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References

ABRAHAMS, S. C. (1956). *Quart. Rev.* **10**, 422.
ARONSON, YU. P. & BELEN'KII, S. M. (1965). *Zashchita Metallov*, **1**, 125.
BRITTS, K. & KARLE, I. L. (1967). *Acta Cryst.* **22**, 308.
CALLERI, M. FERRARIS, G. & VITERBO, D. (1969). *Acta Cryst.* **B25**, 1133.
CUCKA, P. (1963). *Acta Cryst.* **16**, 318.
DOWNIE, T. C., HARRISON, W., RAPER, E. S. & HEPWORTH, M. A. (1972). *Acta Cryst.* **B28**, 283.
FREEMAN, H. C. 1967). *Advanc. Protein Chem.* **22**, 258.
GLUSKER, J. P. VAN DER HELM, R., LOVE, W. E., MINKIN, J. E. & PATTERSON, J. L. (1968). *Acta Cryst.* **B24**, 359.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: The Kynoch Press.
JEFFREY, G. A. & SHIONO, R. (1959). *Acta Cryst.* **12**, 447.
KARLE, I. L. & KARLE, J. (1965). *Acta Cryst.* **19**, 92.
KARLE, I. L., ESTLIN, J. A. & BRITTS, K. (1967). *Acta Cryst.* **22**, 273.

KATRITZKY, A. R. & LAGOWSKI, J. M. (1963). *Advanc. Heterocycl. Chem.* **2**, 64.
KITAIGORODSKI, A. I. (1961). *Organic Chemical Crystallography*. New York: Consultants Bureau.
KREBS, B. & KOENIG, D. F. (1969). *Acta Cryst.* **B25**, 1022.
McDOWELL, J. J. H. (1969). *Acta Cryst.* **B25**, 2175.
MONAHAN, J. E., SCHIFFER, M. & SCHIFFER, J. P. (1967). *Acta Cryst.* **22**, 322.
PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell Univ. Press.
PIMENTEL, G. C. & McCLELLAN, A. L. (1960). In *The Hydrogen Bond*, pp. 225–295. London: Freeman.
SALMOND, W. G. (1968). *Quart. Rev.* **22**, 253.
SHEFFNER, E. & MAUTNER, H. G. (1967). *J. Amer. Chem. Soc.* **89**, 1249.
SINGH, C. (1965). *Acta Cryst.* **19**, 861.
SLETTEN, E. ,SLETTEN, J. & JENSEN, L. H. (1969). *Acta Cryst.* **B25**, 1330.
SUTTON, L. E. (1965). *Tables of Interatomic Distances and Configurations in Molecules and Ions*. Special Publication No. 18. London: The Chemical Society.
TRUTER, M. R. (1960). *J. Chem. Soc.* p. 997.
VALLE, G., COJAZZI, G., BUSETTI, V. & MAMMI, M. (1970). *Acta Cryst.* **B26**, 468.
VALLE, G., BUSETTI, V., MAMMI, M. & CARAZZOLO, G. (1969). *Acta Cryst.* **B25**, 1432.
WHEATLEY, P. J. (1955). *Acta Cryst.* **8**, 224.
ZVONKOVA, Z. V. & KHVATKINA, A. N. (1965). *Kristallografiya*, **10**, 734.

The Crystal and Molecular Structure of Potassium Dinitrotrichlorocyclopentadienide

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Potassium dinitrotrichlorocyclopentadienide crystallizes in space group $P2_1/c$ with $a=13.684$, $b=8.765$, $c=8.065$ Å, $\beta=93.2°$ and with $Z=4$. The structure was determined from photographic data and refined by the least-squares method to $R=0.10$ for 723 reflexions. The analysis established the structure of the anion as 1,2-dinitro-3,4,5-trichlorocyclopentadienide. The three chlorine atoms are in the plane of the five-membered ring but the two nitrogen atoms are displaced on the opposite sides of the plane by about 0.3 Å. The bond distance between the two carbon atoms to which nitro groups are attached (1.46 Å) is longer than the others owing to the repulsion between the two nitro groups. The potassium atom is surrounded irregularly by six oxygen atoms and the unit negative charge of the molecule seems to be distributed on the oxygen atoms.

