The Crystal Structure of π-Cyclopentadienyl(triethylphosphine)copper(I), π-C₅H₅CuP(C₂H₅)₃

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Cyclopentadienyl(triethylphosphine)copper(I), $C_5H_5CuP(C_2H_5)_3$, has the cell dimensions $a = 8.60 \pm 0.02$, $b = 11.04 \pm 0.03$, $c = 7.67 \pm 0.02$ Å and $\beta = 115.3 \pm 0.05°$. The space group of the crystal is $P2_1/m$ and $Z = 2$. The structure was solved, using the intensities obtained from Weissenberg photographs, by three-dimensional Patterson, Fourier and least-squares methods to a final R index of 0.145 when a set of hydrogen atoms was included at chemically expected positions. The analysis revealed the presence of two enantiomers distributed apparently equally and randomly throughout the crystal. The C_5H_5 ring is π-bonded to the copper atom with average bond lengths of 2.24 for Cu–C and 1.38 Å for C–C. The Cu–P bond length is 2.14. The presence of a π-bonded C_5H_5 ring is in accord with the thermal stability of the compound. $C_5H_5CuP(C_2H_5)_3$ is monomeric and obeys the inert gas rule.

Introduction

Cyclopentadienyl(triethylphosphine)copper(I), $C_5H_5CuP(C_2H_5)_3$, is unique among the organometallic compounds of copper in that it is thermally stable well above room temperature, and is not extensively polymerized. Wilkinson & Piper (1956) who first prepared this compound, proposed that the cyclopentadienyl ring was connected to the copper atom by a single σ-bond on the basis of infrared and chemical evidence. Tertiary phosphine complexes of methylcopper of much lower thermal stability were reported by Costa, Pellizer & Rubessa (1964) and by House, Respess & Whitesides (1966) although usually methyl compounds are more stable than their σ-bonded cyclopentadienyl analogues. In the crystal structure of the phenyl-ethynyl(trimethylphosphine)copper tetramer reported by Corfield & Shearer (1966) copper is both π-bonded and σ-bonded to ethynyl groups. This suggests that $C_5H_5CuP(C_2H_5)_3$ may also be stabilized by π-bonding. Because of the special properties of $C_5H_5CuP(C_2H_5)_3$ and the existence of several possible structures, the present authors decided to undertake an X-ray crystal structure analysis.

Experimental

Preparation and purification

$C_5H_5CuP(C_2H_5)_3$ was prepared by the method of Wilkinson & Piper (1956). The crude product was placed in a vacuum sublimer and left overnight at 40 °C and 10^{-3} mmHg pressure. The triethylphosphine oxide present (m.p. 55–56 °C) was removed and the temperature raised to 55 °C. After 24 hours pure colourless crystals of $C_5H_5CuP(C_2H_5)_3$ were obtained (m.p. 122–124 °C *in vacuo*). The infrared spectrum agreed with that of Wilkinson & Piper (1956). Analysis: (micro-analysis by Geller Laboratories) Calculated for $C_{11}H_{20}CuP$: C, 53.5; H, 8.2; Cu, 25.8; P, 12.6. Found: C, 53.8; H, 8.0; Cu, 25.4; P, 12.0.

Crystal data

The colourless crystals were coated with a thin film of a commercial aerosol hair spray (water and/or alcohol base) to prevent oxidation in air. Plastic coatings with organic solvents as a base were found to be unsatisfactory. No difference was seen in short exposure oscillation photographs taken of a crystal before and after coating. The hair spray coating was found to maintain a good 'seal' for several days, but it was reapplied after about a week to ensure that the seal was maintained. Precession and Weissenberg photographs showed that the unit cell is monoclinic with the dimensions:

$$
\begin{aligned}
a &= 8.60 \pm 0.02 \text{ Å} & \beta &= 115.3 \pm 0.05° \\
b &= 11.04 \pm 0.03 \text{ Å} & Z &= 2 \\
c &= 7.67 \pm 0.02 \text{ Å} \\
V &= 658.3 \text{ Å}^3 \\
\varrho_o &= 1.25 \text{ g.cm}^{-3} \text{ (by flotation)} \\
\varrho_c &= 1.24 \text{ g.cm}^{-3} \text{ (for } Z = 2)
\end{aligned}
$$

The only observed systematic absence, $0k0$ present only with $k = 2n$, identifies the space group as $P2_1$ or $P2_1/m$.

