Structures and Properties of Zinc(II) Complexes of *NN*-Bis[(2-hydroxy-5-X-phenyl)phenylmethylene]-4-azaheptane-1,7-diamine (X = Chloro or Methyl): Comparison of d^{10}, d^9, and d^8 Analogues

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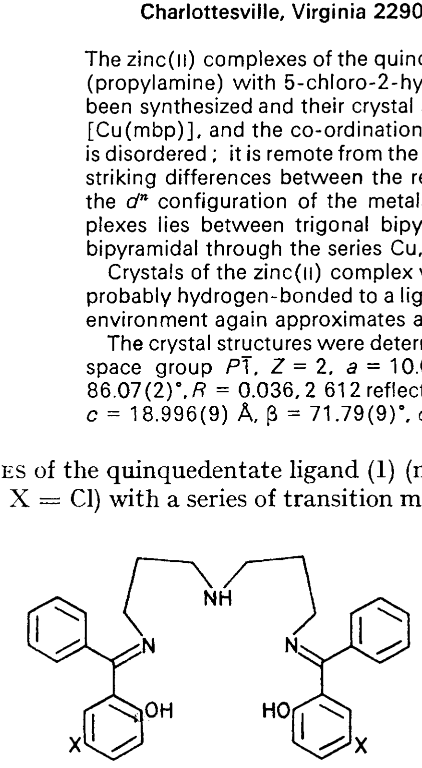
The zinc(II) complexes of the quinquedentate ligands derived from the Schiff-base condensation of 3,3'-iminobis-(propylamine) with 5-chloro-2-hydroxybenzophenone (cbp) and 2-hydroxy-5-methylbenzophenone (mbp) have been synthesized and their crystal structures determined. [Zn(cbp)]·H_2O Is crystallographically isomorphous with [Cu(mbp)], and the co-ordination environment of the zinc is a distorted trigonal bipyramid. The water molecule is disordered; it is remote from the metal atom and appears to produce no significant distortion of the complex. The striking differences between the related nickel(II), copper(II), and zinc(II) complexes must be ascribed mainly to the d^n configuration of the metals. The metal environment in related nickel(II), copper(II), and zinc(II) complexes lies between trigonal bipyramidal and distorted square pyramidal, and progresses increasingly towards bipyramidal through the series Cu, Ni, Zn.

Crystals of the zinc(II) complex with mbp were obtained as a hydrate [Zn(mbp)]·H_2O with the water molecule probably hydrogen-bonded to a ligand atom, but with no apparent distortion due to the water molecule. The metal environment again approximates a trigonal bipyramid.

The crystal structures were determined from full-matrix least-squares refinement of counter data ([Zn(cbp)]·H_2O: space group $P\bar{1}$, $Z = 2$, $a = 10.099(1)$, $b = 12.500(2)$, $c = 13.261(4)$ Å, $\alpha = 74.57(3)$, $\beta = 68.06(1)$, $\gamma = 86.07(2)°$, $R = 0.036$, 2 612 reflections; [Zn(mbp)]·H_2O: space group $P2_1/c$, $Z = 4$, $a = 16.30(1)$, $b = 10.178(4)$, $c = 18.996(9)$ Å, $\beta = 71.79(9)°$, $\alpha = \gamma = 90$, $R = 0.048$, 2 669 reflections).

COMPLEXES of the quinquedentate ligand (1) (mbp, X = Me; cbp, X = Cl) with a series of transition metals have been reported, and the crystal structures of [Ni(mbp)] and [Cu(mbp)] have been determined.[1] The copper(II) and nickel(II) complexes show significant differences in the metal environments, presumably due mainly to crystal-field effects. The nickel is closer to square pyramidal than trigonal bipyramidal and it is also sufficiently different from square planar to make it high spin. The copper environment is somewhat closer again to square pyramidal than for nickel, having one elongated metal–ligand bond. We report here the structure of two related five-co-ordinated zinc(II) complexes to complete the comparison of d^8, d^9, and d^{10} complexes with ligand (1). It was noted[1] that [Zn(cbp)] is isomorphous with [Cu(mbp)], but that [Zn(mbp)] is not isomorphous with any of the related complexes. Thus, in at least one case, the ideal situation exists for the comparison; the two types of molecules are packed in essentially the same unit cells, and any differences in molecular structure must be due to the d^n configuration alone.



(1)

EXPERIMENTAL

The complexes were prepared as previously described, [Zn(cbp)] (Found: C, 62.1; H, 4.9; N, 6.4. $ZnCl_2O_2N_3C_{32}H_{29}$ requires C, 61.6; H, 4.7; N, 6.7%) and [Zn(mbp)]·$\frac{1}{2}H_2O$ (Found: C, 68.6; H, 6.1; N, 6.7. $ZnO_{2.5}N_3C_{34}H_{36}$ requires C, 69.0; H, 6.1; N, 7.1%) were recrystallised from methanol to give crystals suitable for *X*-ray crystallographic studies. Densities were determined by flotation (aqueous potassium iodide), and mass spectra obtained on a Hitachi Perkin-Elmer RMU 6E mass spectrometer.

Crystal Data for [Zn(cbp)]·H_2O.—$M = 621$, Triclinic, $a = 10.099(1)$, $b = 12.500(2)$, $c = 13.261(4)$ Å, $\alpha = 74.57(3)$, $\beta = 68.06(1)$, $\gamma = 86.07(2)°$, $U = 1\,495$ Å^3, $D_m = 1.42$, $Z = 2$, $D_c = 1.41$. Space group $P\bar{1}$. Mo-K_α radiation, $\lambda = 0.710\,7$ Å; μ(Mo-K_α) = 10.5 cm^{-1}.

