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The Crystal and Molecular Structure of *trans*-Tetrakis(miconazole)cobalt(II) Nitrate, $(C_{18}H_{14}Cl_4N_2O)_4Co(NO_3)_2$

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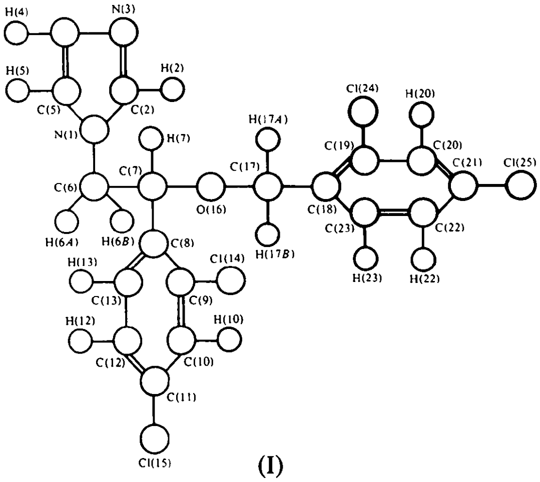
The crystal and molecular structure of (1-{2,4-dichloro-β-[(2,4-dichlorobenzyl)oxy]phenethyl}imidazole)-cobalt(II) nitrate was determined by single-crystal X-ray diffraction techniques (diffractometer, monochromated Cu $K\alpha$ radiation). The compound crystallizes in the triclinic system, space group $P\bar{1}$, with lattice parameters $a = 8{\cdot}797$ (3), $b = 14{\cdot}783$ (3), $c = 15{\cdot}949$ (3) Å, $\alpha = 75{\cdot}8$ (3), $\beta = 82{\cdot}8$ (3), $\gamma = 75{\cdot}1$ (3)°, $Z = 1$ and $\rho_o = 1{\cdot}577$, $\rho_c = 1{\cdot}580$ g cm^{-3}. The structure was solved by direct methods using three-dimensional data (4090 reflections). The two miconazole molecules in the asymmetric unit form an enantiomeric pair. The Co atom, at the centre of a slightly distorted *trans*-octahedron, is coordinated by four pyridine-type N atoms (imidazole rings) and two O atoms (nitrate groups). The final refinement by a three-dimensional least-squares analysis resulted in an R value of 0·072.

Introduction

Polarographic studies, performed in this laboratory, showed that 1-{2,4-dichloro-β-[(2,4-dichlorobenzyl)-oxy]phenethyl}imidazole, or miconazole (I), forms complexes with different metal ions such as Co, Cu, Mn, Zn and Cd. Different stoichiometric compositions can be obtained, depending on the metal-to-miconazole ratio in solution (Willems, 1977).



(I)

In this paper the structure of Co(miconazole)$_4$(NO$_3$)$_2$ is reported. Miconazole is a derivative of 1-phenethylimidazole. The preparation is described by Godefroi, Heeres, van Cutsem & Janssen (1969). It displays potent, broad-spectrum activity against dermatophytes, yeast cells and Gram-positive bacteria (Godefroi, van Cutsem, van der Eycken & Janssen, 1967).

Experimental

Preparation

Transparent red crystals were obtained from acetone after mixing Co(NO$_3$)$_2$.6H$_2$O and miconazole base in the ratio 1:4.

Crystal data

$(C_{18}H_{14}Cl_4N_2O)_4Co(NO_3)_2$ (from elemental analysis), FW 1847·5. Unit-cell parameters (determined from Weissenberg photographs and single-crystal diffractometer data; Cu $K\alpha$ radiation, $\lambda = 1{\cdot}54178$ Å): $a = 8{\cdot}797$ (3), $b = 14{\cdot}783$ (3), $c = 15{\cdot}949$ (3) Å, $\alpha = 75{\cdot}8$ (3), $\beta = 82{\cdot}8$ (3), $\gamma = 75{\cdot}1$ (3)°, $V = 1939$ (2) Å^3, $Z = 1$, $\rho_o = 1{\cdot}577$, $\rho_c = 1{\cdot}580$ g cm^{-3}, μ(Cu $K\alpha$) = 29·33 cm^{-1}, $F(000) = 937$, space group $P\bar{1}$.

