Acta Cryst. (1964). **17**, 592

The Crystal and Molecular Structure of Diiododi-(*o*-phenylenebisdimethylarsine)nickel(II)

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(*Received* 22 *May* 1963)

The crystal structure of $NiI_2(C_6H_4[As(CH_3)_2]_2)_2$ has been determined by single-crystal X-ray methods. The intensities were measured visually. The structure was refined by cycles of differential syntheses and structure factors in which anisotropic thermal parameters were included. The molecule is monomeric and consists of two diarsine ligands arranged about the nickel atom in the form of a square, with two iodine atoms in octahedral sites. The Ni–As bond distances are appreciably shorter than the normal single covalent bond distance and this can be explained in terms of $d\pi$–$d\pi$ bonding between nickel and the diarsine chelate. There is a strong interaction between iodine and the nickel–arsenic plane, which results in a distortion of the tetrahedral distribution of bonds about each arsenic atom.

Introduction

The earlier work on spin-paired complexes of bivalent nickel invariably showed them to contain four ligands arranged about the metal atom in the form of a square-plane, but more recently it has been found that five-coordinate d^8-complexes are more common than formerly supposed. The crystal structure study of $NiBr_2.Me_2As.[CH_2]_3.AsMe.[CH_2]_3.AsMe_2$ by Mair, Powell & Henn (1960) showed that the complex contains a five-coordinate Ni(II) atom. In solution, Harris, Nyholm & Phillips (1960), found that the ditertiary arsine chelate *o*-phenylenebisdimethylarsine (diarsine) formed five-coordinate cations of the type

$$[Ni(diarsine)_2halogen]^+.$$

The crystal structure of $Ni(diarsine)_2I_2$ has been investigated primarily to determine the coordination state of the Ni(II) atom in the crystal. It was noted some years ago that two forms of this compound can be prepared, a brown stable modification and a green unstable one. The possibility that the isomers are *cis* and *trans* forms of a six-covalent complex or that one is a non-electrolyte and the other a salt adds additional interest to the investigation.

Experimental

Single crystals of the brown form were grown from nitrobenzene solution. The following unit-cell dimensions were obtained from Weissenberg photographs taken with Cu $K\alpha$ radiation and zero layer precession photographs taken with Mo $K\alpha$ radiation:

$$a=9{\cdot}49,\ b=9{\cdot}25,\ c=16{\cdot}94\ \text{Å};\ \beta=114{\cdot}0°.$$

The space group was uniquely determined as $P2_1/c$ from the systematic extinctions and the compound is therefore isomorphous with the corresponding platinum complex (Stephenson, 1963). Two formula units (M.W. = 804) per unit cell ($U=1358$ Å^3) give a calculated density of 2·08 g.cm^{-3}. The molecular symmetry is $\bar{1}$.

The intensity data were collected on multiple film equi-inclination Weissenberg photographs (Cu $K\alpha$), taken around [010], ($k=0, \ldots, 7$), and [001], ($l=0, \ldots, 5$). The intensities were estimated visually with the aid of a calibration strip, and the Lorentz and polarization corrections were applied on an IBM 1620 computer with the programs of Shiono (1962). The interlayer scaling factors were determined by the least-squares method of Dickerson (1959) and Rollett & Sparks (1960). In this method the symmetric matrix formed by the normal equation coefficients was calculated on a desk machine and diagonalized, Jacobi's iterative method being used, on the IBM 1620. The scaling factors were the elements of the eigenvector corresponding to the least eigenvalue. The averaging of the structure amplitudes for those reflections which were observed on more than one layer gave 1702 independently observed structure factors. No dispersion or absorption corrections were applied.

Structure determination and refinement

For the initial trial model nickel atoms were placed at the symmetry centers (0, 0, 0) and (0, $\frac{1}{2}$, $\frac{1}{2}$) and the coordinates which had been found in the isomorphous $Pt(diarsine)_2I_2$ were assigned to the arsenic and iodine atoms. The atomic scattering factors of Thomas & Fermi (1935) for nickel, arsenic and iodine were each modified by an exponential temperature factor ($B=3{\cdot}0$ Å^2) and used in the structure factor calculation. The initial reliability factor was $R=0{\cdot}40$.

