

The Crystal Structure of Dichloro-2,2',2''-terpyridylcobalt(II)

BY ELISABETH GOLDSCHMIED AND N. C. STEPHENSON

School of Chemistry, University of N.S.W., P. O. Box 1, Kensington, N.S.W., 2033, Australia

(Received 4 February 1969)

The crystal structure of dichloro-2,2',2''-terpyridylcobalt(II), Co(terpy)Cl_2 , has been determined from three-dimensional data by direct comparison with the known structure of Zn(terpy)Cl_2 , followed by four cycles of full-matrix least-squares refinement. The crystals consist of discrete monomeric molecules in which the cobalt atom is five-coordinate; its environment is best described as being intermediate between that of the zinc atom in Zn(terpy)Cl_2 and that of the cobalt atom in $\beta\text{-Co(paphy)Cl}_2$ (paphy = pyridine-2-aldehyde-2'-pyridylhydrazone). There are significant deviations from planarity in the coordinated terdentate ligand.

Introduction

In a previous study (Harris, Lockyer & Stephenson, 1966) crystals of the anhydrous 1:1 adducts of 2,2',2''-terpyridine (terpy) with the chlorides of Mn^{II} , Co^{II} , Cu^{II} and Zn^{II} were prepared. They are all monoclinic (space group $P2_1/c$) with only small differences in their cell dimensions, thus suggesting isomorphism. Substantiating evidence for this assumption was obtained by a comparison of the intensity distribution observed on single-crystal Weissenberg and $h0l$ and $hk0$ precession photographs of these compounds. The intensity distribution is practically the same on all of them,* so that the films become almost superimposable. In order to confirm this assumption it was decided to collect three-dimensional data on the cobalt complex and to compare them with those calculated from the known parameters of Zn(terpy)Cl_2 . The structure of the latter which had been known for some time (Corbridge & Cox, 1956) had recently been refined (Einstein & Penfold, 1966).

In a similar single-crystal study (Lions, Dance & Lewis, 1967), the cell dimensions and $0kl$ intensity distributions of anhydrous Ni(terpy)Cl_2 were compared with those of the cobalt complex and found to be very similar, thus suggesting isomorphism of the nickel complex also.

In another recent study, based on evidence obtained from X-ray powder photographs, magnetic moments and Mössbauer studies (Judge, Reiff, Intelle, Ballway & Baker, 1967), these findings were confirmed and extended to include all the mono(terpy) adducts of the halides (Cl^- , Br^- , I^-) of the bivalent ions Mn^{II} , Fe^{II} , Co^{II} , Ni^{II} and Zn^{II} : with the sole exception of Fe(terpy)Cl_2 , all were found to be isomorphous with Zn(terpy)Cl_2 .

Pyridine-2-aldehyde-2'-pyridylhydrazone (paphy), which is structurally very similar to 2,2',2''-terpyridine, forms two isomeric mono-complexes with cobalt chloride: a red, octahedral isomer, designated α , and a green β -isomer (Dance, Gerloch, Lewis, Lions & Stevens, 1966). A crystal structure determination on the latter (Gerloch, 1966) revealed it to be pentacoordinated and to display some striking similarities with Zn(terpy)Cl_2 . The details of the crystal structure of Co(terpy)Cl_2 provide an interesting comparison with those of Zn(terpy)Cl_2 on the one hand and $\beta\text{-Co(paphy)Cl}_2$ on the other.

Crystal data

Dichloro-2,2',2''-terpyridylcobalt(II) crystallizes in thin, green needles, elongated along [100]. The space group and unit-cell dimensions were obtained from single-crystal Weissenberg and $h0l$ and $hk0$ precession photographs; unfiltered cobalt radiation was used for the former and zirconium-filtered molybdenum radiation for the latter. The density of the crystals was measured by flotation in a mixture of 1,2-dibromoethane and benzene.

The crystal data are as follows:

$\text{CoC}_{15}\text{H}_{11}\text{N}_3\text{Cl}_2$, $M = 363.1$, $F(000) = 732$
 Monoclinic, space group $P2_1/c$ (from systematic absences)
 $a = 10.84$, $b = 8.21$, $c = 16.24 \text{ \AA}$, $\beta = 95.1^\circ$, $U = 1440 \text{ \AA}^3$
 $D_m = 1.677$, $D_x = 1.675 \text{ g.cm}^{-3}$, $Z = 4$.