Intensity collection

A crystal of dimensions $0.25 \times 0.40 \times 0.40$ mm outlined by forms {100} {010} and {001} was mounted for rotation about the b axis, and then coated with hair spray. Equi-inclination Weissenberg photographs of the levels $h0l$ to $h9l$ were recorded by the triple-film technique using Mo $K\alpha$ radiation with a Zr filter. The

intensities were estimated visually by comparison with those on an intensity scale prepared by taking a set of timed exposures of one reflexion. Six hundred and fifteen structurally different reflexions were recorded, and the Lorentz and polarization corrections were applied to them. Weissenberg photographs were taken of the 0kl and 1kl levels with a different crystal mounted around the a axis, and a correlation of the intensities of the h0l to h9l levels with each of these was attempted but proved to be unsatisfactory. Instead the levels h0l to h9l were scaled by exposure times (about 24 hours for each). For the last cycle of refinement a rescale factor (which proved to vary slightly from the exposure time factor) was calculated for each level by a least-squares method and then applied. No absorption corrections were applied to the reflexions.

Structure determination

A series of Patterson sections parallel to (010) revealed three very strong vectors of about the same peak height. One of these vectors corresponded to the expected Cu–P distance and was nearly coincident with the a axis. Of the other two peaks, occurring on the $y=\frac{1}{2}$ section, one had to correspond to the Cu–Cu vector and the other to two superimposed Cu–P vectors, thus indicating two possible structures. Only one of these possible structures proved capable of refinement; it is the one described here.

With only two molecules in each unit-cell, the space group $P2_1/m$ would necessitate a mirror plane in the molecule itself, and this seemed unlikely. However, leaving this question open at the outset, a first approx-

Table 1. *The observed and calculated structure factors* ($\times 10$)

imate three-dimensional electron density map with phases based only on the copper and phosphorus atoms was computed; this centrosymmetric map clearly revealed the positions of the five carbon atoms in the ring. One ring carbon atom was found to lie on the mirror plane, and the other four were found to occur as two pairs reflected across the mirror plane. The positions of the methyl carbon atoms were also indicated on this map. Thus, the positions of the copper, phosphorus, ring carbon and end carbon atoms of the ethyl groups conform to the space group $P2_1/m$. There remained two sets of chemically possible positions for the inner carbon atoms of the ethyl groups as shown in Fig. 1(a) and (c).

Least-squares calculations based on $P2_1$ symmetry and including only one of the enantiomers (shown in Fig. 1(a) and (c) without ring carbon atoms) in the lattice led to unsatisfactory results. Another model in which each molecule was forced to have a mirror plane by placing C(4) on that plane and by relating C(6) to C(7) by reflexion was also unacceptable. Only a disordered model containing two enantiomers each with one-half occupancy proved capable of refinement. Such a model satisfies the requirements of space group $P2_1/m$. The two enantiomers are shown without the ring carbon atoms in a projection along the Cu–P bond (nearly the a axis) in Fig. 1(a) and (c), with their superposition throughout the structure shown in Fig. 1(b). Fig. 2, which is an electron density map through the mean plane of the methylene carbon atoms using the final structure factors, shows, when compared with Fig. 1(b), the close correlation between the electron distribution and the disordered structure.

Considering the observed reflexions only, refinement of the disordered structure was carried out using several cycles of least-squares fitting of the positional parameters of all the non-hydrogen atoms and of the

temperature factors, initially isotropic but later aniso-tropic; slow convergence led to a final R index of 0·151 $(R=\sum||F_o|-|F_c||/\sum|F_o|)$. The quantity mini-mized was $\sum W (|F_o|-|F_c|)^2$. The weighting scheme employed was $W=1/\{1\cdot23+0\cdot054|F_o|\}$. With the in-clusion of a set of hydrogen atoms at chemically ex-pected positions and refinement of the parameters of all the atoms except the hydrogens, the R index was lowered to 0·145. These refined parameters are within the estimated standard deviations of the refined param-eters before hydrogen atoms were included, the latter being those shown in Table 2.

