Table 4 (*cont.*)

(III) $R = \mathrm{Bu}^t$	x	y	z	U_{eq}† ($\text{Å}^2 \times 10^2$)
Co(1)	0·24494 (3)	0·04942 (3)	0·23987 (2)	1·634 (9)
Co(2)	0·09764 (3)	0·24190 (3)	0·16352 (2)	1·582 (9)
C(1)	0·0646 (3)	−0·1114 (3)	0·27963 (15)	2·32 (8)
O(1)	−0·0480 (3)	−0·2115 (2)	0·30599 (13)	3·87 (7)
C(2)	0·2932 (3)	−0·0347 (3)	0·1267 (2)	2·52 (8)
O(2)	0·3197 (3)	−0·0889 (3)	0·05592 (13)	4·00 (7)
C(3)	0·4052 (3)	0·0026 (3)	0·3216 (2)	2·64 (9)
O(3)	0·5053 (3)	−0·0303 (3)	0·37374 (14)	4·64 (8)
C(4)	−0·1177 (3)	0·1149 (3)	0·1809 (2)	2·29 (8)
O(4)	−0·2508 (2)	0·0352 (2)	0·19206 (12)	3·41 (7)
C(5)	0·1257 (3)	0·2116 (3)	0·0343 (2)	2·10 (8)
O(5)	0·1430 (2)	0·1921 (2)	−0·04617 (11)	3·23 (6)
C(6)	0·0629 (3)	0·4419 (3)	0·1516 (2)	2·52 (9)
O(6)	0·0388 (3)	0·5682 (3)	0·14203 (14)	4·17 (7)
C(10)	0·3296 (3)	0·2950 (3)	0·22794 (14)	1·64 (7)
C(11)	0·4978 (3)	0·4126 (3)	0·2032 (2)	2·30 (8)
C(12)	0·4803 (4)	0·5886 (3)	0·1876 (2)	3·46 (10)
C(13)	0·5566 (3)	0·3591 (3)	0·1090 (2)	2·77 (8)
C(14)	0·6286 (3)	0·4132 (4)	0·2889 (2)	3·25 (9)
C(20)	0·2172 (3)	0·2552 (3)	0·29683 (15)	1·70 (7)
C(21)	0·1775 (3)	0·2983 (3)	0·39810 (15)	2·25 (8)
C(22)	0·2142 (4)	0·4869 (3)	0·4065 (2)	3·61 (10)
C(23)	0·2912 (3)	0·2396 (4)	0·4770 (2)	3·09 (9)
C(24)	−0·0068 (3)	0·2150 (4)	0·4170 (2)	3·18 (9)

† All atoms anisotropically refined.

atoms, assumed to be sp^2, sp^2 and sp^3 hybridized respectively for (I), (II) and (III). Both increase as expected in the order $R = -\mathrm{CO_2Me}, -\mathrm{Ph}, -\mathrm{Bu}^t$, with values of 139, 140, 144° and 1·42 (3), 1·46 (1) and 1·515 (3) Å, respectively. The equivalent values for $R = \mathrm{CF_3}$ are 139° and 1·48 Å. For (I) and (II) the degree of delocalization suggested by the short R—C(≡C) is echoed by the approximate coplanarity of each C—R group [maximum deviation 0·02 (I), 0·01 (II) Å for R-group atoms and 0·1 (I), 0·6 (II) Å for C atoms] although each group is twisted relative to the mean plane of its acetylene [dihedral angles 47, 61 (I) and 52, 19° (II)]. These somewhat random orientations are assumed to derive from steric factors, since with such arrangements there are no short intramolecular contacts. In (III) any close methyl H···H contacts are minimized by a semi-staggered conformation of the Bu^t groups, with respect to the C—C vector.

The Co—Co separations are also sensitive to R and in good agreement with previously recorded Co—Co single-bond distances (Leung, Coppens, McMullan & Koetzle, 1981; Teller, Wilson, McMullan, Koetzle & Bau, 1978; Cirjak, Ginsberg & Dahl, 1982). The bend of the '$\mathrm{Co_2(CO)_2}$' spine (Fig. 3) is more acute for (I) and (II), 148°, than for (III), 152°.

All three structures show a shorter 'axial' (*trans* to Co—Co bond) M—C(O) bond length than those of the '*cis*' equatorial ligands (Table 2), the latter adopting an eclipsed configuration.

We are grateful to Professors P. Coppens, and F. Baert for collaboration and access to unpublished results; to Drs S. A. R. Knox and G. H. Riding for sample preparation and to the ILL for support (DG).

