Table 4. *Crystallographic data for* $REZn_3$ *compounds**

YZn_3
$a = 6{\cdot}690 \pm 0{\cdot}005$, $b = 4{\cdot}405 \pm 0{\cdot}003$, $c = 10{\cdot}111 \pm 0{\cdot}009$ Å
Pnma

	Equipoint	x	y	z	B
Zn(1)	4(*c*)	$0{\cdot}2152 \pm 0{\cdot}0014$	0·25	$0{\cdot}0449 \pm 0{\cdot}0009$	$1{\cdot}22 \pm 0{\cdot}17$ Å^2
Zn(2)	4(*c*)	$0{\cdot}9162 \pm 0{\cdot}0014$	0·25	$0{\cdot}8549 \pm 0{\cdot}0009$	$1{\cdot}27 \pm 0{\cdot}17$
Zn(3)	4(*c*)	$0{\cdot}5362 \pm 0{\cdot}0013$	0·25	$0{\cdot}8956 \pm 0{\cdot}0009$	$1{\cdot}20 \pm 0{\cdot}16$
Y	4(*c*)	$0{\cdot}2773 \pm 0{\cdot}0009$	0·25	$0{\cdot}3387 \pm 0{\cdot}0006$	$0{\cdot}62 \pm 0{\cdot}10$

$DyZn_3$
$a = 6{\cdot}700$, $b = 4{\cdot}398$, $c = 10{\cdot}06$ Å
Pnma

	Equipoint	x	y	z	B
Zn(1)	4(*c*)	0·216	0·25	0·042	1·4 Å^2
Zn(2)	4(*c*)	0·961	0·25	0·853	1·1
Zn(3)	4(*c*)	0·535	0·25	0·897	0·9
Dy	4(*c*)	0·279	0·25	0·336	2·2

$CeZn_3$
$a = 4{\cdot}62 \pm 0{\cdot}01$, $b = 10{\cdot}43 \pm 0{\cdot}01$, $c = 6{\cdot}64 \pm 0{\cdot}01$ Å
*C*2*cm*, *Cmc*2, or *Cmcm*

* YZn_3: Sree Harsha & Ryba (1964)
$DyZn_3$: Sree Harsha (1964)
$CeZn_3$: Lott & Chiotti (1966)

Sree Harsha (1967) has investigated the structure of $CeZn_3$, but full details are not yet available. The lattice parameters are similar to those of the other $REZn_3$ compounds, and it is suspected that only slight atom shifts are necessary to change the symmetry.

We would like to acknowledge the assistance of Mrs Cheryl Ailes in the collection and processing of the intensity data.

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The crystal structure of tris-(2-dimethylaminoethyl)aminemanganese (II), -iron (II) and -zinc (II) bromides.

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The crystal structures of the isomorphous compounds $Mn(Me_6tren)Br_2$, $Fe(Me_6tren)Br_2$ and $Zn(Me_6tren)Br_2$ [$Me_6tren = N(CH_2CH_2N(CH_3)_2)_3$] have been investigated by three-dimensional X-ray analysis and refined to final R values of 0·067, 0·055 and 0·065 respectively. Crystals of the three complexes are cubic, space group $P2_13$, with $a = 12{\cdot}216 \pm 0{\cdot}007$, $12{\cdot}185 \pm 0{\cdot}004$ and $12{\cdot}105 \pm 0{\cdot}003$ Å for the manganese(II), iron(II) and zinc(II) compounds respectively; $Z = 4$. The three structures consist of $M(Me_6tren)Br^+$ and Br^- ions, arranged in a distorted NaCl type arrangement. The coordination polyhedron about the metal atoms is a trigonal bipyramid with C_3 crystallographic symmetry. The structure is essentially identical with that of the cobalt(II), nickel(II) and copper(II) analogues. The manganese(II) compound represents the first example of pentacoordination for this ion so far described by X-ray methods. The iron(II) complex is the first structure determined by X-rays, with trigonal bipyramidal arrangement about this ion.

