

Entwässerungsverlauf unter Wärmeaufnahme wahrscheinlich nach folgendem Schema entsteht:

Ursprüngliche Probe: $6\text{O}-4\text{Si}-4\text{O}+2(\text{OH})-4\text{Al}-6(\text{OH})$
 Teilweise entwässerte Probe: $6\text{O}-4\text{Si}-4\text{O}+x(\text{OH})-4\text{Al}-y\text{O}+z(\text{OH})$

wobei $0 < x < 2$, $0 < y < 4$, $0 < z < 6$ und $2y + x + z = 8$ sind; $x=0$, $y=4$ und $z=0$ entsprechen zum völlig entwässerten Zustand. An der Probe bei 535°C wurde es annähernd $x \approx 1$ und $y + z \approx 4.5$ von der Dichthöhe des Sauerstoffs in der zweidimensionalen Fourier-Projektion geschätzt.

Im Verlauf der Entwässerung fallen zuerst die an Al gebundenen und an der anderen Seite der Schicht angelegerten Hydroxyle OH(2) ab, und danach die Hydroxyle zwischen Al und Si OH(1): es reagieren also solche Hydroxyl-Paare unter Wasseraustritt, die zwei Al-Oktaederkoordinaten mit gemeinsamen Kanten angehören, Hydroxylionen auf Kanten, die auch zu zwei Al-Oktaeder gehören, deren beiden Ecken ein Hydroxyl und ein O um Si [OH(3)-O(4), OH(4)-O(5)] sind, bleiben dagegen übrig. Dabei gehen die 6-Koordinationsoktaeder von Al infolge dieser Hydroxylabfälle in die 4-Koordinations-tetraeder über. Diese Tatsache ist erst von Brindley & McKinstry

(1961) durch Röntgenfluoreszenzanalyse erwiesen worden. Die entstehenden Koordinations-Tetraeder verbiegen sich stark. Sie dehnen sich zu (001) parallel aus, ziehen sich zur Basisebene senkrecht zusammen und ordnen sich in einer Kette mit einer gemeinsamen Kante [110]. So weit wie es um diese Versuchung angeht, konnte eine grosse Veränderung an den Atomanordnungen nicht beobachtet werden; so bei einer Erhitzung über 535°C könnte die gefundene wasserärmere Phase, ohne grosse Veränderung der Atomanordnungen zu veranlassen, leicht zum Zustand des s.g. Metakaolins übergehen. Dies stimmt aber gerade mit der Annahme von Tscheischwili, Büsser & Weyl (1939) überein.

Literatur

- BRINDLEY, G. W. & MCKINSTRY, H. A. (1961). *J. Amer. Ceram. Soc.* **44**, 506.
 BRINDLEY, G. W. & NAKAHIRA, M. (1959). *J. Amer. Ceram. Soc.* **42**, 311.
 NEWNHAM, R. E. (1961). *Miner. Mag.* **32**, 683.
 PAMPUCH, R. (1966). *Polska. Akad. Nauk Proc. Min.* **6**, 53.
 TSCHESCHWILI, L., BÜSSEM, W. & WEYL, W. (1939). *Ber. dtsh. keram. Gesell.* **20**, 249.

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Refinement of a linear group: direct refinement of an interatomic bond length. By JAMES A. IBERS, *Department of Chemistry, Northwestern University, Evanston, Illinois 60201, U.S.A.*

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The refinement of a linear, two-atom group to resolve a problem of the disorder of the group is illustrated as is the direct refinement of the interatomic separation of the group atoms.

Since their development (Scheringer, 1963; La Placa & Ibers, 1963, 1965) group refinement procedures have been used extensively in these and other laboratories. Although the major use has been to enable one to include in the model a given feature of the structure that is believed to be known, better than it can be determined in that particular experiment, other important applications have been made. In particular, the group refinement procedure enables one to handle disorder problems that would otherwise be intractable (Bright & Ibers, 1968).

Recently a new application of group refinement to the resolution of a disorder problem was evolved. In this application not only was the disorder of a linear, two-atom group handled successfully, but the interatomic separation of the group atoms was refined directly. Although this application was developed for use on certain nitrosyl complexes of iridium (Mingos & Ibers, 1970) it will be illustrated for the $\text{Co}(\text{NH}_3)_5(\text{NO})^{2+}$ ion (Pratt, Coyle & Ibers, 1970), where it was also applied. The $\text{Co}(\text{NH}_3)_5(\text{NO})^{2+}$ ion contains a bent Co-N-O linkage. Crystallographically, *mm* symmetry is imposed on the ion leading, of course, to disorder of the oxygen atom. In the initial refinement it was assumed that both Co and N (of the NO group) lie on the intersection of the mirror planes. The result of this initial refinement is shown in Fig. 1(a). Not only is the shape of the thermal ellipsoid of the N atom unreasonable, but the N-O bond length of 0.92 \AA is physically impossible. We therefore postulated a disorder in which the N atom is not restricted to *mm* symmetry, but is allowed to move away from the intersection of the mirror planes. We now indicate how refinement of this disordered N model was carried out by group methods.

