



Fig. 1. The results of two refinements of the  $\text{Co}(\text{NH}_3)_5(\text{NO})^{2+}$  ion. The ion has crystallographically imposed  $mm$  symmetry. In (a) the N atom of the NO group was restricted to the intersection of the two mirror planes and the refinement was carried out by standard methods. In (b) the restriction of the N atom to the intersection of the mirror planes was relaxed and the refinement was carried out by the group method described here. For the sake of clarity neither drawing illustrates the disorder that results from the imposition of  $mm$  symmetry.

respect to  $\mathbf{x}$  and derivatives of  $\mathbf{x}$  with respect to the group variables.

Let us now consider the special case of the linear NO group. One can readily show that the rotation angle  $\varepsilon$  has an arbitrary value and that the matrix  $\mathbf{R}$  takes the form

$$\mathbf{R} = \begin{pmatrix} \cos \delta \cos \eta & -\sin \delta & \cos \delta \sin \eta \\ \sin \delta \cos \eta & \cos \delta & \sin \delta \sin \eta \\ -\sin \eta & 0 & \cos \eta \end{pmatrix}. \quad (5)$$

Moreover, since we may take one axis of the internal coordinate system along the N–O bond we may place the origin of this coordinate system midway between the two atoms. Thus  $\mathbf{x}'(1) = (L, 0, 0)$  and  $\mathbf{x}'(2) = (-L, 0, 0)$  where  $2L$  is the N–O bond length. We thus have

$$x_i(j) = x_{ci}(j) + P(i, 1) (-1)^{j+1} L, \quad i = 1, 2, 3; \quad j = 1, 2 \quad (6)$$

The direct refinement of  $L$  is readily possible through a simple program modification since

$$\partial F / \partial L = \sum_{i=1}^3 P(i, 1) [\partial F / \partial x_i(1) - \partial F / \partial x_i(2)]. \quad (7)$$

In Fig. 1(b) we illustrate the results of such a group refinement of the disordered N model for the  $\text{Co}(\text{NH}_3)_5(\text{NO})^{2+}$  ion. In the final analysis the disordered N atom is approximately 0.3 Å from the intersection of the two mirror planes, and thus refinement of this model by ordinary least-squares procedures would not have been possible. It is interesting that refinement of the ordered N model, with both N and O

anisotropic, leads to agreement factors identical with those from the group method for the disordered N model (with N isotropic and O anisotropic). The number of variables is the same in the two refinements. Moreover, the derived parameters of the O atom, including the thermal parameters, do not differ from those derived in the ordered N model by more than one standard deviation. It should be emphasized that in this present application one has achieved a fit of a different model to the data. The fact that the agreement with the data is equally good in the ordered and disordered N models means that these cannot be distinguished in the experiment. Yet physically the disordered model, refinement of which was effected as described above, is far more satisfying from a chemical point of view, especially when the Co–N–O bond angle and the N–O bond length are considered.

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## Book Reviews

*Works intended for notice in this column should be sent direct to the Book-Review Editor (M.M. Woolfson, Physics Department, University of York, Heslington, York YO1 5DD, England). As far as practicable books will be reviewed in a country different from that of publication.*

**Chimie cristalline.** Par J. ZEMANN. Pp. xiv + 162. Paris: Dunod, 1970. Price not known.

This booklet, originally in German (ca. 1966), is a pocket-sized volume of about 150 pages and is one of a series of some 80 similar monographs, in French. It is meant to be an introductory textbook in the structural chemistry of sol-

ids and it is addressed to 'the student, research worker, engineer and layman'. It is written at about the level of second-year University work.

Some features of this little book are very pleasing, most notably its numerous clear diagrams of crystal structures (very sensibly including also an Å scale in almost every instance).

In any case it is refreshing to meet a different lay-out of familiar material. The main part of the book consists of four short chapters, each of about 15 pages only, on atomic radii, lattice energies, covalent crystals and metallic solids. Although so brief these are quite illuminating being amply illustrated with examples, tables, and diagrams. These chapters are preceded by a relatively very long chapter on the symmetry and geometry of lattices and the book ends with a miscellany of extremely short sections on solid solutions, polymorphism, silicates and other special topics.