A series of five-coordinated high spin complexes with general formula $M^{II}(Me_6tren)X_2$, where $M^{II} = Cr, Mn, Fe, Co, Ni, Cu, Zn$ and $Me_6tren = tris$-(2-dimethylaminoethyl)-amine, $N(CH_2CH_2N(CH_3)_2)_3$, and $X = Cl$, Br, I, NO_3 or ClO_4, has been prepared by Ciampolini & Nardi (1966*a*,*b*).

As a part of an X-ray structural investigation of the isomorphous series of the complex bromides, we have previously reported the structures of the cobalt(II) (Di Vaira

& Orioli, 1967), nickel(II) and copper(II) complexes (Di Vaira & Orioli, 1968). We report here the results of the X-ray analysis on the manganese(II), iron(II) and zinc(II) complexes.

Only a few significant details of the experimental procedure will be given, since the method used for the cobalt(II) complex was closely followed for all the isomorphous complexes. Crystals of the three compounds, kindly supplied by Dr Ciampolini, are tetrahedral in shape and belong to the space group $P2_13$. Data for the three compounds reported below refer to the manganese(II), iron(II) and zinc(II) complexes in that order. Cell dimensions and their standard deviations are: $a = 12{\cdot}216 \pm 0{\cdot}007$, $12{\cdot}185 \pm 0{\cdot}004$ and $12{\cdot}105 \pm 0{\cdot}003$ Å; $\mu = 118{\cdot}6$ (Cu $K\alpha$), 132·0 (Fe $K\alpha$) and

Table 1. *Positional parameters, temperature factors and their estimated standard deviations*

Anisotropic thermal factors are of the form: $\exp(-\sum_{i=1}^{3}\sum_{j=1}^{3} h_i h_j \beta_{ij})$.

Estimated standard deviations are given in parenthesis.

