Table 1 reports the final atomic parameters and the temperature factors with their estimated standard deviations, as calculated from the diagonal terms of the inverse least-squares matrix. Bond lengths and angles in the cation are reported in Table 2. Tables 3, 4 and 5 report the observed and calculated structure factors.

The general features of the structure are the same for each of the three compounds as well as for the other compounds of the series previously reported, as one would expect from their isomorphism. However, some distances and angles in the coordination polyhedra of the various complexes in the series differ by several standard deviations. A detailed study and possible explanation of these small but significant differences, which must depend essentially upon the electronic configuration and size of the metal ions, will form the subject of a future discussion.

The structure of the complexes consists of $M(Me_6tren)Br^+$ and Br^- ions arranged in a distorted NaCl type arrangement. The five ligands about the metal atom are at the apices of a trigonal bipyramid with C_3 crystallographic symmetry (Fig. 1). The symmetry of the coordination polyhedron alone is C_{3v}. The deviation of the metal atom from the equatorial plane of the bipyramid towards the bromine atom is 0·36, 0·32 and 0·27 Å respectively, for the three compounds here reported.

The average Zn–N distance of 2·13 Å and the N(1)–Zn–N(2) angle of 82·6° in the zinc(II) complex can be compared with the analogous values (2·12 Å and 81°) reported for the structure of $Zn(tren)(SCN)_2$ by Jain, Lingafelter & Paoletti (1968). No suitable structures can be found for comparison in the case of the other two complexes, since, to the authors' knowledge, $Mn(Me_6tren)Br_2$ is the first example of a pentacoordinate structure for manganese(II) which has been elucidated by a complete X-ray analysis and $Fe(Me_6tren)Br_2$ is the first case of a pentacoordinate iron(II) complex which exhibits trigonal bipyramidal geometry in the coordination polyhedron.

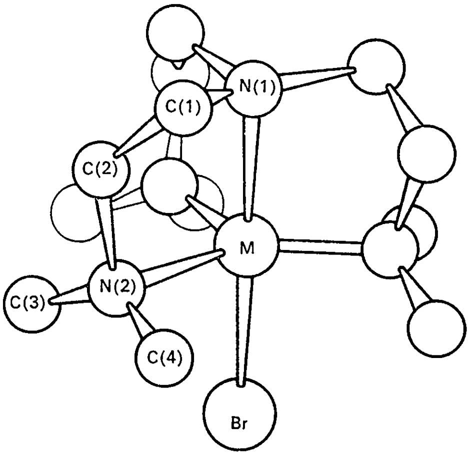

Fig. 1. A perspective drawing of the $M(Me_6tren)Br^+$ ion.

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Evidence for systematic errors in X-ray temperature parameters resulting from bonding effects*.

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Evidence derived from a combination of X-ray and neutron diffraction data for several compounds indicates that bonding introduces significant systematic errors in temperature parameters of first-row atoms. Difference ellipsoids are drawn which represent X-ray minus neutron thermal motion. The principal axes of these ellipsoids generally point along molecular symmetry axes.

Introduction

Refinement of high-order X-ray data has indicated that anisotropic thermal parameters used routinely in crystal structure refinement can absorb deviations from spherical symmetry of the atomic charge cloud. Thus temperature parameters obtained by refinement of all data with spherical atom form factors are systematically in error because of bonding effects (Hall & Maslen, 1967; Stewart, 1968). Further evidence, to be discussed here, has been obtained from comparison of X-ray and neutron diffraction data.‡ The comparison indicates a considerable effect for first row atoms.

Origin of the discrepancies

We want to list three differences between the free atom and an atom in a molecule.

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‡ Our treatment implies that the effect of thermal diffuse scattering on temperature parameters is similar for the two techniques. The physical meaning of the results supports this assumption.

(*a*) *Bond density*. In the localized bond approximation the overlap density is represented by the last term in the following expression for the charge density ϱ in the bond AB

$$\varrho = \psi_A^2 + \psi_B^2 - \frac{S}{1+S}(\psi_A^2+\psi_B^2) + \frac{2}{1+S}\psi_A\psi_B$$

(Coulson, 1961)

in which ψ_A and ψ_B are the atomic bonding hybrids on atoms A and B, and S is the overlap integral between these hybrids. The overlap density which amounts to $2S/(1+S)$ electrons, is centered in the bond. This implies that the valence charge density of the bound atom is more diffuse than the valence electrons in the isolated atom. An apparent increase in thermal motion in the direction of the bonds may be anticipated.