Experimental

Intensity data were collected from single-crystal equi-inclination Weissenberg photographs, taken by rotation about [100], ($h = 0, 1 \dots 7$), using unfiltered Co $K\alpha$ radiation.

The multiple-film technique was used to record the diffraction patterns and the intensities were estimated visually, using a calibrated intensity strip. 1026 independent, non-zero reflexions were observed.

* It should be noted, however, that some differences in the $0kl$ intensity distributions of Co(terpy)Cl_2 and Zn(terpy)Cl_2 were observed in a subsequent study (Lions, Dance & Lewis, 1967).

No corrections were made for absorption or extinction effects, nor was any attempt made at this stage to attain internal inter-layer correlation of the eight zones of data.

Comparisons of the structure amplitudes with those calculated from the parameters of dichloro-2,2',2''-terpyridylzinc(II)

The observed structure amplitudes were then compared with those calculated from the positional and isotropic thermal parameters of the zinc complex (Einstein & Penfold, 1966); this comparison was undertaken separately for each layer of data, and an approximate scale factor, S_h , based on the criterion

$$S_h = \frac{\sum_{k,l} |F_{\text{calc}}|_{hkl}}{\sum_{k,l} |F_{\text{obs}}|_{hkl}}$$

could thus be calculated for each of them.

The unreliability indices R for the eight layers varied from 0.17 to 0.24, with an overall value of 0.20.

Refinement

After scaling the data in accordance with these scale factors, the structure was refined in four full-matrix least-squares cycles, using Cruickshank's (1965) weighting scheme, *i.e.*

$$W = 1/(a + |F_{\text{obs}}| + c|F_{\text{obs}}|^2),$$

where $a = 2|F_o|_{\text{min}}$, $c = 2/|F_o|_{\text{max}}$ and $|F_o|_{\text{min}}$ and $|F_o|_{\text{max}}$ are the lowest and highest observed values of $|F_{\text{obs}}|$ respectively.

The parameters which were varied in the four cycles were:

- Cycle (1) Isotropic temperature factors, one overall scale factor, positional parameters
- Cycle (2) Individual scale factors (one for each layer of data)

Table 1. Atomic parameters and standard deviations

	x/a	y/b	z/c	B	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	$\sigma(B)$
Co	0.2141	0.0847	0.1174	3.46 Å ²	0.0032 Å	0.0032 Å	0.0029 Å	0.09 Å ²
Cl(1)	0.1391	0.0201	0.2400	4.82	0.0054	0.0052	0.0053	0.12
Cl(2)	0.3351	0.3143	0.1302	4.13	0.0051	0.0049	0.0045	0.11

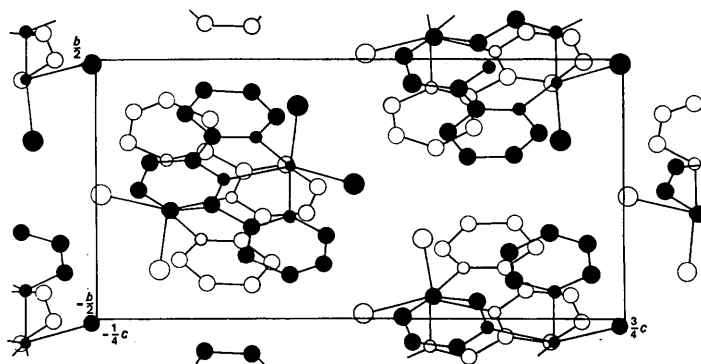


Fig. 1. (100) projection of the unit cell of Co(terpy)Cl₂.

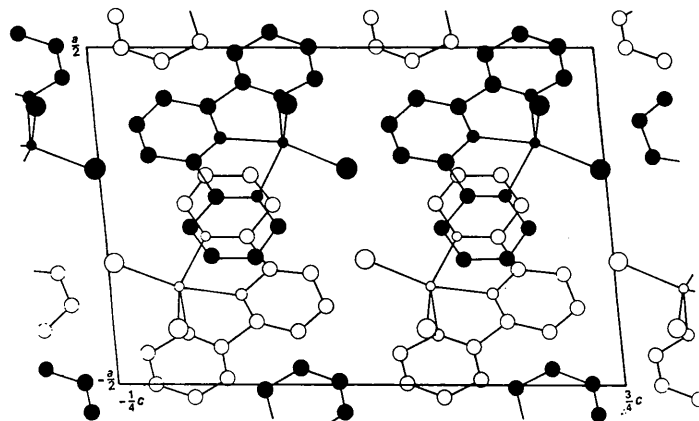


Fig. 2. (010) projection of the unit cell of Co(terpy)Cl₂.