Introduction

Potassium dinitrotrichlorocyclopentadienide was originally synthesized by Haga (1969) by nitration of hexachlorocyclopentadiene with alkali nitrite in an aqueous or alcoholic solution. Potassium dihydroxycyclopenta-

trionide is obtained by hydrolysis of the former, in which the nitro groups and the chlorine atoms are replaced by hydroxyl groups and oxygen atoms respectively. Data from chemical and spectroscopic measurements do not allow an unambiguous distinction between possible molecular structures for these two sub-

stances. Therefore, the structure of potassium dinitro-trichlorocyclopentadienide was determined by X-ray diffraction. Crystals of potassium dihydroxycyclopen-tatrionide were not suitable for X-ray work since they were flaky and twinned.

Experimental

The crystals, recrystallized from aqueous solution, are red needles elongated along the c axis and are stable to X-rays.

The crystal data are: $C_5N_2O_4Cl_3K$, F.W. 297·53, monoclinic, $a=13·684 \pm 0·008$, $b=8·765 \pm 0·007$, $c= 8·065 \pm 0·009$ Å, $\beta=93·2 \pm 0·1°$, $U=965·9$ Å^3, $D_m= 2·043$ g.cm^{-3}, $Z=4$, $D_x=2·046$ g.cm^{-3}, space group $P2_1/c$, linear absorption coefficient for Cu $K\alpha$, $\mu=29·7$ cm^{-1}.

From a crystal of dimensions $0·1 \times 0·1 \times 0·2$ mm, equi-inclination Weissenberg photography with Cu $K\alpha$ radiation of the $h0l$ to $h5l$ and the $hk0$ to $hk1$ layers produced 723 observable reflexions. The visually estimated

data were corrected for Lorentz, polarization and spot shape effects. The structure factors were put on the same scale by the least-squares method and reduced approximately to absolute values by Wilson's method.

Structure determination

The coordinates of the five carbon, two nitrogen and four oxygen atoms were obtained from a three-dimensional electron-density map calculated with all the

Table 1. *The final atomic parameters and their estimated standard deviations* ($\times 10^4$)

The anisotropic temperature factors are of the form:
$$\exp\{-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)\}.$$

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	7228(11)	3338(18)	2290(18)	64(10)	80(36)	98(25)	68(28)	3(27)	-16(36)
C(2)	7111(12)	1699(18)	2498(19)	68(10)	52(34)	121(28)	22(28)	95(27)	-55(37)
C(3)	7954(12)	1037(19)	1869(18)	65(11)	67(34)	144(28)	-31(26)	95(28)	-153(42)
C(4)	8553(10)	2182(18)	1312(18)	42(9)	93(35)	131(26)	19(25)	7(25)	-162(41)
C(5)	8131(12)	3589(18)	1571(18)	72(11)	47(33)	87(25)	30(28)	-2(25)	-27(34)
N(1)	6694(10)	4503(15)	3026(16)	54(9)	106(31)	153(24)	8(22)	-20(24)	0(37)
N(2)	6268(9)	995(15)	2754(14)	46(7)	132(29)	112(22)	-27(20)	108(21)	-15(32)
O(1)	6756(9)	5831(13)	2511(13)	81(9)	84(23)	156(20)	82(20)	35(21)	-43(30)
O(2)	6128(8)	4170(12)	4187(12)	77(8)	110(22)	91(16)	5(20)	72(19)	-55(27)
O(3)	5453(7)	1650(13)	2612(14)	38(5)	132(22)	175(21)	-33(19)	76(18)	-102(30)
O(4)	6301(10)	-387(14)	3168(15)	92(10)	101(27)	215(24)	-15(22)	106(25)	99(35)
Cl(1)	8104(3)	-822(5)	1583(6)	65(3)	57(9)	235(9)	30(7)	77(8)	-39(12)
Cl(2)	9646(3)	1929(6)	435(6)	50(2)	134(10)	233(10)	14(8)	104(8)	-26(14)
Cl(3)	8686(4)	5292(5)	1202(6)	75(3)	68(10)	232(9)	-25(8)	107(9)	17(12)
K	4197(3)	2259(4)	9804(4)	72(2)	68(7)	104(5)	-17(6)	52(6)	31(9)

Fig. 1. A projection of the structure along the b axis.