Intensity data

The intensity data were collected on a single-crystal automated Nonius CAD-4 diffractometer using Cu $K\alpha$ radiation with a graphite monochromator and the θ–2θ scan technique. With a maximum value of $2\theta = 120°$ the number of independent reflections collected was 4791. Of these, 4090 were used in the crystal structure analysis, taking as unobserved the reflections whose intensities were less than three times their standard deviations. The data were corrected in the usual way for Lorentz and polarization factors, but no correction was made for absorption.

Structure determination and refinement

As the proportion of the Co electron number to the whole cell content is rather low, the heavy-atom method was not applied. The structure was solved by direct methods using the *MULTAN* 74 procedure (Main, Woolfson, Lessinger, Germain & Declercq, 1974). Initially the program was run in the automatic mode, choosing its own starting set [including five general reflections: 4$\bar{8}\bar{7}$ ($|E|$ = 4·16), 01$\bar{4}$ ($|E|$ = 3·50), 041 ($|E|$ = 3·40), 743 ($|E|$ = 3·29) and 58$\bar{1}$ ($|E|$ = 2·70)]. The origin-defining reflections [04$\bar{1}$ ($|E|$ = 3·30), 05$\bar{5}$ ($|E|$ = 3·03) and 350 ($|E|$ = 2·94)] were the same for two $E_{\min}$ values (1·9 and 1·6). This choice of the starting set, however, did not lead to the solution of the structure. Examination of the $\sum_2$ listing showed that the failure was due to a lack of interlinking relationships with a whole set of three-dimensional higher-order reflections. For this reason a different starting set was chosen [reflections 4$\bar{8}\bar{7}$($|E|$ = 4·16), $\bar{3}$,11,3 ($|E|$ = 2·38), 3,12,10 ($|E|$ = 2·13) and 05$\bar{5}$ ($|E|$ = 3·03), 3,6,11 ($|E|$ = 2·54), 2,13,11 ($|E|$ = 2·52), 0,13,1 ($|E|$ = 2·32), 3,4,13 ($|E|$ = 1·78)] taking special care over better interlinking properties. The $E_{\min}$ value was set to 1·75 and from the set with the best combined figure of merit (2·61) 34 atoms of the 55 non-hydrogen atoms in the asymmetric unit could be localized.

An electron-density Fourier synthesis with phases determined by the previously identified atoms was then calculated. Subsequently the missing non-hydrogen atoms were readily located in a difference density map. The trial structure was refined by block-diagonal least squares (XRAY system; Stewart, Kruger, Ammon, Dickinson & Hall, 1972). The quantity minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma$. After isotropic and anisotropic refinement, based on all 4090 observed reflections, the residual factor was 0·109. At this stage an ($|F_o| - |F_c|$) synthesis was computed and the positions of 26 of the 28 H atoms were found. The theoretical positions of the two remaining H atoms were computed. The H atoms were included in the subsequent refinement with the isotropic temperature factors of their parent atoms, but none of their parameters have been refined.

The final difference synthesis showed no outstanding features, and the conventional R obtained was 0·072.*

The final atomic coordinates are given in Tables 1 and 2. The atomic scattering factors of Cromer & Mann (1968) were used for O, N, C and Co and those of Stewart, Davidson & Simpson (1965) for H. All the calculations were performed on an IBM 370/158 computer.