Table 4. Details of planes

Plane	1 Trigonal equatorial plane	2 Basal nitrogen plane	3 Mean plane through terpy ligand	4 First pyridine ring	5 Second pyridine ring	6 Third pyridine ring
Least-squares plane of best fit through the atoms	Co, Cl(1), Cl(2), N(2)	N(1), N(2), N(3)	N(1), N(2), N(3) C(1) to C(15)	N(1) C(1) to C(5)	N(2) C(6) to C(10)	N(3) C(11) to C(15)
Perpendicular equation to the plane* $lX' + mY + nZ' = p$	+0.7889 -0.5582 +0.2568 +1.8146	+0.6029 +0.7905 +0.1077 +1.7029	+0.6105 +0.7859 +0.0983 +1.6288	+0.6775 +0.7319 +0.0732 +1.9779	+0.6138 +0.7868 +0.0641 +1.7260	+0.5811 +0.8108 +0.0695 +1.6724
Displacement of atoms from the plane (Å)	Co Cl(1) Cl(2)	+0.348 -0.454	+0.418	+0.128	+0.264	+0.274
	N(1) N(2) N(3)	+0.007 +0.004	+0.088 +0.093 +0.063	-0.018	-0.063 +0.009 -0.060	+0.019
	C(1) C(2) C(3) C(4) C(5)	+0.007	+0.082 -0.060 -0.130 -0.114 +0.041	+0.012 -0.008 +0.008 -0.013 +0.018	-0.107 -0.243 -0.270 -0.214 -0.068	
	C(6) C(7) C(8) C(9) C(10)		+0.050 +0.051 -0.032 +0.019 +0.050	-0.020 +0.028 -0.024 +0.013 -0.004	-0.020 +0.028 -0.024 +0.013 -0.004	
	C(11) C(12) C(13) C(14) C(15)		+0.021 -0.087 -0.079 -0.034 -0.021	-0.057 -0.137 -0.153 -0.157 -0.167	-0.057 -0.137 -0.153 -0.157 -0.167	+0.012 -0.026 +0.012 +0.019 -0.035
Angles between bonds and the plane	Bond	Angle	Bond	Angle	Bond	Angle
	Co-N(1)	72°	Co-Cl(1)	21°		
	Co-N(3)	75	Co-Cl(2)	87		
Dihedral angle between planes		1 and 2		4 and 5		5 and 6
Value		86°		4.9°		2.4°

Angles between bonds and the plane

Dihedral angle between planes
Value

* These equations are referred to orthogonal axes X' , Y , Z' , related to the crystallographic axes X , Y , Z , by the transformation $X' = X + Z \cos \beta$, $Z' = Z \sin \beta$; l , m and n are the direction cosines which the perpendiculars p make with the orthogonal axes a , b and c' respectively.

is no overlap between molecules in adjacent layers. Within each layer centrosymmetrically related molecules are arranged 'end to end'.

The atomic packing in the crystals is shown in the (100) and (010) projections of the unit cell, in Figs. 1 and 2. The shape of the individual molecules can be seen quite clearly in both of these projections, but it is also shown separately in Fig. 3, which is a photograph of a scale model. Table 3 gives the bond distances and bond angles in the molecule and some important intramolecular distances between non-bonded atoms. Reference will be made to several planes within the molecule; details of these are summarized in Table 4.