Crystal Data for [Zn(mbp)]·H_2O—$M = 581$, Monoclinic, $a = 16.30(1)$, $b = 10.178(4)$, $c = 18.996(9)$ Å, $\beta = 71.79(9)$, $\alpha = \gamma = 90°$, $U = 2\,979$ Å^3, $D_m = 1.30$, $Z = 4$, $D_c = 1.33$. Space group $P2_1/c$. μ(Mo-K_α) = 8.8 cm^{-1}. Slow loss of water, which accounts for the difference in hydration between microanalytical and crystallographic samples, is discussed later.

Small irregularly-shaped crystals of [Zn(cbp)]·H_2O and [Zn(mbp)]·H_2O were selected for the crystallographic study. Preliminary cell dimensions were obtained by use of the Enraf–Nonius program SEARCH to locate 15 independent reflections. Refined cell dimensions and their estimated standard deviations were calculated from a least-squares refinement of the preliminary *vs.* observed values of $\pm\theta$ for 28 strong general reflections for [Zn(cbp)]·H_2O, and for 23 for [Zn(mbp)]·H_2O, each centred on the diffractometer for the Mo-K_{α_1} and Mo-K_{α_2} wavelengths.

Diffraction data were collected from small crystals mounted on glass fibres with epoxy resin. The mosaicity of each crystal was examined by the ω scan technique and judged satisfactory. Diffraction data were collected on an Enraf–Nonius four-circle CAD 4 diffractometer controlled by a PDP8/E computer, by use of graphite-monochromated Mo-K_α radiation. The θ—2θ scan technique was used to record the intensities of all reflections for which $0° < 2\theta <$

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[1] P. C. Healy, G. M. Mockler, D. P. Freyberg, and E. Sinn, *J.C.S. Dalton*, 1975, 691, and refs. therein.

25°. The symmetric scans were centred on the calculated peak positions. Scan widths (SW) were based on θ by use of the formula $SW = A + B\tan\theta$, where A is estimated from the mosaicity and $B\tan\theta$ allows for the increase in width of the peak due to separation of Mo-K_{α_1} and Mo-K_{α_2}: $A = 0.6$, $B = 0.2°$ were used for [Zn(cbp)]·H_2O, and $A = 1.5$, $B = 0.4°$ for [Zn(mbp)]·H_2O. For each reflection, the calculated scan angle was extended by 25% at either side to estimate the background count. Reflection data were considered significant if intensities registered 10 counts above background during the prescan, insignificant reflections being rejected automatically by the computer. Of 4 173 independent intensities recorded for [Zn(cbp)]·H_2O 2 612 were considered observed [having $I > 3\sigma(I)$], and of the 3 522 independent intensities for [Zn(mbp)]·H_2O, 2 669 were considered observed [having $I > 2\sigma(I)$].

For each crystal, the intensities of four standard reflections, monitored at 100 reflection intervals, showed no significant fluctuations. Raw intensity data were corrected for Lorentz and polarization effects, but not for absorption because of the small sizes of the crystals.

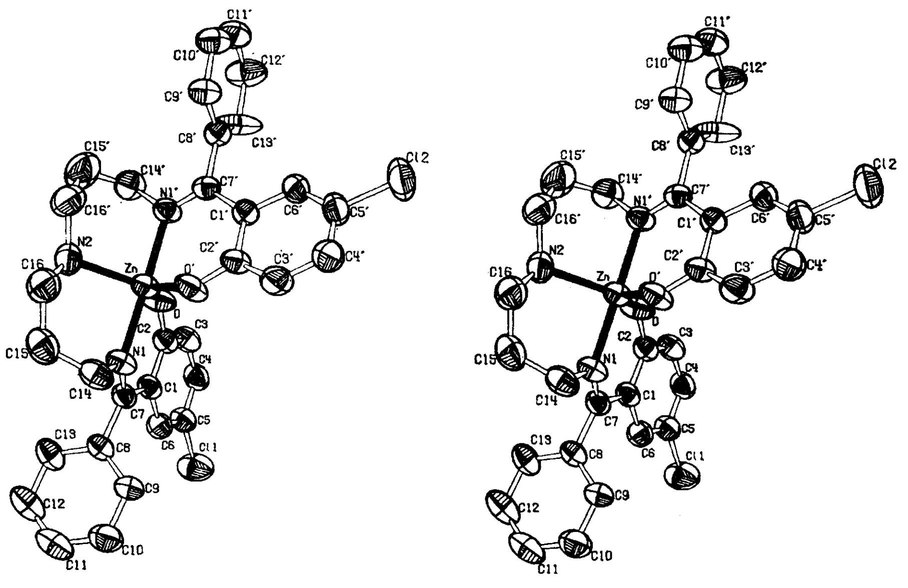

FIGURE 1 Molecular geometry of [Zn(cbp)]·H_2O

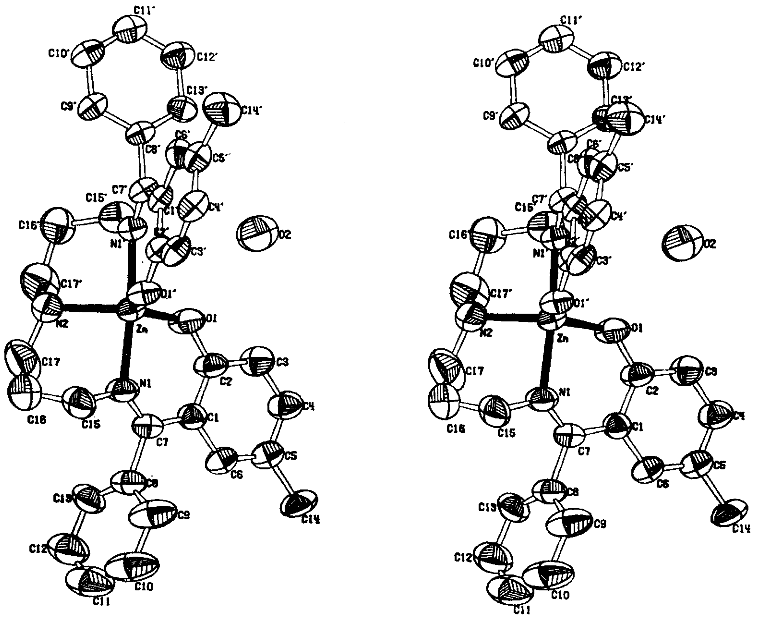

FIGURE 2 Molecular geometry of [Zn(mpb)]·H_2O

Solution and Refinement of the Structures.—Full-matrix least-squares refinement was based on F, and the function was minimized as $\Sigma w(|F_o| - |F_c|)^2$. Atomic scattering factors for non-hydrogen atoms were taken from ref. 2 and

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[2] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 511

for hydrogen from ref. 3, the effects of anomalous dispersion were included in taking values for $\Delta f'$ and $\Delta f''$ from ref. 4.

