14)	0.4063 (3)	0.3298 (8)	0.5449 (4)	0.06 (1)	0.87 (2)
Zn(2)	0.1233 (2)	0.2637 (5)	0.0923 (3)	0.053 (7)	
Hal(21)	0.1559 (3)	0.3046 (7)	-0.0458 (4)	0.067 (1)	0.97 (2)
Hal(22)	0.1498 (2)	0.0252 (5)	0.1420 (3)	0.047 (8)	1.10 (2)
Hal(23)	0.0284 (3)	0.2858 (6)	0.0970 (4)	0.05 (1)	1.01 (2)
Hal(24)	0.1611 (3)	0.4429 (7)	0.1827 (4)	0.064 (9)	0.97 (2)
N(1)	0.492 (1)	0.263 (3)	0.830 (2)	0.053 (3)	
C(11)	0.467 (2)	0.297 (4)	0.742 (3)	0.07 (1)	
C(12)	0.540 (2)	0.163 (5)	0.819 (3)	0.08 (2)	
C(13)	0.511 (2)	0.402 (5)	0.871 (2)	0.05 (1)	
C(14)	0.450 (2)	0.191 (5)	0.886 (3)	0.07 (1)	
N(2)	0.823 (2)	0.235 (3)	0.098 (2)	0.06 (4)	
C(21)	0.799 (2)	0.319 (5)	0.171 (3)	0.08 (2)	
C(22)	0.808 (2)	0.072 (5)	0.111 (3)	0.07 (2)	
C(23)	0.885 (3)	0.265 (5)	0.100 (3)	0.09 (2)	
C(24)	0.802 (2)	0.284 (5)	0.012 (3)	0.06 (1)	
N(3)	0.572 (2)	0.207 (4)	0.405 (2)	0.06 (4)	
C(31)	0.545 (2)	0.311 (6)	0.333 (3)	0.11 (2)	
C(32)	0.559 (2)	0.062 (6)	0.381 (3)	0.08 (2)	
C(33)	0.547 (2)	0.247 (5)	0.487 (3)	0.07 (2)	
C(34)	0.632 (3)	0.251 (6)	0.405 (3)	0.11 (2)	
N(4)	0.747 (2)	0.220 (4)	0.670 (2)	0.083 (4)	
C(41)	0.723 (2)	0.226 (5)	0.761 (3)	0.11 (2)	
C(42)	0.758 (2)	0.066 (6)	0.651 (3)	0.09 (2)	
C(43)	0.703 (2)	0.276 (5)	0.608 (3)	0.09 (2)	
C(44)	0.796 (3)	0.322 (8)	0.666 (4)	0.16 (3)	

1985) and this fact may indicate a trend to decrease the relative rotation around the a axis with increasing Br concentration. All this is reflected in the (x, T) phase diagram of TMA₂ZnCl_{4-x}Br_x (Colla *et al.*, 1984) which shows for the low-temperature region (~ 263 – 173 K) a phase change at $x \approx 3$ from phases with dominant rotation around the a axis to a dominant rotation around the c axis. For $x < 0.5$ there is a weaker dependence of the phase diagram on the Br concentration which may be caused by the supposed high Br occupation probability at the motionless top of the tetrahedra.

Since it is not to be expected that the tetrahedra orient themselves during the growth process with a Br atom pointing along the a direction we can infer that this could be an exceptional case where a random system tends to higher order through phonon excitations.

In continuation of this work X-ray analyses of the structures of a Br-poor sample are in preparation for phases I and IV. We hope to obtain access to useful information about the last question suggested and about the microscopic mechanism driving the phase transitions in this system.

The authors thank Professor H. Arend for crystal growth and Professor R. Blinç for valuable discussions. This work is supported by the Swiss National Fond.