At the latest stage, a difference Fourier synthesis was carried out using the structure factors calculated with the hydrogen atoms included. This revealed a peak of 1·6 e.Å^{-3} between the copper and phosphorus atoms. The remainder of the map was between 1·0 and −1·2 e.Å^{-3} with the maxima and minima occurring on the mirror plane.

In the final least-squares cycle, the largest and the average absolute value of the atomic coordinate shifts, in fractional coordinates, were respectively for the copper atom 6×10^{-5} and 5×10^{-5}, for the phosphorus atom 3×10^{-5} and 2×10^{-5}, and for the carbon atoms 81×10^{-5} and 37×10^{-5}; the maximum positional parameter shift was less than one-third of its estimated standard deviation whereas the average positional parameter shift as a fraction of the e.s.d. was less than one-tenth. The computation was done by an IBM System 360/65 computer using the N.R.C. Crystallo-graphic Programs by F. R. Ahmed, S. R. Hall, M. E. Pippy & G. P. Saunderson. The block-diagonal least-squares program was modified by the present authors into a full-matrix least-squares program. The scattering factors for C, P and Cu^{1+} and the correction for anom-alous dispersion for P and Cu^{1+} were taken from *International Tables for X-ray Crystallography* (1962).

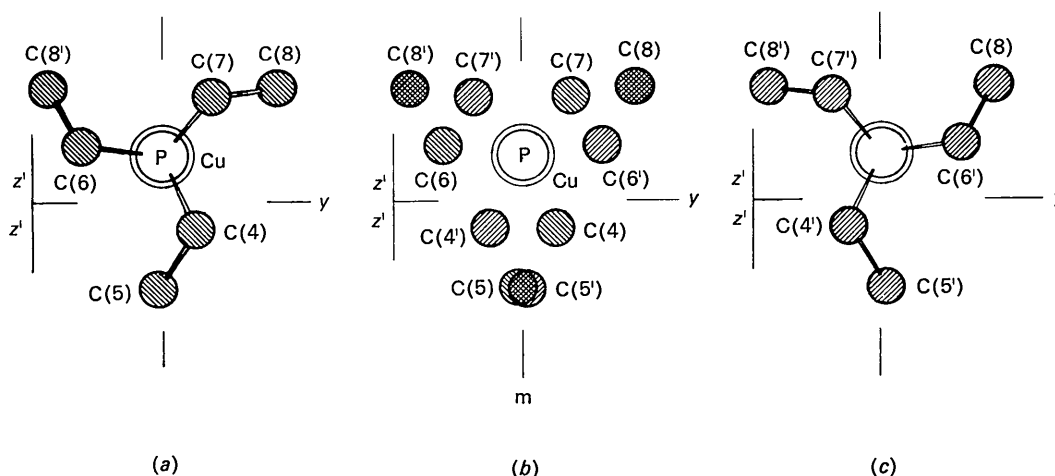
(a)   (b)   (c)

Fig. 1. Projection of the molecule along the Cu–P bond with no ring carbon or hydrogen atoms shown; (a) and (c) show the two enantiomers and (b) their superposition.

Results and discussion

The observed and calculated structure factors using parameters refined before the hydrogen atoms were included are shown in Table 1, the final atomic coordinates are given in Table 2 and the bond distances and interbond angles are given in Table 3. Table 4 gives the thermal vibration tensor components (U_{ij}'s). A projection of the unit cell viewed along the c axis is shown in Fig. 3. The atoms of one enantiomer are shown in solid circles and the non-identical portion of the other is given in dashed circles. The copper, phosphorus, ring carbon and the two end carbon atoms off the mirror plane C(8) and C(8') have identical positions in both enantiomers. Also, within its e.s.d., the end carbon atom C(5) is on the mirror plane. However, best refinement was achieved with this atom treated as two symmetrical half-atoms slightly displaced from this plane. Only the methylene carbon atoms do not conform to $P2_1/m$ symmetry in both enantiomers.