References

Anderson, A. B. (1976). *Inorg. Chem.* **15**, 2598–2602.

Baert, F. & Coppens, P. (1982). Private communication.

Cirjak, L. M., Ginsberg, R. E. & Dahl, L. F. (1982). *Inorg. Chem.* **21**, 940–957.

Cotton, F. A., Jamerson, J. D. & Stults, R. (1976). *J. Am. Chem. Soc.* **98**, 1774–1779.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Leung, P., Coppens, P., McMullan, R. K. & Koetzle, T. F. (1981). *Acta Cryst.* B**37**, 1347–1352.

Sheldrick, G. M. (1981). *SHELXTL. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data.* Univ. of Göttingen, Federal Republic of Germany.

Sly, W. G. (1959). *J. Am. Chem. Soc.* **81**, 18–20.

Teller, R. G., Wilson, R. D., McMullan, R. K., Koetzle, T. F. & Bau, R. (1978). *J. Am. Chem. Soc.* **100**, 3071–3077.

Thorn, D. & Hoffmann, R. (1978). *Inorg. Chem.* **17**, 126–140.

Acta Cryst. (1983). C**39**, 1027–1031

Hexakis(imidazole)manganese(II) Dichloride Tetrahydrate, $[\mathrm{Mn(C_3H_4N_2)_6}]\mathrm{Cl_2.4H_2O}$, and Hexakis(imidazole)zinc(II) Dichloride Tetrahydrate, $[\mathrm{Zn(C_3H_4N_2)_6}]\mathrm{Cl_2.4H_2O}$

By Thomas P. J. Garrett, J. Mitchell Guss and Hans C. Freeman*

Department of Inorganic Chemistry, University of Sydney, Sydney 2006, *Australia*

(*Received* 26 *January* 1983; *accepted* 3 *May* 1983)

Abstract. $[\mathrm{Mn(ImH)_6}]\mathrm{Cl_2.4H_2O}$ (ImH = imidazole, $\mathrm{C_3H_4N_2}$): $M_r = 606{\cdot}4$, triclinic, $P\bar{1}$, $a = 10{\cdot}726$ (3), $b = 9{\cdot}275$ (2), $c = 8{\cdot}846$ (2) Å, $\alpha = 119{\cdot}65$ (1), $\beta = 96{\cdot}87$ (2), $\gamma = 97{\cdot}62$ (2)°, $V = 740{\cdot}3$ (4) Å^3, $Z = 1$, $D_m = 1{\cdot}37$ (1), $D_x = 1{\cdot}360$ g $\mathrm{cm^{-3}}$, $\lambda(\mathrm{Mo}\ K\alpha) = 0{\cdot}71069$ Å, $\mu(\mathrm{Mo}\ K\alpha) = 6{\cdot}53\ \mathrm{cm^{-1}}$, $F(000) = 315$, $T = 291$ K, $R = 0{\cdot}030$ for 3542 unique reflections. $[\mathrm{Zn(ImH)_6}]\mathrm{Cl_2.4H_2O}$: $M_r = 616{\cdot}8$, triclinic, $P\bar{1}$, $a =$

---

* Author to whom correspondence should be addressed.

0108-2701/83/081027-05$01.50

10·635 (6), $b = 9{\cdot}231$ (4), $c = 8{\cdot}835$ (4) Å, $\alpha = 119{\cdot}53$ (2), $\beta = 96{\cdot}85$ (4), $\gamma = 97{\cdot}87$ (4)°, $V = 729{\cdot}8$ (7) Å^3, $Z = 1$, $D_m = 1{\cdot}45$ (2), $D_x = 1{\cdot}409$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ(Mo $K\alpha$) = 11·00 cm^{-1}, $F(000) = 320$, $T = 291$ K, $R = 0{\cdot}029$ for 3504 unique reflections. The two crystal structures are isomorphous. The metal atom in each complex is octahedrally coordinated by six planar imidazole rings. The complex ions form hexagonally packed layers which are separated by layers of water molecules and chloride ions.

Introduction. The imidazole groups of histidine side chains participate in the binding of metal atoms in many metalloproteins and metal–protein complexes. Among the first-row transition metals which are found in metalloproteins, zinc is well known but manganese is a relative newcomer (McEuen, 1981). The crystal structures of the title complexes have been determined to provide additional precise values for zinc(II)–imidazole bond lengths and to relieve the general paucity of model compounds for manganese(II)–protein interactions. In addition, the present work completes the series of metal–N(imidazole) bond lengths in octahedral complexes of the transition-metal ions between Mn$^{\text{II}}$ and Zn$^{\text{II}}$.