A series of three cycles of differential syntheses and

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Table 1. *Final fractional coordinates and standard deviations*

	x/a	y/b	z/c	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
Ni	0·0000	0·0000	0·0000	0·000 Å	0·000 Å	0·000 Å
As(1)	0·2054	0·1534	0·0579	0·002	0·002	0·002
As(2)	0·0671	−0·0908	0·1371	0·002	0·002	0·002
I	0·1849	−0·2462	−0·0527	0·002	0·002	0·002
C(1)	0·2886	0·0186	0·3035	0·03	0·03	0·03
C(2)	0·2321	0·0293	0·2178	0·01	0·03	0·01
C(3)	0·3911	0·1014	0·0456	0·01	0·03	0·03
C(4)	0·3970	0·1092	0·3591	0·03	0·05	0·03
C(5)	0·2875	0·1425	0·1834	0·02	0·02	0·02
C(6)	0·4521	0·2170	0·3232	0·03	0·03	0·03
C(7)	0·4035	0·2377	0·2372	0·03	0·03	0·03
C(8)	0·1861	0·3645	0·0277	0·03	0·02	0·03
C(9)	−0·0847	−0·0914	0·1857	0·02	0·03	0·02
C(10)	0·1491	−0·2766	0·1644	0·03	0·04	0·04

structure factors was computed in which the positional and isotropic thermal parameters of the nickel, arsenic and iodine atoms were allowed to change. The reliability index was reduced to $R=0{\cdot}21$.

A three-dimensional difference Fourier synthesis was then computed using all observed reflections. These reflections were assigned phases on the basis of the heavy atom contribution and these structure factors contributions were subtracted from the scaled data before summation. The resulting electron distribution clearly resolved the positions of the ten carbon atoms. The estimated standard deviation in electron density at this stage was 0·71 e.Å^{-3} and no significant peaks other than those representing the light atoms appeared in the electron distribution. Structure factors calculated with all atoms contributing, assuming an isotropic thermal parameter for the light atoms of $B=3{\cdot}0$ Å^2, gave a reliability index of $R=0{\cdot}17$.

Five cycles of anisotropic refinement were completed by differential synthesis. The scale factor, anisotropic thermal parameters and positional coordinates for each atom were allowed to vary. The refinement was complete since the average shift in parameter was a small fraction of the corresponding standard deviation. The final value of the reliability index was $R=0{\cdot}11$.

In Table 1 the atomic coordinates and their standard deviations are given.

Table 2. *Thermal parameters*

($\times 10^3$)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Ni	40 Å	52 Å	35 Å	−19 Å	12 Å	6 Å
As(1)	27	33	39	−3	0	12
As(2)	31	35	31	0	8	12
I	48	51	51	8	3	20
C(1)	34	53	29	16	8	6
C(2)	37	79	35	4	10	13
C(3)	15	40	47	−11	−8	22
C(4)	77	84	26	−8	−3	23
C(5)	35	10	36	0	−14	7
C(6)	38	87	38	23	−26	3
C(7)	54	71	105	14	−18	8
C(8)	53	28	51	4	7	23
C(9)	37	64	69	10	−9	32
C(10)	89	39	60	−16	9	19

Table 2 shows the final values, referred to the monoclinic axes, for the tensor components describing the anisotropic vibration of the atoms. The tensor components U_{ij} are those occurring in the temperature factor

$$\exp\left[-2\pi^2(h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots)\right],$$

so that, for instance, U_{11} is the mean-square amplitude of vibration of the atom parallel to the a^* axis.

Table 5† lists the final observed and calculated structure factors for comparison.

Dimensions of the molecules

The molecule is monomeric and consists of two diarsine ligands arranged about the nickel in the form of a square, with two iodine atoms in octahedral sites (Fig. 1). The bond lengths and angles are listed in Table 3. The standard deviations in bond lengths are 0·002 Å for Ni–As, 0·002 Å for Ni–I, 0·02–0·04 Å for

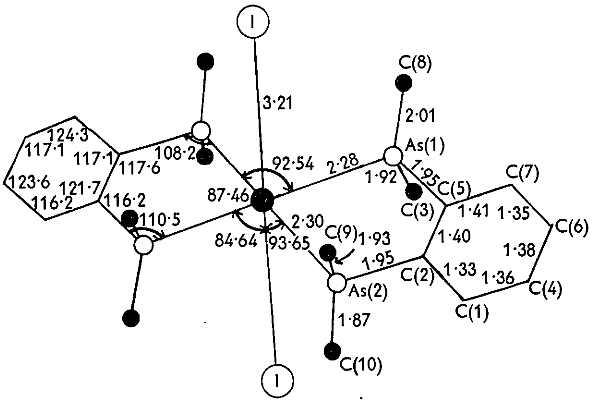

Fig. 1. Intramolecular bond lengths (Å) and angles (°).