Table 2. *Observed and calculated structure factors* ($\times 2$)

terms, the signs of which were determined from the coordinates of one potassium and the three chlorine atoms obtained from a sharpened Patterson function. The positional parameters and isotropic temperature factors were refined by five cycles of the diagonal least-squares method. The R value was 0·20 at this stage. Anisotropic temperature factors were then introduced and ten cycles of block-diagonal least-squares refinement reduced the R-value to 0·10. A weighting scheme $W = (F_{max}/F_o)^2$ if $|F_o| \geq 4F_{min}$ and $W = 1$ otherwise, was employed, where $F_{min} = 4·79$ and $F_{max} = 4F_{min}$. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The final atomic parameters are listed in Table 1 with their standard deviations in parentheses. A comparison of the observed and calculated structure factors is given in Table 2.

Results and discussion

A projection of the structure along the b axis is presented in Fig. 1. The anion conforms to the formula 1,2-dinitro-3,4,5-trichlorocyclopentadienide. It is interesting that nitro groups occupy vicinal positions to form 1,2-dinitro compounds, which suggests a reaction mechanism different from the normal cationic nitration. Unlike cyclopentadienyl complexes of sandwich type (Wilson & Shoemaker, 1957; Berndt & Marsh, 1963; Whitla, Powell & Venanzi, 1966; Ziegler, 1967; Chaiwasie & Fenn, 1968) a potassium ion is exclusively surrounded by six oxygen atoms of nitro groups. Thus, the excess electron of the molecule seems to be distributed on the oxygen atoms of the nitro groups and not on the five-membered ring.

Bond lengths and angles are shown in Fig. 2. From the bond lengths, it may be concluded that the π elec-

trons in the anion are delocalized as in sandwich-type complexes. The average of the C–C bond lengths, except C(1)–C(2), is 1·40 Å which agrees within experimental error with the value observed in related compounds, *e.g.* cyclopentadiene (1·41 Å) (Liebling & Marsh, 1965), π-cyclopentadienyl molybdenum tricarbonyl chloride (1·36 Å) (Chaiwasie & Fenn, 1968) and 1,2,3,4-tetraphenylcyclopentadiene (1·44 Å) (Evrard, Piret, Germain & Van Meerssche, 1971). The distance 1·46 Å between the two carbon atoms to which nitro groups are attached is slightly longer than the other C–C distances, which indicates intramolecular overcrowding. According to Ferguson & Sim (1961), Kurahashi, Fukuyo & Shimada (1967) and Sakore, Tavale & Pant (1967), in the case of *ortho*-substituted benzene derivatives, the strain resulting from the overcrowding of the *ortho*-substituents is relieved by (1) the rotation of the substituents, (2) by displacement of the substituents from the plane of the benzene ring and (3) by increasing the bond angles. In the present case the strain seems to be relieved by elongation of the C(1)–C(2) bond in addition to factors (1) and (2).