Experimental. Procedure of Sandmark & Brändèn (1967): aqueous solution of imidazole (adjusted to pH 6·9 with 10 mol dm^{-3} HCl) added to aqueous solutions of $MnCl_2$ and $ZnCl_2$ in molecular ratios of 20:1 and 10:1, respectively; crystals by slow evaporation. Densities by flotation in toluene/bromobenzene, specimens coated with clear lacquer to inhibit decomposition. Table 1 gives details of data collection (Enraf–Nonius CAD-4/F diffractometer, graphite monochromator). Unit-cell dimensions by least-squares refinement of 2θ values. Profile analysis of a representative reflection from each compound indicated that $\omega/2\theta$ scan would optimize measurement of integrated intensities. Scan speeds determined by required precision $\sigma_{\text{stat}}(I) < 0{\cdot}015I$, subject to a maximum scan time. Extreme one-sixths of scans yielded backgrounds, orientation checked after every 100 reflections. Lorentz, polarization, decomposition and absorption corrections (Busing & Levy, 1957; Coppens, Leiserowitz & Rabinovich, 1956). Error analysis (Freeman & Guss, 1972) showed that systematic variance V_s was in each case dependent only on $|F|$, value of $\sigma^2(F)$ for each reflection recalculated as sum of statistical variance and V_s, where $V_s = a + b|F| + c|F|^2$.

Table 1. *Crystal data and data collection parameters*

	Mn salt	Zn salt
Crystal faces	{100} {01$\underline{0}$} {011}	{1$\underline{0}$0} {11$\underline{0}$} {01$\underline{1}$} {10$\bar{1}$}
Separations between crystal faces in above order (mm)	0·125 0·170 0·175	0·138 0·300 0·350 0·425
Number of reflections used to calculate lattice parameters	19	15
Range of 2θ (°)	41–44	41–44
Max. $(\sin\theta)/\lambda$ (Å^{-1})	0·66	0·66
Min.h, max.h	−14,14	−14,14
Min.k, max.k	−12,12	−12,12
Min.l, max.l	−11,11	−11,11
Number of reflections measured	7490	7008
Number of unique reflections	3542	3504
R_{merge}†	0·012	0·012
Number of unobserved I [$I < 3\sigma_{\text{stat}}(I)$]	751	565
Scan parameters		
Ratio of angles (ω:2θ)	6:4	6:5
Maximum time (s)	60	45
Intensity standards		
Exposure time between measurement(s)	7000	6000
Decrease in $\bar{I}$ (%)	7 (1)	18 (1)
Absorption corrections		
Grid	4×4×4	4×10×10
Min. absorption (A^*)	1·075	1·147
Max. absorption (A^*)	1·134	1·374
Systematic variance, V_s		
a in $V_s = a + b\|F\| + c\|F\|^2$	$3{\cdot}25\times10^{-1}$	1·33
b in $V_s = a + b\|F\| + c\|F\|^2$	$-5{\cdot}9\times10^{-3}$	$-2{\cdot}5\times10^{-2}$
c in $V_s = a + b\|F\| + c\|F\|^2$	$5{\cdot}7\times10^{-5}$	$1{\cdot}6\times10^{-4}$
Refinement criteria		
Final R	0·030	0·029
Final R_w	0·030	0·030
Final S	1·833	1·915
Max. shift/error in last cycle	8×10^{-5}	2×10^{-4}
Av. shift/error in last cycle	3×10^{-6}	9×10^{-6}
Max. e Å^{-3} in final ΔF map	0·2	0·3
Min. e Å^{-3} in final ΔF map	−0·2	−0·5

† $R_{\text{merge}} = \{\sum_{hkl}\sum_i k_i^{-2}[|\bar{F}(hkl)| - k_i|F_i(hkl)|]^2/\sum_{hkl}\sum_i|F_i(hkl)|^2\}^{1/2}$. k_i is the relative scale factor for the ith value, F_i.

