

Pyrazoles and Imidazoles as Ligands. XX.* The Crystal and Molecular Structure of Hexakis-(2-methylimidazole)cadmium(II) Tetrafluoroborate

BY J. REEDIJK§ AND G. C. VERSCHOOR

Department of Chemistry, Sections of Coordination Chemistry and X-ray and Electron Diffraction, State University, Leiden, P. O. Box. 75, The Netherlands

(Received 1 November 1972; accepted 5 December 1972)

The crystal and molecular structure of hexakis-(2-methylimidazole)cadmium(II) tetrafluoroborate, $\text{Cd}(\text{2MIz})_6(\text{BF}_4)_2$, has been determined by single-crystal X-ray diffraction techniques. The compound crystallizes in the trigonal system, space group $R\bar{3}m$, with $a=9.479$ (8) Å, $\alpha=87.71$ (5)° and $Z=1$. Data to $(\sin \theta)/\lambda=0.81$ Å⁻¹ (Mo $K\alpha$ radiation) were collected with a three-circle diffractometer, and the structure was solved and refined by the conventional heavy-atom technique and the least-squares method. The final least-squares cycle gave a conventional R index of 0.041 ($R_w=0.033$) based on 876 reflexions. The compound consists of discrete $\text{Cd}(\text{2MIz})_6^{2+}$ (symmetry D_{3d}) and BF_4^- (symmetry C_{3v}) ions, separated by normal van der Waals distances. The cadmium(II) ion is coordinated octahedrally to the six imine nitrogen atoms of the ligands, with $\text{Cd-N}=2.413$ (3) Å. The octahedron is slightly compressed in the direction of the trigonal axis.

Introduction

Previous investigations on the nature of the complex formation of 2-methylimidazole (2MIz) have shown that compounds having the formula $\text{M}(\text{2MIz})_n\text{X}_2$, with $\text{X}=\text{ClO}_4^-, \text{BF}_4^-$ and NO_3^- , are invariably formed for $\text{M}=\text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}$ and Zn (Goodgame, Goodgame & Rayner Canham, 1969; Reedijk, 1972). This stoichiometry differs from that of complexes with the ligands imidazole and *N*-methylimidazole, for which compounds of type $\text{M}(\text{L})_6\text{X}_2$, with octahedral cations, are found (Goodgame *et al.*, 1969; Reedijk, 1969*a, b*).

The origin of the different stoichiometry for compounds with 2MIz ligands has been tentatively attributed to the steric hindrance of the methyl group next to the donor site of the ligand.

With $\text{Cd}(\text{BF}_4)_2$ and $\text{Cd}(\text{ClO}_4)_2$, however, we observed (Reedijk, 1972) that apart from compounds of type $\text{Cd}(\text{2MIz})_4\text{X}_2$, compounds having the formula $\text{Cd}(\text{2MIz})_6\text{X}_2$ could also be isolated.

Notwithstanding the steric requirements of the ligand, which did not seem to allow an octahedral arrangement of 2MIz ligands around a Cd(II) ion, ligand-field and e.p.r. spectra of the Mn, Ni and Cu(II) doped compounds showed a rather regular octahedral environment for the metal ions in this lattice (Reedijk, 1972).

In order to determine the exact coordination and geometry of the ligands around the cadmium ion, we decided to carry out an X-ray structural analysis of $\text{Cd}(\text{2MIz})_6(\text{BF}_4)_2$.

Experimental

Crystals of $\text{Cd}(\text{2MIz})_6(\text{BF}_4)_2$ were grown, as described previously (Reedijk, 1972), as colourless rhombohedrons {100} from alcoholic solutions of $\text{Cd}(\text{H}_2\text{O})_6(\text{BF}_4)_2$ and an excess of 2MIz.

