817. *Hydrazinium*(1+) *as a Ligand.*

By C. K. PROUT and H. M. POWELL

The crystal structure of hydrazinium(1+) zinc sulphate, $(N_2H_5)_2Zn(SO_4)_2$, has been determined. It contains infinitely extended, essentially one-dimensional complexes of the same overall composition. These consist of zinc ions octahedrally surrounded by four oxygen and two nitrogen atoms. The oxygen atoms belong to sulphate groups which bridge to neighbouring zinc ions. Each co-ordinated nitrogen atom forms one end of a hydrazinium group, which is not co-ordinated to zinc through its other nitrogen atom. There is a system of hydrogen bonding between oxygen atoms and nitrogen atoms of both sorts. These bonds are formed both within the linear complex and between neighbouring complexes, so that the crystal as a whole is a three-dimensionally bonded structure.

ALTHOUGH a great deal is known about ammonia as a group co-ordinated to a variety of metals little has so far been reported concerning hydrazine except that in a large number of compounds it co-ordinates with the same metals. Many of the compounds could be regarded as double salts. Among known types [1] are $(N_2H_5)_2M^{II}(SO_4)_2$ where M is Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, or Ca, $(N_2H_5)M^{III}(SO_4)_2,12H_2O$ where M is Al or Cr, $(N_2H_5)M^{II}Cl_3$ where M is Hg, Cd, Zn, Sn, Cu, Fe, or Mn, $(N_2H_5)_2M^{II}Cl_4,nH_2O$ where M is Cd or Hg ($n = 4$), M is Co or Ni ($n = 2.5$), or M is Cu ($n = 0.5$).

For the chlorides there are the possibilities that the metal may have hydrazine, chlorine, or both in the co-ordination sphere. In double ammonium sulphates, *e.g.*, $(NH_4)_2Zn(SO_4)_2,6H_2O$ a group of water molecules is attached to the metal, and this suggests that in the anhydrous compounds above, the hydrazine is in some way co-ordinated to the metal. Another indication that hydrazine may be acting as a ligand is the extreme stability of the chromous sulphate compound which remains unoxidised in the atmosphere. The hydrazinium double sulphates are also distinguished from the double ammonium sulphates by general insolubility. Structural study of the hydrazinium double sulphates therefore seemed the most promising way of investigating the problem, but most of them could not be obtained as anything but microcrystalline powders unsuitable for the purpose.

X-Ray examination of these powders by Debye–Scherrer methods and also by the Guinier technique gave similar diffraction patterns for the iron, cobalt, nickel, and zinc compounds; the chromium and copper compounds gave diffraction patterns different from these but similar to each other. The manganese compound differed from all the others.

[1] Audrieth and Ogg, " The Chemistry of Hydrazine," Wiley, New York, 1951.

Cruciform twins of the chromous compound appeared too complex for single-crystal work and only the zinc compound readily formed crystals of apparent simplicity. These, however, proved to be multiple twins and crystallisation of the material in varied conditions of the solution failed to modify this form of growth. The alternative being to leave the problem unsolved, it was decided to use a twinned crystal and to adopt whatever methods were possible to diminish the difficulties of structure determination which this introduced. Many apparently single crystals in some orientations extinguished in the usual way between crossed Nicols, but in other orientations showed the extinction behaviour of multiple twins. When oscillated about the needle axis they gave X-ray diffraction patterns superficially normal and symmetrical about the equator. Weissenberg photographs about this axis show two superposed diffraction patterns which have one axial line in common. The equatorial symmetry is thus shown to be false. It is found that each diffraction