(*b*) *Lone pair electrons*. For atoms with lone pairs which are not pure *s* or pure *p* orbitals, but sp^n hybrids, the charge density is no longer spherically symmetric. This gives rise to a small shift in the centroid of the atomic charge density (Coppens & Coulson, 1967), and will also increase apparent thermal motion in the direction of the lone pair orbital axis. Since the total amount of charge centered on the atom is not affected a certain decrease may be expected in other directions from this effect alone.

(*c*) *Ionicity*. Least-squares refinement will tend to produce thermal parameters which properly build up the density at the time-averaged nuclear position. Thus ionicity will generally increase X-ray thermal parameters of electropositive atoms and decrease the parameters of electronegative atoms. When extra density is preferentially located in a particular orbital, such as a π orbital in a conjugated system an overall decrease may be accompanied by an increase in the direction of the π orbital axis.

Evidence from comparison of X-ray and neutron data

A number of accurate X-ray and neutron analyses of organic crystals have been completed. They include α-deuterooxalic acid dideuterate (Delaplane & Ibers, to be published; Coppens & Sabine, to be published), β-deuterooxalic acid dideuterate (Iwasaki & Saito, 1967; Coppens & Sabine, to be published), *s*-triazine (Coppens, 1967) and orthanilic acid (Hall & Maslen, 1968). In all these structures significant discrepancies have been observed. Both α-deuterooxalic acid and *s*-triazine were determined from diffractometer data only. The α-deuterooxalic acid Cu *Kα* X-ray and the neutron data were corrected for anisotropic extinction according to a method developed by Coppens & Hamilton (to be published). The *s*-triazine Mo *Kα* data showed no evidence for extinction. Conventional least-squares refinement techniques were used. Numerical information is given in Table 1. For 16 out of a total of 18 diagonal tensor elements the X-ray values exceed corresponding neutron values, the discrepancies varying between $-0{\cdot}9$ and $+8{\cdot}1\sigma$ or -3 to 50% of the neutron values with an average apparent increase of 11·5%. Theoretical order of magnitude calculations (Stewart & Coppens, 1968) give results which are compatible with these numbers.

Since the X-ray values are generally larger it is possible to obtain a pictorial view of the effect by plotting the difference between X-ray and neutron thermal ellipsoids. The mean square displacement parallel to any unit vector with components $l_i (i=1,2,3)$ is given by $\sum_i \sum_j U_{ij} l_i l_j$. The difference between the X-ray and neutron thermal motion can therefore be plotted as $\sum_i \sum_j (U_{ij,\mathrm{X}} - U_{ij,\mathrm{N}}) l_i l_j$. Such $X-N$ difference ellipsoids for α-deuterooxalic acid dideuterate and *s*-triazine were obtained with the program *ORTEP* (Johnson, 1965) and are reproduced in Fig. 1. Slight negative principal elements of the difference ellipsoids have been replaced with small positive values for the N atom in *s*-triazine (in the direction tangential to the ring), and for the atoms C (⊥ to the C–C bond in the molecular plane) and O(3) (in the D_2O molecular plane ⊥ to the bisectrix of the two OD bonds). The orientation of the difference ellipsoids in *s*-triazine is dictated by symmetry (Coppens, 1967), but it is obvious that the carbon atom has an apparent extra motion in the direction of the overlap density in the C–N bond. According to a CNDO (complete neglect of differential overlap; Pople, Santry & Segal, 1965) molecular orbital calculation of the molecule (Stewart, 1968) the nitrogen atom has a negative charge of almost 0·2 electron. An apparent decrease in thermal motion tangential to the ring is observed, while the net effect is positive both in the direction of the nitrogen lone pair and in the direction of the π orbital.

No symmetry restrictions exist for deuterooxalic acid, nevertheless the principal axes of the difference ellipsoids point along molecular symmetry axes. Both O(3) and C show flat disks with principal axes approximately perpen-

Table 1. *Agreement factors* (%)

	s-Triazine		α-DOX	
	X-rays	Neutrons	X-rays	Neutrons
$R = \dfrac{\Sigma \lvert F_o - \lvert F_c \rvert \rvert}{\Sigma F_o}$	5·0	7·3	2·7	4·5
$R_w = \left\{\dfrac{\Sigma w \lvert F_o - \lvert F_c \rvert \rvert^2}{\Sigma w F_o^2}\right\}^{1/2}$	3·9	5·3	3·3	5·0

Information on diagonal tensor elements U_{ii} (Å²) of atoms other than H

	s-Triazine		α-DOX	
	X-rays	Neutrons	X-rays	Neutrons
Average U_{ii}	0·080	0·071	0·0409	0·0371
Range of U_{ii}	0·053–0·133	0·049–0·115	0·0264–0·0699	0·0234–0·0601
Average $\sigma(U_{ii})$	0·002	0·004	0·0008	0·0007