	Positional parameters × 10⁴			Thermal parameters × 10⁴					
	x/a	*y/b*	*z/c*	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
				$Mn(Me_6tren)Br_2$					
Mn	2260 (4)	2260 (4)	2260 (4)	28 (3)	28 (3)	28 (3)	3 (3)	3 (3)	3 (3)
Br(1)	1083 (3)	1083 (3)	1083 (3)	47 (2)	47 (2)	47 (2)	−6 (2)	−6 (2)	−6 (2)
Br(2)	8181 (3)	8181 (3)	8181 (3)	69 (3)	69 (3)	69 (3)	11 (3)	11 (3)	11 (3)
N(1)	3295 (24)	3295 (24)	3295 (24)	52 (24)	52 (24)	52 (24)	−1 (20)	−1 (20)	−1 (20)
N(2)	2730 (20)	1015 (21)	3553 (19)	34 (18)	35 (18)	43 (17)	3 (19)	−1 (16)	10 (16)
*C(1)	3648 (23)	2704 (28)	4294 (22)	42 (24)	62 (23)	5 (16)	15 (20)	−27 (15)	−3 (17)
C(2)	3785 (27)	1468 (25)	4032 (32)	46 (26)	33 (20)	77 (29)	−9 (20)	−17 (26)	−20 (22)
C(3)	2995 (30)	−86 (27)	3035 (31)	87 (35)	33 (23)	78 (32)	33 (22)	7 (27)	−9 (20)
C(4)	1816 (33)	910 (28)	4370 (29)	82 (31)	27 (25)	67 (26)	21 (24)	35 (25)	12 (21)
				$Fe(Me_6tren)Br_2$					
Fe	2278 (2)	2278 (2)	2278 (2)	53 (2)	53 (2)	53 (2)	2 (2)	2 (2)	2 (2)
Br(1)	1102 (2)	1102 (2)	1102 (2)	56 (1)	56 (1)	56 (1)	−10 (1)	−10 (1)	−10 (1)
Br(2)	8158 (2)	8158 (2)	8158 (2)	65 (1)	65 (1)	65 (1)	7 (1)	7 (1)	7 (1)
N(1)	3323 (11)	3323 (11)	3323 (11)	51 (10)	51 (10)	51 (10)	13 (9)	13 (9)	13 (9)
N(2)	2765 (12)	1064 (12)	3466 (11)	28 (11)	58 (11)	52 (10)	−8 (10)	−12 (10)	1 (9)
C(1)	3667 (14)	2655 (14)	4283 (13)	63 (12)	59 (13)	20 (13)	1 (11)	−28 (11)	−9 (11)
C(2)	3795 (14)	1487 (13)	4008 (14)	50 (12)	52 (12)	47 (12)	7 (11)	−24 (12)	24 (10)
C(3)	2982 (18)	−64 (18)	3038 (18)	93 (18)	39 (18)	90 (17)	14 (15)	−32 (16)	−14 (15)
C(4)	1902 (19)	914 (18)	4292 (17)	88 (17)	64 (17)	68 (17)	−18 (15)	21 (15)	42 (14)
				$Zn(Me_6tren)Br_2$					
Zn	2289 (19)	2289 (19)	2289 (19)	38 (1)	38 (1)	38 (1)	−1 (1)	−1 (1)	−1 (1)
Br(1)	1121 (2)	1121 (2)	1121 (2)	52 (1)	52 (1)	52 (1)	−10 (1)	−10 (1)	−10 (1)
Br(2)	8155 (2)	8155 (2)	8155 (2)	64 (2)	64 (2)	64 (2)	7 (1)	7 (1)	7 (1)
N(1)	3336 (16)	3336 (16)	3336 (16)	59 (15)	59 (15)	59 (15)	−17 (12)	−17 (12)	−17 (12)
N(2)	2752 (13)	1062 (14)	3443 (14)	44 (10)	39 (11)	51 (12)	5 (11)	−23 (10)	14 (11)
C(1)	3671 (18)	2677 (16)	4328 (13)	68 (17)	44 (12)	14 (8)	17 (13)	−15 (11)	−11 (10)
C(2)	3787 (16)	1469 (15)	3963 (16)	36 (13)	40 (11)	31 (11)	−10 (11)	−19 (12)	5 (11)
*C(3)	2958 (17)	−39 (18)	2960 (17)	49 (17)	9 (15)	99 (16)	23 (13)	−26 (13)	1 (12)
C(4)	1886 (23)	918 (19)	4335 (22)	79 (22)	55 (15)	79 (20)	−18 (15)	3 (18)	18 (15)

* The temperature factors of these atoms are nonpositive definite, probably owing to uncorrected absorption.

Table 2. *Distances and angles in the* $M^{II}(Me_6tren)Br^+$ *ion with their estimated standard deviations*

Primes refer to atoms related to the reference atom by the threefold axis.

	Distances (Å)				Angles (°)			
	M = Mn	M = Fe	M = Zn		M = Mn	M = Fe	M = Zn
M—Br(1)	2·491 (6)	2·482 (3)	2·449 (3)	N(1)–M—N(2)	80·7 (1·0)	81·3 (5)	82·6 (7)
M—N(1)	2·19 (3)	2·21 (1)	2·19 (2)	N(2)–M—Br(1)	99·3 (6)	98·7 (4)	97·4 (5)
M—N(2)	2·27 (2)	2·15 (1)	2·11 (2)	N(2)–M—N(2′)	117·4 (9)	117·8 (5)	118·4 (6)
N(1)–C(1)	1·48 (4)	1·48 (2)	1·50 (3)	M—N(1)–C(1)	111 (2)	107 (1)	108 (1)
C(1)–C(2)	1·55 (5)	1·47 (2)	1·53 (3)	C(1)–N(1)–C(1′)	108 (2)	111 (1)	111 (2)
C(2)–N(2)	1·52 (4)	1·51 (2)	1·49 (2)	N(1)–C(1)–C(2)	110 (2)	112 (1)	108 (1)
N(2)–C(3)	1·52 (4)	1·49 (3)	1·48 (3)	C(1)–C(2)–N(2)	110 (2)	110 (1)	111 (2)
N(2)–C(4)	1·50 (4)	1·47 (3)	1·51 (3)	C(2)–N(2)–C(3)	108 (2)	109 (1)	109 (1)
Br(1)-C(3)	3·63 (4)	3·58 (2)	3·44 (2)	C(2)–N(2)–C(4)	114 (2)	110 (1)	109 (2)
Br(1)-C(4)	4·12 (4)	4·01 (2)	4·01 (3)	C(3)–N(2)–C(4)	111 (2)	105 (1)	107 (2)
Br(1)-N(2)	3·63 (3)	3·52 (1)	3·44 (2)	M—N(2)–C(2)	104 (2)	107 (1)	106 (1)
N(2)–N(2′)	3·87 (3)	3·69 (2)	3·63 (2)	M—N(2)–C(3)	111 (2)	117 (1)	115 (1)
				M—N(2)–C(4)	109 (2)	110 (1)	112 (1)