Using an adaptation of our earlier notation (La Placa & Ibers, 1965) we write

$$\mathbf{x}(j) = \mathbf{x}_c + \mathbf{P}\mathbf{x}'(j), \quad j=1, \dots, N \quad (1)$$

where the vector $\mathbf{x}(j)$ represents the fractional coordinates of atom j , where \mathbf{x}_c represents the fractional coordinates of the center of the group coordinate system, and where $\mathbf{x}'(j)$ represents the coordinates of atom j in Å in the internal group axial system. In equation (1) the matrix \mathbf{P} is given by

$$\mathbf{P} = \mathbf{U}^t \mathbf{R} \quad (2)$$

where the rotation matrix \mathbf{R} brings about coincidence, except for translation, of this internal group coordinate system with an external orthonormal system \mathbf{A} . The system \mathbf{A} is related to the crystal axial system \mathbf{a} by the relation

$$\mathbf{A} = \mathbf{U}\mathbf{a} \quad (3)$$

The particular form of \mathbf{U} adopted in our programs is

$$\mathbf{U} = \begin{pmatrix} a^* & b^* \cos \gamma^* & c^* \cos \beta^* \\ 0 & 1/b & 0 \\ 0 & -\cot \alpha/b & \csc \alpha/c \end{pmatrix} \quad (4)$$

where the symbols have their usual meanings. The form of \mathbf{R} adopted here is based on successive counterclockwise rotations, δ , ϵ , and η , about the internal axes 2, 1, and 3. The group refinement is carried out in the following way: The fractional coordinates $\mathbf{x}(j)$ are derived from the various group parameters, \mathbf{x}_c , and $\mathbf{x}'(j)$. The derivatives of the structure factors F with respect to the group variables are derived by direct propagation of derivatives of F with

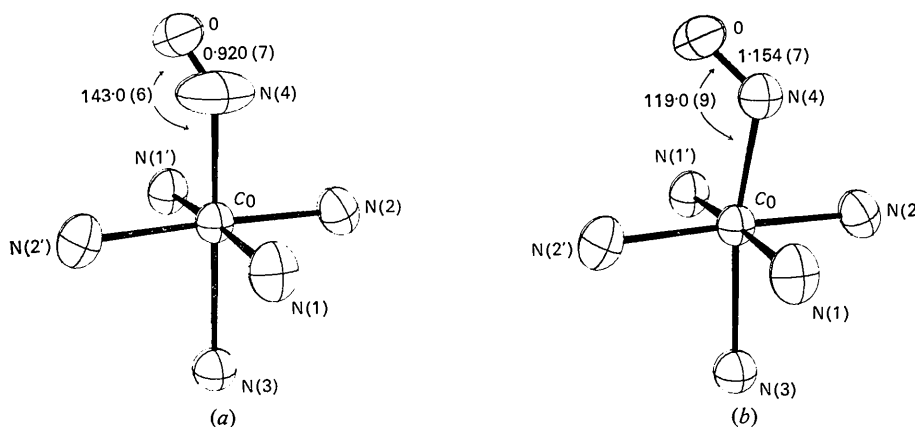


Fig. 1. The results of two refinements of the $\text{Co}(\text{NH}_3)_5(\text{NO})^{2+}$ ion. The ion has crystallographically imposed mm symmetry. In (a) the N atom of the NO group was restricted to the intersection of the two mirror planes and the refinement was carried out by standard methods. In (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 ε 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.

References

- BRIGHT, D. & IBERS, J. A. (1968). *Inorg. Chem.* **7**, 1099.
 LA PLACA, S. J. & IBERS, J. A. (1963). *J. Amer. Chem. Soc.* **85**, 3501.
 LA PLACA, S. J. & IBERS, J. A. (1965). *Acta Cryst.* **18**, 511.
 MINGOS, D. M. P. & IBERS, J. A. (1970). *Inorg. Chem.* In the press.
 PRATT, C. S., COYLE, B. A. & IBERS, J. A. (1970). *J. Chem. Soc.* Submitted for publication.
 SCHERINGER, C. (1963). *Acta Cryst.* **16**, 546.

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).