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A refinement of the crystal structure of potassium hydroxylamine-*N*-sulphonate.

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The crystal structure of potassium hydroxylamine-*N*-sulphonate, $K^+[SO_3NHOH]^-$, was determined by Belt & Baenziger (1957) by least squares using partial three-dimensional data. The final R index was 14·8 %. As a common isotropic temperature factor had been used for all atoms, we thought it worth while refining the structure with individual anisotropic vibration parameters, since rotational corrections to coordinates are sometimes appreciable. The space group of KSO_3NHOH is $P2_12_12_1$ with $a = 7·06$, $b = 12·02$, $c = 5·58$ Å and $Z = 4$.

The data used were the 465 independent $|F_o|$ measured by Belt & Baenziger. These had been collected from $l = 0$, 1, 2, 3 Weissenberg layer photographs with the use of Cu $K\alpha$ radiation, and from the zero-layer a and b axis precession photographs with Mo $K\alpha$ radiation. The linear absorption coefficient μ is $\sim 130\ \text{cm}^{-1}$ for Cu $K\alpha$ and $\sim 14\ \text{cm}^{-1}$ for Mo $K\alpha$ radiation. On the advice of Professor Baenziger we started from the original intensity values. These were corrected for Lp factors, but absorption corrections had to be omitted as the crystal dimensions were not known. We found for the higher layer Weissenberg reflexions that there were large discrepancies, of the order of 15 %, between the new values of $|F_o|$ and those reported earlier; in the extreme cases the errors were as high as 45 %. It transpired that a faulty method of applying the Lp corrections had been used in the earlier work.

Only the Weissenberg data were used in the first stages of the present refinement. After five cycles of isotropic least-squares refinement R was 11·5 %; this fell to 10·3 % after two cycles of anisotropic refinement. The coordinates obtained at this stage are shown in parentheses in Table 1. The maximum shifts are 0·047 Å and 0·041 Å in the z parameters of N and O(4).

It has recently been realized (Lingafelter & Donohue, 1966) that when layer data are collected about only one axis, i, a singularity in the equations prevents the evaluation of the anisotropic U_{ii} and the individual layer-scale factors. Accordingly the $0kl$ and $h0l$ precession data were added to the $|F_o|$ list, though not without caution, for there were discrepancies of the order of 25 % between the reflexions common to the Weissenberg and precession data. The extreme ratios of the $|F_o|$ from the different sources were 0·55 and 1·45 and, though the ratios varied more or less at random, there was a slight indication that the ratio was some function of sin θ. This could be partly due to the large difference in absorption for Cu $K\alpha$ and Mo $K\alpha$ radiation. Four cycles,

Table 1. *Atomic coordinates and e.s.d.'s*

The values in parentheses are from the Weissenberg data alone

Atom	x	y	z
K	1·311 ± 0·003 (1·309) Å	4·085 ± 0·003 (4·087) Å	2·892 ± 0·004 (2·905) Å
S	0·109 ± 0·003 (0·108)	1·680 ± 0·003 (1·685)	0·175 ± 0·004 (0·170)
N	1·689 ± 0·012 (1·682)	1·157 ± 0·011 (1·150)	0·447 ± 0·013 (0·478)
O(1)	2·013 ± 0·010 (2·024)	1·373 ± 0·008 (1·368)	1·878 ± 0·010 (1·892)
O(2)	−0·108 ± 0·010 (−0·104)	2·951 ± 0·009 (2·963)	0·862 ± 0·013 (0·875)
O(3)	0·111 ± 0·012 (0·113)	1·820 ± 0·011 (1·810)	−1·276 ± 0·013 (−1·271)
O(4)	−0·757 ± 0·009 (−0·763)	0·639 ± 0·009 (0·646)	0·721 ± 0·012 (0·744)

Table 2. *Bond distances and angles*

The values in parentheses are from the Weissenberg data alone

Bond	Distance	Bond	Distance
S–O(2)	1·460 ± 0·010 (1·475) Å	K···O(1)	2·980 ± 0·009 (2·988) Å
S–O(3)	1·458 ± 0·014 (1·446)	K···O(3)	2·926 ± 0·013 (2·931)
S–O(4)	1·460 ± 0·010 (1·472)	K···O(2)	2·725 ± 0·012 (2·716)
S–N	1·687 ± 0·012 (1·690)	K···O(1)	2·992 ± 0·009 (2·974)
N–O(1)	1·483 ± 0·017 (1·472)	K···O(2)	2·973 ± 0·012 (2·967)
N···O(2)	2·573 ± 0·015 (2·575)	K···O(3)	2·838 ± 0·013 (2·852)
N···O(3)	2·429 ± 0·018 (2·440)	K···O(4)	2·750 ± 0·010 (2·764)
N···O(4)	2·515 ± 0·015 (2·510)	K···O(4)	2·767 ± 0·010 (2·736)
O(2)···O(3)	2·429 ± 0·017 (2·446)	N–H···O(2)	2·888 ± 0·016 (2·911)
O(2)···O(4)	2·405 ± 0·013 (2·412)	O(1)–H···N	2·877 ± 0·015 (2·875)
O(3)···O(4)	2·477 ± 0·017 (2·486)		

Angles	
N–S–O(2)	109·5 ± 0·6° (108·7°)
N–S–O(3)	100·9 ± 0·7 (101·8)
N–S–O(4)	105·9 ± 0·6 (104·9)
O(2)–S–O(3)	112·6 ± 0·7 (113·7)
O(2)–S–O(4)	110·9 ± 0·6 (109·9)
O(3)–S–O(4)	116·2 ± 0·7 (116·8)
S–N–O(1)	108·4 ± 0·8 (110·2)

which included the refinement of the scales of the individual Weissenberg and precession layers, led to $R = 11{\cdot}3\,\%$, and after averaging the $|F_o|$ values of all common reflexions two further cycles reduced R to $9{\cdot}3\,\%$.