Crystal symmetry and approximate cell parameters were determined from zero and upper level Weissenberg photographs. The condition $I(hkl)=I(khl)$ limited the possible space groups to $R32$, $R3m$ and $R\bar{3}m$; the choice of space group $R\bar{3}m$ was confirmed by subsequent refinement. The precise unit-cell parameters were determined on a single-crystal diffractometer at 20°C. Some relevant data are listed in Table 1.

Table 1. Crystal data for $\text{Cd}(\text{2MIz})_6(\text{BF}_4)_2$

$\text{CdB}_2\text{F}_4\text{N}_{12}\text{C}_{24}\text{H}_{36}$	M.W. 779
Space group	$R\bar{3}m$
Lattice constant	$a=9.479$ (8) Å
Rhombohedral angle	$\alpha=87.71$ (5)°
Cell volume	$V=849$ Å ³
Radiation	Mo $K\alpha=0.71069$ Å
Calculated density for $Z=1$	1.51 g cm ⁻³
Observed density (floatation)	1.50 (2) g cm ⁻³
Linear absorption coefficient	$\mu=7.27$ cm ⁻¹
Number of measured reflexions	4400
Number of independent reflexions	1044
Number of observed independent reflexions	876

A crystal with dimensions 0.5×0.5×0.5 mm was mounted on an Enraf-Nonius three-circle single-crystal diffractometer, with the plane (100) perpendicular to the φ axis. Intensities were recorded by the θ - 2θ scan method for all reflexions between 3 and 35°. Mo $K\alpha$ radiation, monochromated by graphite, was

* Part XIX. Reedijk (1973). Submitted to *Rev. Trav. Chim.*

§ Present address: Department of Chemistry, Technological University, Julianalaan 136, Delft, The Netherlands.

Table 3. Positional parameters of the non-hydrogen atoms ($\times 10^4$)

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Cd	0	0	0
B	3825 (3)*	3825 (3)	3825 (3)
F(1)	3036 (3)	3036 (3)	3036 (3)
F(2)	4640 (1)	4640 (1)	2940 (2)
N(3)	1659 (2)	1659 (2)	8990 (2)
N(1)	2947 (2)	2947 (2)	7543 (2)
C(2)	1958 (2)	1958 (2)	7619 (2)
C(4)	2472 (3)	2472 (3)	9712 (4)
C(5)	3292 (3)	3293 (3)	8846 (5)
C(6)	1381 (4)	1381 (4)	6391 (4)

* Estimated standard deviations (e.s.d.) in the least significant digits are in parentheses throughout.

Table 4. Positional parameters ($\times 10^3$) and isotropic temperature factors ($\text{\AA}^2 \times 10^2$) for the hydrogen atoms

The first figure of the atomic numbering (in parentheses) corresponds to the atom to which the hydrogen is attached.

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	U_{iso}
H(1)	333 (4)	333 (4)	713 (5)	11 (2)
H(4)	267 (3)	267 (3)	87 (5)	11 (2)
H(5)	392 (4)	392 (4)	903 (5)	10 (2)
H(61)*	56 (4)	56 (4)	649 (6)	5 (2)
H(62)*	77 (8)‡	222 (8)	579 (8)	17 (3)
H(63)†	154 (10)	154 (10)	567 (15)	8 (4)
H(64)†	135 (15)‡	26 (14)	614 (12)	15 (5)

* Hydrogens belonging to the first set of CH_3 groups.

† Hydrogens belonging to the second CH_3 group.

‡ H(61) and H(63) are in special positions; H(62) and H(64) are in general positions.

Table 5. Anisotropic temperature factors of the non-hydrogen atoms ($\text{\AA}^2 \times 10^4$)

The general anisotropic temperature factor has the form: $\exp[-2\pi^2(\sum_i U_{ii}h_i^2 + \sum_j U_{jj}k_j^2 + \sum_k U_{kk}l_k^2 + \sum_{ij} U_{ij}h_i h_j a_i^* a_j^*)]$.