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† Table 5 has been deposited as Document number 7632 with the A.D.I. Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D.C., U.S.A. A copy may be secured by citing the Document number and by remitting $3·75 for photoprints, or $2·00 for 35 mm microfilm. Advance payment is required. Make check or money orders payable to: Chief, Photoduplication Service, Library of Congress.

Table 3

(*a*) Bond lengths with standard deviations

	d (Å)	*σ*(*d*) (Å)		*d* (Å)	*σ*(*d*) (Å)
Ni–As(1)	2·284	0·002	C(1)–C(2)	1·33	0·04
Ni–As(2)	2·302	0·002	C(2(–C(5)	1·40	0·03
Ni–I	3·215	0·002	C(5)–C(7)	1·41	0·04
As(1)–C(3)	1·92	0·03	C)7)–C(6)	1·35	0·04
As(1)–C(5)	1·95	0·02	C(6)–C(4)	1·38	0·04
As(1)–C(8)	2·01	0·03	C(4)–C(1)	1·36	0·04
As(2)–C(2)	1·95	0·02			
As(2)–C(9)	1·93	0·02			
As(2)–C(10)	1·87	0·04			

(*b*) Bond angles with standard deviations

	β (°)	*σ*(*β*) (°)		*β* (°)	*σ*(*β*) (°)
As(1)–Ni–As(2)	87·46	0·23	C(5)–As(1)–C(3)	97·4	1·1
As(1)–Ni–I	95·31	0·20	C(2)–As(2)–C(10)	102·5	1·4
As(2)–Ni–I	93·65	0·20	C(2)–As(2)–C(9)	103·2	0·9
Ni–As(1)–C(5)	110·5	0·9	C(9)–As(2)–C(10)	101·6	1·4
Ni–As(2)–C(2)	108·2	0·9	C(2)–C(5)–As(1)	116·2	1·5
Ni–As(1)–C(8)	121·4	0·9	C(5)–C(2)–As(2)	117·6	1·5
Ni–As(1)–C(3)	117·3	0·9	C(1)–C(2)–C(5)	117·2	2·2
Ni–As(2)–C(9)	118·9	0·6	C(2)–C(5)–C(7)	121·7	2·5
Ni–As(2)–C(10)	120·1	1·2	C(5)–C(7)–C(6)	116·2	2·7
C(8)–As(1)–C(3)	102·0	1·3	C(7)–C(6)–C(4)	123·6	3·1
C(8)–As(1)–C(5)	106·4	1·1	C(6)–C(4)–C(1)	117·1	3·3
			C(4)–C(1)–C(1)	124·3	3·0

As–C and 0·03–0·04 Å for C–C. The standard deviations in bond angles are shown in Table 3(*b*).

The best least-squares planes through various atoms in the molecule have been calculated following Schomaker, Waser, Marsh & Bergman (1959) using a diagonal weight matrix. The equation of the plane through the Ni, As(1), and As(2) atoms is

$$0{\cdot}716X-0{\cdot}678Y-0{\cdot}442=0$$

where the coordinates X, Y and Z are in Å and refer to the crystallographic axes. The benzene ring is also planar, the equation being

$$0{\cdot}792X\text{–}0{\cdot}610Y\text{–}0{\cdot}337Z\text{–}0{\cdot}327=0$$

and the maximum deviation from it is $-0{\cdot}016$ Å for C(5). The arsenic atoms do not lie in the plane of the benzene ring. The deviations are $+0{\cdot}021$ Å ($\Delta/\sigma=10$) for As(1) and $-0{\cdot}094$ Å ($\Delta/\sigma=47$) for As(2). The two planes are inclined to each other at an angle of 10·4°.