Table 3 lists the displacements of the atoms from the best plane of the five-membered ring. The two oxygen atoms O(1) and O(4) are nearly on the plane of the five-membered ring, whereas the two nitrogen atoms, N(1) and N(2), are displaced by 0·27 and 0·33 Å on the opposite sides of the plane. The two C–NO$_2$ groups are kept planar. In other words, the two planar C–NO$_2$ groups are tilted around the lines through C(1) and O(1) and through C(2) and O(4) at angles of 23 and 25° respectively. The dihedral angle N(1)C(1)C(2)N(2) is 32°. The two nitro groups seem to make contact with each other at oxygen atoms, the O(2)···O(3) distance being 2·69 Å.
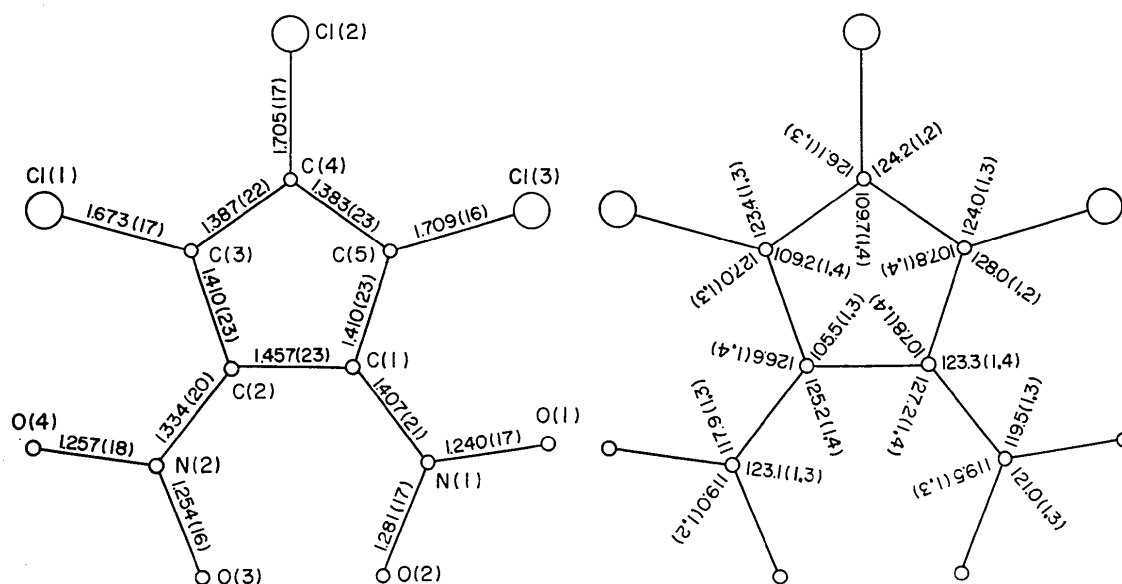

Fig. 2. Bond lengths (Å) and angles (°), with their standard deviations in parentheses.

Table 3. *Deviations of atoms from the plane of the five membered ring*

	Shift (Å)		Shift (Å)
C(1)	−0·005	Cl(2)	−0·022
C(2)	0·002	Cl(3)	0·135
C(3)	0·001	O(1)	−0·001
C(4)	−0·004	O(2)	0·762
C(5)	0·006	O(3)	−0·858
N(1)	0·270	O(4)	−0·074
N(2)	−0·325	K	0·042
Cl(1)	−0·168		

Each potassium ion is surrounded irregularly by six oxygen atoms. K···O distances are indicated in Fig. 1. Other intermolecular distances are listed in Table 4. The potassium ions form a layer parallel to the (100) plane. The potassium ions and the anions are evidently linked by electrostatic forces between the potassium ion and the excess negative charge distributed on the oxygen atoms of the nitro groups. The anions are arranged on both sides of the layer of potassium ions, with the oxygen atoms oriented towards the cations, thus forming layers parallel to the (100) plane. These double layers of the sequence, anion–cation–anion, are held together by van der Waals forces between chlorine atoms. The anions are stacked parallel to form columns parallel to the c axis. The closest approach between adjacent molecules occurs at N(2) of one molecule and O(2) of the other molecules (see Fig. 1). This might sug-
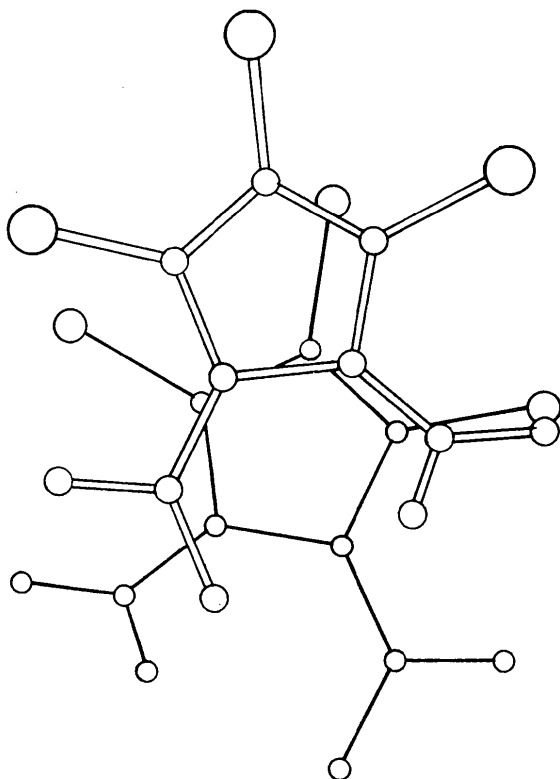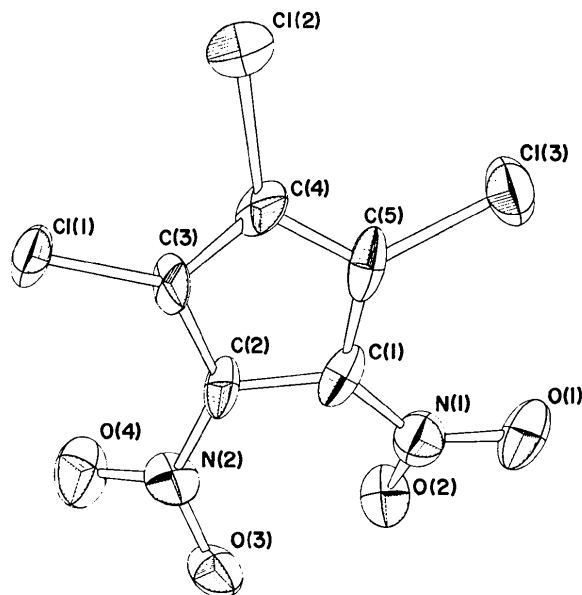

