

119. Five-covalent Terpyridyl Complexes of Bivalent Metals. Part I. The Stereochemistry of the Zinc, Cadmium, and Copper Compounds.

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The structure of terpyridylzinc chloride has been investigated by three-dimensional X-ray analysis in sufficient detail to determine its main stereochemical features. The lattice is molecular, the zinc atom in each Zn(terpy)Cl_2 molecule being linked in a distorted trigonal bipyramid to five atoms, three nitrogens at 2.2 Å and two chlorines at 2.29 Å. The distortion consists chiefly in a deflection of the two axial bonds of the bipyramid to accommodate the terpyridyl molecule, the external bonds of which are also deflected. These deflections are all in the plane of the terpyridyl molecule, which remains flat; thus, approximately the complex has two planes of symmetry intersecting in a two-fold axis which passes through the zinc atom and bisects both the central pyridine ring and the ClZnCl angle.

The corresponding cadmium and copper compounds are isomorphous with the zinc compound and although they have not been investigated in such detail there is no doubt that their structures are essentially the same. The copper compound contains two molecules of water of crystallisation accommodated apparently in holes in the structure which remain empty (and are possibly smaller) in the anhydrous zinc and cadmium lattices.

MORGAN and BURSTALL (*J.*, 1937, 1649) prepared a number of compounds of the type M(terpy)X_2 where $\text{M} = \text{Ag, Cu, Pd, Pt, Zn, Cd, and Hg}$, $\text{terpy} = \text{ter-2-pyridyl}$, and X is a univalent anion. The copper, palladium, and platinum chlorides were hydrated and might conceivably therefore contain octahedral complexes, but the others were anhydrous and were formulated tentatively by Morgan and Burstall as $[\text{M(terpy)X}]\text{X}$ which suggests a planar distribution of four valencies around M since the terpyridyl could hardly be distorted enough to span three tetrahedral positions. However, there were clearly several other possibilities to consider such as a tetrahedral configuration involving only two nitrogen atoms of the terpyridyl molecule, and these could best be discriminated by X-ray analysis, since the insoluble nature of the compounds made it difficult to investigate their properties in solution. We have now examined a large number of metal terpyridyl compounds by means of X-rays and the present paper gives the stereochemical results for Zn(terpy)Cl_2 and the corresponding cadmium and copper compounds, which we find to be five-coordinated molecular complexes.

The crystallographic constants for these and for two iodides are given in Table I, from

TABLE I. Crystallographic data for compounds $\text{MX}_2(\text{terpy})$.

M X	Form I; space-group Ia or $I2/a$.				Form II; space-group $P2_1/a$.		
	Zn	I	Cd	I	Zn	Cd	Cu *
a (Å)	13.95	14.05	14.02	14.09	16.21	16.42	16.20
b (Å)	9.12	9.62	9.35	9.92	8.25	8.22	8.26
c (Å)	11.48	11.73	11.57	11.72	10.97	11.15	10.66
β	96°	95°	96°	96°	93.5°	93°	95°
$d_{\text{calc.}}$	1.71	—	1.82	—	1.70	1.84	1.88
$d_{\text{obs.}}$	1.72	—	1.82	—	1.69	1.84	1.86
n	4	4	4	4	4	4	4

The accuracy of the above cell dimensions is about $\frac{1}{2}\%$.

* This compound is a dihydrate, $\text{CuCl}_2(\text{terpy}) \cdot 2\text{H}_2\text{O}$.

which it will be seen that the zinc and the cadmium compound are isodimorphous, and that notwithstanding the presence of two molecules of water of crystallisation, the copper compound appears to be isomorphous with the second form of the anhydrous zinc and cadmium compounds.

These results suggest very strongly that the compounds are monomeric with four molecules of M(terpy)X_2 per unit cell. An arrangement of two molecules of $[\text{M(terpy)X}_2]_2$ per unit cell

is not permitted by the symmetry of the space-groups Ia and $I2/a$ and while it would be possible in the space-group $P2_1/a$ the similarity of cell dimensions and the easy inter-convertibility by recrystallisation of forms I and II suggest that they are simple isomorphs of the same molecular structure differing only in the manner of packing in the crystals. The molecules being assumed to be monomeric, the space-group symmetry does not however discriminate between molecules $[M(\text{terpy})X_2]$, salts $[M(\text{terpy})X]X$, and continuous structures $[M(\text{terpy})X_2]_\infty$ in which the metal atoms achieve octahedral co-ordination by sharing X atoms. If the space-group of form I is $I2/a$ the metal atoms must lie on two-fold axes, and this would exclude continuous structures and also structures in which only two of the three terpyridyl nitrogen atoms were co-ordinated to the metal: in spite of the absence of pyroelectric effects in the liquid-air test, form I may however have the lower symmetry Ia in which case no symmetry requirements are imposed in the molecule by the space-group.