Computations were performed on a PDP 11/45 computer with 32K of core memory, magnetic tape and magnetic disc storage being used in calculations with larger memory requirements, such as full-matrix least-squares refinements and Fourier mapping. The programmes used were local or adapted from those specifically written for Enraf–Nonius diffraction systems by Y. Okaya, B. Frenz, K. O. Hodgson, E. Sinn, and others; others were from '*X*-Ray '72' (ed. J. M. Stewart), ORTEP (C. K. Johnson), and the University of Canterbury crystallographic programmes.[5] The validity of calculated outputs from our programme system was thoroughly checked and compared with the results of previously tested systems such as '*X*-Ray '72' and the University of Canterbury programmes.

Structure of [Zn(cbp)]·H_2O.—All non-hydrogen atoms were inserted at calculated positions of the isomorphous complex [Cu(mbp)]. This gave *R* 0.48, and six cycles of full-matrix least-squares refinement of this model produced *R* 0.083. The disordered water molecule was located in a Fourier difference map. Anisotropic temperature factors were introduced, and hydrogen atoms were inserted geometrically as fixed atoms, assuming C–H 0.95 Å, with isotropic temperature factors of 5.0. After convergence, they were inserted at their new calculated positions. After further refinement, the model converged with *R* 0.036 and *R'* 0.048 [$R' = \Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2$]. The error in an observation of unit weight was 1.113.

Structure of [Zn(mbp)]·H_2O.—A standard Patterson map calculated from all data enabled location of the zinc atom in a general position (*R* 0.483). All the remaining non-

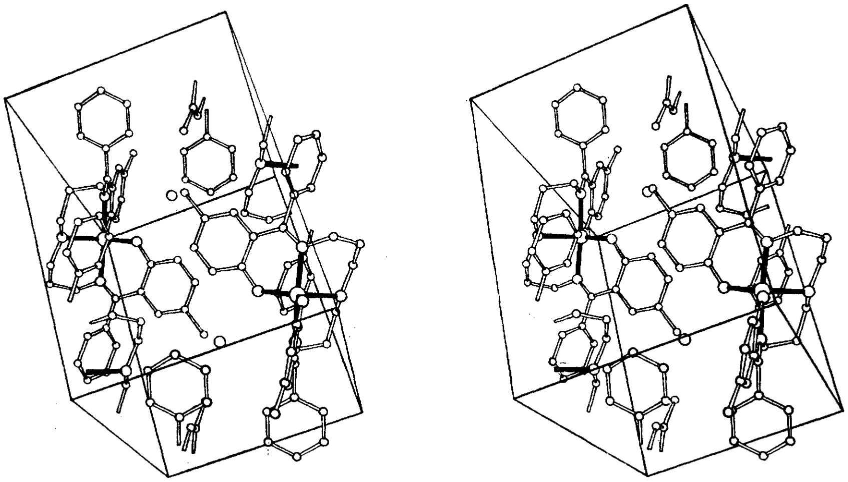

FIGURE 3 Packing diagram for [Zn(cbp)]·H_2O

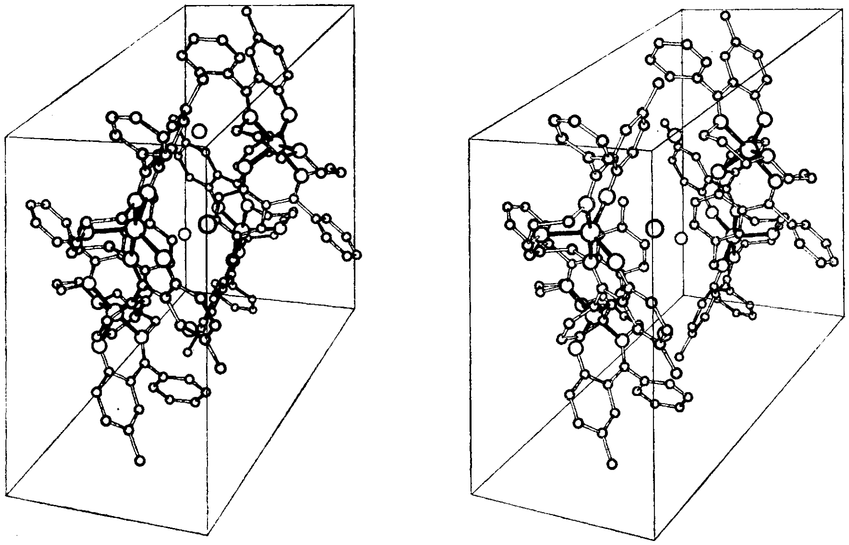

FIGURE 4 Packing diagram for [Zn(mpb)]·H_2O

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[3] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[4] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

[5] R. M. Countryman, W. T. Robinson, and E. Sinn, *Inorg. Chem.*, 1974, **13**, 2013; W. T. Robinson and E. Sinn, *J.C.S. Dalton*, 1975, 726.

