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Structure of Hexakis(methylimidazole)cobalt(II) Dichloride Dihydrate, $[Co(CH_3-C_3H_3N_2)_6]Cl_2.2H_2O$

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Abstract. $[Co(C_4H_6N_2)_6]Cl_2.2H_2O$, $M_r = 658{\cdot}5$, monoclinic, $P2_1/n$, $a = 15{\cdot}064\ (2)$, $b = 13{\cdot}300\ (2)$, $c = 8{\cdot}100\ (1)$ Å, $\beta = 97{\cdot}90\ (3)°$, $V = 1607{\cdot}4\ (6)$ Å^3, $Z = 2$, $D_x = 1{\cdot}360$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 6{\cdot}8$ cm^{-1}, $F(000) = 690$, $T = 294$ K, final $R = 0{\cdot}076$ for 1682 Mo $K\alpha$ unique observed $[I > 3\sigma(I)]$ reflections. The presence of a methyl group in the imidazole moiety does not significantly modify the molecular conformation found in the Co^{II} imidazole complex but, unexpectedly, changes the Co^{II}—N distances thus accounting for the observed features in the EPR spectra. The elongation of the Co^{II}—N distances in octahedral imidazole complexes with respect to the Zn^{II}—N distances in tetrahedral analogues suggests that the easy replacement of Zn^{2+} by Co^{2+} in metalloenzymes may occur with retention of biological activity if the tetrahedral structure around the metal environment is maintained.

Introduction. Cobalt is present in the human body at a concentration of 0·016 p.p.m. and naturally occurs in vitamin B_{12}; Co^{2+} is able to replace Zn^{2+} in metalloenzymes, *e.g.* carboxypeptidase, carbonic anhydrase, alkaline phosphatase *etc.* (Sigel & Dekker, 1974) which retain their catalytic properties. The imidazole group and its derivatives, contained in several metalloenzymes, provide the binding site for metal ions such as Zn^{2+}. The active site of these enzymes usually also involves the bonding of the metal atom with the imidazole groups of the histidine residues. We have therefore undertaken the study of the product obtained by reacting vitamin B_{12} models with imidazole derivatives. In the development of the Co—N bond chemistry of biomolecules, such as vitamin B_{12}, we have observed that *N*-methylimidazole (*N*-Meim) replaces all the N atoms in the coordination sphere of hemiporphyrazinecobalt(II) dichloride yielding the octahedral complex $[Co(N\text{-Meim})_6]Cl_2$. The determination of the molecular dimensions in such a complex is justified since the molecular structures of $[Co(Him)_6](NO_3)_2$ (Him=Imidazole) (Price, Mighell, Reimann & Santoro, 1972) and $[Zn(Him)_2]Cl_2$ (Lundberg, 1966) are known and other divalent metal complexes of the $[M(Him)_6]^{2+}$ type (M=Ni^{2+},Cd^{2+} or Cu^{2+}) have already been studied (Santoro, Mighell, Zocchi & Reimann, 1969; Mighell & Santoro, 1971; McFadden, McPhail, Garner & Mabbs, 1975).

Table 1. *Crystal and refinement data of* $[Co(CH_3-C_3H_3N_2)_6]Cl_2.2H_2O$

Data collection method	θ–2θ
2θ range	$2 \leq 2\theta \leq 50°$
Scan width	1·2°
Range of h	−17, 17
k	0, 15
l	0, 9
Number of reflections measured	3452
Number of unique reflections	2824 ($R = 0{\cdot}025$)
Number of reflections used	1682 $[I > 3\sigma(I)]$
Weighting scheme	$w = 1$ for all reflections
Final R_F value	0·076
Final S	2·54
Final largest shift/e.s.d.	< 1·0

Experimental. The cobalt(II) methylimidazole complex was obtained as a crystalline product after dissolving hemiporphyrazine cobalt(II) dihydrochloride, $[Co(C_{26}H_{14}N_8)(HCl)_2]$, in pure *N*-methylimidazole at 298 K. Brilliant sky-blue-green crystals were obtained by recrystallization from acetone. Analytical data: Found: %C 43·69; %H 6·18; %N 25·48; %Cl 10·67; Calculated for $[Co(CH_3-C_3H_3N_2)_6]Cl_2.2H_2O$: %C 43·73; %H 6·12; %N 25·53; %Cl 10·77.