Discussion

The molecular packing, as seen by projection down the *b* axis, is shown in Fig. 2. All intermolecular separations less than 5·5 Å were calculated; there were no abnormally short values, and some of the more important ones are shown in Fig. 2. There are three atoms which approach the iodine atom more closely than others. They are C(4) (non-bonded approach

Table 4. *Atomic peak heights* (eÅ^{-3}) *and curvatures* (eÅ^{-5})

Atom		*ϱ*	−*A*(*HH*)	−*A*(*KK*)	−*A*(*LL*)	*A*(*HK*)	*A*(*KL*)	*A*(*HL*)
Ni	obs.	48·3	427	331	425	−83	54	138
	calc.	53·3	480	371	471	−73	45	162
As(1)	obs.	76·8	758	618	663	−25	11	263
	calc.	77·3	771	617	676	−21	9	270
As(2)	obs.	75·7	720	578	704	−22	36	260
	calc.	77·7	748	594	725	−18	28	270
I	obs.	103·4	917	790	856	44	2	323
	calc.	104·1	937	795	879	37	2	330
C(1)	obs.	6·5	44	43	49	1	−3	21
	calc.	7·5	53	47	59	0	−3	27
C(2)	obs.	9·0	97	46	108	−5	−5	34
	calc.	8·7	92	46	102	−6	−6	33
C(3)	obs.	7·6	99	50	56	−1	−1	35
	calc.	9·5	120	66	75	1	0	44
C(4)	obs.	6·3	41	25	49	2	−9	9
	calc.	6·2	41	30	45	3	−9	9
C(5)	obs.	8·8	64	71	81	−1	−12	12
	calc.	9·8	79	78	92	−4	−11	14
C(6)	obs.	6·7	52	43	41	−2	4	7
	calc.	7·2	58	50	47	−4	6	11
C(7)	obs.	6·5	51	40	55	4	−3	24
	calc.	6·0	49	38	54	2	−1	24
C(8)	obs.	6·3	39	59	47	5	−25	22
	calc.	8·3	58	76	67	8	−29	29
C(9)	obs.	7·3	82	54	63	6	−5	42
	calc.	7·9	87	60	72	6	−5	44
C(10)	obs.	6·6	53	37	42	−2	5	20
	calc.	6·3	57	35	43	−1	4	22