Fig. 1. *Electron density projected perpendicular to [010]. Contours at approx. 2 electrons/Å², starting with the broken line at zero. For the zinc atom heavier contours are at intervals of approx. 9 electrons/Å².*
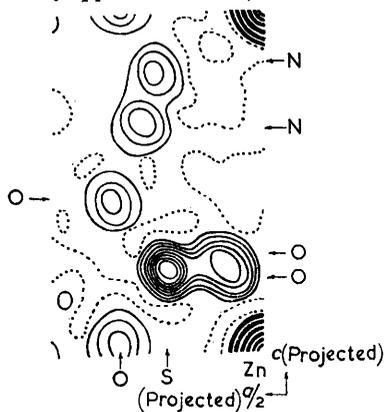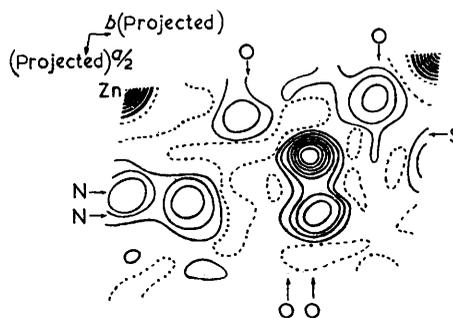
Fig. 2. *Electron density projected perpendicular to [001]. Contours as in Fig. 1 except that the interval is 8 electrons/Å² for the zinc atom.*

pattern may be indexed on the basis of an anorthic cell, the two components of the twin having b and c common.

Results. $(N_2H_5)_2Zn(SO_4)_2$, $M = 323\cdot8$, triclinic pinacoidal, $a = 7\cdot36 \pm 0\cdot03$, $b = 5\cdot33 \pm 0\cdot03$, $c = 5\cdot82 \pm 0\cdot03$ Å, $\alpha = 99° 42' \pm 10'$, $\beta = 87° 27' \pm 10'$, $\gamma = 105° 42' \pm 10'$, $U = 216\cdot7$ Å³, $D_m = 2\cdot47 \pm 0\cdot02$ (by flotation), $Z = 1$, $D_c = 2\cdot48$, $F(000) = 164$. Space group, $P\bar{1}$ (C^1_i, No. 2) Cu-K_α radiation, single crystal oscillation and Weissenberg photographs. Optically biaxial, twinned.

Most reflexions from the two components of the twin do not overlap on the films, and their intensities may be estimated separately. It is also possible by comparison of reflexions of the same indices to estimate the ratio of intensities produced by the separate parts of the twin. The intensities of the necessarily overlapping axial reflexions were divided in the appropriate ratio so as to give the intensity due to one part of the twin only. A number of non-axial reflexions happen to overlap. Those used in the analysis were all $hk0$ reflexions with $k = 4$, but the h values for each overlapping pair were different. These intensities cannot be divided in a similar way at the start of the analysis. They were provisionally shared equally between the two reflexions and thus one in eight of the reflexions in this zone was introduced with a very uncertain error. These errors were not sufficient to prevent the derivation of an approximate structure. Once this was obtained, the overlapping reflexions were divided in the ratio of the corresponding calculated quantities, with proper allowance for the fact that non-overlapping reflexions of the same

indices due to the two parts of the twin have different intensities because the two parts have different masses. As the structure refined the ratios were further modified.

There is one zinc atom per unit cell. Whether in a special position of $P\bar{1}$ or the general position of $P1$ this may be taken at the origin. Patterson projections perpendicular to b and c were evaluated and their most prominent peaks could be explained as due to the vectors from a zinc atom to two sulphur atoms related by a centre of symmetry at the zinc atom. A more complex system of peaks would have been expected if there had been two crystallographically distinct sulphur atoms in the space group $P1$. In order that no unnecessary chemical assumptions should be made the structure was then developed by means of F_o syntheses at first based only on positive signs arising from the zinc atom at the origin. The first projections showed sulphur atoms in positions consistent with those already deduced from the Patterson functions. Other peaks made it possible to assign positions to all oxygen atoms, and gave less certain indications of the hydrazine. A re-phasing was therefore made with the contributions of zinc, sulphur, and oxygen only. There were some sign changes, and the resulting electron-density map showed the nitrogen positions more clearly. Another F_o synthesis phased on the contributions of all atoms led to a set of atomic parameters which were then refined by F_o-F_c syntheses. The R value for F_{hk0} fell steadily from 0·42 to 0·26 and for F_{h0l} from 0·35 to 0·17. The final electron-density projections calculated from F_{h0l} and F_{hk0} are reproduced in Figs. 1 and 2.