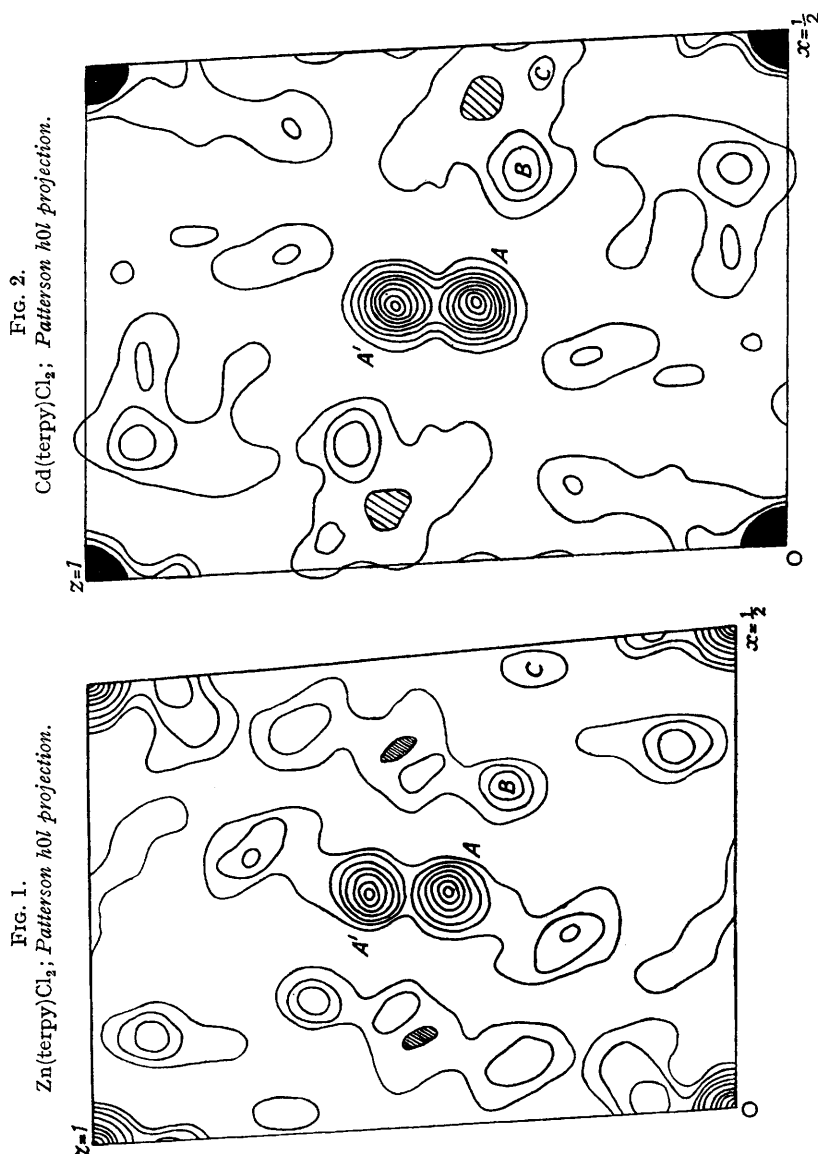
After a preliminary survey of the problem we decided to carry out a structure analysis on form II of $Zn(\text{terpy})Cl_2$ using data from the isomorphous $Cd(\text{terpy})Cl_2$ to resolve ambiguities where necessary. The intensities of 1934 hkl reflections from the zinc compound were estimated visually and another 561 which should have been observed were recorded as too small to measure; about 850 of the strongest reflections were used to carry out the analysis described below. About 150 $h0l$ intensities from the cadmium compound were measured. The structure amplitudes were calculated in the usual way and Patterson projections for the $h0l$ zones were obtained (Figs. 1 and 2); that for the cadmium compound is probably less accurate because of higher absorption and because fewer terms were used in the synthesis (152 as against 186 for the zinc compound). The large peaks A corresponding to the metal-metal vectors were readily identifiable in these projections, and the co-ordinates of one of the chlorine atoms were found by noting that the three peaks A , B , and C were nearly equally spaced in a straight line and were of descending order of magnitude as would be expected for $Zn-Zn$, $Zn-Cl_I$ and Cl_I-Cl_I vectors. The position of the second chlorine atom could not at first be recognised and it was assumed that the $Zn-Cl_{II}$ peak fell too close to the $Zn-Zn$ peak A to be resolved; this was later found to be the case, and in the $h0l$ Patterson projection for the copper compound (Fig. 3) the resolution is sufficient to separate the peaks so that another equally spaced linear triad ADE can be recognised corresponding to the $Cu-Cu$, $Cu-Cl_{II}$, and $Cl_{II}-Cl_{II}$ vectors.

