observed some additional very weak X-ray reflexions when a crystal of copper formate tetrahydrate was cooled below its transition temperature.

In the present work a crystal, lightly smeared with Vaseline to prevent dehydration, was mounted in a Weissenberg camera and cold gas from boiling liquid nitrogen was passed round it. Filtered Cu $K\alpha$ radiation was used with the generator running at 40 kV and 20mA to take equi-inclination photographs about the a and c axes. With exposure times of four hours and use of Ilford Industrial G film many weak spots were observed in addition to the spots appearing on photographs taken at room temperature.

The unit cell was determined to be $a = 8{\cdot}17 \pm 0{\cdot}03$ $b = 8{\cdot}12 \pm 0{\cdot}03$, $c = 12{\cdot}64 \pm 0{\cdot}06$ Å, $\beta = 101 \pm 1°$ and is thus the same as that of the room-temperature structure except for a doubling of the c axis. As far as could be judged by eye the intensities of all hkl reflexions were equal to those of $h\bar{k}l$ reflexions so that the cell is almost certainly monoclinic. The only systematic absences observed were for $0k0$ with k odd: many weak reflexions were observed which preclude the space groups $P2_1/a$ and $P2_1/n$. The space group $P2_1/m$ must also be precluded for the following reason. No noticeable change in the intensities of the spots common to the high and the low temperature phases resulted when the crystal was cooled below the transition temperature. This means that only minor shifts in the positions of the heavy atoms can occur during the transition, whereas very large shifts would be required to construct a structure with the symmetry of $P2_1/m$. The only possible space group is thus $P2_1$.

Some of the additional reflexions observed occur at high angles, $(\sin\theta)/\lambda > 0{\cdot}6$ Å^{-1}, at which hydrogen atoms contribute negligibly to the diffracted intensities. Thus, although there is convincing evidence that rearrangement of hydrogen atoms in the water layers is chiefly responsible for the antiferroelectric properties below the critical temperature, the present work shows that small displacements of heavy atoms also occur during the transition.

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Monosemicarbazide hydrobromide

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The new salt of semicarbazide with HBr: CH_6N_3OBr has cell constants $a = 7{\cdot}800$ (3), $b = 13{\cdot}509$ (3), $c = 4{\cdot}725$ (5) Å. Solubility and pleochroism of the compound are explained in terms of a ribbon like structure.

Crystal data

While studying the combinations of halogenidric acids with semicarbazide: $H_2NNHCONH_2$ (SEM from now on), a second salt of HBr with the base has been characterized. The components here being equimolar, the new salt will have to be called monosemicarbazide hydrobromide, to distinguish it from the disemicarbazide which presents an acid-base ratio of one to two (Boldrini, 1971).

Pseudohexagonal, white, shining, elongated prisms of SEMHBr separate by evaporating 50 ml of a 50% ethanol–water solution containing 7·5 g of freshly prepared SEM and 67·6 g of an aqueous solution of hydrobromic acid at 48%. The preparative stoichiometry is one mole of SEM and four of HBr. Crystals of SEMHBr appear always regularly shaped, sometimes one inch long, with prominent forms: {010}, {121}, {120}, and {100}. They are pleochroic, optically biaxial, birefringent and present extinction parallel to the elongation axis. In a dry atmosphere the compound is stable, but it is slightly hygroscopic in open air, and when it is exposed to X-ray radiation it decomposes, rapidly becoming yellowish.

A preliminary X-ray investigation has shown that SEMHBr is orthorhombic. Crystallographic data for it and for SEMHCl (Michael, 1919), measured by precession methods with Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å) and $PbCl_2$ as calibrating substance ($a = 7{\cdot}61892$, $b = 9{\cdot}04443$, $c = 4{\cdot}53345$ Å), are reported in Table 1. The specific gravity has been obtained by flotation in $CHBr_3$–CCl_4 mixtures. Referring to the estimated standard deviations (e.s.d.'s) of Table 1, the difference in accuracy between columns 2 and 3 is due to the more rapid decomposition of SEMHBr. Also comparison of columns 3 and 4 shows that accuracy has been markedly improved for SEMHCl, while the more recent values on the same substance, column 5, appear inaccurate (Nardelli, Fava & Giraldi, 1965). For determining the space group of SEMHBr, extinctions were found only along the three crystallographic axes for reflexions with odd indices. This establishes for SEMHBr the same space group $P2_12_12_1$ as for SEMHCl (Johnson, 1960).