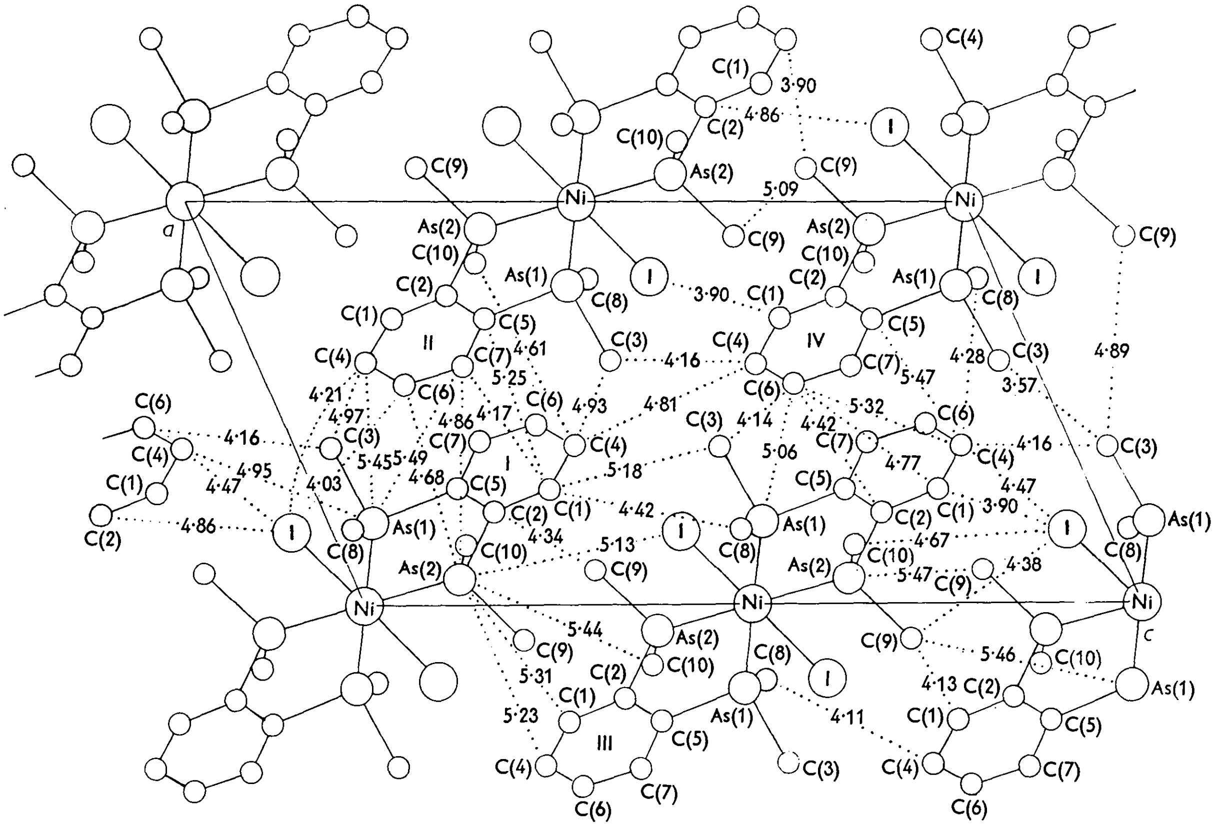

Fig. 2. Projection along the b axis showing packing and the closest intermolecular contacts. Molecule: (I) x, y, z; (II) $x, y-\frac{1}{2}, \frac{1}{2}-z$; (III) $1-x, y-\frac{1}{2}, \frac{1}{2}-z$; (IV) $1-x, 1-y, 1-z$.

distance 4·21 Å) and C(6) (at 4·03 Å) on molecule II and C(1) (at 3·90 Å) on molecule III. These approach distances are very close to the sums of the van der Waals radii as given by Pauling (1960), *i.e.* carbon (methyl group) 2·0 Å and iodine (2·15 Å). The asymmetric environment of the iodine atom is responsible for it shifting slightly away from the precise octahedral position. Thus the angles I–Ni–As(1) and I–Ni–As(2) are significantly distorted from the right angle ($\Delta/\sigma=27$ and 18 respectively).

The benzene rings of adjacent sets of molecules (*e.g.* I and II) pack together in a manner illustrated in Fig. 3. They are inclined to each other at an angle of 75·2°. It is apparent from the non-bonding approach distances and this unfavourable angle of inclination that there is very little interaction between π-electron systems of the benzene rings.

The Ni–As bond distances are appreciably shorter than the sum of the square covalent radius for nickel(II) and the tetrahedral covalent radius for arsenic ($1{\cdot}39+1{\cdot}18=2{\cdot}57$ Å). A short Ni–As bond length (2·27 Å) is also observed in the compound NiBr$_2$ triarsine (Mair, Powell & Henn, 1960). If we suppose that the dative σ-bond is first formed, then this confers a positive charge on the ligand and a negative one on the metal and respectively increases and decreases the exponents for the ultimate $d\pi$ and penultimate $d\pi$ orbitals on the two atoms. Consequently these two orbitals become more nearly matched, and overlap between them is improved. If

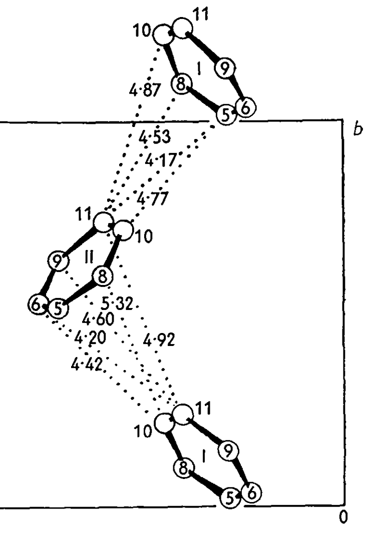

Fig. 3. The mode of packing of benzene rings on adjacent molecules, viewed down the c axis.

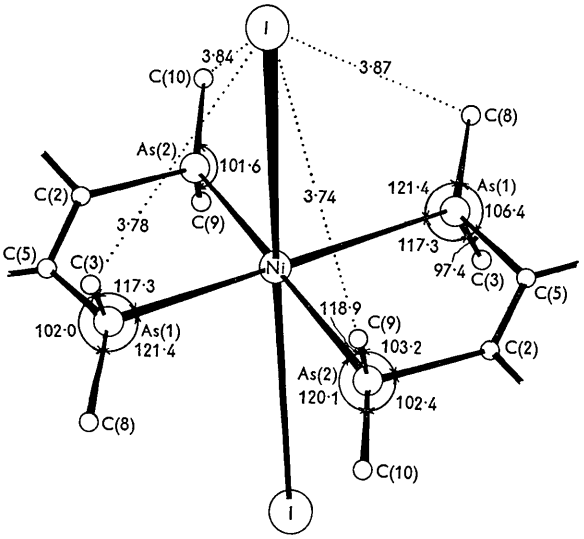

Fig. 4. Schematic depiction of the approach of the iodide ion to the nickel–arsenic plane, showing approach distances and distortions of the tetrahedral distributions of bonds about the arsenic atoms.

a dative π-bond from metal to ligand is now formed, the charges will be partly neutralized. The formation of either bond favours the development of the other and the final charge asymmetry will depend upon the electronegativities of the two centres. This double bonding, which can only arise in transition metal complexes, is thus responsible for an appreciable shortening of the Ni–As bond length from the normal single covalent bond distance.