Table 1 gives the observed and calculated structure factors. In calculations, the atomic scattering factors for zinc, oxygen, and nitrogen were taken from data by Berghuis

TABLE 1. *Observed structure amplitudes and calculated structure factors for hkl. In each set of three columns the first gives h, the second $\frac{1}{2}F_{\mathrm{obs.}}$ and the third $\frac{1}{2}F_{\mathrm{calc.}}$. The values recorded are rounded from the computer figures used to calculate R.*

l00
h	$\frac{1}{2}F_{o}$	$\frac{1}{2}F_{c}$
1	12	20
2	11	-7
3	15	18
4	12	10
5	6	5
6	4	3
7	4	-4
8	6	3
9	8	9

h01
h	$\frac{1}{2}F_{o}$	$\frac{1}{2}F_{c}$
-8	5	-5
-7	5	6
-6	15	15
-5	10	10
-4	9	10
-3	16	19
-2	30	25
-1	24	27
0	14	14
1	0	1
2	7	-3
3	3	1
4	15	11
5	9	7
6	0	-2
7	8	6
8	11	15

h02
h	$\frac{1}{2}F_{o}$	$\frac{1}{2}F_{c}$
-6	17	16
-5	8	6
-4	5	3
-3	23	21

(second block)
h	$\frac{1}{2}F_{o}$	$\frac{1}{2}F_{c}$
-2	21	15
-1	6	-4
0	8	-6
1	8	-4
2	17	17
3	23	20
4	0	-1
5	6	6
6	17	17
7	0	8
8	2	5

h03
h	$\frac{1}{2}F_{o}$	$\frac{1}{2}F_{c}$
-8	9	7
-7	11	10
-6	5	3
-5	4	4
-4	12	12
-3	13	11
-2	8	6
-1	0	4
0	11	9
1	18	14
2	23	23
3	11	8
4	0	1
5	13	12
6	11	12
7	3	4
8	2	1

h04
h	$\frac{1}{2}F_{o}$	$\frac{1}{2}F_{c}$
-8	0	2
-7	4	4
-6	3	3
-5	9	10

(third block)
h	$\frac{1}{2}F_{o}$	$\frac{1}{2}F_{c}$
-4	6	7
-3	3	3
-2	3	5
-1	12	12
0	23	19

h05
h	$\frac{1}{2}F_{o}$	$\frac{1}{2}F_{c}$
-6	6	8
-5	8	8
-4	9	8
-3	0	1
-2	8	6
-1	22	22
0	10	-7
1	10	7
2	5	7
3	9	10
4	7	6
5	5	5
6	0	0

h06
h	$\frac{1}{2}F_{o}$	$\frac{1}{2}F_{c}$
-5	0	1
-4	5	5
-3	8	8
-2	7	8
-1	0	5
0	0	4
1	0	4

(fourth block)
h	$\frac{1}{2}F_{o}$	$\frac{1}{2}F_{c}$
2	7	7
3	8	9
4	4	5

h07
h	$\frac{1}{2}F_{o}$	$\frac{1}{2}F_{c}$
-3	7	10
-2	0	2
-1	2	0
0	3	

h10
h	$\frac{1}{2}F_{o}$	$\frac{1}{2}F_{c}$
-9	0	1
-8	10	17
-7	9	12
-6	9	-2
-5	9	10
-4	7	14
-3	4	9
-2	10	17
-1	0	2
0	4	0
1	18	24
2	12	12
3	11	10
4	10	9
5	0	0
6	17	12
7	15	13

h20
h	$\frac{1}{2}F_{o}$	$\frac{1}{2}F_{c}$
-8	0	2
-7	12	10
-6	15	13
-5	12	11
-4	8	7
-3	15	-9

