# FIVE-COORDINATED 2,2′,2″-TERPYRIDYL COMPLEXES OF COBALT(II), MANGANESE(II), AND COPPER(II)*

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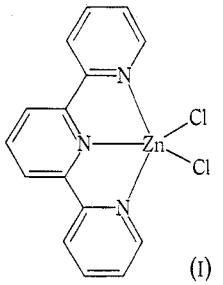
The chelating ability of 2,2′,2″-terpyridyl (terpy) was originally demonstrated by the classic chemical work of Morgan and Burstall.[1] Confirmation of the tridentate nature and virtual planarity of this ligand was provided by the structure of the zinc complex, $ZnCl_2$ terpy, determined by Corbridge and Cox[2] using single crystal X-ray diffraction methods. They found that each zinc atom was surrounded by a distorted trigonal bipyramidal arrangement of three nitrogen and two chlorine atoms (see (I)).



(I)

Einstein and Penfold[3] have recently carried out a least squares refinement of the data of Corbridge and Cox[2] and confirmed their original results with some small changes in bond distances, angles, and planarities.

Morgan and Burstall[1] originally proposed that the compounds $MCl_2$ terpy (M = $Cu^{II}$, $Pd^{II}$, $Pt^{II}$, $Zn^{II}$, $Cd^{II}$, and $Hg^{II}$) possessed structures involving the four-coordinated $[MCl\ terpy]^+$ species. It has been suggested[4] that in some cases 2,2′,2″-terpyridyl may function as a bidentate chelating agent.

The properties of various metal complexes of 2,2′,2″-terpyridyl have recently received further attention by a number of workers.[5–7] A systematic study of a number of mono- and bis-complexes have been recently completed in these laboratories[8] and evidence adduced to indicate that various mono-complexes of copper(II), cobalt(II), and manganese(II) contain five-coordinated metal atoms. To confirm this the crystallographic properties of the anhydrous chloro compounds $MCl_2$ terpy (M = Cu, Co, and Mn) have been examined to see if these compounds are isostructural with the corresponding zinc complex. Single crystals of the compounds were prepared by the slow dropwise addition of an ethanol solution of 2,2′,2″-terpyridyl to a boiling ethanol

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[1] Morgan, G. T., and Burstall, F. H., *J. chem. Soc.*, 1937, 1649.
[2] Corbridge, D. E. C., and Cox, E. G., *J. chem. Soc.*, 1956, 594.
[3] Einstein, F. W. B., and Penfold, B. R., *Acta crystallogr.*, in press.
[4] Brandt, W. W., Dwyer, F. P., and Gyarfas, E. C., *Chem. Rev.*, 1954, **54**, 972.
[5] Basolo, F., Gray, H. B., and Pearson, R. G., *J. Am. chem. Soc.*, 1960, **82**, 4200.
[6] Dwyer, F. P., and Broomhead, J. A., *Aust. J. Chem.*, 1961, **14**, 250.
[7] Hogg, R., and Wilkins, R. G., *J. chem. Soc.*, 1962, 341.
[8] Lockyer, T. N., Ph.D. Thesis, University of New South Wales, 1962.

solution containing a slight excess of the appropriate metal(II) chloride. The analytical results are shown in Table 1.

Single crystals of the compounds are invariably elongated along [001], except the copper compound which is elongated in a direction perpendicular to [010]. The diffraction data were recorded on films using Weissenberg and precession methods. The unit cell dimensions are listed in Table 2, and were measured from zero level precession photographs, and are considered to be accurate to 0·5%. The standard deviation in cell volume is thus 12 Å$^3$.

TABLE 1

ANALYSES (%)

| | | C | H | N | Metal | Cl |
|---|---|---|---|---|---|---|
| $CuCl_2(C_{15}H_{11}N_3)$ | Calc. | 49·0 | 3·0 | 11·4 | 17·3 | |
| | Found | 48·9 | 2·9 | 11·1 | 17·3 | |
| $ZnCl_2(C_{15}H_{11}N_3)$ | Calc. | 48·8 | 3·0 | 11·4 | | 19·2 |
| | Found | 48·7 | 3·1 | 11·4 | | 19·3 |
| $MnCl_2(C_{15}H_{11}N_3)$ | Calc. | 50·2 | 3·1 | 11·7 | | |
| | Found | 49·7 | 3·0 | 11·7 | | |
| $CoCl_2(C_{15}H_{11}N_3)$ | Calc. | 49·6 | 3·1 | 11·6 | 16·3 | |
| | Found | 49·4 | 3·2 | 11·2 | 16·2 | |

The compounds are obviously isomorphous. It is reasonable to assume that in each case the metal atom is bonded to the three nitrogen atoms of the terpyridyl molecule and to two chlorine atoms, so that the stereochemistry is that of a distorted trigonal bipyramid. Substantiating evidence arises from X-ray intensity statistics—

TABLE 2

UNIT CELL DIMENSIONS OF SOME 2,2′,2″-TERPYRIDYL COMPLEXES

Space group $P2_1/c$, 4 molecules per cell. Molecular symmetry 1

| Compound | Colour | $a$ (Å) | $b$ (Å) | $c$ (Å) | $\beta$ | $V$ (Å$^3$) | Ref. |
|---|---|---|---|---|---|---|---|
| $CuCl_2$ terpy,$2H_2O$ | green | 10·66 | 8·26 | 16·20 | 95° | 1421 | 2 |
| $CuCl_2$ terpy | green | 10·67 | 8·17 | 16·19 | 95° | 1406 | this work |
| $ZnCl_2$ terpy | light brown | 10·97 | 8·25 | 16·21 | 93·5° | 1464 | 2 |
| $ZnCl_2$ terpy | cream | 10·95 | 8·32 | 16·22 | 93·5° | 1474 | this work |
| $CdCl_2$ terpy | green–yellow | 11·15 | 8·22 | 16·42 | 93·0° | 1503 | 2 |
| $MnCl_2$ terpy | yellow | 10·97 | 8·25 | 16·35 | 94·0° | 1476 | this work |
| $CoCl_2$ terpy | green | 10·84 | 8·21 | 16·24 | 95·1° | 1439 | this work |

the distribution of intensities of the same reflection for different compounds is practically identical, so that the X-ray films become superimposable. Marked deviations from the above stereochemistry, such as the terpyridyl molecule acting as a bidentate, would cause the intensity distribution to change noticeably from that observed for the zinc or copper compounds. This is not the case. To test this assumption completely the structure of $CoCl_2$ terpy is being refined using three-dimensional single crystal X-ray data.

It is of interest to note that distorted trigonal–bipyramidal structures have been recently reported to occur in five-coordinated copper(II) complexes[9] such as iodobis-(2,2′-bipyridyl)copper(II) iodide[10] and in the dimers of bis(*N*-methylsalicylaldiminato)zinc(II), cobalt(II), and manganese(II).[11] The manganese(II) and cobalt(II) complexes are of the "high-spin" type, as is the case for the 2,2′,2″-terpyridyl compounds of manganese(II) and cobalt(II) chloride discussed here.

[9] Harris, C. M., Lockyer, T. N., and Waterman, H., *Nature*, 1961, **192**, 424.
[10] Barclay, G. A., and Kennard, C. H. L., *Nature*, 1961, **192**, 425; Barclay, G. A., Hoskins, B. F., and Kennard, C. H. L., *J. chem. Soc.*, 1963, 5691.
[11] Orioli, P. L., Di Viara, M., and Sacconi, L., *Chem. Commun.*, 1965, **6**, 103.