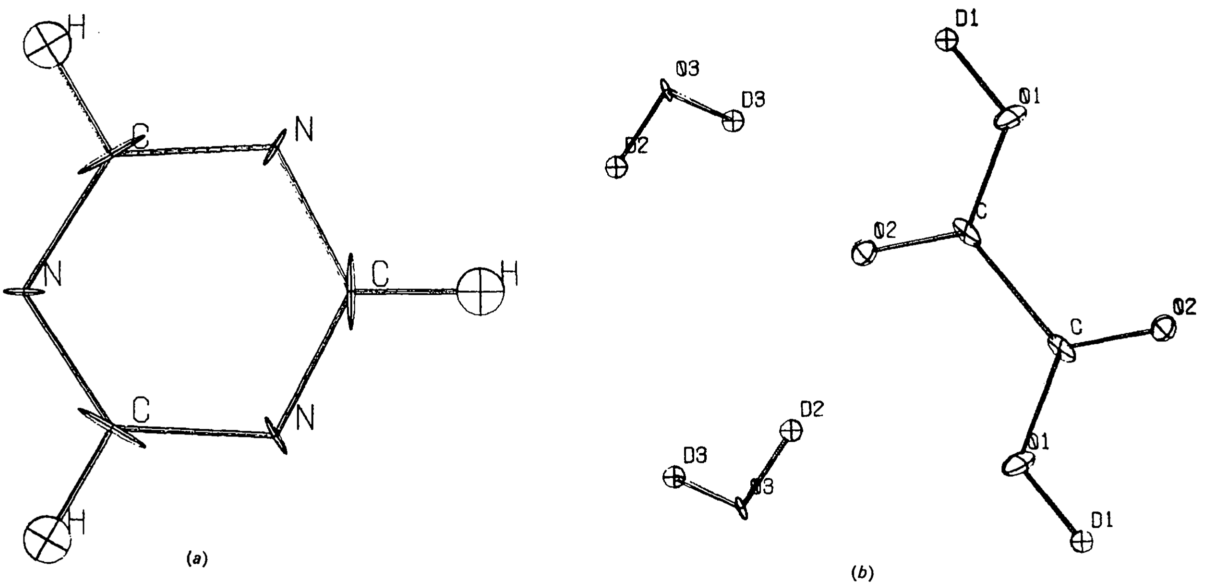

Fig. 1. *X–N* difference ellipsoids. The hydrogen atoms are indicated by circles. (*a*) *s*-Triazine viewed along the *c* axis, 70% probability ellipsoids. (*b*) α-Deuterooxalic acid dideuterate viewed along **b**, 80% probability ellipsoids.

dicular to the molecular plane and in the plane bisecting two bonds. The O(3) thermal parameters are obviously affected by the lone pair electrons, like the *s*-triazine nitrogen, while the carbon atom shows the effect of π density and the C–C bond, but not the C–O bonds. The atom O(1) is extended in a direction tangential to the lone pair and the C–O bond while the effect on O(2) which has two lone pairs and density in the C–O bond is fairly symmetric.

Conclusion

Comparison of X-ray and neutron data confirms that X-ray thermal parameters are affected by bonding. X-ray difference maps calculated with such parameters will show an unreasonably good agreement with the spherical atom model. Temperature parameters obtained with free-atom form factors are of limited usefulness in detailed studies of molecular motion. It seems doubtful that a sufficiently reliable correction formula can be derived. Therefore further improvements in the thermal motion treatment to include effects such as anharmonicity will only yield meaningful results if bonding is properly taken into account.

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Notes and News

Announcements and other items of crystallographic interest will be published under this heading at the discretion of the Editorial Board. The notes (in duplicate) should be sent to the General Secretary of the International Union of Crystallography (G. Boom, Laboratorium voor Fysische Metaalkunde der Rijksuniversiteit, Universiteitscomplex Paddepoel, Groningen, The Netherlands). Publication of an item in a particular issue cannot be guaranteed unless the draft is received 8 *weeks before the date of publication.*

International Union of Crystallography

Eighth General Assembly and International Congress of Crystallography. Buffalo, N.Y.; Stony Brook, N.Y.; Washington, D.C.; U.S.A. August 7–27, 1967

The attention of those persons interested in attending the Congress is directed to the announcement of the Congress in 'Notes and News', *Acta Cryst.* (1968), A**24**, 251 and B**24**, 159, and to a preliminary announcement already mailed to all known crystallographers. Those interested persons who have not responded to the preliminary announcement are requested to write immediately to

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