Assuming that the terpyridyl molecule lay on the side of the zinc atom remote from Cl_I , we were able to show by means of models that the x and z co-ordinates for Zn (0.12, 0.22) and Cl_I (0.24, 0.14) were compatible with various reasonable arrangements of the molecules in the crystal lattice. We therefore calculated a Fourier synthesis with 63 $h0l$ terms, allocating signs to the coefficients determined by the zinc and chlorine contributions, and assuming Cl_{II} to have approximately the same (x, z) co-ordinates as Zn. The map of this synthesis showed Zn and Cl_I in almost the same positions as had been deduced from the Patterson synthesis, but Cl_{II} was clearly resolved with co-ordinates (0.13, 0.35) which thus gave rise in the Patterson synthesis to a $Zn-Cl_{II}$ peak coinciding, not with the $Zn-Zn$ peak A , but with the symmetrically related $Zn-Zn$ peak A' . With this information it was found possible to account for nearly all the main features of the Patterson syntheses. The (x, z) co-ordinates of the three heavy atoms were next determined more accurately by means of a Harker $P(x\frac{1}{2}z)$ synthesis of about 800 hkl terms and this synthesis also showed a weak $Zn-Cl_I$ peak, indicating that Zn and Cl_I had approximately the same y co-ordinates. This result showed that Zn and Cl_I were about 2.3 Å apart and therefore bonded together, and it also showed that the structure could not consist of chains of octahedral complexes since the only way of achieving this would be through linking Cl_{II} atoms along the b -axis, and the distance between successive zinc atoms in this direction is much too great for such binding.

In order to carry the analysis further, a comparison of corresponding $h0l$ intensities for the zinc and cadmium compounds was made and the signs of a few structure factors were determined in this way, but the method was not pursued because (a) the high absorption factor (160 cm.^{-1}) for the cadmium compound reduced the accuracy of the intensity measurements and (b) the Patterson syntheses showed that the assumption that the atomic positions were exactly the same in the two substances was not strictly valid. Attempts to determine signs by means of Harker-Kasper inequalities (*Acta Cryst.*, 1948, 1, 70) were not successful,

but successive synthesis and recalculation of structure factors enabled us to obtain a $h0l$ projection of 180 terms in which two of the three pyridine rings were resolved, the third being obscured by the corresponding centrosymmetrically related ring of another molecule (Fig. 4).

The y co-ordinates were determined by Patterson three-dimensional line syntheses,



$hk0$ Patterson and Fourier projections, and finally by a section projection (Booth, *Trans. Faraday Soc.*, 1945, **41**, 434) between $z = 0$ and $z = \frac{1}{2}$. At this stage it was clear that the molecule had a somewhat distorted trigonal bipyramidal structure which would not be fully resolved in any projection, and the final co-ordinates were therefore determined by means of a series of three-dimensional Fourier sections and lines. The first stage consisted in determining the signs of about 850 hkl structure factors; in many cases these were determined by the contributions of the heavy atoms, but where necessary the contributions

of the carbon and nitrogen atoms were calculated. The electron density was then calculated over seven sections of the unit cell from $y = 1/30$ to $y = 7/30$, the calculation in each section extending from $x = 0$ to $x = 1$ and $z = 0$ to $z = 1$ at intervals of $1/60$ in both

FIG. 4.
Comparison of $h0l$ Fourier projections of Zn(terpy)Cl_2
and Cu(terpy)Cl_2

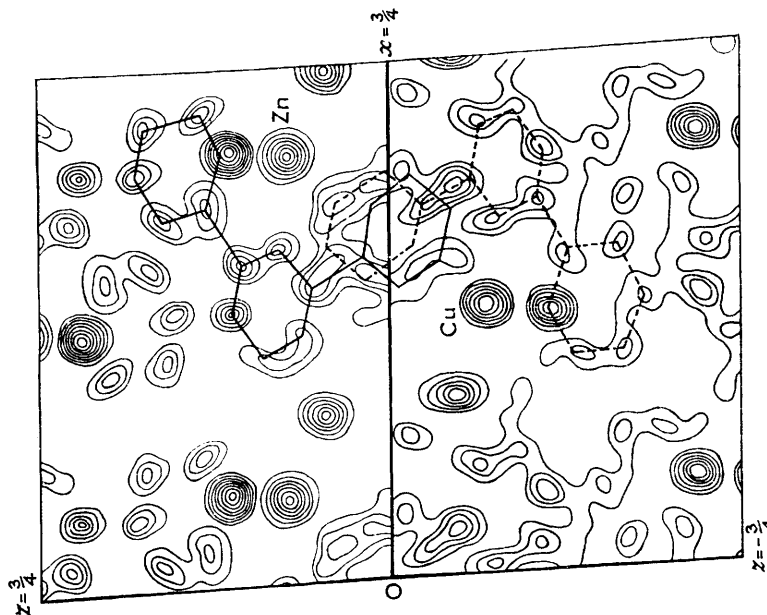
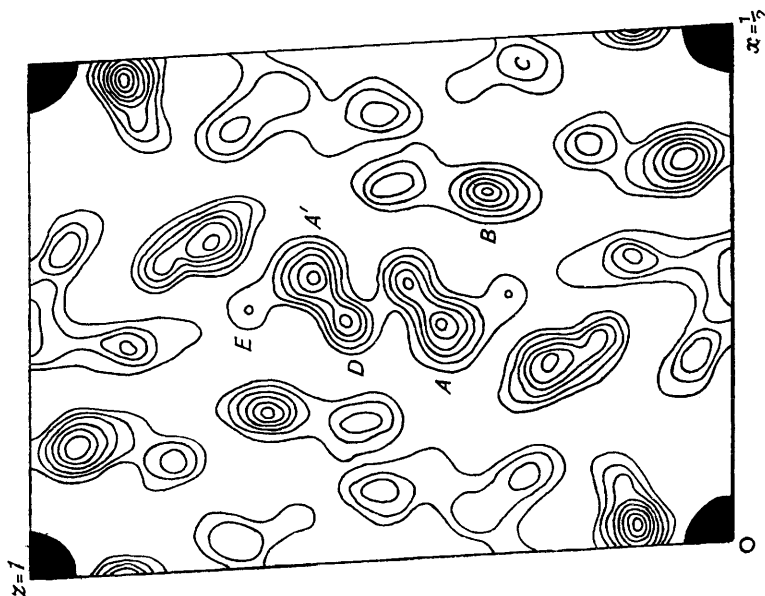