(fifth block)
h	$\frac{1}{2}F_{o}$	$\frac{1}{2}F_{c}$
-2	4	3
-1	22	25
0	0	0
1	2	-3
2	19	17
3	19	16
4	20	17
5	12	12
6	8	-2
7	7	5

h30
h	$\frac{1}{2}F_{o}$	$\frac{1}{2}F_{c}$
-9	26	24
-8	0	2
-7	12	10
-6	15	13
-5	12	11
-4	9	7
-3	15	-9
-2	4	3
-1	22	25
0	26	24
1	10	10
2	3	-3
3	5	1
4	6	4
5	9	9
6	11	7
7	4	1

h40
h	$\frac{1}{2}F_{o}$	$\frac{1}{2}F_{c}$
-8	7	8
-7	9	11
-6	3	5
-5	4	3
-4	6	7

(sixth block)
h	$\frac{1}{2}F_{o}$	$\frac{1}{2}F_{c}$
-3	15	12
-2	18	14
-1	4	6
0	1	2
1	5	4
2	7	6
3	8	9
4	2	3
5	5	-3

h50
h	$\frac{1}{2}F_{o}$	$\frac{1}{2}F_{c}$
-8	2	2
-7	3	0
-6	5	4
-5	7	9
-4	8	3
-3	8	-6
-2	9	3
0	8	12
1	0	2
2	5	5
3	5	9
4	9	8

h60
h	$\frac{1}{2}F_{o}$	$\frac{1}{2}F_{c}$
-6	4	1
-5	3	6
-4	7	9
-3	7	6
-2	6	3
-1	6	2
0	8	4
1	6	8

TABLE 2. *Atomic co-ordinates.*

	x	y	z			x	y	z
Zn	0·000	0·000	0·000	O(3)		0·347	0·632	0·449
S	0·215	0·630	0·247	O(4)		0·337	0·714	0·050
O(1)	0·079	0·372	0·213	N(1)		0·257	0·041	0·828
O(2)	0·090	0·786	0·286	N(2)		0·288	0·259	0·672

TABLE 3.   *Co-ordinates (in Å) referred to orthogonal axes with Z′ parallel to c,*
X′ perpendicular to c in the ac plane, and Y′ perpendicular to X′ and Z′.

	X′	Y′	Z′		X′	Y′	Z′
Zn	0	0	0	O(4)	1·476	3·615	0·240
S	0·697	3·190	0·942	N(1)	1·832	0·208	4·866
O(1)	0·059	1·883	0·932	N(2)	1·754	1·311	3·773
O(2)	−0·442	3·979	0·988				
O(3)	1·664	3·200	2·159				

TABLE 4.   *Interatomic distances (in Å) and some bond-angles calculated from the*
parameters of Table 2.   (Letters a—f are as in Fig. 3.)

Zn–O(1)	2·10	N(1)–O(4)	2·98 a	O(1)–Zn–O(2)	93°
Zn–O(2)	2·38	N(1)–O(4)	2·54 e	O(1)–Zn–N(1)	85°
Zn–N(1)	2·08	N(2)–O(3) *	2·49 d	O(2)–Zn–N(1)	87°
S–O(1)	1·45	N(2)–O(3)	2·68 b	Zn–N(1)–N(2)	110°
S–O(2)	1·39	N(2)–O(2)	2·73 c		
S–O(3)	1·55	N(2)–O(4)	2·95 f		
S–O(4)	1·48				
N(1)–N(2)	1·55				

* O(3) of another unit.

et al.,[2] and that for sulphur from Viervoll's.[3]   A general temperature factor $B = 0.8$ Å^2 was used.   Table 2 gives the atomic parameters deduced.   Table 3 gives atomic co-ordinates referred to a set of orthogonal axes, with a zinc atom at the origin.   Table 4 gives interatomic distances and some angles.   High accuracy is precluded by the nature of the twinned crystals.   Although the errors in bond lengths may be as much as 0·1 Å the accuracy attained is sufficient to provide answers to the main chemical questions that were being studied.   From the immediate surroundings of the atoms several geometrical complexes may be identified in the structure.   The simpler ones are the linked nitrogen atoms of an N_2H_5 group and the tetrahedral SO_4.   The zinc ion is at the centre of an irregular octahedron of surrounding atoms.   This consists of two nitrogen atoms N(1) of two separate N_2H_5 groups, and four oxygen atoms, two each of types O(1) and O(2).   Each of these oxygens belongs to a different sulphate group.   Single-bond distances, Zn–N = 2·06 and Zn–O = 2·05 and 2·27 Å, have been observed in an octahedral complex with 8-hydroxyquinoline.[4]   An acetylacetone complex [5] of different stereochemistry has Zn–O distances in the range 1·92—2·13 Å.   The present rather inaccurately observed distances are consistent with the view that the zinc is joined by single bonds to its six neighbours.   Each N(1) is certainly linked covalently to Zn as is shown by the Zn–N distance and by the angle Zn–N(1)–N(2) which is very near to the expected tetrahedral value, although a larger angle would result in greater separation of the positive charges on Zn and N(2).   If the longer Zn–O distance is not regarded as a bond the zinc would have four co-planar bonds.