Discussion: comparison with $\text{Zn}(\text{terpy})\text{Cl}_2$ and $\beta\text{-Co}(\text{paphy})\text{Cl}_2$

The striking similarity in the pentacoordinated stereochemistry of the metal atom in $\text{Zn}(\text{terpy})\text{Cl}_2$ and $\beta\text{-Co}(\text{paphy})\text{Cl}_2$ was pointed out by Gerloch (1966); it is not surprising that the structure of $\text{Co}(\text{terpy})\text{Cl}_2$ displays the same salient features and it is interesting to note that, although the individual differences in bond lengths and angles around the metal atoms of the three complexes is so small as to be barely significant, especially in view of the somewhat large standard deviations reported for the zinc complex, yet in almost every instance where significant differences in geometrical detail do occur, $\text{Co}(\text{terpy})\text{Cl}_2$ is intermediate between the limits set by $\text{Zn}(\text{terpy})\text{Cl}_2$ on the one hand, and $\beta\text{-Co}(\text{paphy})\text{Cl}_2$ on the other.

The environment of the zinc atom in $\text{Zn}(\text{terpy})\text{Cl}_2$ was originally described by Corbridge & Cox (1956) as being '... much closer to a trigonal bipyramid, than to any other recognized arrangement, and in particular it is certainly not that of a tetragonal pyramid...'; yet although the salient features of the stereochemistry were not significantly altered as a result of the subsequent refinement by Einstein & Penfold (1966), it was nevertheless suggested by Gerloch (1966) and by Lions *et al.* (1967) that it might be better described as being tetragonal pyramidal, by analogy with the structure of $\beta\text{-Co}(\text{paphy})\text{Cl}_2$.

In what follows, the stereochemistry of the metal atom in $\text{Co}(\text{terpy})\text{Cl}_2$ will be presented in terms of its deviations from both idealized geometries and compared with that found in its zinc-terpy and cobalt-paphy analogues.

Gerloch used the difference of 0.05 Å in the lengths of the two M-Cl bonds in $\beta\text{-Co}(\text{paphy})\text{Cl}_2$ as an argument in favour of describing its stereochemistry as square pyramidal and he pointed out that a significantly longer apical bond is a common feature in this type of stereochemistry (see also Muetterties & Schunn, 1966); yet no such significant difference was found in either of the terpyridine complexes. While it must be pointed out that Gerloch's standard deviations for the M-Cl bonds are less than half of those which were obtained for either of the terpyridine com-

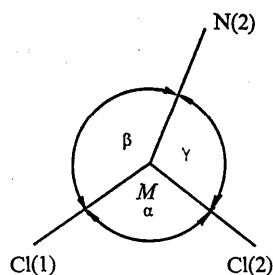
plexes, nevertheless it should also be pointed out that in both of the latter the corresponding difference is only 0.02 Å, which could not be regarded as physically meaningful, even if it were significant statistically. In a trigonal bipyramidal stereochemistry, the two M-Cl bonds would, of course, be expected to be equivalent.

In all three of the complexes the central M-N bond appears to be slightly shorter than the mean value of the external ones, though the difference is barely significant in any of them, and if real, it is more likely to be due to ligand constraints imposed on the bonding around the metal atom, than to any inherently 'preferred' stereochemistry.

As in the other two complexes, the metal atom, the two chlorine atoms and the central nitrogen atom in $\text{Co}(\text{terpy})\text{Cl}_2$ are coplanar (plane 1, Table 4). However the deviations from trigonal bipyramidal symmetry lie in the facts that the axial Co-N bonds are not perpendicular to this plane, the angle between them being 72 and 75° respectively, and that there is considerable distortion from trigonal symmetry of the bond angles within this plane. It can be seen from Table 5 that this distortion is 13° smaller in $\text{Zn}(\text{terpy})\text{Cl}_2$ and 12° larger in $\beta\text{-Co}(\text{paphy})\text{Cl}_2$.

Table 5. Deviation from trigonal symmetry in the equatorial planes of $\text{Zn}(\text{terpy})\text{Cl}_2$, $\text{Co}(\text{terpy})\text{Cl}_2$ and $\beta\text{-Co}(\text{paphy})\text{Cl}_2$

	$\text{Zn}(\text{terpy})\text{Cl}_2$	$\text{Co}(\text{terpy})\text{Cl}_2$	$\beta\text{-Co}(\text{paphy})\text{Cl}_2$
α	112°	111°	110°
β	143	150	157
γ	105	99	94
$(\beta-\gamma)$	38	51	63



All three of the angles Cl(2)-M-N lie within $100 \pm 6^\circ$ in the three complexes under discussion. According to Gillespie (1963) this is the optimum value for the angle between an axial and a basal bond in a tetragonal pyramidal complex. It follows that in such a structure the central atom will be slightly displaced from the basal plane in the direction of the apical atom. This displacement is in fact observed in all three of the complexes (Table 6). Furthermore, as would be expected in a tetragonal pyramidal structure, the apical M-Cl(2) bond is nearly perpendicular to this plane. In $\text{Co}(\text{terpy})\text{Cl}_2$, the Co-Cl(2) bond is inclined at 87° to the basal plane defined by the three nitrogen atoms (plane 2) and the trigonal equatorial plane (plane 1),

which contains this bond, makes a dihedral angle of 86° with the nitrogen-atoms plane; this orthogonality has also been observed in the other two complexes.