FIG. 3.
 Cu(terpy)Cl_2 ; Patterson $h0l$ projection.



directions. The summations were carried out by Hollerith methods (Cox and Jeffrey, *Acta Cryst.*, 1949, 2, 65; Greenhalgh, *Proc. Leeds Phil. Soc.*, 1950, 5, 301) and occupied about 12 days. A composite map of the result is shown in Fig. 5. The y -co-ordinates were found by calculating the electron densities along lines parallel to the b -axis and passing through the maxima in the (x, z) maps. The results (in thousandths of the cell edges) are given in Table 2, and the bond lengths and bond angles around the zinc atom in Table 3.

TABLE 2. Atomic co-ordinates in $\text{ZnCl}_2(\text{terpy})$.

	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
Zn	118	097	217	C ₈	827	000	261
Cl _I	239	027	135	C ₉	858	093	170
Cl _{II}	133	323	334	C ₁₀	935	107	155
C ₁	186	844	405	C ₁₁	971	186	050
C ₂	184	760	523	C ₁₂	925	263	969
C ₃	108	707	536	C ₁₃	950	366	874
C ₄	025	767	473	C ₁₄	033	377	880
C ₅	040	850	386	C ₁₅	077	293	975
C ₆	966	917	325	N ₁	124	900	350
C ₇	889	913	350	N ₂	994	030	236
				N ₃	051	203	057

TABLE 3. Bond lengths (Å) and bond angles.

Zn-Cl _I	2.28 ₃	Zn-N ₂	2.11	Cl _I ZnCl _{II} ...	111°	N ₂ ZnN ₃ ...	72°
Zn-Cl _{II}	2.29 ₅	Zn-N ₃	2.34	N ₁ ZnN ₂ ...	79	N _{1,3} ZnCl ...	100 (average)
Zn-N ₁	2.19						

Since the primary object in determining the structure was to elucidate the stereochemistry of the metal atom, the analysis has not yet been carried far enough to enable standard deviations of bond lengths to be calculated, but from the variations of the co-

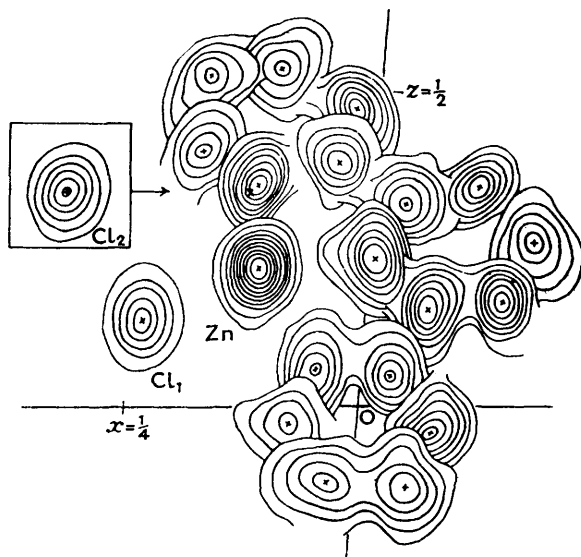


FIG. 5.
 $\text{Zn}(\text{terpy})\text{Cl}_2$; composite three-dimensional Fourier diagram.

ordinates during the later stages it seems reasonable to assign approximate probable errors of ± 0.03 Å and ± 0.1 Å to the mean Zn-Cl and Zn-N distances respectively, and $\pm 2^\circ$ to the ClZnCl angle. (It should be noted that the analysis of this stage does not distinguish with certainty between carbon and nitrogen atoms; the three atoms of the terpyridyl molecule bonded to zinc can, however, be assumed to be nitrogen and not carbon.) A list of observed and calculated structure factors is given in Table 4; the reliability factor *R* is about 25%.