hydrogen atoms were unambiguously located from subsequent three-dimensional Fourier syntheses, and full-matrix least-squares refinement gave R 0.098. With anisotropic temperature factors and hydrogen atoms calculated as before, the model converged with R 0.048

TABLE 1

Positional parameters* and their estimated standard deviations

(*a*) $[Zn(mbp)]\cdot H_2O$

Atom	*x*	*y*	*z*
Zn	0.25730(7)	0.8914(1)	0.44431(6)
O(1)	0.3209(3)	0.7375(6)	0.4608(3)
O(1′)	0.2005(3)	0.9025(6)	0.3682(3)
O(2)	0.2094(5)	0.5115(8)	0.4809(4)
N(1)	0.3771(4)	0.9755(7)	0.3824(4)
N(1′)	0.1421(4)	0.8147(7)	0.5186(3)
N(2)	0.2363(4)	1.0645(8)	0.5160(4)
C(1)	0.4693(5)	0.7944(8)	0.3892(4)
C(2)	0.4042(5)	0.7078(9)	0.4308(5)
C(3)	0.4290(5)	0.5804(9)	0.4395(5)
C(4)	0.5157(6)	0.5387(9)	0.4089(5)
C(5)	0.5820(6)	0.6216(9)	0.3697(5)
C(6)	0.5569(5)	0.7475(9)	0.3615(5)
C(7)	0.4535(5)	0.9272(9)	0.3710(4)
C(8)	0.5284(5)	1.0191(9)	0.3363(5)
C(9)	0.5677(6)	1.0209(11)	0.2597(5)
C(10)	0.6362(6)	1.1071(14)	0.2295(6)
C(11)	0.6637(6)	1.1872(13)	0.2735(7)
C(12)	0.6263(6)	1.1875(11)	0.3488(7)
C(13)	0.5582(5)	1.1022(10)	0.3792(5)
C(14)	0.6761(5)	0.5742(10)	0.3377(5)
C(15)	0.3613(5)	1.1101(10)	0.3599(5)
C(16)	0.3395(7)	1.2063(11)	0.4226(7)
C(17)	0.3072(8)	1.1571(11)	0.4968(6)
C(1′)	0.0632(5)	0.7900(8)	0.4297(4)
C(2′)	0.1269(5)	0.4876(8)	0.3676(4)
C(3′)	0.1084(5)	0.8466(9)	0.2996(4)
C(4′)	0.0327(5)	0.7899(9)	0.2947(4)
C(5′)	−0.0281(6)	0.7251(9)	0.3528(4)
C(6′)	−0.0110(5)	0.7335(9)	0.4188(4)
C(7′)	0.0725(5)	0.7827(8)	0.5037(4)
C(8′)	−0.0055(5)	0.7374(9)	0.5657(4)
C(9′)	−0.0680(5)	0.8277(8)	0.6013(4)
C(10′)	−0.1410(5)	0.7867(10)	0.6587(5)
C(11′)	−0.1519(5)	0.6570(9)	0.6787(5)
C(12′)	−0.0894(6)	0.5651(9)	0.6438(5)
C(13′)	−0.0170(5)	0.6079(9)	0.5874(4)
C(14′)	−0.1060(5)	0.6531(10)	0.3415(5)
C(15′)	0.1483(5)	0.8064(10)	0.5945(4)
C(16′)	0.1466(6)	0.4912(11)	0.6287(5)
C(17′)	0.2231(7)	1.0287(10)	0.5918(7)
H(3)	0.3863(0)	0.5194(0)	0.4666(0)
H(4)	0.5290(0)	0.4493(0)	0.4166(0)
H(6)	0.5998(0)	0.8081(0)	0.3360(0)
H(9)	0.5484(0)	0.9665(0)	0.2275(0)
H(10)	0.6609(0)	1.1099(0)	0.1770(0)
H(11)	0.7137(0)	1.2385(0)	0.2450(0)
H(12)	0.6458(0)	1.2481(0)	0.3781(0)
H(13)	0.5308(0)	1.1016(0)	0.4316(0)
H(15A)	0.3135(0)	1.1141(0)	0.3380(0)
H(15B)	0.4110(0)	1.1454(0)	0.3206(0)
H(16A)	0.2925(0)	1.2644(0)	0.4186(0)
H(16B)	0.3887(0)	0.2650(0)	0.4155(0)
H(17A)	0.3002(0)	1.2355(0)	0.5295(0)
H(17B)	0.3631(0)	1.1181(0)	0.5032(0)
H(3′)	0.1472(0)	0.8843(0)	0.2561(0)
H(4′)	0.0208(0)	0.7966(0)	0.2480(0)
H(3′)	0.4483(7)	0.1804(7)	0.3303(6)
H(4′)	0.4599(7)	0.1624(7)	0.5039(7)
H(6′)	0.0373(7)	0.1909(6)	0.6431(5)
H(9′)	−0.1497(8)	0.0155(6)	0.5945(6)
H(10′)	−0.3444(8)	−0.0416(6)	0.7658(6)
H(11′)	−0.4666(8)	0.0865(7)	0.8562(6)
H(12′)	−0.4078(10)	0.2727(7)	0.7763(7)
H(13′)	−0.2159(9)	0.3321(7)	0.6057(7)
H(14′A)	−0.2115(8)	0.3207(7)	0.3282(6)
H(14′B)	−0.2698(8)	0.2435(7)	0.4495(6)
H(15′A)	−0.2874(9)	0.1900(10)	0.2884(9)
H(15′B)	−0.2827(9)	0.1028(10)	0.3944(9)
H(16′A)	−0.1389(9)	0.0592(7)	0.2321(7)
H(16′B)	−0.0524(9)	0.0740(7)	0.3028(7)

TABLE 1 (*Continued*)

