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Errors in bond lengths from using wrong scattering factors. By ALAN HAZELL, *Institute of Chemistry, Århus University, DK-8000 Århus C, Denmark*

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Abstract

The incorrect assignment of atom type leads not only to incorrect thermal parameters but in unfavourable circumstances, such as having a limited data set or through over-weighting low-order reflections, to incorrect bond distances.

During crystal structure determinations there is sometimes doubt as to which type of atom a peak in an electron density map corresponds. This problem is frequently solved by performing least-squares refinements with different scattering curves and finding which gives the most plausible thermal parameters. In the determination of the structure of $[\text{Ir}(\text{bpy})_2\text{bpy}\cdot\text{C}^3, \text{N}'][(\text{ClO}_4)_3]\cdot\text{H}_2\text{O}^*$ (Hazell & Hazell, 1984) there was doubt as to whether one of the bipyridine ligands was bonded to iridium by (a) two N atoms, (b) one N and one C, or (c) one N and one C but disordered so that the atoms X, bound to Ir, scattered as the mean of C and N. Refinements showed (c) to be the most probable, they also showed however that Ir–X was too long for X = N and too short for X = C. Further refinements were then tried in which a genuine N atom of one of the other bipyridines was assumed to be O or C showing a similar but larger effect (Fig. 1).

The contribution of an atom towards the structure factor is, for a centrosymmetric structure, $a(\mathbf{h}) = fe^{-M} \cos 2\pi(\mathbf{h}\cdot\mathbf{r})$, where f is the scattering factor and e^{-M} the temperature factor where $M = B \sin^2 \theta / \lambda^2$. If f is replaced by a wrong scattering curve, g , the correct value of $a(\mathbf{h})$ can be approximated by changing M or r . As the changes should have as little effect as possible on other reflections the change will

* $\text{bpy} = 2,2'$ -bipyridine- N, N' , $\text{bpy}\cdot\text{C}^3, \text{N}' = \text{NH}^+\cdot 2,2'$ -bipyridinium-3-yl- N' .

mainly be in B . For low-order reflections where $\sin^2 \theta$ is small e^{-M} is close to 1 and is insensitive to changes in M , a very large shift in B would be required and instead there will be some small shifts in r . There is a balance between the contradictory requirements of wanting to improve $a(\mathbf{h})$ whilst not worsening the higher-order reflections. Changes in scale factor will also correct for the wrong scattering curve but for light atoms in a large heavy-atom structure the change should be small, particularly so in those cases where two atoms, e.g. C and N, are interchanged. For a light atom close to (i.e. scattering in phase with) a heavy atom the shift in r will be such as to increase the interatomic distance if $g > f$ and to decrease it if $g < f$. This is just the effect observed for the iridium complex. The effect of obtaining wrong bond lengths should be more noticeable in structures containing heavy atoms, i.e. where the two atoms forming the bond scatter in phase with the structure

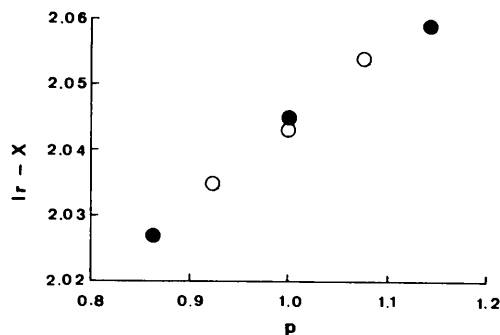


Fig. 1. Ir–X distances vs occupation factors p for $[\text{Ir}(\text{bpy})_3(\text{ClO}_4)_3]\cdot\text{H}_2\text{O}$. The open circles are for $X = (\text{C} + \text{N})/2$, i.e. for the disordered bipyridinium ligand, the filled circles are for $X = \text{N}$ for one of the N-bonded bipyridines.

Table 1. Bond distances M – N obtained for differing occupation factors, and with different $\sin \theta / \lambda$ ranges

The R values are for unit occupation factors. N_0 and N_v are the number of reflexions and the number of variables.

	Occupation factor for N			$\sin \theta / \lambda_{\text{max}}$ (\AA^{-1})	N_0	N_v	R
	0.86	1.0	1.14				
$[\text{Ir}(\text{bpy})_2\text{bpy}\cdot\text{C}^3, \text{N}']X_3\cdot\text{H}_2\text{O}^*$	2.027 (7)	2.045 (7)	2.059 (7)	0.48	2531	514	0.031
$[\text{Ir}(\text{bpy})_3]X_3\cdot 2\frac{1}{2}\text{H}_2\text{O}^\dagger$	2.007 (18)	2.032 (18)	2.055 (18)	0.54	2870	490	0.040
$[\text{Pd}(\text{phen})_2](\text{ClO}_4)_2^\ddagger$	2.060 (4)	2.060 (4)	2.061 (4)	0.65	2294	209	0.046
$[\text{Pd}(\text{phen})_2](\text{ClO}_4)_2$	2.055 (6)	2.059 (6)	2.064 (6)	0.50	1094	209	0.041
$[\text{Pd}(\text{phen})_2](\text{ClO}_4)_2$	2.050 (9)	2.060 (9)	2.070 (9)	0.45	798	209	0.041
$[\text{Pd}(\text{phen})_2](\text{ClO}_4)_2$	2.030 (17)	2.063 (17)	2.084 (17)	0.40	578	209	0.041
$[\text{Co}(\text{ama}_3)]\text{Cl}_3\cdot 3\text{H}_2\text{O}^\S$	1.994 (4)	2.001 (4)	2.005 (4)	0.65	2465	390	0.049
$\text{Pt}(\text{TPP})^\P$	2.006 (3)	2.005 (3)	2.004 (3)	0.56	1051	118	0.012
$\text{Pt}(\text{TPP})$	2.006 (4)	2.006 (4)	2.006 (4)	0.45	561	118	0.010
$\text{Pt}(\text{TPP})$	1.969 (8)	2.000 (7)	2.021 (7)	0.40	385	118	0.009

* $P2_1/c$, $X = \text{ClO}_4$, data from Hazell & Hazell (1984).