The main difficulty in describing the structures of the two terpyridine complexes as distorted tetragonal pyramidal lies in the absence of a basal tetragonal plane, defined by the atoms N(1), N(2), N(3) and Cl(1). In the case of Co(terpy)Cl_2 , Cl(1) lies 0.45 \AA 'below' the plane defined by the three nitrogen atoms; this corresponds to approximately a fifth of a bond length. The cobalt atom lies 0.35 \AA on the opposite side of this plane. Table 6 gives the corresponding parameters for Zn(terpy)Cl_2 and $\beta\text{-Co(paphy)Cl}_2$. It can be seen from this Table that the displacement of

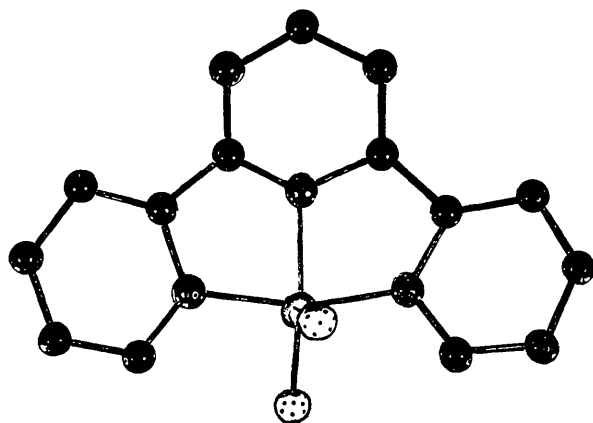


Fig. 3. The shape of the molecule of Co(terpy)Cl_2 - a scale model.

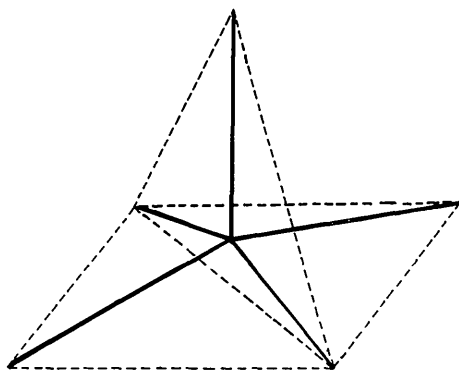


Fig. 4. The relation between tetragonal pyramidal and trigonal bipyramidal coordination.

the 'basal' chlorine atom [Cl(1)] from the 'basal' plane increases markedly from $\beta\text{-Co(paphy)Cl}_2$ to Zn(terpy)Cl_2 ; in the former it may be regarded as a slight distortion, but in the other two complexes it is so great that it is difficult to reconcile this with the concept of a basal tetragonal plane.

It has been repeatedly pointed out that in five-coordinate complexes, the energy differences involved between trigonal bipyramidal and tetragonal pyramidal structures are very small and that, in fact, the geometrical features of the two types of stereochemistry are not very different. Nevertheless, having made this point, most authors then proceed to classify even distorted five-coordinate structures as tending to conform to a greater extent to one or the other of the idealized geometries in accordance with certain criteria, such as equivalence of axial bond lengths, etc.

If the magnitude of the mean angular deviations from the idealized models is to be taken as a measure of the extent to which the stereochemistry of the three complexes approaches one or the other of the idealized polyhedra, then it is found [Table 7 (a)] that all three of the complexes approach a square-pyramidal model with an angle of 99.4° * between axial and basal bonds to a greater extent than they do the trigonal bipyramidal one. However, it could be argued that the very fact that the metal atom in this model is raised above the basal plane is in itself a distortion in the direction of trigonal bipyramidal geometry, since such an arrangement may equally well be regarded as a distorted trigonal bipyramid, such that the axial bonds are bent at the metal atom (Fig. 4), a condition which in these complexes is necessarily brought about by the geometry of the terdentate ligands.