	$U_{11} = U_{22}^*$	U_{33}	$2U_{12}$	$2U_{23} = 2U_{31}^*$
Cd	361 (2)	361 (2)	29 (3)	29 (3)
B	316 (11)	316 (11)	-84 (36)	-84 (36)
F(1)	119 (17)	119 (17)	-678 (51)	-678 (51)
F(2)	761 (9)	941 (15)	106 (23)	66 (21)
N(3)	515 (9)	412 (13)	-93 (26)	136 (21)
N(1)	833 (16)	547 (20)	540 (40)	343 (33)
C(2)	613 (13)	440 (17)	-21 (37)	209 (30)
C(4)	681 (14)	474 (18)	-517 (40)	20 (30)
C(5)	891 (20)	638 (27)	-941 (53)	143 (41)
C(6)	1089 (28)	425 (22)	-500 (77)	148 (43)

* Because of the special positions of all the non-hydrogen atoms, $U_{11} = U_{22}$ and $U_{23} = U_{31}$; in addition, for Cd, B and F(1) on the trigonal axis: $U_{22} = U_{33}$ and $U_{12} = U_{23}$.

Table 6. Intramolecular distances in $\text{Cd}(\text{2Miz})_6(\text{BF}_4)_2$ and their estimated standard deviations (\AA)

Atoms marked with a prime are related to the unprimed atoms by a rotation about the threefold axis. A double prime denotes a rotation about a twofold axis.

E.s.d.'s include errors in the cell parameters.			
Cd—N(3)	2.413 (3)	N(1)—C(2)	1.350 (5)
B—F(1)	1.347 (7)	C(2)—N(3)	1.341 (3)
B—F(2)	1.358 (3)	N(3)—C(4)	1.337 (5)
N(1)—H(1)	0.7 (1)	C(4)—C(5)	1.352 (5)
C(4)—H(4)	1.1 (1)	C(5)—N(1)	1.347 (7)
C(5)—H(5)	0.9 (1)	C(2)—C(6)	1.444 (6)
C(6)—H(6) _{av}	1.0 (1)*	N(3)···N(3')	3.507 (5)
		N(3)···N(3'')	3.315 (6)
		N(3)···C(6'')	3.385 (5)
		N(3)···C(2'')	3.612 (5)
		C(2)···C(6'')	3.584 (6)
		F(1)···F(2)	2.190 (5)
		F(2)···F(2')	2.234 (3)

* The averaged C—H distance for both methyl conformations.

less than one-fifth of the estimated standard deviations, (e.s.d.) and the refinement was terminated. A final difference Fourier synthesis was structureless, with the highest peaks less than 0.3 e \AA^{-3} . Structural parameters are listed in Tables 2–5.

Description of the structure

Intramolecular distances and their e.s.d.'s are listed in Table 6, while bond angles with e.s.d.'s are given in Table 7. The stereochemistry of one unit $\text{Cd}(\text{2Miz})_6(\text{BF}_4)_2$ is depicted in Fig. 1, together with the labelling system of the ring atoms. All ring atoms are numbered according to the organic chemical nomenclature.

Table 7. Bond angles and their e.s.d.'s in $\text{Cd}(\text{2Miz})_6(\text{BF}_4)_2$

The primed and double primed atoms are explained in Table 6. The e.s.d.'s include errors in the cell parameters.

N(3)—Cd—N(3')	93.2 (1)°	N(1)—C(2)—N(3)	107.6 (3)°
N(3)—Cd—N(3'')	86.8 (1)	C(2)—N(3)—C(4)	106.2 (3)
N(3)—Cd—B*	57.05 (8)	N(3)—C(4)—C(5)	112.0 (4)
Cd—N(3)—C(2)	127.9 (2)	C(4)—C(5)—N(1)	103.6 (5)
Cd—N(3)—C(4)	125.9 (3)	C(5)—N(1)—C(2)	110.6 (3)
F(1)—B—F(2)	108.2 (3)	N(1)—C(2)—C(6)	123.3 (3)
F(2)—B—F(2')	110.8 (3)*	N(3)—C(2)—C(6)	129.1 (3)

* The angle with the rhombohedral body diagonal; for octahedral geometry it is expected to be 54.75° .