The revised coordinates and their e.s.d.'s are given in Table 1. The maximum change from the values of Belt & Baenziger is 0·030 Å; the effect of adding the precession data has been to reduce the changes. The anisotropic vibration parameters are not given, as they seem to be considerably affected by the neglect of absorption; however, they provide no hint of a need for rotational corrections. Table 2 shows the revised distances and angles. They are not significantly different from those given by Belt & Baenziger, so that their main results are confirmed despite the errors in the Weissenberg Lp corrections. They are also fairly consistent with the results obtained from the Weissenberg reflexions alone in the first stage of the refinement.

The N–O(1) bond length has changed from 1·51 ± 0·02 Å to 1·483 ± 0·017 Å, which agrees better with the values reported by Jerslev (1948) in hydroxylammonium chloride (1·47 Å) and by Meyers & Lipscomb (1955) in hydroxylamine (1·48 Å). The S–O lengths average 1·459 ± 0·007 Å and S–N is 1·687 ± 0·012 Å, as compared with 1·453 ± 0·005 and 1·662 ± 0·005 Å in the $[NH(SO_3)_2]^{2-}$ ion (Cruickshank & Jones, 1963). The slight lengthening of S–N may be correlated with a more pyramidal distribution of the valencies about nitrogen, for S–N–O(1) = 108·4° as compared with S–N–S = 125·5° in the imidodisulphate. Nevertheless it remains shorter than the formal S–N single bond length of 1·74 Å, so there is some measure of S(d)–N(p) π-bonding, though not so much as in $[NH_2SO_3]^-$ (1·60 ± 0·03 Å, Jeffrey & Stadler, 1951) or $SO_2(NMe_2)_2$ (1·623 ± 0·007 Å, Jordan, Smith, Lohr & Lipscomb, 1963).

The angle between the planes NSO(3) and SNO(1) is about 18°, so that with respect to the S–N bond O(1) is nearly *trans* to O(3). O(1) is 2·83 Å from O(2), 3·09 Å from O(4), but only 2·57 Å from S. The O(1)–S repulsion is therefore the main cause of the irregularities in the angles at S. In particular the fact that O(3)–S–N = 101° is the smallest angle is consistent with the *trans* position of O(1).

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Evaluations of particle size and strain values from X-ray line breadths and line shapes in α-AgCd alloys.

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In X-ray studies of cold-worked metals and alloys the conventional methods of line profile analysis involve estimates of various quantities (*e.g.* particle size and strain) from measurements of line shapes (Warren, 1959) and line breadths. The former analysis assumes a Gaussian peak profile while the latter assumes either a Gaussian or a Cauchy peak shape for both particle size and strain broadening. However, it turns out that particle size broadening tends to give a Cauchy line and strain broadening a Gauss or $1/(1+k^2x^2)^2$ line (Warren, 1959; Taylor, 1961). Recently, Schoening (1965) has given a method for evaluating particle size and strain values from line breadth analysis with the use of these more realistic profiles. In the present note Schoening's method has been considered and a comparative study of the peak broadening of cold-worked α-AgCd alloys by the Warren–Averbach method and integral breadth measurements has been made.

The experimental procedure and the results of Fourier analysis of line shapes in α-AgCd alloys have been reported earlier (Sen Gupta & Quader, 1966). The integral breadths of the 111, 200, 222 and 400 peaks of cold-worked and annealed materials were evaluated after the separation of the α_2 component by Rachinger's (1948) method and corrected for instrumental broadening by the parabolic relation (Wagner & Aqua, 1963) $b_{\text{true}} = B_{\text{CW}} - b_A^2/B_{\text{CW}}$. In the Cauchy peak shape, separation of particle size and strain has been effected by using the linear relation $b_t \cos\theta_0/\lambda = 1/D_C + 4\varepsilon_c \sin\theta_0/\lambda$ and in the Gaussian peak shape the separation has been made by using the square relation $(b_t \cos\theta_0/\lambda)^2 = 1/(D_G)^2 + 16\varepsilon_G^2 (\sin\theta_0/\lambda)^2$, θ_0 being the peak maximum position. For Schoening's method both cases were considered and the separation of strain broadening from particle size has been done by the method outlined (Schoening, 1965). The values of the fault probabilities have been also deduced from the effective particle sizes (Wagner & Aqua, 1963) and the results are summarized in Tables 1 and 2.

It is apparent from Tables 1 and 2 that, in general, the Warren–Averbach technique and line breadth measurements lead to different values of particle sizes and strains. But it can be seen from Table 1 that there exists a close agreement between the particle size values $[D_e]_{hkl}$ and $[D_G]_{hkl}$ obtained from two methods, $[D_G]_{hkl}$ being slightly higher. The values obtained from the Cauchy relation are larger ($[D_C]_{hkl} \sim 2[D_e]_{hkl}$) and there exists a fair agreement between all the Cauchy values. Schoening's method gives lower values and for the case where the strain assumes a Gaussian form values of $[L]_{hkl}$ approach those of $[D_G]_{hkl}$. Regarding compound fault probability $(1{\cdot}5\alpha+\beta)$ evaluated from particle size values and from peak-shift and peak asymmetry measurements, line shape analysis gives good agreement and a fair agreement has been observed in the values obtained with the Cauchy assumption. The strains