Fig. 4. Thermal ellipsoids of the molecule.

gest a charge-transfer interaction between these atoms. It is to be noted that the nitro group O(1)N(1)O(2) is asymmetric and the donor atom O(2) has a longer N–O distance than has O(1). The other nitro group, of which nitrogen atom N(2) acts as an acceptor, is symmetrical within experimental error. Also the N(1)–C(1) distance is significantly longer than the N(2)–C(2) distance. Fig. 3 shows the overlap of the two adjacent anions, the perpendicular distance between the molecular planes being 3·56 Å.

Table 4. *Intermolecular approaches less than* 3·8 Å, *with their standard deviations in parantheses*

No symbol	x	y	z				
i	$1-x$	$1-y$	$1-z$	vi	x	$\frac{1}{2}-y$	$-\frac{1}{2}+z$
ii	$1-x$	$-y$	$1-z$	vii	x	$\frac{3}{2}-y$	$\frac{1}{2}+z$
iii	$2-x$	$1-y$	$-z$	viii	$1-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
iv	$2-x$	$-y$	$-z$	ix	$1-x$	$\frac{1}{2}+y$	$\frac{3}{2}-z$
v	x	$\frac{1}{2}-y$	$\frac{1}{2}+z$	x	$2-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$

C(1)···O(2^{vi})	3·597 (18) Å	N(1)···O(3^{viii})	3·502 (17) Å
C(2)···C(4^v)	3·693 (21)	N(1)···K^{ix}	3·259 (14)
C(2)···C(5^v)	3·506 (21)	N(2)···K^{ii}	3·557 (13)
C(2)···N(1^{vi})	3·770 (20)	N(2)···O(2^{vi})	2·786 (15)
C(2)···O(2^{vi})	3·019 (18)	N(2)···K^{vi}	3·692 (13)
C(3)···N(1^{vi})	3·493 (20)	O(1)···Cl(1^{vii})	3·713 (13)
C(3)···O(2^{vi})	3·216 (19)	O(2)···Cl(1^{vii})	3·604 (12)
C(3)···Cl(3^v)	3·766 (16)	Cl(1)···Cl(2^{iii})	3·621 (8)
C(4)···C(1^{vi})	3·655 (21)	Cl(1)···K^i	3·588 (7)
C(4)···Cl(2^v)	3·653 (16)	Cl(1)···Cl(3^{vii})	3·783 (8)
C(5)···Cl(2^v)	3·673 (16)	Cl(2)···Cl(2^{iv})	3·598 (7)
N(1)···K^i	3·800 (14)	Cl(3)···Cl(2^{iii})	3·635 (7)
N(1)···Cl(1^{vii})	3·601 (14)	Cl(3)···Cl(2^x)	3·732 (8)

Thermal ellipsoids of 50% probability calculated from the anisotropic temperature factors listed in Table 1 are shown in Fig. 4. The motion appears mainly to be a rotational libration about the axis through the

Fig. 3. Molecular overlap as seen perpendicular to the molecular plane.

centre of the ring and perpendicular to the molecular plane.