The tables and figures show that the symmetry of the cation $\text{Cd}(\text{2Miz})_6^{2+}$ is D_{3d} , implying that all ring atoms of one molecule of 2Miz (with the exception of two of the methyl hydrogens) are in one plane with the cadmium ion. Moreover, two rings are related by the inversion centre. The three planes containing the ring are related by the threefold axis.

The high symmetry of the cation is surprising in view of the asymmetry of the ligand 2Miz. This may be accounted for by the position of the methyl group in the imidazole ring, which prevents the rings from being tilted from the mirror planes. As mentioned above, the octahedral coordination of the cation with this ligand is unexpected for steric reasons. The large cationic radius of Cd^{2+} , however, seems to allow an octahedral ion $\text{Cd}(\text{2Miz})_6^{2+}$ with the present geometry. On the other hand, the Cd—N distance of 2.413 \AA is quite long compared with 2.361 \AA in Cd(imidazole)₆.

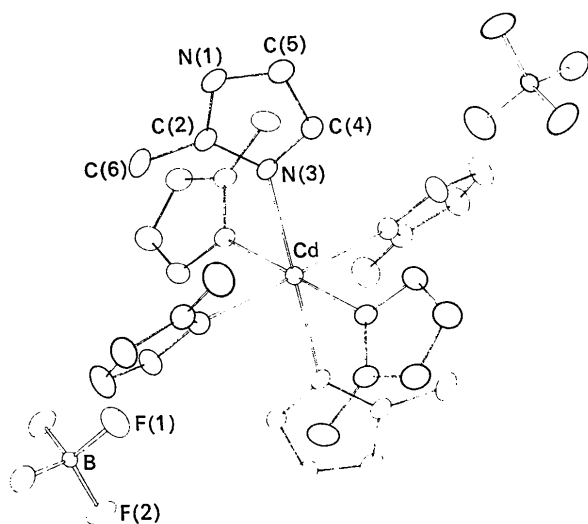


Fig. 1. Perspective view of $\text{Cd}(\text{2MIz})_6(\text{BF}_4)_2$; hydrogen atoms have been omitted for clarity. Non-hydrogen atoms are drawn on a 30% probability level. The trigonal axis runs through the atoms $\text{B}-\text{F}(1)-\text{Cd}$ and through the $\text{B}-\text{F}$ bond of the opposing BF_4^- ion.

$(\text{NO}_3)_2$ (Mighell & Santoro, 1971) and to 2.30–2.35 Å in $\text{Cd}(\text{pyridine})_3(\text{NO}_3)_2$ (Cameron, Taylor & Nuttall,

1972), which might originate from the steric hindrance mentioned.

The distortion of the octahedral coordination of $\text{Cd}(\text{II})$ can best be described by a compression along the threefold axis, making the angles between this axis and the $\text{Cd}-\text{N}$ bonds 57.05° instead of the octahedral value of 54.75° .

Imidazole rings

Table 8 presents a comparison of the ring bond lengths and bond angles with some literature compounds. Comparisons with some older work are given by Antti & Lundberg (1971) and by Mighell & Santoro (1971). The Table shows that there is reasonable agreement with literature values for the bond distances. That all the ring distances are almost equal indicates the aromatic character of the ligand. The bond angles in the present compound show some minor deviations compared with unsubstituted imidazole. The small value of the angle around $\text{N}(3)$, the coordinating atom, may be due to the size of the ligand, since in this way the CH_3 group is held away from the other ligands and from the metal ion. Unfortunately Akhtar, Huy & Skapski (1972) did not list the bond angles of 2MIz in $\text{Co}(\text{2MIz})_4(\text{NO}_3)_2$.