(*b*) $[Zn(cpp)]\cdot H_2O$

Atom	*x*	*y*	*z*
Zn	0.09491(9)	0.30231(7)	0.21397(6)
Cl	0.3226(3)	0.8839(2)	−0.0810(2)
Cl′	0.2626(2)	0.1681(2)	0.7178(2)
O(1)	0.0325(5)	0.4549(4)	0.2031(3)
O(1′)	0.2339(4)	0.2256(4)	0.2731(3)
O(2A)	0.1131(11)	0.5076(8)	0.5758(8)
O(2B)	0.9793(13)	0.5113(16)	0.4649(12)
N(1)	0.2459(5)	0.3597(4)	0.0482(4)
N(1′)	−0.0610(5)	0.2496(4)	0.3784(4)
N(2)	−0.0065(6)	0.1938(5)	0.1595(4)
C(1)	0.2159(6)	0.5558(5)	0.0280(5)
C(2)	0.0992(7)	0.5470(5)	0.1358(5)
C(3)	0.0563(7)	0.6470(6)	0.1634(5)
C(4)	0.1216(8)	0.7488(6)	0.1003(5)
C(5)	0.2357(7)	0.7566(5)	−0.0005(5)
C(6)	0.2787(7)	0.6618(6)	−0.0348(5)
C(7)	0.2758(6)	0.4592(5)	−0.0137(5)
C(8)	0.3794(6)	0.4832(5)	−0.1357(5)
C(9)	0.5219(7)	0.5024(6)	−0.1646(5)
C(10)	0.6149(7)	0.5211(6)	−0.2761(6)
C(11)	0.5654(8)	0.5216(7)	−0.3587(5)
C(12)	0.4226(8)	0.5028(7)	−0.3300(5)
C(13)	0.3295(7)	0.4830(6)	−0.2193(5)
C(14)	0.3157(8)	0.2653(6)	0.0051(6)
C(15)	0.2119(9)	0.1961(6)	−0.0123(6)
C(16)	0.0967(8)	0.1288(7)	0.0905(6)
C(1′)	0.1057(6)	0.2053(5)	0.4732(5)
C(2′)	0.2305(6)	0.2093(5)	0.3746(5)
C(3′)	0.3603(7)	0.1869(6)	0.3922(5)
C(4′)	0.3704(7)	0.1744(7)	0.4959(6)
C(5′)	0.2483(7)	0.1795(6)	0.5878(5)
C(6′)	0.1201(7)	0.1916(6)	0.5781(5)
C(7′)	−0.0400(6)	0.2160(5)	0.4707(5)
C(8′)	−0.1641(6)	0.1790(5)	0.5831(5)
C(9′)	−0.2020(7)	0.0690(6)	0.6310(5)
C(10′)	−0.3174(7)	0.0349(6)	0.7333(6)
C(11′)	−0.3900(7)	0.1104(6)	0.7856(6)
C(12′)	−0.3544(9)	0.2200(6)	0.7393(6)
C(13′)	−0.2412(8)	0.2553(6)	0.6378(6)
C(14′)	−0.2022(7)	0.2513(6)	0.3750(6)
C(15′)	−0.2294(8)	0.1598(8)	0.3316(7)
C(16′)	−0.1041(8)	0.1109(7)	0.2582(7)
H(3)	−0.0240(8)	0.6443(6)	0.2307(6)
H(4)	0.0892(8)	0.8133(6)	0.1256(6)
H(6)	0.3551(7)	0.6682(7)	−0.1050(6)
H(9)	0.5578(8)	0.5031(7)	−0.1081(5)
H(10)	0.7141(8)	0.5337(7)	−0.2950(7)
H(11)	0.6291(9)	0.5347(7)	−0.4349(6)
H(12)	0.3870(8)	0.5034(7)	−0.3869(6)
H(13)	0.2307(8)	0.4692(7)	−0.2006(6)
H(14A)	0.3519(8)	0.2199(6)	0.0577(6)
H(14B)	0.3922(8)	0.2930(6)	−0.0647(6)
H(15A)	0.2661(10)	0.1460(7)	−0.0531(6)
H(15B)	0.1669(10)	0.2450(7)	−0.0563(6)
H(16A)	0.1403(9)	0.0814(7)	0.1368(7)
H(16B)	0.0453(9)	0.0852(7)	0.0676(7)
H(6′)	−0.0536(0)	0.6975(0)	0.4605(0)
H(9′)	−0.0616(0)	0.9177(0)	0.5875(0)
H(10′)	−0.1838(0)	0.8463(0)	0.6851(0)
H(11′)	−0.2051(0)	0.6274(0)	0.7185(0)
H(12′)	−0.0973(0)	0.4746(0)	0.6580(0)
H(13′)	0.0256(0)	0.5427(0)	0.5640(0)
H(15′A)	0.2003(0)	0.7643(0)	0.5932(0)
H(15′B)	0.1004(0)	0.7594(0)	0.6256(0)
H(16′A)	0.1479(0)	0.9329(0)	0.6780(0)
H(16′A)	0.0966(0)	0.9873(0)	0.6280(0)
H(17′A)	0.2763(0)	0.9852(0)	0.5878(0)
H(17′B)	0.2206(0)	1.1097(0)	0.6154(0)

* The form of the anisotropic thermal parameter is: $\exp -[(b(1.1)*h*h + b(2.2)*k*k + b(3.3)*l*l + b(1.2)*h*k + b(1.3)*h*l + b(2.3)*k*l)]$.