The structure of one molecule is shown in Fig. 6, and the arrangement of the molecules in the lattice in Fig. 7. The bond lengths and the general arrangement of the molecules show quite clearly that the molecule is a five-co-ordinated complex and that there is no possibility of either polymerisation or ionisation (this does not of course exclude the possibility of the Zn-Cl bonds' having some ionic character, although their length, 2.29 Å, is almost exactly what would be expected for covalent bonds). The terpyridyl molecule is flat within experimental error and lies in a plane approximately at right angles to the plane of the Zn-Cl bonds; thus approximately the complex has two planes of symmetry intersecting in a two-fold axis which bisects the ClZnCl angle and the central pyridine ring. The

configuration of the five bonds to the zinc atom is that of a distorted trigonal bipyramid; the two axial bonds are deflected from the ideal position to accommodate the terpyridyl molecule, and the deflection appears to be shared between the zinc and the terpyridyl since, as can be seen from Figs. 5 and 6, neither the two outer N–Zn bonds nor the two pyridine–pyridine bonds are in line with the corresponding ring diameters, all having been deflected inwards. This is understandable, but there seems to be no obvious explanation at present for the significant deviation of the ClZnCl angle from 120° ; nevertheless, the configuration is much closer to a trigonal bipyramid than to any other recognised arrangement, and in particular it is certainly not that of a tetragonal pyramid.

The intermolecular distances are normal and do not call for any special comment except to note that neither the zinc nor the chlorine atoms have any atoms in other molecules near

FIG. 6. $\text{Zn}(\text{terpy})\text{Cl}_2$; bond lengths and bond angles.

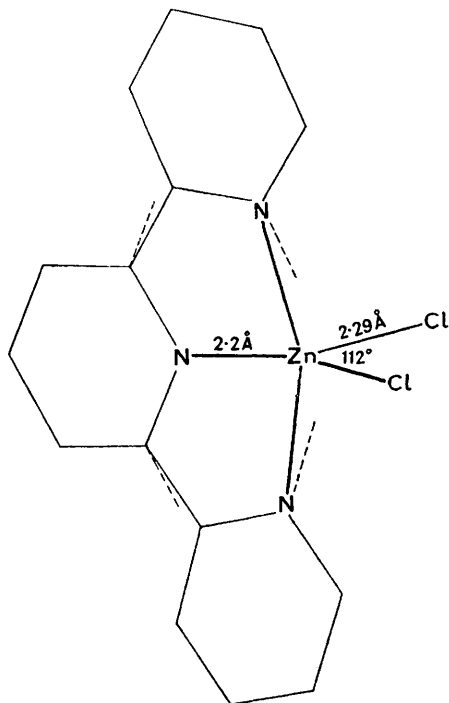
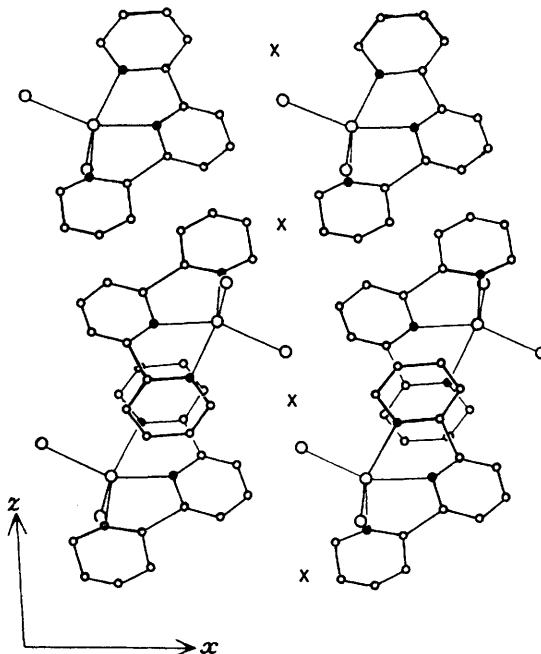


FIG. 7. $\text{Zn}(\text{terpy})\text{Cl}_2$; arrangement of molecules in the lattice.



enough to suggest anything but van der Waals forces between them; the nearest neighbour to zinc is a carbon atom at 4.1 \AA and the shortest Cl . . . Cl distance is 5.1 \AA . The packing of the molecules is good except along the a -axis where there are some gaps the projected positions of which are shown approximately at X in Fig. 7.

No detailed analysis has been made of the cadmium compound, but the similarity of the Patterson projection (Fig. 2) to that of the zinc compound (Fig. 1) leaves no doubt that its structure is essentially the same. The same conclusion could be drawn with regard to the copper compound (Fig. 3) but because of its rather different properties (higher solubility, reaction for chloride ion, water of crystallisation), and because the stereochemistry of copper does not normally show much resemblance to that of zinc, we have carried the analysis further. Proceeding in the same way as with the zinc compound, we have made $h0l$ and $hk0$ Fourier projections; comparison of the $h0l$ projection with that for the zinc compound at about the same stage of the analysis (Fig. 4) leaves no doubt as to the very close similarity of their structures. The approximate co-ordinates derived from these projections, and the bond distances and angles calculated from them, are only slightly different from the corresponding figures for the zinc compound. The analysis has not yet been

TABLE 4. Observed and calculated structure factors for Zn(terpy)Cl₂.