Computations

All the calculations were carried out using the IBM 360/75 computer at Mitsubishi Computer Centre and the MELCOM 9100 computer in our laboratory. Calculations of $|F_o|$ and $|F_c|$, Fourier syntheses, diagonal least-squares and block-diagonal least-squares analyses, bond lengths, bond angle and best plane calculations were carried out by RDTR-3, RSSFR-4, RSDLS-3, HBLS IV, RSDA-4 and RSBP-3 of UNICS computer program system respectively (Crystallographic Society of Japan, 1967). The program for computation of dihedral angles was BOND written by Iitaka. Thermal ellipsoids were plotted by the ORTEP program written by Johnson (1965).

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References

BERNDT, A. F. & MARSH, R. E. (1963). Acta Cryst. 16, 118.
CHAIWASIE, S. & FENN, R. H. (1968). Acta Cryst. B24, 525.
EVRARD, P. G., PIRET, P., GERMAIN, G. & VAN MEERSSCHE, M. (1971). Acta Cryst. B27, 661.
FERGUSON, G. & SIM, G. A. (1961). Acta Cryst. 14, 1262.
HAGA, T. (1969). Japan Patent 574642.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
JOHNSON, C. K. (1965). ORTEP. Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
KURAHASHI, M., FUKUYO, M. & SHIMADA, A. (1967). Bull. Chem. Soc. Japan, 40, 1296.
LIEBLING, G. & MARSH, R. E. (1965). Acta Cryst. 19, 202.
SAKORE, T. D., TAVALE, S. S. & PANT, L. M. (1967). Acta Cryst. 22, 720.
WHITLA, W. A., POWELL, H. M. & VENANZI, L. M. (1966). Chem. Commun. p. 310.
WILSON, F. C. & SHOEMAKER, D. P. (1957). J. Chem. Phys. 27, 809.
ZIEGLER, M. (1967). Z. anorg. allg. Chem. 355, 12.

The Structure of Zr2Ni7*

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Zr2Ni7 has been found to crystallize with monoclinic symmetry: $a = 4.698 \pm 0.009$, $b = 8.235 \pm 0.013$, $c = 12.193 \pm 0.016$ Å, and $\beta = 95.83 \pm 0.13°$. The crystal structure, with $C2/m$ space group symmetry, is compatible with observed intensities of X-ray reflections. The unit cell contains four formulae of Zr2Ni7. An R index of 0.091 was obtained from three-dimensional intensity data totaling 2031 independent reflections. The intensity data were accumulated diffractometrically with the $\theta-2\theta$ scan technique. Zirconium atoms occur in two independent sets, each with coordination number 16. The coordination atmospheres of the independent zirconium atoms are remarkably similar, with geometries related to Laves–Friauf polyhedra. Nickel atoms occur in four independent sets, each with coordination number 12. The coordination atmospheres of each of two pairs of independent nickel atoms are closely comparable, but differ between pairs. Nickel coordination atmospheres can for both pairs be considered as irregular icosahedra; however, the irregularity for one pair of the coordination icosahedra is so severe that two adjacent faces are coplanar to within the precision of the structure determination. Thus, this coordination polyhedron is not truly an icosahedron but has only 19 faces.

Introduction

Kirkpatrick & Larsen (1961) have examined the phase relationships in the zirconium–nickel binary system across the complete composition range and have reported the existence of seven intermediate phases: Zr2Ni, ZrNi, Zr7Ni10, Zr9Ni11, Zr2Ni5, Zr2Ni7, and ZrNi5. The crystal structures of Zr2Ni and ZrNi have been determined by Kirkpatrick, Bailey & Smith (1962), the structure of Zr7Ni10 has been determined by

Kirkpatrick, Smith & Larsen (1962), and the structure of ZrNi5 has been determined by Smith & Guard (1957).

Crystallographic data on the three remaining compounds are incomplete and must be considered tentative; these data include a limited amount of symmetry information and some values for lattice parameters. In the particular case of Zr2Ni7, Kirkpatrick & Larsen (1961) found that attempts to isolate single crystals of the phase by mechanical means always resulted in plastic deformation. Diffraction patterns from crystals they were able to obtain were indicative of a layered structure, and rough values for orthogonal

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