Table 7(b) compares the angular deviations of the three complexes from the idealized trigonal bipyramid with those from a square pyramid in which the metal atom lies in the basal plane. From this point of view it might be argued that Zn(terpy)Cl_2 is $(1 - \frac{4.6}{12.6}) \times 100\% = 62\%$ trigonal-bipyramidal in character, while $\beta\text{-Co(paphy)Cl}_2$ is 61% tetragonal-pyramidal in character and the stereochemistry of Co(terpy)Cl_2 lies just half way between these two extremes.

The configuration of the ligand atoms in the three complexes brings to light another interesting point of distinction between them.

* The mean value of the Cl(2)-M-N angles in the three complexes.

Table 6. Displacement of metal and basal chlorine atoms from the basal planes of Zn(terpy)Cl_2 , Co(terpy)Cl_2 and $\beta\text{-Co(paphy)Cl}_2$

Compound	Zn(terpy)Cl_2	Co(terpy)Cl_2	$\beta\text{-Co(paphy)Cl}_2$
Reference plane through	middle ring	N(1), N(2), N(3)	planar ligand
Distance of metal atom 'above' the plane (\AA)	0.39	0.35	0.39
Distance of Cl(1) 'below' the plane			
(i) in \AA	0.62	0.45	0.17
(ii) expressed as a fraction of a bond length	0.28	0.20	0.07

Both free ligand molecules are presumably planar, like uncoordinated 2,2'-bipyridine (Merritt & Schroeder, 1956), but while the coordinated paphy ligand is reported to remain strictly planar, this is not the case in the two terpyridine complexes both of which experience some rotation about the single bonds joining the outer rings to the central ring; however this rotation produces different orientations of the rings relative to each other and to the metal atom, in the two complexes. The planes of all three pyridine rings in Co(terpy)Cl_2 point to the same side of the cobalt atom, while the planes of the external and central rings point towards opposite sides of the zinc atom in Zn(terpy)Cl_2 . This is, in fact, the only physically significant difference in the structures of the two terpyridine complexes.

It can be seen from Table 4 that, while the individual rings in Co(terpy)Cl_2 remain planar, the ligand as a whole shows significant deviations from planarity. Inspection of the second-last column in Table 4 shows that all the atoms in the external rings lie on one side of the mean plane through the middle ring (plane 5), *i.e.* the side away from the cobalt atom. The twisting of the rings with respect to each other is reflected in

dihedral angles of 4.9 and 2.4° respectively, between the planes of the external rings and the middle ring.

Presumably in order to attain the closest possible approach to the cobalt atom, the displacement of each of the nitrogen atoms from the ligand mean plane (plane 3) in the direction of the cobalt atom is greater than that of any of the carbon atoms in the given ring. The arrangement is illustrated in Fig. 5.

The inward bending of the external rings about the two C-C bonds joining them to the central ring, which has been observed in both Zn(terpy)Cl_2 and $\beta\text{-Co(paphy)Cl}_2$ is apparent in Co(terpy)Cl_2 also. This inward bending is reflected in the differences (both 0.43 \AA) between the C(4)-C(7) and N(1)-N(2) distances and between the corresponding C(9)-C(12) and N(2)-N(3) distances, and in the fact that the four external C-C bond angles of the type C(4)-C(5)-C(6) have a mean value which is 9° greater than the mean value of the four internal N-C-C bond angles of the type N(1)-C(5)-C(6).

It is apparent from the mode of packing of the molecules in the unit cell that no association or bonding interaction of any kind exists between molecules of

Table 7. Angular deviations of (i) Zn(terpy)Cl_2 , (ii) Co(terpy)Cl_2 , (iii) $\beta\text{-Co(paphy)Cl}_2$ from the idealized trigonal bipyramidal and square pyramidal models