† $R3c$, $X = \text{ClO}_4$, data from Hazell & Hazell (1984).

‡ $I2/c$, phen = 1,10-phenanthroline, data from Rund & Hazell (1980).

§ $P1$, ama = 3-aminomethyl-3-methylazetidide, data from Larsen & Jørgensen (1983).

¶ $I42d$, TPP = 5,10,15,20-tetraphenylporphyrinato, data from Hazell (1984).

factors, and where the low-order reflections make a relatively large contribution towards the least-squares matrix elements, this could be because the data set was limited or because an inappropriate weighting scheme was employed. The effect should be decreased if an extinction parameter is refined as this can also soak up errors for low-order reflections.

Refinements were carried out for five structures, with models where a N atom was given occupation factors 0.86, 1.0 and 1.14. 0.86 corresponds to replacing N by C, and 1.14 to replacing N by O. The occupation factor for a C

atom was adjusted so that the total scattering power of the molecule was constant. The effect was observed for all the structures although in some cases only for limited data sets (Table 1). The effect increases as $(\sin \theta / \lambda)_{\max}$ decreases.

References

- HAZELL, A. C. (1984). *Acta Cryst.* In the press.
 HAZELL, A. C. & HAZELL, R. G. (1984). *Acta Cryst.* In the press.
 LARSEN, F. K. & JØRGENSEN, P. (1983). Private communication.
 RUND, J. V. & HAZELL, A. C. (1980). *Acta Cryst.* B36, 3103–3105.

International Union of Crystallography

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Union Office Computer

With the help of a generous donation from the Japanese crystallographic community, a minicomputer with 384K bytes of memory and 15M bytes of hard disc storage (with magnetic cartridge tape back-up) has been installed in the Union office at Chester. Six VDU terminals and two printers, together with the software supplied, allow timely accounting for all the Union's financial transactions. A

balance sheet and accounts, comparable to those published in the annual Executive Committee reports [*cf. Acta Cryst.* (1984). A40, 68–85], can now be produced at short notice. In addition, the progress of all papers throughout the journal production process will be monitored, duplications identified, status reports listed and subject index, chemical name index, author index and formula indexes maintained. Production of the next cumulative index will save approximately the total cost of the microcomputer.

An engraved wall plaque commemorating the Japanese gift has been placed in the Chester office.

Book Reviews

Works intended for notice in this column should be sent direct to the Book-Review Editor (J. H. Robertson, School of Chemistry, University of Leeds, Leeds LS2 9JT, England). As far as practicable books will be reviewed in a country different from that of publication.

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Points, lines and walls in liquid crystals, magnetic systems and various ordered media. By M. KLÉMAN. Pp. 322. Chichester–New York–Brisbane–Toronto–Singapore: John Wiley & Sons, 1983. £29.95.

The technical importance of liquid crystals has challenged many papers, especially in the theoretical interpretation of their outstanding properties which are essentially determined by defects. Approximately 30 years ago a similar development took place in the theory of plastic deformation of metals. It could be shown then that edge and screw dislocations as defined by the direction of a line and their Burgers vector, given by the well known Burgers circuit, suffice to explain the dynamic behaviour of crystals during plastic deformation. Since structural details of the kernel of dislocation lines were irrelevant, the extension of this theory to materials other than metals was very simple. Now, a more generalized treatment of similar defects is offered in Kléman's book, which explains the topology of defects in media which are in general characterized by a tensor field, e.g. a director field in the case of first-order tensors.

The author starts by showing many pictures of defects predominantly taken with the optical microscope using crossed nicols. It is regrettable that no direct correlation between these pictures and the defects described in the text

book is given; this could have been done at least in some cases. Then a classification of defects is given, beginning with the symmetry of nematic, smectic and cholesteric phases. The formal topological description of most of the defects is explained in terms of the so called 'Volterra process', which is a valuable means whereby an adequate description of many types of dislocation, disclination *etc.* is possible. In the following chapters a systematic review of the most important defects in liquid crystals is given. Obviously these defects also play an important role in the magnetic properties of crystals where spin orientation and spin density are the relevant factors describing their properties (e.g. Bloch walls, Néel walls, helimagnets *etc.*). In the last chapter Kléman gives a review of a generalized group-theoretical classification of topologically stable defects. This method yields a unique treatment of singularities including lines and walls, which are partially described in a more or less artificial manner by the Volterra process. Obviously a better understanding of the relevant basic mathematics is necessary in this part of the book. The treatment of the dynamics of liquid crystals, which is an important field of present and future development in this field lies beyond the scope of this textbook.

Apparently the author has endeavoured to keep the mathematical background necessary for full understanding of a complicated subject as low as possible. Consequently, advanced students as well as scientists may use it as a good