Table 1. *Atomic coordinates with e.s.d.'s for the non-hydrogen atoms*

	x	y	z
Co	0·0	0·5	0·0
N(1)	−0·1598 (5)	0·5086 (3)	0·1112 (3)
C(2)	−0·2955 (6)	0·4831 (4)	0·1329 (4)
N(3)	−0·3581 (5)	0·5009 (3)	0·2103 (3)
C(4)	−0·2540 (7)	0·5395 (4)	0·2410 (4)
C(5)	−0·1362 (7)	0·5434 (4)	0·1807 (4)
C(6)	−0·5100 (7)	0·4842 (4)	0·2514 (4)
C(7)	−0·4956 (7)	0·3806 (4)	0·3031 (4)
C(8)	−0·6585 (6)	0·3740 (4)	0·3459 (3)
C(9)	−0·7036 (7)	0·3860 (4)	0·4293 (4)
C(10)	−0·8544 (6)	0·3884 (4)	0·4672 (4)
C(11)	−0·9618 (6)	0·3750 (4)	0·4177 (4)
C(12)	−0·9257 (7)	0·3627 (4)	0·3340 (4)
C(13)	−0·7736 (7)	0·3612 (4)	0·2989 (4)
Cl(14)	−0·5687 (2)	0·4039 (1)	0·4916 (1)
Cl(15)	−1·1540 (2)	0·3768 (1)	0·4624 (1)
O(16)	−0·4515 (5)	0·3247 (3)	0·2386 (3)
C(17)	−0·4011 (7)	0·2218 (4)	0·2743 (5)
C(18)	−0·2337 (7)	0·1961 (4)	0·2987 (4)
C(19)	0·1928 (8)	0·1613 (4)	0·3829 (5)
C(20)	−0·0360 (9)	0·1298 (5)	0·4075 (5)
C(21)	0·0767 (8)	0·1382 (4)	0·3386 (6)
C(22)	0·0419 (8)	0·1744 (5)	0·2540 (5)
C(23)	−0·1124 (8)	0·2037 (5)	0·2343 (5)
Cl(24)	−0·3372 (3)	0·1515 (2)	0·4687 (2)
Cl(25)	0·2740 (3)	0·0981 (2)	0·3683 (3)
N(1′)	0·0724 (5)	0·6218 (3)	0·0177 (3)
C(2′)	0·2168 (7)	0·6231 (4)	0·0421 (4)
N(3′)	0·2119 (5)	0·7151 (3)	0·0467 (3)
C(4′)	0·0665 (7)	0·7728 (4)	0·0244 (4)
C(5′)	−0·0176 (6)	0·7142 (4)	0·0067 (4)
C(6′)	0·3470 (7)	0·7497 (4)	0·0604 (4)
C(7′)	0·3173 (6)	0·7921 (4)	0·1397 (4)
C(8′)	0·4313 (6)	0·8564 (4)	0·1345 (4)
C(9′)	0·3847 (6)	0·9549 (4)	0·1194 (4)
C(10′)	0·4899 (7)	1·0142 (4)	0·1158 (4)
C(11′)	0·6443 (7)	0·9674 (4)	0·1273 (4)
C(12′)	0·6998 (7)	0·8704 (4)	0·1394 (4)
C(13′)	0·5914 (7)	0·8153 (4)	0·1440 (4)
Cl(14′)	0·1891 (2)	1·0137 (1)	0·1036 (1)
Cl(15′)	0·7773 (2)	1·0373 (1)	0·1261 (1)
O(16′)	0·3426 (4)	0·7147 (3)	0·2144 (3)
C(17′)	0·3051 (7)	0·7401 (4)	0·2972 (4)
C(18′)	0·1353 (7)	0·7851 (4)	0·3124 (4)
C(19′)	0·0175 (8)	0·7366 (4)	0·3203 (4)
C(20′)	−0·1412 (7)	0·7745 (5)	0·3371 (4)
C(21′)	−0·1803 (8)	0·8682 (5)	0·3469 (4)
C(22′)	−0·0650 (9)	0·9193 (5)	0·3392 (5)
C(23′)	0·0869 (8)	0·8789 (5)	0·3217 (5)
Cl(24′)	0·0709 (2)	0·6158 (1)	0·3120 (1)
Cl(25′)	−0·3801 (3)	0·9186 (2)	0·3662 (2)
N(26)	0·3144 (6)	0·3608 (4)	0·0711 (3)
O(27)	0·1734 (4)	0·4023 (3)	0·0868 (2)
O(28)	0·3546 (5)	0·2716 (3)	0·0867 (3)
O(29)	0·4170 (5)	0·4076 (3)	0·0443 (3)

Description of the structure

The asymmetric unit of the Co complex, as found by the structure analysis, is shown in Fig. 1. Bond lengths and angles are given in Figs. 2 and 3. It should be noted that the two miconazole molecules are present in both enantiomeric forms.