Crystal approximately 0·15 × 0·16 × 0·12 mm, Philips PW 1100 diffractometer, graphite-monochromated Mo $K\alpha$. Cell constants from setting angles of 25

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Table 2. *Positional parameters and equivalent isotropic thermal parameters* ($U_{eq} \times 10^2$) *and their estimated standard deviations for* $[Co(CH_3-C_3H_3N_2)_6]Cl_2.2H_2O$

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}(Å^2)
Co	1·0000	1·0000	0·0000	3·5 (1)
N(1)A	0·8844 (4)	0·9531 (5)	0·1088 (10)	4·0 (3)
N(2)A	0·7951 (5)	0·8775 (6)	0·2638 (10)	4·8 (3)
C(1)A	0·8740 (6)	0·8755 (7)	0·2037 (11)	4·2 (3)
C(2)A	0·7516 (6)	0·9634 (7)	0·2025 (13)	5·1 (4)
C(3)A	0·8052 (6)	1·0090 (8)	0·1087 (11)	4·4 (3)
C(4)A	0·7600 (7)	0·8003 (9)	0·3671 (15)	7·2 (4)
N(1)B	0·9905 (5)	0·8696 (6)	−0·1711 (10)	3·9 (3)
N(2)B	0·9584 (5)	0·7243 (5)	−0·2944 (9)	4·6 (3)
C(1)B	0·9543 (7)	0·7801 (8)	−0·1580 (13)	4·4 (4)
C(2)B	1·0009 (7)	0·7796 (8)	−0·4016 (12)	4·9 (4)
C(3)B	1·0192 (8)	0·8687 (8)	−0·3257 (14)	5·0 (4)
C(4)B	0·9254 (10)	0·6203 (9)	−0·3208 (15)	7·1 (5)
N(1)C	1·0901 (5)	0·9165 (6)	0·1834 (10)	4·3 (3)
N(2)C	1·1720 (5)	0·7960 (6)	0·3142 (10)	4·7 (3)
C(1)C	1·1059 (6)	0·8192 (7)	0·1922 (12)	4·4 (3)
C(2)C	1·2012 (7)	0·8840 (9)	0·3888 (14)	5·7 (4)
C(3)C	1·1505 (8)	0·9559 (8)	0·3090 (15)	6·2 (4)
C(4)C	1·2010 (9)	0·6926 (9)	0·3574 (15)	7·6 (5)
Cl	0·4306 (2)	0·8783 (2)	0·7010 (4)	4·7 (4)
O	0·3987 (6)	0·0783 (7)	0·4847 (12)	7·4 (5)

Table 3. *Selected bond distances* (Å) *and angles* (°) *in* $[Co(CH_3-C_3H_3N_2)_6]Cl_2.2H_2O$

	Ring A	Ring B	Ring C
Co—N(1)	2·149 (7)	2·212 (8)	2·174 (7)
N(1)—C(1)	1·309 (12)	1·320 (13)	1·316 (12)
C(1)—N(2)	1·345 (13)	1·339 (13)	1·339 (12)
N(2)—C(2)	1·375 (12)	1·363 (14)	1·362 (14)
C(2)—C(3)	1·329 (14)	1·346 (15)	1·334 (15)
C(3)—N(1)	1·406 (11)	1·380 (14)	1·372 (13)
N(2)—C(4)	1·468 (15)	1·475 (14)	1·471 (14)
C(1)—N(1)—C(3)	104·3 (7)	104·4 (9)	103·9 (8)
N(1)—C(3)—C(2)	109·9 (8)	110·6 (10)	111·2 (9)
N(2)—C(2)—C(3)	106·8 (9)	105·6 (9)	105·8 (9)
C(1)—N(2)—C(2)	106·7 (8)	107·8 (8)	106·9 (8)
N(1)—C(1)—N(2)	112·3 (8)	111·5 (9)	112·1 (8)
Co—N(1)—C(1)	129·7 (6)	130·4 (7)	129·1 (6)
Co—N(1)—C(3)	125·6 (6)	125·0 (7)	126·8 (6)

Angles around the Co atom

N(1)A—Co—N(1)B	92·5 (3)	N(1)B—Co—N(1)C	90·5 (3)
N(1)A—Co—N(1)C	92·1 (3)		

independent reflections ($15 \leq \theta \leq 25°$). Three standard reflections, no significant intensity decay. Crystal data and additional details of the data collection and refinement are presented in Table 1. Absorption corrections were made by using the empirical method of North (North, Phillips & Mathews, 1968). A total of 3452 reflections were collected and the averaging over symmetry equivalents gave a final set of 2824 reflections, 1682 of which have $I_{obs} > 3\sigma(I_{obs})$. The agreement factor (on F) between symmetry equivalent reflections was 2·5%.