(R' 0.048). The error in an observation of unit weight was 1.655. Structure factor calculations with all observed and unobserved reflections included (no refinement) gave R 0.063 for [Zn(cbp)]·H_2O and R 0.081 for [Zn(mbp)]·H_2O; on this basis it was decided that careful measurement of reflections rejected automatically during data collection would not significantly improve the result. Final observed and calculated structure factors and thermal parameters are listed in Supplementary Publication No. SUP 21579 (32 pp., 1 microfiche).*

TABLE 2

Bond distances (Å)

(*a*) [Zn(cbp)]

Zn–O(1)	1.964(5)	Zn–O(1′)	1.947(5)
Zn–N(1)	2.113(5)	Zn–N(1′)	2.114(5)
Zn–N(2)	2.160(6)		
Cl–C(5)	1.735(8)	Cl′–C(5′)	1.754(7)
O(1)–C(2)	1.295(8)	O(1′)–C(2′)	1.297(7)
N(1)–C(7)	1.279(8)	N(1′)–C(7′)	1.279(8)
N(1)–C(14)	1.478(8)	N(1′)–C(14′)	1.445(9)
N(2)–C(16)	1.474(10)	N(2′)–C(16′)	1.483(10)
C(1)–C(2)	1.456(9)	C(1′)–C(2′)	1.431(8)
C(1)–C(6)	1.405(9)	C(1′)–C(6′)	1.419(9)
C(1)–C(7)	1.468(9)	C(1′)–C(7′)	1.485(9)
C(2)–C(3)	1.397(9)	C(2′)–C(3′)	1.418(9)
C(3)–C(4)	1.372(10)	C(3′)–C(4′)	1.386(10)
C(4)–C(5)	1.386(9)	C(4′)–C(5′)	1.387(10)
C(5)–C(6)	1.373(9)	C(5′)–C(6′)	1.348(9)
C(7)–C(8)	1.523(8)	C(7′)–C(8′)	1.522(8)
C(8)–C(9)	1.365(9)	C(8′)–C(9′)	1.365(9)
C(8)–C(13)	1.382(9)	C(8′)–C(13′)	1.380(9)
C(9)–C(10)	1.389(9)	C(9′)–C(10′)	1.398(9)
C(10)–C(11)	1.365(11)	C(10′)–C(11′)	1.342(10)
C(11)–C(12)	1.367(11)	C(11′)–C(12′)	1.356(10)
C(12)–C(13)	1.381(10)	C(12′)–C(13′)	1.382(9)
C(14)–C(15)	1.517(11)	C(14′)–C(15′)	1.493(12)
C(15)–C(16)	1.498(11)	C(15′)–C(16′)	1.495(12)

(*b*) [Zn(mbp)]

Zn–O(1)	1.957(5)	Zn–O(1′)	1.949(5)
Zn–N(1)	2.119(6)	Zn–N(1′)	2.114(6)
Zn–N(2)	2.187(8)		
O(1)–C(2)	1.333(8)	O(1′)–C(2′)	1.327(10)
N(1)–C(7)	1.294(10)	N(1′)–C(7′)	1.295(9)
N(1)–C(15)	1.481(12)	N(1′)–C(15′)	1.479(10)
N(2)–C(17)	1.45(2)	N(2′)–C(17′)	1.43(2)
C(1)–C(2)	1.42(1)	C(1′)–C(2′)	1.43(1)
C(1)–C(6)	1.44(1)	C(1′)–C(6′)	1.41(1)
C(1)–C(7)	1.44(1)	C(1′)–C(7′)	1.46(1)
C(2)–C(3)	1.38(1)	C(2′)–C(3′)	1.41(1)
C(3)–C(4)	1.42(1)	C(3′)–C(4′)	1.39(1)
C(4)–C(5)	1.39(1)	C(4′)–C(5′)	1.40(1)
C(5)–C(6)	1.37(1)	C(5′)–C(6′)	1.37(1)
C(5)–C(14)	1.54(1)	C(5′)–C(14′)	1.54(1)
C(7)–C(8)	1.52(1)	C(7′)–C(8′)	1.51(1)
C(8)–C(9)	1.39(1)	C(8′)–C(9′)	1.38(1)
C(8)–C(13)	1.37(1)	C(8′)–C(13′)	1.38(1)
C(9)–C(10)	1.40(2)	C(9′)–C(10′)	1.40(1)
C(10)–C(11)	1.34(2)	C(10′)–C(11′)	1.37(1)
C(11)–C(12)	1.37(2)	C(11′)–C(12′)	1.39(1)
C(12)–C(13)	1.39(1)	C(12′)–C(13′)	1.39(1)
C(15)–C(16)	1.50(2)	C(15′)–C(16′)	1.52(1)
C(16)–C(17)	1.43(2)	C(16′)–C(17′)	1.51(1)

RESULTS AND DISCUSSION

The molecular geometries and numbering systems of [Zn(cbp)]·H_2O and [Zn(mbp)]·H_2O are shown in Figures 1 and 2 respectively. Owing to positional disorder, the

TABLE 3

Bond angles (°)