Table 3. *Observed and calculated structure factors for* $Mn(Me_6tren)Br_2$

Columns are: K index, $10F_o$, $10|F_c|$. Reflexions considered affected by extinction are marked by an E. Unobserved reflexions have not been reported. The maximum value of F_c for the unobserved reflexions is 389.

Table 4. *Observed and calculated structure factors for* $Fe(Me_6tren)Br_2$

Columns are: K index, $10F_o$, $10|F_c|$. Reflexions considered affected by extinction are marked by an E. Unobserved reflexions have not been reported. The maximum value of F_c for the unobserved reflexions is 179.

77·7 cm^{-1} (Cu $K\alpha$). There are four formula units in the unit cell. The crystals selected for data collection had the shape of regular tetrahedra, with the edge varying from 0·25 to 0·30 mm. Since the crystals are sensitive to moisture, they were dipped in collodion, which formed a thin protective film. In the case of the manganese(II) and iron(II) compounds, which easily oxidize, three and four different crystals respectively were used. Because of an extremely fast decomposition due to the X-rays, the structure of the chromium(II) analogue could not be determined.

Reflexions were collected by means of integrated Weissenberg photographs and their intensities measured on a Nonius microdensitometer. 279, 385, and 334 independent reflexions, respectively, were measured for the three compounds and used for the refinement. The initial parameters for the atoms were taken from the last isotropic least-squares cycle of the refinement on the cobalt(II) complex. Scaling of the data was done by comparison with the F_c. Two isotropic least-squares cycles, followed by two anisotropic cycles, were performed in each case. The final R values for the three compounds are 0·067, 0·055 and 0·065 respectively. Reduction of the intensities, structure factor calculations and least-squares refinement were performed with an IBM 7090 computer at the CNUCE in Pisa, with programs written or adapted by Stewart (1964).

Table 5. *Observed and calculated structure factors for* $Zn(Me_6tren)Br_2$

Columns are: H index, $10F_o$, $10|F_c|$. Reflexions considered affected by extinction are marked by an E. Unobserved reflexions have not been reported. The maximum value of F_c for the unobserved reflexions is 386.

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.

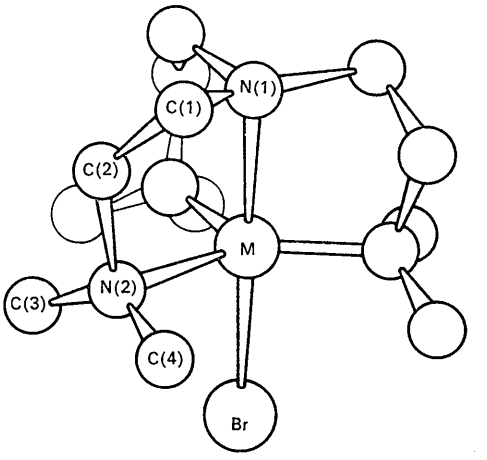

Fig. 1. A perspective drawing of the $M(Me_6tren)Br^+$ ion.

We wish to thank Dr Ciampolini for supplying crystals of the compounds. Thanks are expressed to Prof. L. Sacconi for his continuous interest. The financial support of the Italian Consiglio Nazionale delle Ricerche is gratefully acknowledged.

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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.