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33364 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Atomic coordinates for the hydrogen atoms*

The number of the H atom corresponds to that of the parent atom.

	x	y	z
H(2)	−0·3835	0·4737	0·0898
H(4)	−0·2972	0·5487	0·2987
H(5)	−0·0480	0·5670	0·1885
H(6*A*)	−0·6024	0·4737	0·1776
H(6*B*)	−0·5732	0·5199	0·2881
H(7)	−0·3858	0·3421	0·3503
H(10)	−0·8631	0·3698	0·5415
H(12)	−0·9956	0·3421	0·2874
H(13)	−0·7417	0·3684	0·2293
H(17*A*)	−0·5350	0·2105	0·3190
H(17*B*)	−0·3499	0·1842	0·1970
H(20)	−0·0026	0·1380	0·4739
H(22)	0·1690	0·1809	0·2142
H(23)	−0·1492	0·2489	0·1603
H(2′)	0·1500	0·6053	0·0567
H(4′)	0·0463	0·8684	−0·0053
H(5′)	−0·1227	0·7359	−0·0086
H(6′*A*)	0·3618	0·8041	0·0097
H(6′*B*)	0·4310	0·6842	0·0928
H(7′)	0·1910	0·8421	0·1506
H(10′)	0·4318	1·1053	0·1010
H(12′)	0·8087	0·8348	0·1685
H(13′)	0·6168	0·7413	0·1503
H(17′*A*)	0·3828	0·8892	0·2974
H(17′*B*)	0·3498	0·6712	0·3436
H(20′)	−0·2289	0·7336	0·3416
H(22′)	−0·0963	0·9923	0·3472
H(23′)	0·1936	0·8947	0·3207

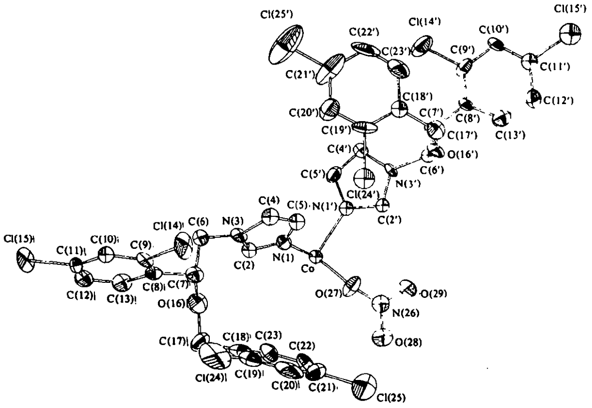

Fig. 1. *ORTEP* plot of the asymmetric unit with atomic numbering. The thermal ellipsoids correspond to the 50% probability limit.

The Co atom, at a symmetry centre of the crystal structure, is six-coordinated by N(1), N(1′), O(27) and their symmetry-related equivalents. The coordination polyhedron is quite a regular octahedron. The bond distances Co–N(1) and Co–N(1′) are respectively 2·14 (4) and 2·15 (2) Å. The distance between Co and the binding O(27) of the nitrate group is 2·18 (5) Å. The angles around the Co atom, N(1)–Co–N(1′), O(27)–Co–N(1) and O(27)–Co–N(1′), are 91·2 (2), 88·9 (2) and 87·3 (2)° respectively.

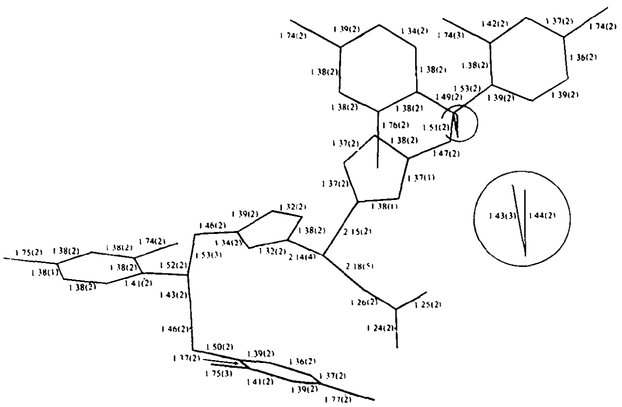

Fig. 2. Bond lengths (Å) in the asymmetric unit.

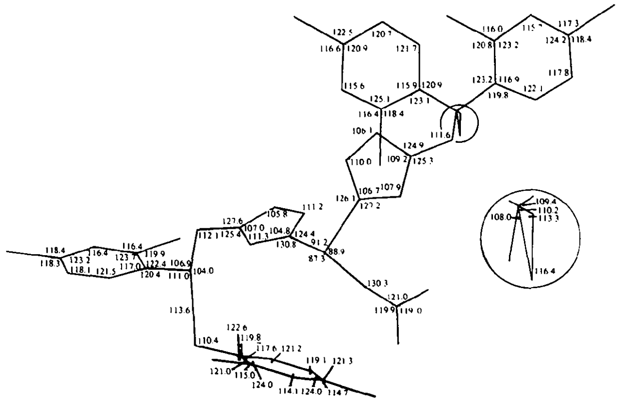

Fig. 3. Bond angles (°) in the asymmetric unit. The average of the e.s.d.'s is 0·4°.