Table 2. Atomic coordinates and their estimated standard deviations ($\times 10^4$)

	x/a	σ	y/b	σ	z/c	σ
Cu	$-0\cdot1288$	(4)	$0\cdot2500$	(—)	$0\cdot1110$	(6)
P	$0\cdot1348$	(8)	$0\cdot2500$	(—)	$0\cdot1589$	(11)
C(1)	$-0\cdot3237$	(31)	$0\cdot2500$	(—)	$0\cdot2347$	(48)
C(2)	$-0\cdot3501$	(24)	$0\cdot3528$	(24)	$0\cdot1159$	(36)
C(3)	$-0\cdot3979$	(28)	$0\cdot3151$	(28)	$-0\cdot0632$	(33)
C(4)	$0\cdot1701$	(62)	$0\cdot3146$	(66)	$-0\cdot0488$	(91)

Table 2 (cont.)

C(5)	$0\cdot0760$ (50)	$0\cdot2408$ (94)	$-0\cdot2436$ (72)
C(6)	$0\cdot2367$ (46)	$0\cdot0945$ (41)	$0\cdot2053$ (52)
C(7)	$0\cdot2809$ (40)	$0\cdot3451$ (42)	$0\cdot3632$ (70)
C(8)	$0\cdot2214$ (44)	$0\cdot4703$ (37)	$0\cdot3750$ (40)

Table 3. Interatomic distances and angles and their estimated standard deviations

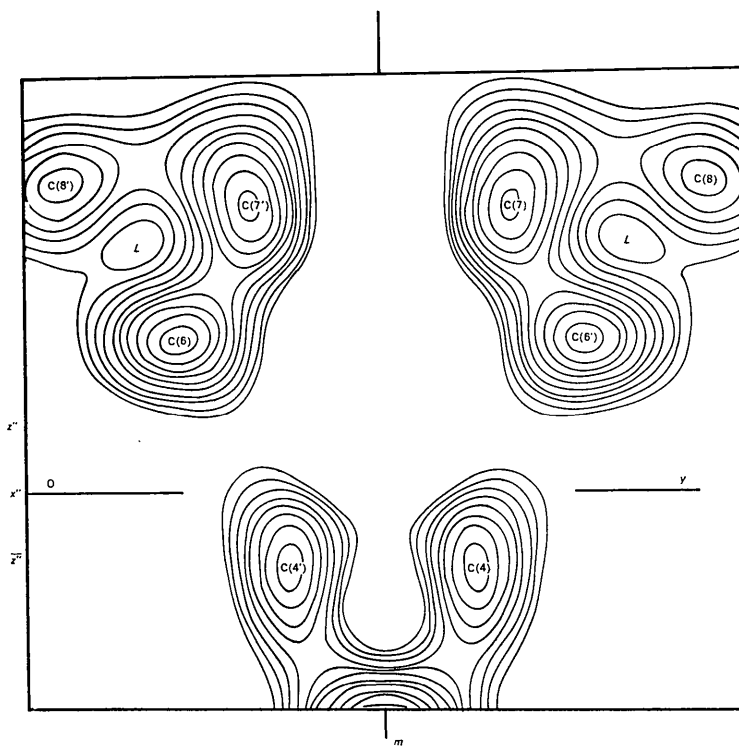|		σ
Cu—P	2·136	0·009 Å
P —C(4)	1·885	0·065
P —C(6)	1·891	0·044
P —C(7)	1·858	0·047
Average P–C	1·878	0·053
C(4)–C(5)	1·587	0·095
C(7)–C(8)	1·489	0·062
C(6)–C(8')	1·540	0·052
Average ethyl C–C	1·539	0·072
Cu—C(1)	2·252	0·031
Cu—C(2)	2·229	0·024
Cu—C(3)	2·239	0·026
Average Cu–C	2·238	0·026
C(1)–C(2)	1·412	0·032
C(2)–C(3)	1·321	0·034
C(3)–C(3')	1·438	0·044
Average ring C–C	1·381	0·035
P —Cu—C(1)	148·7	0·7°
P —Cu—C(2)	148·0	0·7
P —Cu—C(3)	148·5	0·7
Average P–Cu–C	148·4	0·7

Fig. 2. Electron density map of the mean plane through the methylene carbon atoms; the lowest contour is 1 e.Å^{-3} with the contour interval 0·2 e.Å^{-3}; L denotes 'low'.

Table 3 (cont.)