Note: These figures are on one-quarter of the absolute scale. Calculations were made with the *f* values given in the International Tables, with a temperature factor *B* = 1.0.

<i>hkl</i>	F (obs.)	F (calc.)	<i>hkl</i>	F (obs.)	F (calc.)	<i>hkl</i>	F (obs.)	F (calc.)	<i>hkl</i>	F (obs.)	F (calc.)
200	22	29	809	14	21	506	21	-20	1020	0	-1
400	29	-27	1001	37	-33	507	9	-11	1220	7	4
600	14	-9	1002	11	-6	508	17	17	1420	5	-3
800	31	27	1003	14	9	509	3	11	1620	4	4
1000	8	-6	1004	24	26	5010	10	-14	1820	4	7
1200	18	-18	1005	16	13	501	19	-13	240	13	-11
1400	14	-14	1006	~10	-13	502	46	-42	440	28	23
1600	16	16	1007	10	-12	503	7	4	640	3	-1
1800	3	1	1008	12	12	504	7	4	840	9	-10
2000	7	-8	1009	3	-4	505	12	4	1040	6	-2
			1201	7	8	506	7	6	1240	19	22
001	8	10	1202	10	11	507	14	-12	1440	3	3
002	24	-20	1203	4	6	508	0	-2	1640	7	-4
003	15	-10	1204	13	14	509	17	22	1840	4	4
004	6	-4	1205	9	-11	5010	10	-11	260	8	-7
005	11	8	1206	5	-13	1001	20	14	460	13	14
006	17	12	1207	16	21	1002	0	0	660	5	4
007	20	17	1208	2	6	1003	10	-13	860	6	-5
008	3	0	1401	19	17	1004	8	9	1060	6	-9
009	19	18	1402	5	-2	1005	4	8	1260	5	8
0010	5	-10	1403	0	1	1006	0	-4	1460	4	4
0011	14	-20	1404	0	2	1007	—	-9	280	0	-1
0012	4	-8	1405	4	4	1008	10	-16	480	5	4
			1406	11	22	1009	10	10	*110	3	35
020	0	2	1407	5	3	10010	8	14	310	18	-15
040	14	-12	1408	9	-15	1201	6	3	510	2	-5
060	7	-6	1601	7	9	1202	14	14	710	9	5
080	0	2	1602	0	5	1203	14	-13	910	24	17
0100	10	12	1603	5	-4	1204	14	-13	1110	8	-6
			1604	9	-8	1205	—	1	1310	6	-6
201	27	-21	1605	6	9	1206	7	8	1510	5	-6
202	17	13	1606	3	7	1207	13	16	1710	13	13
203	23	23	1607	8	-13	1208	2	9	130	13	4
204	13	12	1801	10	-12	1209	11	-21	330	9	-8
205	1	4	1802	10	-10	12010	6	-5	530	2	0
206	26	-22	1803	2	-6	1401	14	-11	730	7	3
207	12	-9	1804	7	11	1402	9	7	930	9	5
208	18	13	1805	7	10	1403	16	18	1130	5	-6
209	5	7	1806	9	-11	1404	0	-2	1330	11	11
2010	14	-15	2001	2	2	1405	8	-3	1530	0	—
401	19	15	2002	2	-2	1406	12	-11	1730	0	—
402	23	24	2003	2	4	1407	0	4	150	21	-17
403	13	-4	201	37	43	1408	9	6	350	22	19
404	18	-12	202	3	2	1409	0	2	550	30	30
405	40	-31	203	0	-1	14010	6	-11	750	13	-13
406	18	-10	204	8	7	1501	10	-8	950	16	-16
407	29	-27	205	5	3	1502	22	-27	1150	4	6
408	11	14	206	24	19	1503	4	-3	1350	11	11
409	17	-17	207	17	-12	1504	10	11	1550	8	-12
4010	3	3	208	24	-23	1505	5	7	1750	4	-5
601	13	8	209	0	-6	1506	3	-3	170	8	-7
602	9	-4	2010	12	19	1507	2	1	370	0	-1
603	26	-16	401	16	13	1508	0	-3	570	7	4
604	13	7	402	25	29	1509	5	9	770	6	-6
605	8	-1	403	25	-16	1801	12	13	970	4	-3
606	14	11	404	20	-20	1802	3	-7	1170	6	7
607	0	0	405	11	-7	1803	6	-8	1370	7	9
608	22	-24	406	0	-2	1804	0	10	190	5	7
609	4	-8	407	21	23	2001	7	-1	380	6	-10
6010	14	18	408	7	9	2002	8	8	590	7	7
801	12	8	409	~10	-15	2003	5	-11	210	13	-12
802	18	-12	4010	5	-9	2004	8	-10	410	2	-1
803	13	-14	501	45	-45				610	28	26
804	3	-4	502	3	0	220	24	-18	810	8	5
805	11	7	503	35	32	420	14	8	1010	18	-15
806	10	7	504	8	5	620	5	-6	1210	3	7
807	19	-19	505	5	-6	820	22	15	1410	8	6
808	0	1									

* This discrepancy is not understood; it may in part be due to extinction.