(a) Angle between axial and basal bonds in the square-pyramidal model = 99.4° *											
Angle	Idealized values		Actual values			Deviations from idealized values					
	Trigonal bipyramidal	Square pyramidal	(i)	(ii)	(iii)	Trigonal bipyramidal			Square pyramidal		
			(i)	(ii)	(iii)	(i)	(ii)	(iii)	(i)	(ii)	(iii)
Cl(1)-M-Cl(2)	120°	99°	112°	111°	110°	8°	9°	10°	13°	12°	11°
Cl(1)-M-N(1)	90	88	97	97	100	7	7	10	9	9	12
Cl(1)-M-N(2)	120	161	143	150	157	23	30	37	18	11	4
Cl(1)-M-N(3)	90	88	101	102	102	11	12	12	13	14	14
Cl(2)-M-N(1)	90	99	102	102	99	12	12	9	3	3	0
Cl(2)-M-N(2)	120	99	105	99	94	15	21	26	6	0	5
Cl(2)-M-N(3)	90	99	98	96	100	8	6	10	1	3	1
N(1)-M-N(2)	90	88	74	74	74	16	16	16	14	14	14
N(2)-M-N(3)	90	88	73	76	75	17	14	15	15	12	13
N(1)-M-N(3)	180	161	145	147	(146)†	35	33	34	16	14	15
			Mean angular deviation			15	16	18	11	9	9

(b) Angle between axial and basal bonds in the square-pyramidal model = 90°												
Angle	Idealized values			Actual values			Deviations from idealized values					
	Trigonal bipyramidal	Square pyramidal	Difference	(i)	(ii)	(iii)	Trigonal pyramidal			Square pyramidal		
				(i)	(ii)	(iii)	(i)	(ii)	(iii)	(i)	(ii)	(iii)
Cl(1)-M-Cl(2)	120°	$\neq 90^\circ$	30°	112°	111°	110°	8°	9°	10°	22°	21°	20°
Cl(1)-M-N(1)	90	90		97	97	100						
Cl(1)-M-N(2)	120	$\neq 180$	60	143	150	157	23	30	37	37	30	23
Cl(1)-M-N(3)	90	90		101	102	102						
Cl(2)-M-N(1)	90	90		102	102	99						
Cl(2)-M-N(2)	120	$\neq 90$	30	105	99	94	15	21	26	15	9	4
Cl(2)-M-N(3)	90	90		98	96	100						
N(1)-M-N(2)	90	90		74	74	74						
N(2)-M-N(3)	90	90		73	76	75						
N(1)-M-N(3)	180	180		145	147	(146)†						
			Sum	120			46	60	73	74	60	47

* The mean value of the Cl(2)-M-N angles in the three complexes.

† Estimated value.

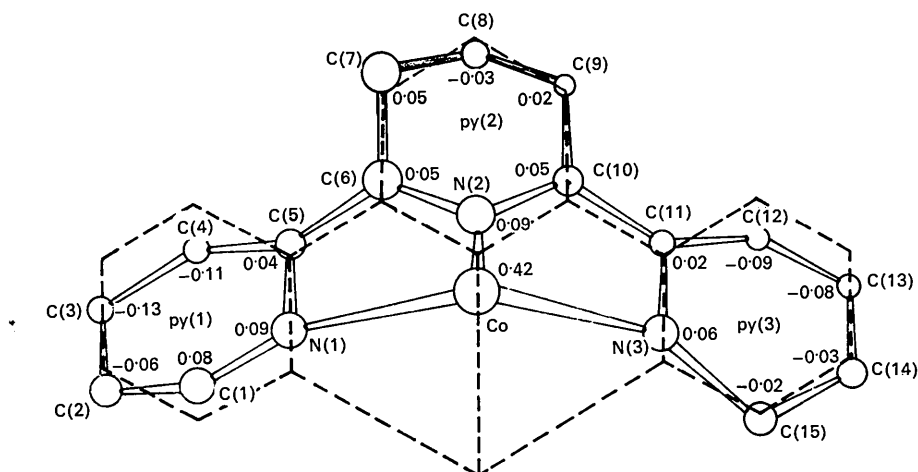


Fig. 5. The shape of the coordinated 2,2',2''-terpyridine ligand in $\text{Co}(\text{terpy})\text{Cl}_2$. The least-squares mean plane through the three rings is shown by dotted lines. The displacements (\AA) of atoms from the mean plane are shown.