Cu—P —C(4)	113·4	2·0
Cu—P —C(6)	113·9	1·3
Cu—P —C(7)	115·5	1·4
Average Cu-P-C	114·3	1·6
P —C(4)-C(5)	113·6	4·5
P —C(7)-C(8)	116·7	3·0
P —C(6)-C(8')	112·4	2·7
Average P-C-C	114·2	3·5
C(4)-P —C(6)	105·8	2·4
C(4)-P —C(7)	101·8	2·5
C(6)-P —C(7)	105·2	1·9
Average C-P-C	104·3	2·3
C(1)-C(2)-C(3)	108·1	2·3
C(2)-C(3)-C(3')	108·3	2·4
C(2)-C(1)-C(2')	107·0	2·2
Average ring C-C-C	107·8	2·3

An examination of Table 3 shows that each individual bond length is equal (within its e.s.d.) to the average bond length of all chemically equivalent bond lengths (within its e.s.d.).

The Cu-P distance is 2·14 Å. From the sum of the covalent radii given by Pauling (1967) the expected value is 2·45 Å for a Cu-P bond length. However, our experimental value can be compared with the experimental average value of 2·23 Å obtained by Corfield & Shearer (1966) in the structure of phenylethynyl-(triethylphosphine)copper(I). The P-C bond distances average 1·88 Å. Summing the covalent radii of Pauling (1967) gives 1·87 Å for a P-C bond length whereas the average experimental value of 1·83 Å was obtained by Corfield & Shearer (1966).

The Cu-C ring distances, presented in Table 3, average 2·24 Å. Table 5 shows that the distance of the copper atom from the ring plane is 1·90 Å, and that the Cu-P bond is normal to the mean ring plane. Clearly the cyclopentadienyl ring in $C_5H_5CuP(C_2H_5)_3$ is π-bonded to the copper atom. This is the first X-ray structure determination of a C_5H_5 ring bonded to a copper atom. The presence of a π-bonded C_5H_5 ring is in accord with the thermal stability of the compound. In $C_5H_5CuP(C_2H_5)_3$ copper achieves an inert gas configuration making the molecule isoelectronic with cyclopentadienyl(nitrosyl)nickel, C_5H_5NiNO. A Ni-C bond distance of 2·11 Å in C_5H_5NiNO was found by Cox, Thomas & Sheridan (1958) by microwave spectroscopy. This distance may be compared with our average Cu-C ring distance of 2·24 Å. The average C-C bond length in the ring is 1·38 Å. This is similar to the average C-C bond length of 1·40 Å in the π-cyclopentadienyl ring of $(\pi\text{-}C_5H_5)Fe(\sigma\text{-}C_5H_5)(CO)_2$ whose crystal structure was determined by Bennett, Cotton, Davidson, Faller, Lippard & Morehouse (1966).

Table 5. *Cyclopentadienyl ring: mean plane and distances*

Equation of the plane of C_5H_5:

$$-0.9877X + 0.0002Y - 0.1564Z - 3.2382 = 0$$

where X, Y, Z refer to the orthogonal set of axes, X along **a**, Y along **b**, and Z along **c***.

Distances of atoms from the plane

C(1)	0·018 Å
C(2)	−0·014
C(2')	−0·015
C(3)	0·006
C(3')	0·006
Cu	−1·904
P	−4·040

The difference between the copper and phosphorus distances to the mean plane through the C_5H_5 ring is equal to the Cu-P bond length. Therefore the Cu-P bond is normal to this mean plane.

The random distribution of the enantiomers can be understood from a consideration of possible intermolecular interactions. The positions of the methyl carbon atoms, which form an almost equilateral triangle as shown in Fig. 1, are those that might be expected from packing considerations. Since C(5) lies on the mirror plane within its e.s.d., all of the atoms except the methylene carbon atoms form a set which conforms to $P2_1/m$ symmetry. Because of this symmetry this set can show no preference in its interactions with right- or left-handed molecules. Once the posi-