Atomic positions of non-hydrogen atoms for $[Mn(ImH)_6]Cl_2.4H_2O$ determined by Patterson and Fourier methods, full-matrix least-squares refinement, isotropic, $R = 0{\cdot}088$, $R_w = 0{\cdot}089$, $w = 1/\sigma^2(F)$, only observed reflections used, atomic scattering factors for Mn^{2+}, Zn^{2+}, Cl^-, O, N and C from Cromer & Mann (1968), for H from Stewart, Davidson & Simpson (1965), anomalous-dispersion corrections for Mn, Zn and Cl applied (*International Tables for X-ray Crystallography*, 1974), program for structure analysis and refinement: XRAY76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). After two cycles of anisotropic refinement, difference Fourier map showed imidazole H atoms, which were included in the refinement with thermal parameters 1·25 times $\langle U_{ii}\rangle$ for the attached C or N atoms. Difference Fourier map calculated after two more cycles of refinement and positions of the remaining H atoms deduced from it. Each of the two independent water molecules had one H atom in a site with occupancy 1·0 and the other hydrogen distributed over two sites each with occupancy 0·5. Positions of the latter were kept fixed at 0·8 Å from the O(water) atom in the directions of neighbouring O(water) atoms. Thermal parameters were assigned to H atoms as before. Thermal parameters for O(2) indicated that it was disordered ($U_{11} = 0{\cdot}146$, $U_{22} = 0{\cdot}067$, $U_{33} = 0{\cdot}070$ Å^2). Attempts to resolve alternate positions unsuccessful. H(200), in the fully occupied position near O(2), fixed 0·8 Å from O(2) along the line to a chloride ion; the positional parameters, which were not refined, were recalculated after every third cycle.

Refinement of $[Zn(ImH)_6]Cl_2.4H_2O$ commenced with coordinates taken from refinement of $[Mn(ImH)_6]Cl_2.4H_2O$ when all thermal parameters isotropic. Two cycles of full-matrix least-squares refinement, isotropic, $R = 0{\cdot}078$, $R_w = 0{\cdot}084$. After two further cycles of anisotropic refinement, difference Fourier map showed all hydrogen atoms, parameters for hydrogen atoms assigned as above. In further refinement O(2) again appeared disordered ($U_{11} = 0{\cdot}100$, $U_{22} = 0{\cdot}065$, $U_{33} = 0{\cdot}068$ Å^2); treatment of disorder and assignment of hydrogen-atom parameters as described for Mn complex. Since Sandmark & Brändèn (1967) had refined $[Zn(ImH)_6]Cl_2.4H_2O$ in $P1$, we tested the hypothesis that correct space group is $P1$ and not $P\bar{1}$ by repeating the structure analysis without averaging $F(hkl)$ and $F(\bar{h}\bar{k}\bar{l})$. The first Fourier map was calculated with phases based on the zinc and one chlorine atom. The positions of all non-hydrogen atoms were obtained. Isotropic full-matrix least-squares refinement commenced in $P1$. Parameters of pairs of pseudo-symmetrically related atoms were highly correlated and oscillated as could be expected when a centre of symmetry has been omitted (Schomaker & Marsh, 1979). Maximum and average ratios of shift to error were 9·5 and 1·5, respectively. It was concluded that the space group is $P\bar{1}$.*

Discussion. Final atomic parameters are given in Tables 2 and 3. Bond lengths and angles for both structures are given in Table 4.

The $[M(ImH)_6]^{2+}$ cations (M = Mn, Zn) have octahedral coordination (Fig. 1). There is a slight tetragonal distortion. The metal—N(imidazole) bond lengths in both cations differ by 3σ–4σ of the differences. Each imidazole ring is parallel to the ring *trans* to it, as required by symmetry, and approximately co-planar with four of the metal—N(imidazole) bonds. Thus the three pairs of rings lie in approximately orthogonal planes; the angles between them are 82·2–89·9 (2)° in the Mn complex, and 84·2–89·1 (1)° in the Zn complex, respectively.

The complex cations form hexagonally packed layers parallel to the *yz* plane. They are anchored to layers of chloride ions and water molecules by N—H···Cl hydrogen bonds (see Fig. 2). Each complex is hydrogen bonded to six Cl^- ions, three on each side of the cation layer. Each Cl^- is hydrogen bonded to three complexes and to two water molecules. Curiously, the five hydrogen-bond partners all lie on one side of the Cl^- ion. The water molecule represented by O(1) is hydrogen bonded (i) to an equivalent water molecule O(1′) related to it by a centre of symmetry at (½,0,0),

Table 2. *Atomic positional parameters* (×10⁴ *for non-hydrogen atoms,* ×10³ *for hydrogen atoms) and equivalent isotropic thermal parameters,* U_{eq} (Å^2 × 10^3; U_{iso} *for* H) *for* $[Mn(ImH)_6]Cl_2.4H_2O$

E.s.d.'s of positional parameters in parentheses. E.s.d.'s of U_{eq}'s and U_{iso}'s are 2 in the least significant digit for Cl, 1 in the least significant digit for other atoms. Asterisks * denote hydrogen sites with occupancy 0·5.