$\text{Co}(\text{terpy})\text{Cl}_2$. Although there are no fewer than seventy-six approaches between non-bonded atoms in neighbouring molecules, whose distances from each other lie between 3.25 and 4.0 \AA , yet only two of these involve contacts between non-bonded atoms whose separation from each other is significantly shorter than the sum of their van der Waals radii,* *i.e.* 3.28 \AA between C(5) in (x, y, z) and C(14) in $(\bar{x}, \bar{y}, \bar{z})$, and 3.61 \AA between Co in (x, y, z) and C(12) in $(\bar{x}, \bar{y}, \bar{z})$. These are attributable solely to steric factors.

All computations in this work were carried out on the IBM 360/50 computer at the University of N.S.W. and the programs used included the Oak Ridge Fortran Least Squares and Function and Error (*ORFLS* and *ORFE*) programs, written by W.R. Busing, K. O. Martin and H. A. Levy, a three-dimensional Fourier synthesis program by B. Craven and a *Best least-*

squares plane program by S. Chu. All these programs were converted into FORTRAN IV-G by D. C. Craig, who also wrote the intensity reduction and structure factor programs used in this work. We should like to express our appreciation to these authors, for allowing us to use their programs.

References

- CORBRIDGE, D. E. C. & COX, E. G. (1956). *J. Chem. Soc.* p. 594.
- CRUICKSHANK, D. W. J. (1965). In *Computing Methods in Crystallography*. Ed. J. S. ROLETT, Ch. 14, p. 114. New York: Pergamon Press.
- DANCE, I. G., GERLOCH, M., LEWIS, J., LIONS, F. & STEVENS, F. S. (1966). *Nature, Lond.* **210**, 298.
- EINSTEIN, F. W. B. & PENFOLD, B. R. (1966). *Acta Cryst.* **20**, 924.
- FIGGIS, B. N., GERLOCH, M. & MASON, R. (1964). *Acta Cryst.* **17**, 506.
- GERLOCH, M. (1966). *J. Chem. Soc. A*, p. 1317.
- GILLESPIE, R. J. (1963). *J. Chem. Soc.* pp. 4672, 4679.
- HARRIS, C. M., LOCKYER, T. N. & STEPHENSON, N. C. (1966). *Austr. J. Chem.* **19**, 1741.
- HÖNL, H. (1933a). *Z. Phys.* **84**, 1.
- HÖNL, H. (1933b). *Ann. Phys.* **18**, 625.
- International Tables for X-ray Crystallography* (1962). Vol. II. Birmingham: Kynoch Press.
- JAMES, R. W. (1954). *The Optical Principles of the Diffraction of X-rays, Appendix III*, pp. 608–610. London: Bell.
- JUDGE, J. S., REIFF, W. M., INTELLE, G. M., BALLWAY, P. & BAKER, W. A., JR. (1967). *J. Inorg. Nucl. Chem.* **29**, 1711.
- LIONS, F., DANCE, I. G. & LEWIS, J. (1967). *J. Chem. Soc. A*, p. 565.
- MERRITT, L. L., JR & SCHROEDER, E. D. (1956). *Acta Cryst.* **9**, 801.
- MUETTERTIES, E. L. & SCHUNN, R. A. (1966). *Quart. Rev. Chem. Soc. Lond.* **20** (2), 245.
- PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithica: Cornell Univ. Press.
- * The van der Waals radii for the carbon and nitrogen atoms in the pyridine rings were taken as 1.70 \AA , *i.e.* the half thickness of an aromatic ring, according to Pauling (1960). The van der Waals radius of chlorine (1.80 \AA) was obtained from the same source.
- The van der Waals radius of cobalt(II) was estimated as follows:
- Using a value of 0.99 \AA for the covalent radius of chlorine (Pauling, 1960) the covalent radius of Co^{II} in this complex was estimated as 1.30 \AA , from the mean value of the two Co–Cl bond distances. This value lies between 1.32 and 1.25 \AA , which are the estimated values for the octahedral and tetrahedral radii of Co^{II} respectively. (Pauling, 1960; Figgis, Gerloch & Mason, 1964). The van der Waals radius was then estimated as 2.1 \AA , in accordance with Pauling's observation that the van der Waals radius of an element or ion is generally 0.80 ± 0.05 \AA greater than the corresponding single-bond covalent radius.
- A similar argument based on the observed Co–N bond distances, leads to values for the covalent and van der Waals radii of cobalt(II), which are from 0.05–0.10 \AA greater than those quoted above.