(*a*) [Zn(cbp)]·H_2O

O(1)–Zn–O(1′)	130.4(2)	N(1)–Zn–N(1′)	177.9(2)
O(1)–Zn–N(1)	87.8(2)	O(1)–Zn–N(1′)	90.4(2)
O(1)–Zn–N(2)	118.1(2)	O(1′)–Zn–N(2)	111.5(2)
O(1′)–Zn–N(1)	94.1(2)	O(1′)–Zn–N(1′)	87.8(2)
N(1)–Zn–N(2)	90.4(2)	N(1′)–Zn–N(2)	89.6(2)
Zn–O(1)–C(2)	129.5(5)	Zn–O(1′)–C(2′)	126.7(4)
Zn–N(1)–C(7)	128.6(5)	Zn–N(1′)–C(7′)	127.3(5)
Zn–N(1)–C(14)	110.4(4)	Zn–N(1′)–C(14′)	110.6(5)
C(7)–N(1)–C(14)	121.0(6)	C(7′)–N(1′)–C(14′)	122.0(6)
Zn–N(2)–C(16)	112.5(5)	Zn–N(2)–C(16′)	110.2(5)
C(16)–N(2)–C(16′)	105.5(7)		
C(2)–C(1)–C(6)	117.5(7)	C(2′)–C(1′)–C(6′)	119.3(6)
C(2)–C(1)–C(7)	123.2(6)	C(2′)–C(1′)–C(7′)	122.7(6)
C(6)–C(1)–C(7)	119.2(6)	C(6′)–C(1′)–C(7′)	118.0(6)
O(1)–C(2)–C(1)	124.4(7)	O(1′)–C(2′)–C(1′)	26.0(6)
O(1)–C(2)–C(3)	119.7(7)	O(1′)–C(2′)–C(3′)	117.9(6)
C(1)–C(2)–C(3)	115.9(7)	C(1′)–C(2′)–C(3′)	116.0(6)
C(2)–C(3)–C(4)	124.7(7)	C(2′)–C(3′)–C(4′)	122.7(7)
C(3)–C(4)–C(5)	119.3(7)	C(3′)–C(4′)–C(5′)	119.2(7)
Cl–C(5)–C(4)	120.4(6)	Cl′–C(5′)–C(4′)	119.0(6)
Cl–C(5)–C(6)	120.9(6)	Cl′–C(5′)–C(6′)	120.3(6)
C(4)–C(5)–C(6)	118.7(7)	C(4′)–C(5′)–C(6′)	120.7(7)
C(1)–C(6)–C(5)	123.8(7)	C(1′)–C(6′)–C(5′)	121.7(6)
N(1)–C(7)–C(1)	122.7(6)	N(1′)–C(7′)–C(1′)	122.0(6)
N(1)–C(7)–C(8)	120.8(7)	N(1′)–C(7′)–C(8′)	121.2(6)
C(1)–C(7)–C(8)	116.5(6)	C(1′)–C(7′)–C(8′)	116.8(6)
C(7)–C(8)–C(9)	121.5(6)	C(7′)–C(8′)–C(9′)	120.1(6)
C(7)–C(8)–C(13)	119.7(6)	C(7′)–C(8′)–C(13′)	121.0(6)
C(9)–C(8)–C(13)	118.8(6)	C(9′)–C(8′)–C(13′)	118.8(6)
C(8)–C(9)–C(10)	120.5(7)	C(8′)–C(9′)–C(10′)	120.3(7)
C(9)–C(10)–C(11)	120.7(8)	C(9′)–C(10′)–C(11′)	120.0(7)
C(10)–C(11)–C(12)	118.9(8)	C(10′)–C(11′)–C(12′)	120.7(7)
C(11)–C(12)–C(13)	120.8(8)	C(11′)–C(12′)–C(13′)	120.1(7)
C(8)–C(13)–C(12)	120.3(7)	C(8′)–C(13′)–C(12′)	120.1(7)
N(1)–C(14)–C(15)	111.4(6)	N(1′)–C(14′)–C(15′)	112.1(7)
C(14)–C(15)–C(16)	117.6(7)	C(14′)–C(15′)–C(16′)	118.3(8)
N(2)–C(16)–C(15)	115.0(7)	N(2)–C(16′)–C(15′)	113.9(8)

(*b*) [Zn(mbp)]

O(1)–Zn–O(1′)	124.3(2)	N(1)–Zn–N(1′)	172.5(3)
O(1)–Zn–N(1)	88.3(3)	O(1)–Zn–N(1′)	90.1(2)
O(1)–Zn–N(2)	122.2(3)	O(1′)–Zn–N(2)	113.4(3)
O(1′)–Zn–N(1)	97.7(2)	O(1′)–Zn–N(1′)	89.3(2)
N(1)–Zn–N(2)	87.6(3)	N(1′)–Zn–N(2)	87.0(3)
Zn–O(1)–C(2)	129.3(7)	Zn–O(1′)–C(2′)	128.6(6)
Zn–N(1)–C(7)	127.7(8)	Zn–N(1′)–C(7′)	127.1(7)
Zn–N(1)–C(15)	108.7(6)	Zn–N(1′)–C(15′)	110.8(6)
C(7)–N(1)–C(15)	123.3(9)	C(7′)–N(1′)–C(15′)	122.1(8)
Zn–N(2)–C(17)	114.3(7)	Zn–N(2)–C(17′)	111.5(8)
C(17)–N(2)–C(17′)	106.0(11)		
C(2)–C(1)–C(6)	118.8(10)	C(2′)–C(1′)–C(6′)	118.6(9)
C(2)–C(1)–C(7)	124.1(11)	C(2′)–C(1′)–C(7′)	123.2(9)
C(6)–C(1)–C(7)	117.1(11)	C(6′)–C(1′)–C(7′)	118.2(10)
O(1)–C(2)–C(1)	125.7(11)	O(1′)–C(2′)–C(1′)	126.1(10)
O(1)–C(2)–C(3)	117.3(11)	O(1′)–C(2′)–C(1′)	117.6(10)
C(1)–C(2)–C(3)	117.1(10)	C(1′)–C(2′)–C(3′)	116.3(9)
C(2)–C(3)–C(4)	121.5(10)	C(2′)–C(3′)–C(4′)	120.8(9)
C(3)–C(4)–C(5)	123.3(10)	C(3′)–C(4′)–C(5′)	124.5(10)
C(4)–C(5)–C(6)	114.7(11)	C(4′)–C(5′)–C(6′)	113.3(10)
C(4)–C(5)–C(14)	122.3(11)	C(4′)–C(5′)–C(14′)	121.8(11)
C(6)–C(5)–C(14)	123.1(10)	C(6′)–C(5′)–C(14′)	124.9(10)
C(1)–C(6)–C(5)	124.6(10)	C(1′)–C(6′)–C(5′)	126.2(9)
N(1)–C(7)–C(1)	123.5(10)	N(1′)–C(7′)–C(1′)	124.0(10)
N(1)–C(7)–C(8)	116.2(11)	N(1′)–C(7′)–C(8′)	119.3(9)
C(1)–C(7)–C(8)	120.3(10)	C(1′)–C(7′)–C(8′)	116.7(8)
C(7)–C(8)–C(9)	120.4(13)	C(7′)–C(8′)–C(9′)	119.4(10)
C(7)–C(8)–C(13)	120.7(11)	C(7′)–C(8′)–C(13′)	121.9(10)
C(9)–C(8)–C(13)	118.9(11)	C(9′)–C(8′)–C(13′)	118.7(9)
C(8)–C(9)–C(10)	118.9(13)	C(8′)–C(9′)–C(10′)	119.9(9)
C(9)–C(10)–C(11)	120.5(18)	C(9′)–C(10′)–C(11′)	120.5(10)
C(10)–C(11)–C(12)	121.8(19)	C(10′)–C(11′)–C(12′)	120.3(10)
C(11)–C(12)–C(13)	118.1(16)	C(11′)–C(12′)–C(13′)	118.4(10)
C(8)–C(13)–C(12)	121.9(12)	C(8′)–C(13′)–C(12′)	122.2(9)
N(1)–C(15)–C(16)	113.3(10)	N(1′)–C(15′)–C(16′)	111.7(9)
C(15)–C(16)–C(17)	118.5(12)	C(15′)–C(16′)–C(17′)	115.6(10)
N(2)–C(17)–C(16)	119.6(14)	N(2)–C(17′)–C(16′)	117.3(11)