$$U_{eq} = (U_{11}U_{22}U_{33})^{1/3}.$$

	x	*y*	*z*	U_{eq}/U_{iso}
Mn	0	0	0	31·3
Cl	5024·7 (4)	2060·3 (6)	5070·6 (6)	43·3
O(1)	5259 (2)	1724 (3)	1322 (2)	80
O(2)	4864 (2)	4560 (2)	1232 (2)	88
N(1)	1225 (1)	2428 (2)	2407 (2)	38
N(3)	2731 (2)	4761 (2)	4044 (3)	49
N(6)	1302 (1)	−1543 (2)	487 (2)	38
N(8)	2848 (2)	−2134 (3)	1801 (3)	60
N(11)	1246 (1)	363 (2)	−1748 (2)	40
N(13)	2829 (2)	285 (3)	−3117 (3)	62
C(2)	2258 (2)	3385 (3)	2425 (3)	45
C(4)	1977 (3)	4696 (3)	5130 (3)	58
C(5)	1050 (2)	3263 (3)	4121 (3)	52
C(7)	2343 (2)	−907 (3)	1766 (3)	46
C(9)	2106 (3)	−3648 (3)	478 (4)	68
C(10)	1154 (2)	−3277 (3)	−324 (3)	50
C(12)	2279 (2)	−239 (3)	−2147 (3)	51
C(14)	2125 (3)	1286 (4)	−3359 (4)	81
C(15)	1147 (2)	1320 (3)	−2529 (3)	63
H(2)	267 (2)	314 (3)	144 (3)	58
H(3)	336 (2)	555 (3)	431 (3)	63
H(4)	213 (2)	554 (3)	633 (3)	74
H(5)	36 (2)	284 (3)	444 (3)	64
H(7)	268 (2)	27 (3)	255 (3)	62
H(8)	346 (2)	−199 (3)	251 (3)	76
H(9)	226 (2)	−471 (3)	21 (3)	87
H(10)	45 (2)	−405 (3)	−133 (3)	65
H(12)	261 (2)	−93 (3)	−179 (3)	62
H(13)	342 (2)	2 (3)	−352 (3)	77
H(14)	231 (3)	178 (3)	−398 (4)	97
H(15)	47 (2)	187 (3)	−243 (3)	78
H(100)	507 (3)	182 (4)	212 (4)	97
H(101)*	514	255	130	97
H(102)*	511	74	57	97
H(200)	489	541	216	111
H(201)*	498	374	126	111
H(202)*	494	482	50	111

Table 3. *Atomic parameters for non-hydrogen atoms in* $[Zn(ImH)_6]Cl_2.4H_2O$

Details as in Table 2.

	x	*y*	*z*	U_{eq}
Zn	0	0	0	29·5
Cl	5038·3 (4)	2063·3 (6)	5082·7 (6)	40·8
O(1)	5263 (2)	1728 (3)	1326 (3)	79
O(2)	4863 (2)	4562 (2)	1227 (3)	87
N(1)	1183 (1)	2355 (2)	2330 (2)	34
N(3)	2701 (2)	4712 (2)	3986 (3)	45
N(6)	1270 (1)	−1483 (2)	487 (2)	35
N(8)	2827 (2)	−2074 (3)	1810 (3)	55
N(11)	1219 (1)	357 (2)	−1682 (2)	35
N(13)	2803 (2)	243 (3)	−3083 (3)	57
C(2)	2220 (2)	3337 (3)	2354 (3)	40
C(4)	1945 (3)	4616 (3)	5072 (3)	52
C(5)	1015 (2)	3166 (3)	4052 (3)	46
C(7)	2313 (2)	−841 (3)	1786 (3)	42
C(9)	2090 (3)	−3596 (3)	459 (4)	61
C(10)	1132 (2)	−3232 (3)	−350 (3)	45
C(12)	2252 (2)	−268 (3)	−2092 (3)	45
C(14)	2102 (3)	1254 (4)	−3326 (3)	72
C(15)	1123 (2)	1317 (3)	−2471 (3)	56

---

* Lists of structure factors, hydrogen-atom parameters for $[Zn(ImH)_6]Cl_2.4H_2O$, anisotropic thermal parameters, bond lengths and angles involving hydrogen atoms, hydrogen bonds and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38568 (53 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. *Bond lengths* (Å) *and angles* (°) *in* [Mn(ImH)$_6$]Cl$_2$.4H$_2$O *and* [Zn(ImH)$_6$]Cl$_2$.4H$_2$O

E.s.d.'s in parentheses. Atomic labels refer to ImH(1) in each complex; for ImH(2), add 5 to the numeral in each atomic label; for ImH(3) add 10 (see Fig. 1). M = Mn or Zn.