TABLE 4. (Continued.)

<i>hkl</i>	F (obs.)	F (calc.)	<i>hkl</i>	F (obs.)	F (calc.)	<i>hkl</i>	F (obs.)	F (calc.)	<i>hkl</i>	F (obs.)	F (calc.)
1610	0	2	049	12	-10	343	8	-11	531	5	5
1810	8	-4	0410	4	-7	344	8	-6	332	17	-13
230	20	-20	061	5	-1	211	6	-1	333	17	-14
430	0	-4	062	11	7	212	23	23	334	12	11
630	10	11	063	10	12	213	13	-6	121	7	4
830	8	9	064	12	14	214	5	-3	122	51	-49
1030	18	-17	065	13	-11	411	25	24	123	9	-6
1230	13	-14	066	0	-2	412	9	-6	124	38	28
1430	3	1	067	10	13	413	13	-10	321	2	-5
1630	10	11	081	3	3	414	16	-12	322	3	-2
250	0	2	082	0	0	221	13	-12	323	27	-25
450	0	-1	083	11	-12	222	24	-19	324	6	1
650	9	-7	0101	4	5	223	11	9	141	12	-13
850	4	4	0102	6	-11	224	22	20	142	14	-9
1050	0	—	011	19	-25	225	2	-4	143	19	11
1250	0	—	012	15	-7	421	6	2	144	16	10
1450	0	—	013	23	16	422	7	5	341	11	17
1650	7	11	014	5	6	423	13	8	342	12	-10
270	0	1	015	4	-1	424	11	-11	343	12	-11
470	2	4	016	9	-6	425	8	-12	344	10	11
670	6	-6	017	9	-9	621	10	5	211	16	16
870	3	-1	018	14	15	622	0	5	212	30	-28
1070	2	5	019	4	3	623	8	5	213	22	15
1270	8	16	0110	3	-4	624	5	4	214	3	2
290	7	12	031	17	-18	625	15	17	411	22	30
490	4	5	032	25	-26	821	23	22	412	7	-5
690	5	-4	033	21	20	822	0	2	413	15	-9
120	8	-4	034	29	23	823	13	-10	414	8	-6
320	7	-5	035	15	-10	241	14	17	221	24	-18
520	0	-1	036	12	-13	242	3	6	222	3	1
720	23	21	037	0	2	243	5	-4	223	2	2
920	0	1	051	6	-5	244	9	-1	224	8	-7
1120	12	-10	052	14	-11	441	2	3	225	13	13
1320	7	-5	053	4	-5	442	16	-10	421	6	2
1520	9	11	054	13	12	443	15	-9	422	7	-1
1720	4	9	055	1	2	444	0	-1	423	4	-5
140	22	-21	056	0	6	641	18	-22	424	13	-12
340	9	-11	057	13	13	642	15	-11	425	5	-8
540	10	3	071	—	—	643	8	7	621	1	-1
740	15	11	072	8	5	644	13	15	622	3	-1
940	13	-11	073	14	-13	841	7	-2	623	17	16
1140	12	-10	074	14	-18	842	8	8	624	19	20
1340	0	-1	075	10	12	843	2	0	625	10	-6
1540	8	7	111	14	-16	844	10	-10	821	6	0
160	4	1	112	35	-40	261	6	3	822	4	-2
360	9	11	113	10	-7	262	13	14	823	14	-10
560	12	-17	114	28	24	263	11	-11	824	7	3
760	8	-1	115	17	17	264	11	-8	825	9	5
960	0	-2	311	6	-6	461	13	11	241	23	-27
1160	7	7	312	19	17	462	13	-8	242	9	3
180	6	3	313	24	30	463	14	-11	243	21	18
380	11	14	314	13	7	464	0	1	244	18	22
580	7	-12	315	25	-28	—	—	—	441	1	1
760	0	—	511	6	-5	111	15	14	442	19	-20
—	—	—	512	7	7	112	14	4	443	11	-7
—	—	—	513	7	-4	113	3	2	444	7	7
021	12	13	514	11	-11	114	10	-5	641	6	8
022	41	-36	515	1	0	115	21	15	642	2	1
023	22	-19	121	20	-23	311	12	12	643	11	-9
024	8	-7	122	39	-26	312	5	8	644	4	3
025	9	5	123	25	26	313	0	-1	841	5	-1
026	5	-6	124	3	3	314	9	9	842	9	8
027	6	5	321	2	2	315	14	13	843	9	-6
028	6	10	322	18	20	511	8	-2	844	18	-15
029	5	6	323	10	-7	512	7	6	261	5	-4
041	8	5	324	34	-31	513	14	19	262	7	-7
042	18	19	141	15	-14	514	8	-1	263	12	14
043	0	0	142	17	12	515	4	-2	264	12	13
044	11	7	143	10	9	131	3	5	461	10	8
045	13	-14	144	22	16	132	5	2	462	12	-10
046	0	0	145	21	19	133	6	12	463	13	-16
047	12	13	341	21	19	134	11	5	464	8	7
048	0	5	342	13	11	—	—	—	—	—	—

carried far enough to locate the water molecules, which have a comparatively small effect on the intensities, but no evidence has been found contrary to the view that they occupy the cavities *X* (Fig. 7). It is reasonably certain that they cannot in any case be co-ordinated to the copper atom since the disposition of the two chlorine atoms and the terpyridyl molecule in a trigonal bipyramid around the central atom would prevent the water from coming closer than $3\frac{1}{2}$ —4 Å to the latter. It is proposed to make a more detailed analysis to determine the bond lengths accurately, and in the course of this work it is hoped to locate the water molecules with certainty.