Table 4. *Thermal vibrational tensor components U_{ij} (Å²)*

The largest estimated standard deviations are 0·003 for the copper atom, 0·006 for the phosphorus atom while the standard deviations range from 0·011-0·103 for the carbon atoms.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu	0·050	0·087	0·094	0·0	0·029	0·0
P	0·043	0·068	0·071	0·0	0·021	0·0
C(1)	0·027	0·169	0·087	0·0	0·028	0·0
C(2)	0·060	0·065	0·132	0·032	0·050	0·013
C(3)	0·073	0·133	0·082	0·014	0·041	0·006
C(4)	0·081	0·183	0·161	−0·005	0·088	−0·012
C(5)	0·094	0·368	0·130	0·236	0·046	0·054
C(6)	0·059	0·060	0·058	−0·028	−0·002	0·027
C(7)	0·033	0·051	0·124	−0·035	0·014	−0·012
C(8)	0·141	0·142	0·108	−0·068	0·046	−0·031

tions of the members of this set are fixed, only inter-molecular interactions between methylene groups could induce ordering of the enantiomers. However, the shortest distance between methylene carbon atoms is 4·43 Å. If hydrogen atoms are considered, the closest distance of approach is approximately 2·3 Å. The closest intermolecular distance between any pair of non-hydrogen atoms is 3·76 Å. Hence any inter-molecular interactions are relatively weak which is in accord with the high volatility of the compounds.

The room temperature nuclear magnetic resonance spectrum of C₅H₅CuP(C₂H₅)₃ was obtained by Piper & Wilkinson (1956) and showed a single sharp peak for the protons of the C₅H₅ ring. More recently a low temperature study was performed by Whitesides & Fleming (1967). These authors found that in some, but not all, solvents the single sharp peak for the cyclo-pentadienyl ring protons splits into several peaks below −50°C. Because of this, these authors assigned a σ-bonded structure to the compound. However, it must be remembered that this n.m.r. study refers to the compound in solution whereas in an X-ray structure determination one is dealing with the molecule in the solid state.
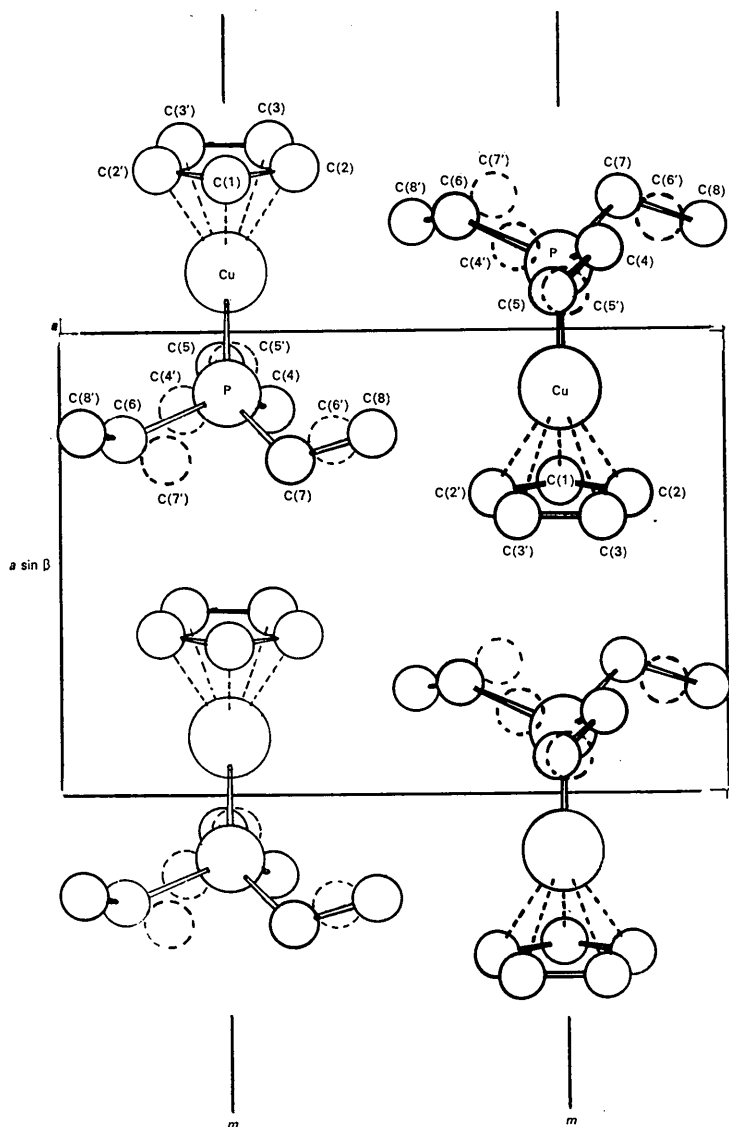
Fig. 3. Projection of the unit-cell viewed along the c axis. For explanation of dashed circles, see text.