The thermal vibrational ellipsoids of the ring atoms have their largest movement in a direction perpendicular

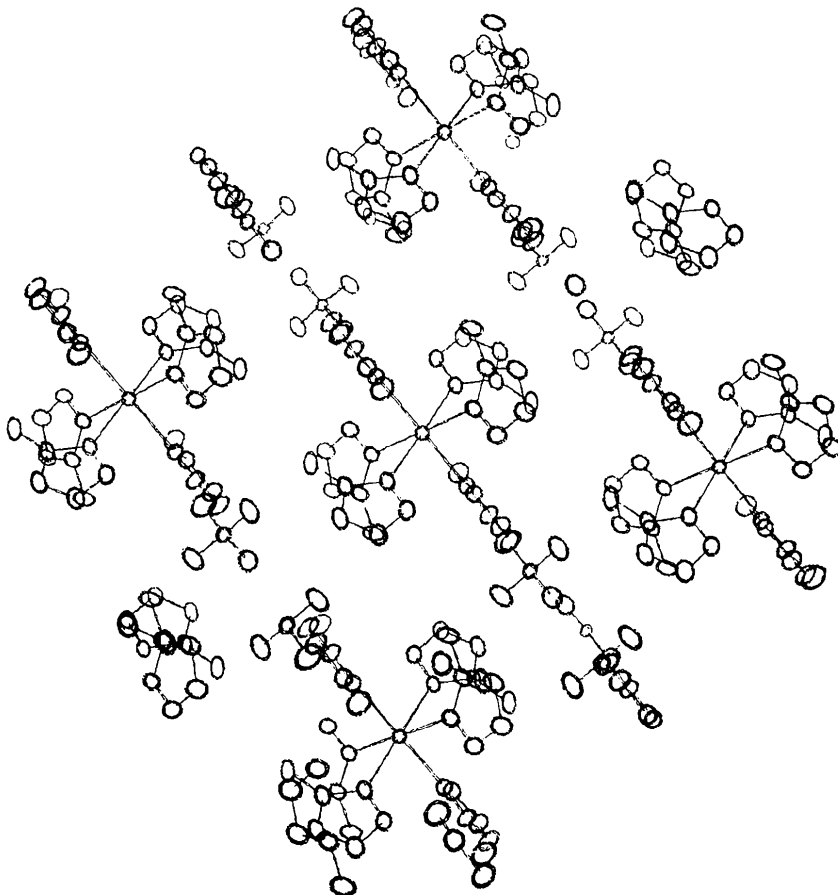


Fig. 2. Perspective view of the packing in $\text{Cd}(\text{2MIz})_6(\text{BF}_4)_2$ as seen along the crystallographic c axis.

Table 8. Comparison of mean bond lengths (Å) and angles (°) in some imidazole and 2-methylimidazole complexes

	Iz*	Cd(Iz) ₆ (NO ₃) ₂ †	Ag(Iz) ₂ NO ₃ ‡	Co(2MIz) ₄ (NO ₃) ₂ §	Cd(2MIz) ₆ (BF ₄) ₂
M—N(3)	—	2.361	2.126	1.96–2.25	2.413
N(1)—C(2)	1.349	1.325	1.335	1.32	1.350
C(2)—N(3)	1.326	1.316	1.322	1.34	1.341
N(3)—C(4)	1.378	1.316	1.363	1.33	1.337
C(4)—C(5)	1.358	1.366	1.363	1.35	1.352
C(5)—N(1)	1.369	1.340	1.404	1.36	1.347
C(2)—C(6)	—	—	—	1.49	1.444
N(3)—Cd—(111)	—	56.3	—	—	57.05
N(1)—C(2)—N(3)	111.3	110.6	110.9	—	107.6
C(2)—N(3)—C(4)	105.4	106.1	107.1	—	106.2
N(3)—C(4)—C(5)	109.8	108.9	109.4	—	112.0
C(4)—C(5)—N(1)	106.3	106.6	105.5	—	103.6
C(5)—N(1)—C(2)	107.2	107.7	107.1	—	110.6

* Martinez-Carrera (1966).