The trigonal bipyramidal arrangement of dsp^3 bonds was predicted by Kimball (*J. Chem. Phys.*, 1940, **8**, 188) and is known to occur in a small number of compounds, but this appears to be the first example of this configuration for zinc, copper, or cadmium or involving a chelate group. On the other hand Daudel and Bucher (*J. Chim. phys.*, 1945, **42**, 6) have suggested that when the *d* orbitals involved in hybridisation have a lower principal quantum number than the *s* and *p* orbitals (as in Ni^{II} and perhaps Cu^{II}) the configuration should be that of a tetragonal pyramid (with the central atom in the plane of the base and not above it as suggested by Kimball for d^2sp^2 hybridisation), and Jensen and Nygaard (*Acta Chem. Scand.*, 1949, **3**, 474) have shown that the compound $NiBr_3 \cdot 2PEt_3$ almost certainly has this configuration. In our case it is to be expected that the zinc orbitals involved in binding will all be in the fourth quantum group, so that the conditions postulated by Daudel and Bucher do not apply and our results are in agreement with Kimball's theory. The case of the cadmium compound is precisely analogous.

It should be possible for cupric complexes to exist with the tetragonal pyramidal configuration corresponding to $3d4s4p^3$ hybridisation (although the fifth bond might be weak) and there is some evidence for the existence of the ion $[Cu(en)_2NH_3]^{++}$ which might be expected to have this structure. If, however, Daudel and Bucher's theory is accepted, our finding that $Cu(terpy)Cl_2$ is trigonal bipyramidal indicates that the hybridisation in this case is $4d4s4p^3$. The nature of the ligands no doubt has considerable influence, but it cannot be argued that the terpyridyl molecule has a "straight-jacket" effect since three bonds suitably disposed to co-ordinate with the three nitrogen atoms are available equally with either a trigonal or a tetragonal configuration of the central atom. It is possible that the energy difference between the two configurations is in many cases not very great, and precise identification of the factors which determine the configuration actually adopted in various circumstances can therefore probably not be made on the data available at present.

A detailed account of the structure of terpyridylcopper chloride and also an account of the crystallography of a number of other polypyridyl complexes will be published later.

EXPERIMENTAL

The zinc and cadmium compounds were supplied by the late Sir Gilbert Morgan and (the late) Dr. F. H. Burstall. The copper compound was prepared by Morgan and Burstall's method (*loc. cit.*).

Terpyridylzinc chloride was obtained from aqueous solutions in two crystalline forms, both monoclinic and both pale greenish-yellow, which were readily interconvertible by crystallisation. Crystals of form I were acicular combinations of $\{110\}$ and $\{011\}$ elongated parallel to $[c]$ and those of form II were prismatic combinations of $\{110\}$, $\{100\}$, $\{001\}$ and $\{20\bar{1}\}$ also elongated parallel to $[c]$. Both forms were diamagnetic and did not show pyroelectricity when tested in liquid air.

Terpyridylcadmium chloride had a darker colour than the zinc compound, and had a higher density (Table I) but otherwise resembled it closely in every respect.

Terpyridylcupric chloride dihydrate was obtained as bluish-green prisms which were very similar to form II of the zinc and the cadmium compound. Recrystallisation did not yield any other type of crystal. The crystals were paramagnetic.

Terpyridylzinc bromide and iodide were only very slightly soluble. A few small needles of form I were obtained by slow evaporation of aqueous solutions over a period of many weeks. No crystals of form II were obtained.

All X-ray photographs were taken with copper K_α radiation. The cell dimensions were determined by means of rotation and Weissenberg photographs and the intensity measurements were made by visual estimation on Weissenberg photographs. Three films were used for each

photograph, which was taken twice with exposures of 4 hr. and 32 hr. so that a set of six films was obtained for each crystal setting, covering a wide range of intensities. Developing, fixing, and washing of the films was done under controlled conditions. Visual estimation of the intensities was controlled by sets of calibration spots obtained from the actual crystals being examined. No corrections for absorption of X-rays in the crystal were made ($\mu = 56 \text{ cm.}^{-1}$ for the zinc compound) but errors were minimised by using equant crystals of appropriate size (about 0.3 mm.). The intensities were measured on an arbitrary scale, and the structure amplitudes calculated from them in the usual way and at a later stage put on the proper scale by comparison with calculated structure amplitudes.

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