The structure was solved by direct methods and refined on F by full-matrix least-squares techniques according to *SHELX76* programs (Sheldrick, 1976). An E map, based on 350 phases from a starting set with the highest combined figure of merit, revealed coordinates for almost all the atoms, the remaining non-H atoms were located from a successive difference Fourier map. Scattering factors from *SHELX76*. The model structure was refined by a full-matrix least-squares analysis with the weighting scheme $w = 1$ for all the reflections. A final value of $R = \sum||F_o| - |F_c||/\sum|F_o| = 0{\cdot}076$ was obtained. During the course of the refinement a water molecule became apparent, its occupation factor was estimated to be 85%. The relatively high R factor may be attributed to the disorder of the water molecules.

In the final three cycles of refinement the H atoms were also included. A difference Fourier map showed the highest residual density near the Co and Cl atoms, with a value of *ca* 1·0 e Å^{-3}. Final atomic parameters are listed in Table 2. The bond lengths and angles are given in Table 3.*

Discussion. The structure consists of discrete $[Co(CH_3-C_3H_3N_2)_6]^{2+}$ complex cations, chloride anions and water molecules packed in a monoclinic cell. The Co atom lies at a center of symmetry, bonded to six *N*-methylimidazole groups only three of which are crystallographically independent (Fig. 1).

The three $Co^{II}-N$ distances, crystallographically equivalent (through the $\bar{3}$ axis) in the $[Co(Him)_6](NO_3)_2$ complex (Price, Mighell, Reimann & Santoro, 1972), are now different, being 2·149 (7), 2·174 (7) and 2·212 (8) Å, but their mean value of 2·178 (8) Å

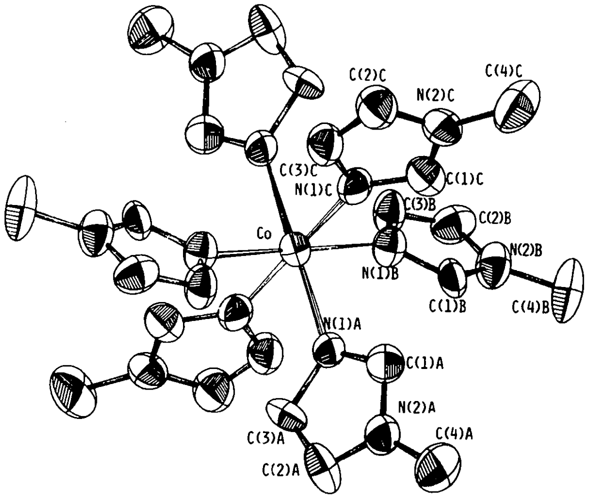

Fig. 1. *ORTEP* (Johnson, 1976) view of the complex cation $[Co(N\text{-}Meim)_6]^{2+}$ with atom numbering.

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and least-squares-planes results have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51521 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

compares well with the Co^{II}—N distance of 2·173 (2) Å found in the $[Co(Him)_6](NO_3)_2$ complex after a very accurate neutron study. A slightly shorter Ni^{II}—N distance of 2·129 Å was found in $[Ni(Him)_6](NO_3)_2$ (Santoro, Mighell, Zocchi & Reimann, 1969) but this is due to the slightly shorter octahedral radius of Ni^{II} compared to that of Co^{II}. The Zn^{II}—N distance of 2·008 Å, found in the tetrahedral complex $[Zn(Him)_2]Cl_2$ (Lundberg, 1966), is remarkably shorter than that of our octahedral Co complex and this is certainly due to the elongation of the metal radii on changing from tetrahedral to octahedral geometry. In fact, in $[Co(RCOO)_2(2\text{-}X\text{-}Him)_2]$ compounds ($R = CH_3$, C_2H_5; $X = H$, CH_3, C_2H_5) (Horrocks, Ishley & Whittle, 1982) that are distorted tetrahedral or octahedral complexes, the Co^{II}—N distances range between 1·987 and 2·069 Å, a value slightly smaller than ours and an explanation is that in true octahedral complexes the Co^{II} radius is longer (Shannon, 1976).