	[Mn(ImH)$_6$]Cl$_2$.4H$_2$O			[Zn(ImH)$_6$]Cl$_2$.4H$_2$O		
Imidazole ring	ImH(1)	ImH(2)	ImH(3)	ImH(1)	ImH(2)	ImH(3)
M—N(1)	2·266 (1)	2·276 (2)	2·276 (2)	2·183 (2)	2·199 (2)	2·196 (2)
N(1)—C(2)	1·317 (3)	1·318 (2)	1·313 (3)	1·319 (3)	1·320 (3)	1·317 (3)
C(2)—N(3)	1·336 (2)	1·336 (4)	1·334 (4)	1·339 (3)	1·337 (4)	1·337 (4)
N(3)—C(4)	1·346 (4)	1·353 (3)	1·349 (5)	1·350 (4)	1·355 (3)	1·350 (5)
C(4)—C(5)	1·347 (3)	1·351 (4)	1·345 (4)	1·348 (3)	1·349 (4)	1·349 (4)
C(5)—N(1)	1·371 (3)	1·375 (3)	1·375 (4)	1·373 (3)	1·381 (3)	1·378 (4)
M—N(1)—C(2)	126·3 (1)	125·3 (1)	126·6 (2)	126·2 (1)	125·5 (1)	126·3 (2)
M—N(1)—C(5)	128·9 (1)	129·8 (1)	128·7 (1)	128·9 (1)	129·6 (1)	128·8 (1)
C(5)—N(1)—C(2)	104·8 (2)	104·7 (2)	104·6 (2)	104·9 (2)	104·8 (2)	104·9 (2)
N(1)—C(2)—N(3)	111·4 (2)	111·5 (2)	111·6 (3)	111·3 (2)	111·4 (2)	111·3 (3)
C(2)—N(3)—C(4)	107·7 (2)	107·8 (2)	107·7 (2)	107·7 (2)	107·8 (2)	107·9 (2)
N(3)—C(4)—C(5)	106·3 (2)	105·9 (3)	106·0 (3)	106·3 (2)	106·2 (3)	106·1 (3)
C(4)—C(5)—N(1)	109·8 (2)	110·0 (2)	110·0 (3)	109·9 (2)	109·8 (2)	109·8 (3)
N(1)—M—N(6)		90·36 (6)			90·32 (7)	
N(1)—M—N(11)		89·61 (6)			89·90 (7)	
N(6)—M—N(11)		90·72 (7)			90·68 (7)	

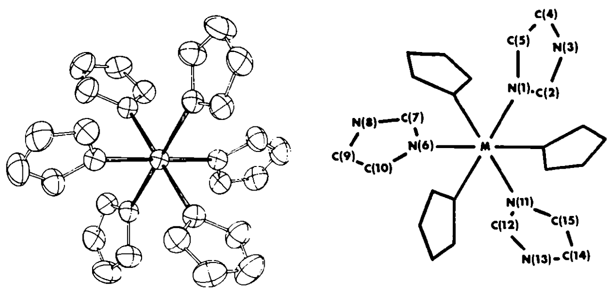

Fig. 1. The [M(ImH)$_6$]$^{2+}$ cation (M = Mn, Zn), showing (left) thermal ellipsoids (Johnson, 1976) taken from the Mn complex at the 50% probability level and (right) atomic labels.

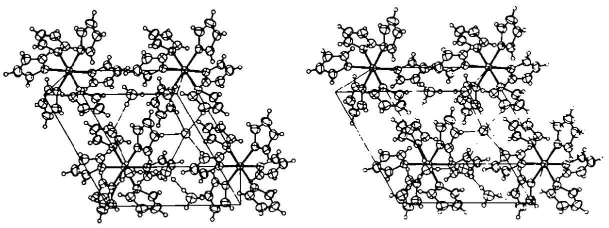

Fig. 2. Stereoview (Johnson, 1976) showing the packing and hydrogen bonding in crystals of [M(ImH)$_6$]Cl$_2$.4H$_2$O (M = Mn, Zn). Origin at the bottom left rear corner, x axis out of the paper, y axis left to right. Hydrogen-atom positions in O—H···Cl bonds are fully occupied; those in O—H···O bonds are half occupied (see text).