One particular feature catches the eye and may be worth mention in this review: the *crystallochemical formulae*, which follow the 1946 notation of Machatschki. These attempt to represent in symbolism the essentials of the stereochemistry of a particular structure by taking a kind of middle course between the bare chemical formula at one extreme and the full structure diagram at the other. The connectivity of the structural unit is indicated and the coordination of each member is given. Thus, diamond becomes  ${}^3_3C^{[4]}$ , while graphite is  ${}^2_3C^{[3]}$ ; metallic selenium is  ${}^3_3Se^{[2]}$ , copper,  ${}^3_3Cu^{[12]}$ , and rutile is  ${}^3_3Ti^{[6]}O_2^{[3]}$ . Sometimes these can formulae be quite complex even for simple materials, e.g. cementite,  ${}^3_3Fe_2^{[2C+11Fe]}Fe^{[2C+12Fe]}C^{[6Fe]}$ . The limitations of such formulae are obvious but the idea is interesting and of some value. Frequent and effective use is made of these formulae throughout the book.

Considering the small size of the book it is remarkable what a range of topics receive mention: intermetallic phases, order-disorder phenomena, non-stoichiometry, crystal defects, boron hydrides, hydrogen bonding, the  $\alpha$ -helix, metal-metal bonding (but not  $\pi$ -bonds) in organometallics, and others. On the other hand, it is a pity that so much space, relatively, is taken up by the over-detailed account of lattice geometry given in the first chapter. Here, not only are the 7 crystal systems defined, and formulae given for their cell volumes, and all the 32 crystal classes set out with their classical epithets (...scalenohedral...), but all 230 space groups are listed, with elaborate attention to the symbols, nomenclature and symmetry operations. None of this technical detail is of any material value to the reader interested in structural chemistry, nor is it used in later chapters. More valuable background would have been provided by some expansion of the very short section which mentions how, by the use of X-rays, the crystallographer is able to measure diffraction intensities and so to discover the atomic positions and molecular structures which the book describes.

On balance, an attractive booklet, considering its size.

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**Progress in stereochemistry. 4.** Edited by B. J. AYLETT and M. M. HARRIS. Pp. vii + 389. London: Butterworths, 1969. Price £7.10s (£7.50).

This, the fourth volume of the series, continues the standard of excellence set by the first three. There are eight

chapters, all very well written, each covering a completely different branch of stereochemistry. Hall describes with authority recent work on bridged biphenyls. Ferrier discusses configurational analysis in carbohydrates, a useful complement to recent reviews of conformational analysis in that field. In an exceptionally useful chapter Klyne and Scopes update correlations of absolute and relative configurations: their tabulations of molecules which have been studied with those ends in mind should prove extremely valuable to chiralists. White emphasizes the value of nuclear magnetic resonance spectroscopy in inorganic problems, citing numerous examples. The chapter by Aylett also is concerned with inorganic compounds, but restricted to the elements of main group IV; nevertheless, over 160 references are cited, testimony to how active group IV stereochemists have become recently. Mills and Speakman carefully explain, for the benefit of non-specialists, what the X-ray method is all about; they do not, unfortunately, discuss the numerous pitfalls which are often encountered therein, nor how easy it is for an X-ray crystallographer to arrive at an incorrect answer. The complete stereochemistry of myoglobin is detailed by H. C. Watson; this discussion includes treatment of the helical, non-helical, hydrophobic, and non-polar portions of this interesting protein. Also included (courtesy of J. C. Kendrew, F.R.S.) is a table of the atomic coordinates; although these have been 'tidied' it is possible that this will not impair their usefulness to those interested in the details of this molecule. In the final chapter Walton describes numerous types of molecular models which are commercially available, together with their advantages, shortcomings, and prices.

Because this review is for the readers of *Acta Crystallographica*, I must include an excerpt from one of the chapters written by an organic chemist: 'Diffraction techniques provide in principle the most powerful general means for determining configurations of crystalline compounds, and only the formidable practical difficulties involved and the complexity of the analysis of the scattering patterns prevent their offering complete solutions to almost all problems. The combined power of the other available methods has almost completely eliminated the necessity to apply diffraction techniques, and they need only be relied upon as a last resort with particularly difficult compounds.' It would appear that after all these years we crystallographers are still considered a world apart, working in a difficult field with obscure methods, interested only in our own results. The nadir of this point of view appeared in a recent issue of *Nature, Lond.* (1970) **226**, 404, in which our branch of science was referred to as 'the trade'. If our work is thus ignorantly classified as mundane and non-U, perhaps it behooves all of us to spend at least one hour a week educating our colleagues across the campus on just what it is that we do, how, and why.

This book is highly recommended to organic, physical, and inorganic chemists, crystallographers, stereochemists, and even to molecular biologists.

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