The remarkable difference of the Co^{II}—N and Zn^{II}—N distances on passing from an octahedral to tetrahedral geometry reinforces the idea that, when Co^{II} replaces Zn^{II} in metalloenzymes, a retention of the (tetrahedral) geometry at the metal site is a prerequisite for retaining full biological activity.

The coordination polyhedron is a distorted octahedron, the N—Co—N angles all being greater than 90° (Table 3) and the observed distortion can be described as a trigonal compression along the nearly ternary axis through the N(1)A—N(1)B—N(1)C atoms (see below) as seen for the above mentioned analogous complexes (Banci, Bencini, Benelli, Gatteschi & Zanchini, 1982; Bencini, Benelli, Gatteschi & Zanchini, 1983). Since the other known octahedral metal-hexakisimidazole complexes have the crystallographic rotoinversion $\bar{3}$ axis of space group $R\bar{3}$ (No. 148) coincident with the ternary axis of the octahedron, we have investigated the extent of the distortion due to the introduction of the CH_3 group. A rough estimate of this is the spread of the dihedral angles between the three imidazole rings, ranging from 65·2 (4) to 76·5 (3)°, and a more precise analysis involves the measurement of the angles between the three *N*-methylimidazole rings and the four pseudo-ternary axes of our octahedral complex. Results showed these angles to be different; nevertheless the pseudo-ternary axis perpendicular to the N(1)A—N(1)B—N(1)C plane forms dihedral angles [72·6 (4), 73·8 (3) and 65·1 (4)° respectively] with the three methylimidazole rings A, B and C, roughly similar to each other, so that the axis is a nearly ternary axis (Fig. 2). We can conclude that the introduction of a methyl group unexpectedly produces few changes to the molecular symmetry but has a much greater consequence for the Co—N bond lengths.

The EPR spectra of trigonal-octahedral high-spin Co^{II} complexes show marked *g*-anisotropies due to the splitting of the $^4T_{1g}$ level by low-symmetry components (Reedijk & Van der Put, 1974; Banci, Bencini, Benelli, Gatteschi & Zanchini, 1982; Bencini, Benelli, Gatteschi & Zanchini, 1983). Almost all complexes, with the inclusion of $[Co(N\text{-}Meim)_6]^{2+}$, have $g_{\parallel} < g_{\perp}$ while only $[Co(Him)_6]^{2+}$ and $[Co(H_2O)_6]^{2+}$ have $g_{\parallel} > g_{\perp}$. When $g_{\parallel} < g_{\perp}$ an orbitally non-degenerate state (singlet-state) is present as a ground state, while when $g_{\parallel} > g_{\perp}$ a lower orbital doublet ground state is hypothesized. Bencini *et al.* (1983) explain the existence of the orbital singlet ground state as resulting solely from the asymmetry of the σ-components of the metal—ligand bonding, while for the $[Co(N\text{-}Meim)_6]^{2+}$ complex they claim an e_π value for $[Co(Him)_6]^{2+}$ larger than that of $[Co(N\text{-}Meim)_6]^{2+}$. The wide range of Co^{II}—N bond distances found by us for the last complex strongly suggests that, in this case too, the singlet ground state has its origin principally in the asymmetry of the σ-components rather than in the π-components.

The imidazole rings were found by least-squares analysis to be planar within experimental error, while the Co atom is slightly out of the three ring planes. The bond distances and angles are very similar to those found in related compounds but are systematically smaller than those found in molecular imidazole [with the exception of N(1)—C(3)] at 123 K (Martinez-Carrera, 1966), probably due to thermal motion. The shortest observed and calculated distances are between atoms involved in usual C—N double bonds. Moreover, the spread of Co^{II}—N bond distances arises from intermolecular and intramolecular non-bonded interactions rather than electronic features. The pentaatomic ring B, that is the farthest from Co^{II}, presents short intramolecular contacts C(1)B···HC(1)C = 2·57 Å, HC(1)B···HC(1)C = 2·28 Å and C(1)B···C(1)C =