(ii) to the second water molecule represented by O(2), and (iii) to a Cl$^-$ ion. The second water molecule, in turn, is hydrogen bonded (i) to an equivalent water molecule O(2″) related to it by a centre of symmetry at $(\frac{1}{2},\frac{1}{2},0)$, (ii) to the original water O(1), and (iii) to a Cl$^-$ ion related to the first Cl$^-$ ion by a centre of symmetry at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. The centres of symmetry impose occupancies of 0·5 on the hydrogen-atom sites between O(1) and O(1′), and between O(2) and O(2″), respectively. As a result, all the O(water)···O(water) hydrogen bonds [including those between O(1) and O(2)] are disordered, O—$\frac{1}{2}$H···$\frac{1}{2}$H—O, and the structure is a superposition of two equivalent configurations for the chains of hydrogen bonds.

The crystals of [Mn(ImH)$_6$]Cl$_2$.4H$_2$O (present work) and [Zn(ImH)$_6$]Cl$_2$.4H$_2$O (Sandmark & Brädèn, 1967; present work) are isomorphous with [Ni(ImH)$_6$]Cl$_2$.4H$_2$O (Konopelski, Reimann, Hubbard, Mighell & Santoro, 1976.* With one exception, the structures of the octahedral hexakis(imidazole) complexes of the first-row transition metals from Mn^{II} to Zn^{II} are now known. The exception is represented by Fe^{II} where, however, the structure of a complex containing two imidazole and four imidazolate ligands has been reported (Lehnert & Seel, 1978). As expected,

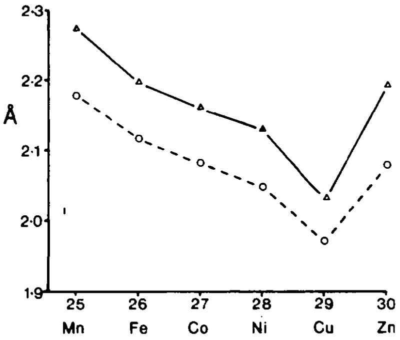

Fig. 3. Plot of average metal—N(imidazole) (——) and metal—O(water) (– – –) bond lengths in ML_6^{2+} complexes *vs* atomic number. Values are taken from present work (Mn—N, Zn—N), Lehnert & Seel (1978) (Fe—N), Prince, Mighell, Reimann & Santoro (1972) (Co—N), Konopelski *et al.* (1976) and Finney, Hitchman, Raston, Rowbottom & White (1981) (Ni—N), McFadden *et al.* (1975) (Cu—N, equatorial bonds), Carrell & Glusker (1973) (Mn—O), Strouse, Layten & Strouse (1977) (Fe—O), Ray, Zalkin & Templeton (1973*a*) (Co—O, Ni—O, Zn—O), Ray, Zalkin & Templeton (1973*b*) (Cu—O, equatorial bonds).

---

* The transformation from the unit cells of the Mn^{II} and Zn^{II} complexes to that report for the Ni^{II} complex is (—**b** — **c**, **c**, —**a**).

the hexakis(imidazole)Cu^{II} complex shows a marked tetragonal distortion (McFadden, McPhail, Garner & Mabbs, 1975). The complexes containing Mn^{II}, Fe^{II}, Co^{II} and Ni^{II} are high spin. In Fig. 3, the metal–ligand bond lengths in $[M(ImH)_6]^{2+}$ and $[M(H_2O)_6]^{2+}$ (M = Mn to Zn) are compared. The parallelism of the two curves suggests that coordination of the imidazole rings is not significantly affected by steric hindrance.

Bond lengths in the coordinated imidazole rings are not significantly different from those in free imidazole as determined by neutron diffraction (Craven, McMullan, Bell & Freeman, 1977; McMullan, Epstein, Ruble & Craven, 1979; *cf.* also Martinez-Carrera, 1966).

This work has been supported by grant (C80/15377) from the Australian Research Grants Scheme.