The structural analogy between the two substances, suspected from the similarity of the two anions and of the cell parameters, is confirmed by a detailed study of their diffraction patterns. They are in fact superimposable and show equal trends of intensities. The four strongest reflexions of SEMHCl, for instance, are also the strongest for SEMHBr, and of comparable orders of magnitude; their indices are reported above as the main crystalline forms found for SEMHBr. It can be concluded then that both salts have the same crystal structure and are made up of halogen anions and SEMH$^+$ cations, the latter being hydrogen bonded in the direction of the elongation axis

Table 1. *Crystallographic data for monosemicarbazide hydrobromide* (SEMHBr) *and monosemicarbazide hydrochloride* (SEMHCl)

Standard deviations are given in parenthesis.

	SEMHBr	SEMHCl	SEMHCl (Johnson, 1960)	SEMHCl (Nardelli *et al.*, 1965)
Mol. formula	CH_6N_3OBr	CH_6N_3OCl	CH_6N_3OCl	CH_6N_3OCl
Mol. wt.	155·987	111·531	111·531	111·5
a	7·800 (3) Å	7·545 (1) Å	7·543 (15) Å	7·51 (1) Å
b	13·509 (3)	13·215 (3)	13·224 (26)	13·13 (1)
c	4·725 (5)	4·668 (1)	4·668 (15)	4·64 (1)
V	497·874 Å^3	465·433 Å^3	465·626 Å^3	457·8 Å^3
D_m (25°C)	2·088 g.cm^{-3}	1·594 g.cm^{-3}	1·58 g.cm^{-3}	
D_c	2·081	1·592	1·59	1·618
Space group	$P2_12_12_1$–19	$P2_12_12_1$–19	$P2_12_12_1$–19	$P2_12_12_1$–19
Z	4	4	4	4
Z_{calc}	4·01	4·01	3·97	3·94

(Johnson, 1960). Since the crystallographic data of SEMHBr agree very well with those of SEMHCl, and the two substances are isostructural, it has been thought unnecessary to make a full chemical analysis of the new crystals. Only Br^- has been checked by weighing it as AgBr or by titration with NaOH. Calculated percentages of the elements in SEMHBr are:

Br 51·23, O 10·26, N 26·94, C 7·70, H 3·88.

Physical properties

Some of the physical properties were measured for SEMHBr as well as SEMHCl. They can be explained in terms of the crystal structure, as known for the latter (Johnson, 1960; Nardelli, Fava & Giraldi, 1965). At the same time further evidence is given that the two salts are isostructural.

Pleochroism is exhibited by both compounds along the elongation axis. It is stronger in SEMHBr because Br^-, when compared with Cl^-, is a better scatterer of electromagnetic radiation. Therefore, from what has been suggested about the dependence of color in the direction of vibration of light (Mandarino, 1959), it can be deduced that the SEMHBr structure is made up of a stringlike arrangement of Br^- ions along the c axis, as it is found for Cl^- in SEMHCl.

It is known that SEMHCl is very soluble in water and slightly soluble in ethanol (Michael, 1919). In order to elaborate on this, accurate titrations were performed with NaOH and phenolphthalein, and both SEM compounds were found to be soluble in seven solvents. Their solubilities in the most effective of these solvents are quantitatively reported in Table 2; the SEM compounds are also slightly soluble in aniline, aqueous ammonia and ethylene glycol.

As can be judged from the data of Table 2 for water and methanol, the high solubility of the two SEM halides is remarkable, particularly if we remember that only 35·7 g of NaCl dissolve in 100 ml of water at 0°C. This may be explained by the long ribbons of $SEMH^+$ cations which extend indefinitely along the c axis and exhibit intramolecular hydrogen bonds (Robertson, 1953). Alternatively, it could be said that the small lattice energy of both SEM halides is easily compensated by their energy of hydration (Evans, 1964). On the same lines the elongated crystal shape of the compounds can also be justified.

Table 2. *Solubility* (g/100 ml) *of* SEMHCl *and* SEMHBr *at* 26°C

Solvent	SEMHCl	SEMHBr
Water	24·21	43·61
Methanol	1·88	5·72
Ethanol	0·22	0·41
Cyclohexanol	0·04	0·06

Finally, two methods have been attempted to determine the melting point of SEMHBr, the Thiele and the electrothermal methods. Both lead to a value of 174°C, which is however not very sharp. It has to be remembered, though, that the substance starts subliming at 165°C, with decomposition beginning at 170°C.

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