† Mighell & Santoro (1971).

‡ Antti & Lundberg (1971).

§ Akhtar, Huq & Skapski (1972).

ular to the ring plane, especially for those atoms further removed from the Cd(II) ion.

The packing of the cations and the anions

Each Cd(2MIz)₆²⁺ cation is surrounded by two BF₄⁻ anions on the trigonal axes (closest Cd—F distance = 5.180 Å) and six BF₄⁻ anions in the neighbouring cells (closest Cd—F distance = 7.141 Å).

The BF₄⁻ anions are nearly tetrahedral, as can be seen from the bond distances (Table 5) and bond angles (Table 6). Although strictly speaking the symmetry of the anion is C_{3v}, indications for such a distortion were not found in the infrared spectra of the BF₄⁻ ions (Reedijk, 1972). In fact the distortion is too small to be observed in vibrational spectra; it may be caused by weak hydrogen bonding with the N—H group of the imidazole ring. The closest N—F(2) distance of 3.130 Å may be an indication of this effect.

All other contacts between fluorine, nitrogen and carbon atoms are normal van der Waals contacts. In Table 9 the closest non-bonding neighbours of each of the boundary atoms are listed. An illustration of the packing of the cations and the anions is given in Fig. 2.

Table 9. Non-bonding contacts in Cd(2MIz)₆(BF₄)₂

F(1)···C(4)	3.286 Å	F(1)···H(4)	2.1 Å
F(1)···C(6)	3.801	F(2)···C(6)	3.776
F(2)···N(1)	3.130	F(2)···H(1)	2.6
F(2)···C(5)	3.213	F(2)···H(5)	2.7
F(2)···F(2)	3.415	C(6)···C(5)	3.596
C(4)···N(3)	3.809		

All crystallographic calculations were carried out using the Leyden University IBM 360/65 computer, with the aid of a set of computer programs written or modified by Mrs E. W. Rutten-Keulemans and Mr R. A. G. de Graaff.

The authors are indebted to Mr H. J. Gijzemijter for experimental assistance, to Dr C. Romers for many stimulating discussions and to Dr W. L. Groeneveld for his interest in this investigation.

References

- AKHTAR, F., HUQ, F. & SKAPSKI, A. C. (1972). *J. Chem. Soc. Dalton*, pp. 1353–1356.
- ANTTI, C. J. & LUNDBERG, B. K. S. (1971). *Acta Chem. Scand.* **23**, 1758–1766.
- CAMERON, A. F., TAYLOR, D. W. & NUTTALL, R. H. (1972). *J. Chem. Soc. Dalton*, pp. 1603–1608.
- CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.
- GOODGAME, D. M. L., GOODGAME, M. & RAYNER CANHAM, G. W. (1969). *Inorg. Chim. Acta*, **3**, 399; 406–410.
- GRAAFF, R. A. G. DE (1973). Forthcoming thesis.
- IBERS, J. A. (1962). *International Tables for X-ray Crystallography*, Vol. III, pp. 210–212. Birmingham: Kynoch Press.
- MARTINEZ-CARRERA, S. (1966). *Acta Cryst.* **20**, 783–789.
- MIGHELL, A. D. & SANTORO, A. (1971). *Acta Cryst.* **B27**, 2089–2097.
- REEDIJK, J. (1969a). *Rec. Trav. Chim.* **88**, 1451–1470.
- REEDIJK, J. (1969b). *Inorg. Chim. Acta*, **3**, 517–522.
- REEDIJK, J. (1972). *Rec. Trav. Chim.* **91**, 507–516.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.