By means of the octahedral co-ordination each sulphate group is linked through an O(1) and an O(2) to two separate zinc ions.   In this way the sulphate groups and zinc ions link to form a complex which extends indefinitely parallel to *b*.   Each zinc is linked to the next through two sulphate groups.   The hydrazinium groups are also attached to the zinc ions and the total composition of the complex is the same as that of the compound.

Only one nitrogen atom of the hydrazinium is co-ordinated to zinc.   This is assumed to be the NH_2 end and its co-ordination is analogous to that of ammonia.

This is believed to be the only established * case of a small *positive* ion acting as a ligand

* The case for NO^+ is strong, though alternatives have been discussed.   In the present instance there is no reasonable alternative.

[2] Berghuis, Haanapel, Potters, Loopstra, MacGillavry, and Veenendal, *Acta Cryst.*, 1955, **8**, 478.
[3] Viervoll, *Acta Cryst.*, 1949, **2**, 277.
[4] Merritt, Cady, and Mundy, *Acta Cryst.*, 1954, **7**, 473.
[5] Lippert and Truter, *J.*, 1960, 4996.

to a metal ion such as Zn^{2+}. The positive charge of the hydrazinium which might be expected to oppose such ligand action is presumed to be concentrated on the nitrogen atom which is not linked to zinc. The action of this positive charge is further reduced by the environment of these non-co-ordinated nitrogen atoms. Each such atom is surrounded by oxygen atoms, two in its own complex and two from neighbouring complexes.

It is expected that hydrazine itself should be an efficient co-ordinating group. In the absence of positive charge it might form links through both ends though it seems unlikely that these would both be joined to the same atom since the lone pairs of electrons are in spatially unsuitable orientation. In one sense hydrazine may be said to be so co-ordinated in this compound to two positive ions, zinc at one end and a proton at the other. Co-ordination of hydrazine to separate metal ions at the two ends would lead to polymeric structures. These may occur in the numerous metal salt hydrazinates which, almost without exception, are reported to be very insoluble powders.

When the hydrazinium is taken into account the complex has approximately the shape of a cylinder. This, as a whole, is electrically neutral but positive and negative charges alternate on its surface.

A set of such essentially one-dimensional complexes is further linked by hydrogen

FIG. 3. *The linear complex is shown in the centre. Hydrogen bonds within the complex and between a pair of neighbouring complexes are shown by broken lines. They are lettered as in Table 4. In addition there is a hydrogen bond* d *from* N(2) *to an oxygen atom similar to* O(3)' *but belonging to another complex nearer to the observer.*
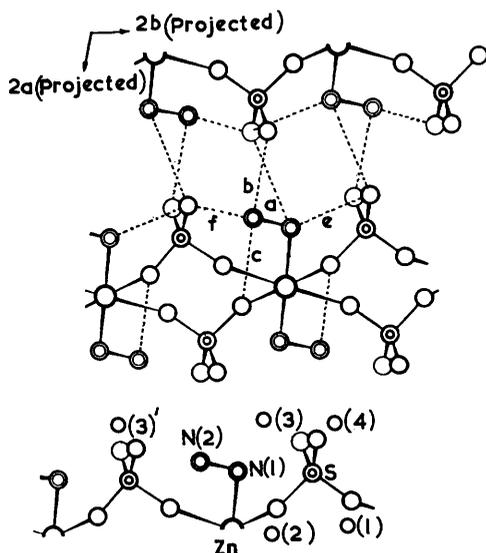
bonds so that the whole crystal is a three-dimensional complex network. Both nitrogens of the hydrazinium play a part in the linking to neighbouring complexes. The inner NH_2, which is directly joined to the zinc, is at distances corresponding to hydrogen bonds from two oxygen atoms, one belonging to its own linear complex and the other to a neighbouring chain. The outer NH_3 group is at hydrogen-bond distances from four oxygens, two within its own linear complex, and two others each in a neighbouring complex. The N(1) and N(2) atoms of any one hydrazinium are linked through hydrogen bonds to the same neighbouring complex (Fig. 3). N(2) is also linked to a neighbouring complex nearer to the observer than that shown in the Figure. It seems probable that the hydrogen bond system contributes to the stabilisation of this type of compound.