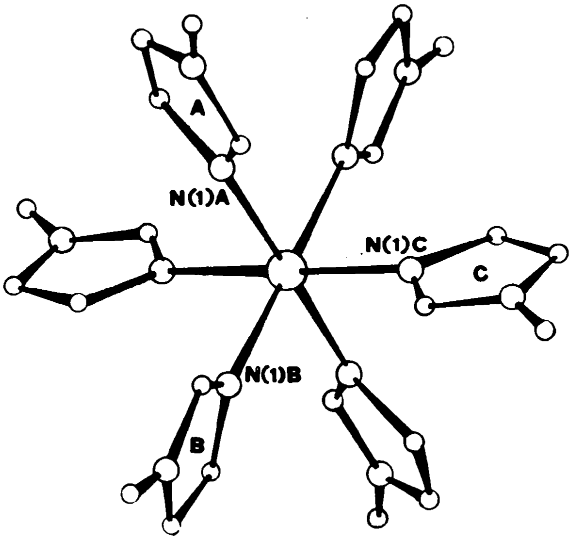

Fig. 2. View of the complex cation $[Co(N\text{-}Meim)_6]^{2+}$ along the pseudo-ternary axis perpendicular to the N(1)A—N(1)B—N(1)C plane (see text).

3·43 Å. An analysis of the shortest intermolecular contacts shows that the chlorine ion and water molecules strongly contribute to hydrogen bonding, $\mathrm{Cl^{i}\cdots OH_2} = 3{\cdot}19\,(1)$ Å [(i) = x, $y-1$, z] and $\mathrm{Cl^{ii}\cdots OH_2} = 3{\cdot}21\,(1)$ Å [(ii) = $1-x$, $1-y$, $1-z$].

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Structure of Dimesityldioxomolybdenum(VI)

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Abstract. Dioxodimesitylmolybdenum(VI), $[\mathrm{MoO_2(C_9H_{11})_2}]$, $M_r = 366$, monoclinic, $C2/c$, $a = 13{\cdot}617\,(4)$, $b = 9{\cdot}174\,(3)$, $c = 13{\cdot}681\,(4)$ Å, $\beta = 103{\cdot}75\,(5)^\circ$, $V = 1660\,(2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}461$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 7{\cdot}7$ cm^{-1}, $F(000) = 752$, $T = 263$ K, $R = 0{\cdot}029$ for 1447 unique diffractometer data with $I > 3\sigma(I)$. The coordination around the metal center, corresponding to a regular tetrahedron, and the geometry of the complex are compared to $\mathrm{ReO_2(mes)_2}$ and $\mathrm{OsO_2(mes)_2}$.

Introduction. In spite of abundant literature on the chemistry of transition-metal complexes involving the oxo ligand (Griffith, 1970; Holm, 1987) it is only rather recently that oxo complexes bearing other functionalities, such as alkyl (Mayer & Tulip, 1984; Cai, Hoffman, Lappas & Woo, 1987) and (or) carbene groups, have been receiving much attention (Schrock, Rocklage, Wengrovius, Rupprecht & Fellman, 1980).

During the past few years, we have been interested in both the oxo ligand and metal–oxygen bond reactivity in metal–oxo complexes. Most of our preliminary results have been obtained with a dioxo complex of molybdenum(VI), $\mathrm{MoO_2(mes)_2}$ (mes = mesityl: $\mathrm{C_6H_2}$-$\mathrm{Me_3}$-2,4,6) (Arzoumanian, Baldy, Lai, Metzger, Nkeng Peh & Pierrot, 1985; Lai, Le Bot, Baldy, Pierrot & Arzoumanian, 1986; Lai, Le Bot & Faure, 1987). This complex belongs to the rare class of metal oxoaryls and was perhaps the only example of a d^0 σ-organometal bearing only oxo and aryl ligands until the rhenium and osmium analogs were recently reported (Stravropoulos, Edwards, Behling, Wilkinson, Motevalli & Hursthouse, 1986). Since some of our results are rather unexpected and could be related to the presence of both the oxo and aryl ligands, and also to the structure of the coordinatively unsaturated dimesityldioxomolybdenum species, we have carried out an X-ray structure determination of this molecule prepared by the literature method (Heyn & Hoffmann, 1976).

Experimental. Crystal (0·4 × 0·2 × 0·3 mm) grown from THF solution, sealed in a capillary under inert atmosphere, mounted on a CAD-4 Enraf–Nonius diffractometer (graphite monochromator for Mo $K\alpha$). Unit-cell parameters refined by least squares on $\sin\theta/\lambda$ values for 25 reflections ($16 < \theta < 18^\circ$). Density obtained by flotation: $D_m = 1{\cdot}46\,(1)$ g cm^{-3}. Intensities measured using ω–2θ scan of 0·91 to

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