References

- ALTERMATT, D., AREND, H., GRAMLICH, V., NIGGLI, A. & PETTER, W. (1984). *Acta Cryst.* **B40**, 347–350.
- AREND, H., PERRET, R., WÜEST, H. & KERKOC, P. (1986). *J. Cryst. Growth*, **74**, 321–325.
- COLLA, E. (1987). In preparation.
- COLLA, E., MURALT, P., AREND, H., EHRENSPERGER, M., PERRET, R., GODEFROY, G. & DUMAS, C. (1984). *Solid State Commun.* **52** (12), 1033–1036.
- CROMER, D. T. (1965). *Acta Cryst.* **18**, 17–23.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
- JANNOT, B. (1986). Private communication.
- MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England, and Louvain, Belgium.
- STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. W. & HALL, S. R. (1972). The XRAY72 system – version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.
- TROUÉLAN, P., LEFEBVRE, J. & DEROLLEZ, P. (1984). *Acta Cryst.* **C40**, 386–389.
- TROUÉLAN, P., LEFEBVRE, J. & DEROLLEZ, P. (1985). *Acta Cryst.* **C41**, 846–850.

Acta Cryst. (1987). **C43**, 1073–1075

Structure of the Charge-Transfer Salt Bis(methylenedithio)tetrathiafulvalene Hexafluoroantimonate(V)

BY PAUL J. NIGREY

Sandia National Laboratories, PO Box 5800, Albuquerque, New Mexico 87185, USA

EILEEN DUESLER

Department of Chemistry, University of New Mexico, Albuquerque, New Mexico 87131, USA

AND HAU H. WANG AND JACK M. WILLIAMS

Chemistry and Materials Science Divisions, Argonne National Laboratory, Argonne, Illinois 60439, USA

(Received 18 August 1986; accepted 15 January 1987)

Abstract. $C_8H_4S_8^+AsF_6^-$, $M_r = 592.38$, triclinic, $P\bar{1}$, $a = 5.664$ (1), $b = 7.488$ (1), $c = 9.614$ (2) Å, $\alpha = 91.24$ (2), $\beta = 91.63$ (2), $\gamma = 100.46$ (1)°, $V = 400.7$ (1) Å³, $Z = 1$, $D_m = 2.43$, $D_x = 2.45$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu(\text{Mo } K\alpha) = 28.0$ cm⁻¹, $F(000) = 285$, $T = 293$ K, $R = 0.014$ for 1388 observed reflections. The cation radicals stack along **b** to form columns with intrastack separations of about 3.867 Å. Shortest interstack S...S separations range from 3.575 to 3.696 Å. The central C=C bond of the cation is 1.388 (4) Å.

Introduction. Charge-transfer salts derived from the π -electron donor molecule bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) and linear centrosymmetric charge-compensating anions exhibit superconductivity at atmospheric pressure and temperatures as high as 8 K [Schirber *et al.* (1986) and references cited therein]. The crystal structure of these organic superconductors consists of donor cation-radicals arranged in a 'corrugated sheet network' (Williams *et al.*, 1984) in which the short interstack S...S separations predominate and little or no columnar stacking occurs. These interstack interactions are thought to be responsible for the

two-dimensional character exhibited by these materials. In view of the importance of these interstack interactions (Leung *et al.*, 1985) for stabilizing the tendency of these materials to undergo lattice distortions, we have concentrated on preparing charge-transfer salts based on the donor bis(methylenedithio)tetrathiafulvalene (BMDT-TTF). This choice was motivated by the belief that the highly symmetrical and planar structure of BMDT-TTF (Kato, Kobayashi, Kobayashi & Sasaki, 1985) is likely to lead to increased two-dimensional interactions. A similar approach has been reported for the preparation of two 3:1 complexes, (BMDT-TTF)₃PF₆(DCE), DCE = dichloroethane (Kato, Kobayashi, Kobayashi & Sasaki, 1984), and (BMDT-TTF)₃ClO₄(DCE) (Kobayashi, Kato, Mori, Kobayashi, Sasaki, Saito & Inokuchi, 1985). We have previously reported preliminary structural data on a 2:1 complex, (BMDT-TTF)₂Au(CN)₂ (Nigrey, Morosin, Kwak, Venturini & Baughman, 1986). In this paper, we report the crystal structure of the 1:1 complex, (BMDT-TTF)SbF₆.

Experimental. The crystals were prepared by electrochemical oxidation of BMDT-TTF (1.4 mg) in 10 ml of