References

Busing, W. R. & Levy, H. A. (1957). *Acta Cryst.* **10**, 180–182.
Carrell, H. L. & Glusker, J. P. (1973). *Acta Cryst.* B**29**, 638–640.
Coppens, P., Leiserowitz, L. & Rabinovich, D. (1965). *Acta Cryst.* **18**, 1035–1038.
Craven, B. M., McMullan, R. K., Bell, J. D. & Freeman, H. C. (1977). *Acta Cryst.* B**33**, 2585–2589.
Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321–324.
Finney, A. J., Hitchman, M. A., Raston, C. L., Rowbottom, G. L. & White, A. H. (1981). *Aust. J. Chem.* **34**, 2113–2123.
Freeman, H. C. & Guss, J. M. (1972). *Acta Cryst.* B**28**, 2090–2096.
International Tables for X-ray Crystallography (1974). Vol. IV, p. 149. Birmingham: Kynoch Press.
Johnson, C. K. (1976). *ORTEP*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
Konopelski, J. P., Reimann, C. W., Hubbard, C. R., Mighell, A. D. & Santoro, A. (1976). *Acta Cryst.* B**32**, 2911–2913.
Lehnert, R. & Seel, F. (1978). *Z. Anorg. Allg. Chem.* **444**, 91–96.
McEuen, A. R. (1981). *Inorganic Biochemistry*, Vol. 2, edited by H. A. O. Hill, pp. 249–282. London: The Royal Society of Chemistry.
McFadden, D. L., McPhail, A. T., Garner, C. D. & Mabbs, F. E. (1975). *J. Chem. Soc. Dalton Trans.* pp. 263–268.
McMullan, R. K., Epstein, J., Ruble, J. R. & Craven, B. M. (1979). *Acta Cryst.* B**35**, 688–691.
Martínez-Carrera, S. (1966). *Acta Cryst.* **20**, 783–789.
Prince, E., Mighell, A. D., Reimann, C. W. & Santoro, A. (1972). *Cryst. Struct. Commun.* **1**, 247–252.
Ray, S., Zalkin, A. & Templeton, D. H. (1973*a*). *Acta Cryst.* B**29**, 2741–2747.
Ray, S., Zalkin, A. & Templeton, D. H. (1973*b*). *Acta Cryst.* B**29**, 2748–2751.
Sandmark, C. & Brändèn, C.-I. (1967). *Acta Chem. Scand.* **21**, 993–999.
Schomaker, V. & Marsh, R. E. (1979). *Acta Cryst.* B**35**, 1933–1934.
Stewart, J. M., Machin, P. A., Dickinson, C. W., Ammon, H. L., Heck, H. & Flack, H. (1976). The XRAY76 system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.
Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
Strouse, J., Layten, S. W. & Strouse, C. E. (1977). *J. Am. Chem. Soc.* **99**, 562–572.

Acta Cryst. (1983). C**39**, 1031–1034

trans-Diaquatetrakis(imidazole)manganese(II) Dichloride, $[Mn(C_3H_4N_2)_4(H_2O)_2]Cl_2$

By Thomas P. J. Garrett, J. Mitchell Guss and Hans C. Freeman*

Department of Inorganic Chemistry, University of Sydney, Sydney 2006, *Australia*

(*Received* 26 *January* 1983; *accepted* 3 *May* 1983)

Abstract. $M_r = 434{\cdot}19$, monoclinic, $C2/c$, $a = 12{\cdot}488\,(2)$, $b = 11{\cdot}121\,(1)$, $c = 14{\cdot}526\,(2)$ Å, $\beta = 107{\cdot}7\,(1)^\circ$, $V = 1921{\cdot}5\,(7)$ Å^3, $Z = 4$, $D_m = 1{\cdot}51\,(1)$, $D_x = 1{\cdot}501$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu(\text{Mo } K\alpha) = 9{\cdot}63$ cm^{-1}, $F(000) = 892$, $T = 291$ K, $R = 0{\cdot}030$ for 2096 unique reflections. The metal atom is octahedrally coordinated [Mn—N(imidazole) = 2·282 (2), 2·213 (6) Å; Mn—O(water) = 2·230 (2) Å]. The Mn—O(water) bonds are longer and two Mn—N(imidazole) bonds are shorter than the corresponding bonds in $[Mn(H_2O)_6]^{2+}$ and $[Mn(imidazole)_6]^{2+}$ ions. The two remaining Mn—N(imidazole) bonds are similar in length to those in the $[Mn(imidazole)_6]^{2+}$ ion.

Introduction. More than 25 manganese-containing metalloproteins and manganese-activated enzymes are now known (McEuen, 1981). Structural data for the types of bonds to be expected in manganese–protein interactions are, however, still limited. The present structure is a Mn^{II} complex in which the ligands are water and imidazole ($ImH = C_3H_4N_2$, the functional group of the amino acid histidine).

Experimental. Crystals of $[Mn(H_2O)_2(ImH)_4]Cl_2$ appeared during attemps to crystallize $[Mn(ImH)_6]Cl_2.4H_2O$ (Garrett, Guss & Freeman, 1983), when a warm ethanolic solution of $MnCl_2$ and imidazole in a molecular ratio of 1:4 was slowly cooled. Density by

---

* Author to whom correspondence should be addressed.

0108-2701/83/081031-04$01.50