The iodide ion approaches the nickel arsenic plane from a position of minimum electrostatic potential energy (Fig. 4). It is cushioned on the four methyl groups C(3), C(8), C(9) and C(10), and the non-bonding approach distance to these atoms is in each case less than the sum of the van der Waals radii for a methyl group and an iodine atom. The strong bonding between iodine and nickel also results in the methyl groups being pushed aside, as it were, to make room for a closer nickel–iodine interaction. Thus the angles C(3)–As(1)–Ni, C(10)–As(2)–Ni, C(8)–As(1)–Ni and C(9)–As(2)–Ni are all significantly distorted beyond the tetrahedral angle whilst the remaining angles between the arsenic–carbon bonds are all less than the normal tetrahedral angle.

It seems reasonable to assume that the charge on the nickel(II) atom lies between 0 and 1+ (Barclay, Nyholm & Parish, 1961). If the nickel–iodine interaction were purely electrostatic then an estimate of the equilibrium approach distance could be made by adding to the ionic radius of the iodide ion (2·15 Å) the non-bonded radius of a nickel atom. The nickel atoms in the bisdimethylglyoximatonickel(II) structure (Godycki & Rundle, 1953) at a distance of 3·25 Å form a bond between the d_{z^2} pair of electrons on one metal atom and the vacant p-orbital on the next: so that the non-bonded nickel(II) radius is in excess of 1·62 Å. The observed length of the Ni–I bond (3·215 Å) is therefore considerably less than the estimated bond distance for an electrostatic interaction ($>3\cdot77$ Å).

Hybridization of these orbitals is most favoured if their energies are not too different. The energy separation between atomic orbitals increases with the formal charge on the metal atom and also with its effective nuclear charge (Slater, 1960). The effective nuclear charge on nickel is low, due to the $d\pi$–$d\pi$ bonding with the diarsine chelate and the $(n-1)d-np$ separation energies for this d^8 complex are also low (Nyholm, 1961). Conditions are therefore favourable for the formation of a six-coordinate complex.

The author would like to express his thanks to Dr G. A. Jeffrey of the University of Pittsburgh for his encouragement, to Prof. R. S. Nyholm of University College, London, for helpful discussion about the bonding in the complex and to Dr C. M. Harris of the University of New South Wales, Sydney, for supplying the crystals used. The computing associated with this work was supported by the National Science Foundation; other support was provided by the U.S. Army Research Office through grant No. DA-ORD-31-124-61-G63.

References

Barclay, G. A., Nyholm, R. S. & Parish, R. V. (1961). *J. Chem. Soc.* p. 4433.

Dickerson, R. E. (1959). *Acta Cryst.* **12**, 610.

Godycki, L. E. & Rundle, R. E. (1953). *Acta Cryst.* **6**, 487.

Harris, C. M., Nyholm, R. S. & Phillips, D. J. (1960). *J. Chem. Soc.* p. 4379.

Mair, G. A., Powell, H. M. & Henn, D. E. (1960). *Proc. Chem. Soc.* p. 415.

Nyholm, R. S. (1961). *Proc. Chem.* Soc. p. 273.

Pauling, L. (1960). *The Nature of the Chemical Bond.* 3rd Ed. Ithaca: Cornell Univ. Press.

Rollett, J. S. & Sparks, R. A. (1960). *Acta Cryst.* **13**, 273.

Schomaker, V., Waser, J., Marsh, R. E. & Bergman, G. (1959). *Acta Cryst.* **12**, 600.

Shiono, R. (1962). Unpublished work.

Slater, J. C. (1960). *Quantum Theory of Atomic Structure.* New York: McGraw Hill.

Stephenson, N. C. (1963). *J. Inorg. Nuclear Chem.* **24**, 791.

Thomas, L. H. & Fermi, E. (1935). *Internationale Tabellen zur Bestimmung von Kristallstrukturen.* Berlin: Borntraeger.