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The Crystal and Molecular Structure of Hexapyrazolenickel(II) Nitrate, Ni(C3H4N2)6(NO3)2

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The crystal structure of hexapyrazolenickel(II)nitrate, $Ni(C_3H_4N_2)_6(NO_3)_2$, was determined by single-crystal diffraction techniques. Crystals of $Ni(C_3H_4N_2)_6(NO_3)_2$ are trigonal with $a = 9\cdot958$, $c = 7\cdot278$ Å, space group $P\bar{3}$, $Z = 1$, $\varrho_o = 1\cdot57$, $\varrho_c = 1\cdot57$ g.cm^{-3}. Three-dimensional counter data were collected (1115 reflections) and the structure was solved by an analysis of the Patterson map. The complex cation, $Ni(C_3H_4N_2)_6^{2+}$, formed by the coordination of six planar pyrazole molecules to the nickel ion, has $\bar{3}$ point symmetry. The nickel ion lies at the center of a nearly regular octahedron of coordinated nitrogen atoms. These complex cations and nitrate anions are linked by hydrogen bonds between each pyrrole type nitrogen atom ($>$N–H) in the pyrazole ring and an oxygen atom in the nitrate group. The final refinement by full-matrix anisotropic least-squares analysis resulted in an R value of 0·053.

Introduction

Five membered ring molecules which contain more than one nitrogen atom form a variety of complexes with transition metal ions. In these complexes important structural details depend upon the type and relative location of the nitrogen atoms. In each of several structures studied in this laboratory, the pyridine type nitrogen atoms ($>$N) are coordinated to a transition metal ion, and the pyrrole type nitrogen atoms ($>$N–H) participate in hydrogen bonding. The influence of the relative location of the nitrogen atoms in the ligand molecule on the structure of the complex is illustrated by some features of imidazole (I) and pyrazole (II) complexes
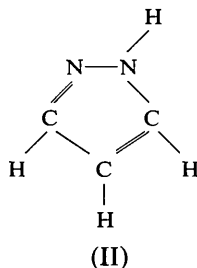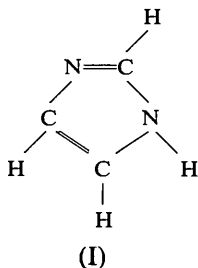
In hexaimidazolenickel(II)nitrate, $Ni(Im)_6(NO_3)_2$ (Santoro, Mighell, Zocchi & Reimann, 1969), the coordinate bond and the N–H direction make an angle of $\sim 144°$. In this complex the N–H groups form hydrogen bonds with oxygen atoms in NO_3^- groups located above and below neighboring $Ni(Im)_6^{2+}$ cations. In dichlorotetrapyrazolenickel(II), $Ni(Pz)_4Cl_2$ (Reimann, Mighell & Mauer, 1967) and dibromotetrapyrazolenickel(II), $Ni(Pz)_4Br_2$ (Mighell, Reimann & Santoro, 1969) in which the coordinate bond and the N–H direction make an angle of $\sim 72°$, the N–H group points toward the coordinated halogen atom to form an internal hydrogen bond.

Another pyrazole complex compound hexapyrazolenickel(II)nitrate, $Ni(Pz)_6(NO_3)_2$, was prepared to compare its structural and spectroscopic properties with those of related complexes. The visible spectrum of $Ni(Pz)_6(NO_3)_2$ was found to be almost identical with that of the related imidazole complex, $Ni(Im)_6(NO_3)_2$. This indicates that the coordination about the nickel ion in these complexes is similar. However, the decrease from ~ 144 to $\sim 72°$ in the angle between the coordinate bond and N–H direction would rule out a network of hydrogen bonds similar to that found in the imidazole complex. Moreover, internal hydrogen

(I)   (II)