The number of oxygen-to-nitrogen distances of hydrogen-bond length is, for N(2), one more than the number of its hydrogen atoms. A similar condition has been found in a few other structures, *e.g.*, orthorhombic hydrazine sulphate [6] and glycine.[7]

[6] Nitta, Tomie, and Sakuri, *Acta Cryst.*, 1951, **4**, 289.
[7] Marsh, *Acta Cryst.*, 1958, **11**, 654.

The observed twinning can be explained in terms of the structure found. Let a plane parallel to (100) and cutting the axis at $a/2$ divide the structure, and let the upper part be rotated relative to the lower through 180° about an axis through the body-centre of the unit cell and perpendicular to the dividing plane. Let the upper half then be displaced approximately through $0.65b + 0.5c$. The nitrogen and oxygen atoms near to the junction plane are then in positions such that the system of hydrogen bonds could continue from one half to the other. At the junction plane the positions of O(3) and O(4) are interchanged, as are those of N(1) and N(2). Although an exact interchange of their rôles does not seem possible, sufficient hydrogen bonding between neighbouring layers could occur to account for the twin formation.

EXPERIMENTAL

Preparation of Materials.—"AnalaR" hydrazine sulphate and "AnalaR" metal salts were used. All compounds were prepared by the method of Curtius and Schrader [8] except the chromous salt. For this compound the method of Traube and Passage [9] was considered but rejected since the product is often found [10] to be contaminated with zinc from the amalgam used in the reduction of Cr(III) to Cr(II). Electrolytic reduction, which avoids this difficulty, was used instead. For compounds $(N_2H_5)_2M^{II}(SO_4)_2$ where M = Mn, Fe, Co, Ni, Cu, or Zn, analyses agreed with those of Curtius and Schrader. The analytical results for the chromous salt were consistent with the formula $(N_2H_5)_2Cr(SO_4)_2$ first quoted by Traube and Passage, but not with that of Palmer [11] who suggests $(N_2H_5)_2Cr(SO_4)_2,H_2O$ for material prepared by the same method [Found: Cr, 16.4; SO_4, 61.9; N_2H_4, 21.3. Calc. for $(N_2H_5)_2Cr(SO_4)_2$: Cr, 16.8; SO_4, 61.5; N_2H_4, 21.3%].

Intensities of Reflexions.—The unit-cell dimensions were obtained from calibrated Weissenberg films taken about two principal axes, and one non-principal axis. The intensities of reflexions $h0l$ and $hk0$ were measured from Weissenberg films. Multiple-film technique was used. Lorentz and polarisation corrections were applied but no attempt was made to correct for absorption and extinction effects.

Magnetic Measurements.—Magnetic susceptibilities of a number of the double sulphates of the form $(N_2H_5)_2M^{II}(SO_4)_2$ were measured by the Gouy method at 21°. The results, expressed as magnetic moments (B.M.), are: Cr 4.96, Mn 5.79, Fe 5.24, Co 4.86, Ni 3.16, and Cu 1.91. These values correspond very closely to the spin-only values for octahedral high-spin complexes.

CHEMICAL CRYSTALLOGRAPHY LABORATORY,
    SOUTH PARKS ROAD, OXFORD.

[8] Curtius and Schrader, *J. prakt. Chem.*, 1894, **50**, 311.
[9] Traube and Passage, *Ber.*, 1913, **46**, 1505.
[10] L. A. K. Staveley, personal communication.
[11] Palmer, "Experimental Inorganic Chemistry," Cambridge, 1954.