The Co and the four pyridine-type N atoms are coplanar because of the $P\bar{1}$ symmetry. As a consequence of packing, the imidazole rings (1–5) and (1′–5′) are rotated, with respect to the Co–N coordination plane, by 68·7 and 29·0° respectively. The dihedral angle between the two imidazole rings is 70·9°. The plane of the nitrate group makes an angle of 49·4° with the Co–N plane.

The observed distances and angles in the imidazole rings are in agreement with those found in the comparable imidazole complex hexakis(imidazole)-nickel(II) nitrate (Santoro, Mighell, Zocchi & Reimann, 1969). Bond distances and angles relating to the phenyl and other groups are generally satisfactory.

From Fig. 1 it can be seen that all substituted Cl atoms, together with their parent atoms, undergo large thermal vibrations.

It is a pleasure to thank 'Janssen Pharmaceutica', Beerse, for providing the miconazole and carrying out the elemental analysis of the complex, Dr H. Schenk, University of Amsterdam, for the collection of the intensities, Professor G. King, KU Leuven, for assistance in using the XRAY system, and Mr R. Minner for preparing the single crystals.

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A Square-Cluster Platinum Complex with Short Metal–Metal Bonds: X-ray Crystal Structure of the Tetragonal Form of *cyclo*-Tetrakis[di-μ-acetato-platinum(II)]

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The structure of $[Pt(CH_3COO)_2]_4$ has been refined with 2894 counter reflexions to $R = 0{\cdot}032$. Eight tetrameric molecules occupy a tetragonal cell with $a = 10{\cdot}254$ (1), $c = 50{\cdot}494$ (5) Å; the space group is $P4_32_12$. The molecular structure is based on a strongly metal–metal bonded square cluster of four Pt atoms, with Pt–Pt lengths in the range 2·492–2·498 Å. Eight bridging acetate groups are arranged around the square such that four groups are in the plane of the cluster and four are alternately above and below it, giving Pt an octahedral coordination. The eight Pt–O bonds in the plane of the cluster are rather long, with a mean distance of 2·162 Å, while those approximately normal to the plane have a mean length of 2·002 Å. A second crystal form of platinum(II) acetate has been found which is monoclinic, with $a = 12{\cdot}031$ (1), $b = 10{\cdot}583$ (1), $c = 20{\cdot}090$ (2) Å, $\beta = 91{\cdot}10$ (1)°, space group $P2_1/c$.

Introduction

Pd acetate, a useful catalyst for a number of oxidation reactions of olefins, was shown to have a cyclic trimeric structure in which three Pd atoms are connected by double acetate bridges, with no metal–metal bonding (Skapski & Smart, 1970). It was originally suggested that Pt acetate was also trimeric, though not isomorphous with $[Pd(acetate)_2]_3$ (Stephenson, Morehouse, Powell, Heffer & Wilkinson, 1965). Attempts to obtain a crystalline specimen of Pt acetate revealed that the method of preparing this compound by the reduction of Pt^{IV} in nitric acid–acetic acid (Stephenson *et al.*, 1965; Davidson & Triggs, 1966) may lead to N-containing products, such as $Pt_4(acetate)_6(NO)_2$. An X-ray structure determination of this compound showed it to be tetranuclear with bridging nitrosyl as well as bridging acetate groups (de Meester, Skapski & Heffer, 1972; de Meester & Skapski, 1973).

A more recent method of preparing Pt acetate (ICI Ltd, 1970) from Ag acetate is simpler and more reliable. Starting from a specimen obtained by this route we have been able to obtain (Phillips & Skapski, 1975) crystals suitable for X-ray analysis. This has shown that the crystal form studied has a cyclic tetrameric molecular structure in which double acetate bridges span a strongly metal–metal bonded square of Pt atoms.

A preliminary report has been published (Carrondo & Skapski, 1976).

Experimental

Crystals of $[Pt(CH_3COO)_2]_4$ were obtained as thin plates by recrystallizing from glacial acetic acid the