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* See Notice to Authors No. 7, in *J.C.S. Dalton*, 1975, Index issue.

water molecule in [Zn(cbp)]·H_2O is not shown. Table 1 gives final positional parameters, and Tables 2 and 3 bond lengths and angles. Estimated standard deviations (in parentheses) are derived from the inverse matrix in the course of normal least-squares refinement calculations. As is evident from the packing diagram (Figures 3 and 4), and from the nearest intermolecular contact distances (Table 4), the crystal structures consist of well-separated neutral complex molecules.

TABLE 4

Nearest intermolecular contact distances (Å)

(*a*) [Zn(cbp)]·H_2O			
Zn · · · O(2A)	4.054(11)	O(1) · · · O(2B)	3.57(3)
O(1) · · · O(2A)	2.901(12)	N(1′) · · · O(2B)	3.84(3)
N(1′) · · · O(2A)	3.234(13)		
Cl · · · C(11′)	3.752(9)	C(10) · · · C(3′)	3.556(11)
Cl · · · C(16′)	3.773(9)	C(10) · · · C(12′)	3.724(12)
Cl′ · · · C(15)	3.535(8)	C(11) · · · C(3′)	3.647(13)
O(1) · · · C(13)	3.640(9)	C(11) · · · C(4′)	3.736(12)
O(1′) · · · C(10)	3.617(9)	C(11) · · · C(13′)	3.771(12)
O(1′) · · · C(9′)	3.561(9)	C(12) · · · C(14′)	3.750(11)
O(1′) · · · C(10′)	3.338(9)	C(2′) · · · C(9′)	3.537(10)
N(2) · · · C(5)	3.610(9)	C(2′) · · · C(10′)	3.717(12)
C(1) · · · C(9)	3.680(10)	C(3′) · · · C(10′)	3.717(12)
C(10) · · · C(2′)	3.506(10)	C(5′) · · · C(16′)	3.738(12)
(*b*) [Zn(mbp)]·H_2O			
Zn · · · O(2)	3.964(12)	C(3) · · · C(10)	3.69(2)
O(1) · · · O(2)	2.883(13)	C(4) · · · C(4)	3.43(2)
N(1′) · · · O(2)	3.279(14)	C(14) · · · C(14′)	3.665(13)
O(1) · · · C(10)	3.71(2)	C(5′) · · · C(12′)	3.53(2)
O(1′) · · · C(11)	3.64(2)	C(5′) · · · C(13′)	3.72(2)
C(1) · · · C(10)	3.76(2)	C(6′) · · · C(12′)	3.48(2)
C(2) · · · C(10)	3.47(2)	C(6′) · · · C(13′)	3.50(2)
C(3) · · · C(4)	3.494(14)	C(10′) · · · C(14′)	3.743(14)

The *X*-ray data unambiguously indicate the presence of one water molecule per zinc atom in [Zn(mbp)]·H_2O and [Zn(cbp)]·H_2O, though microanalytical data suggest a hemihydrate for [Zn(mbp)] and an anhydrous complex for [Zn(cbp)]. This is attributed to slow efflorescence of the powdered samples used for microanalysis while in the single crystals water loss is insignificant, at least during the time required for data collection. The position of the water molecules suggest that weak hydrogen bonding to the ligand is preferred over co-ordination with the metal atom. In [Zn(mbp)]·H_2O the oxygen of the water molecule is near to one ligand oxygen atom (2.88 Å), and one nitrogen (3.28 Å), suggesting hydrogen bonding to the oxygen, and possibly also to the nitrogen. The nearest approach of the oxygen of the water molecule to a zinc atom is 3.96(1) Å. In [Zn(cbp)]·H_2O, the water molecule is disordered between two sites *A* and *B* for the oxygen atom. Of these, *A* is similar to the water in [Zn(mbp)]·H_2O: 2.90 from the nearest ligand oxygen, 3.23 from the nearest ligand nitrogen, and 4.05 Å from the nearest zinc. Site *B* is 3.56 Å from the nearest ligand oxygen. The mass spectra of [Zn(mbp)]·H_2O and [Zn(cbp)]·H_2O exhibit the anhydrous molecular ions and characteristic fragmentation patterns,[1] and, as expected from the rather weak mode of binding of the water molecules, no molecular ion of the hydrated species [Zn(mbp)]·H_2O is observed.

Figures 5 and 6 illustrate the co-ordination about the zinc atom in the two complexes, and give bond distances and angles. Analogous views of the co-ordination about copper in [Cu(mbp)] and the nickel in [Ni(mbp)] are given in Figures 7 and 8. The crystallographic two-fold symmetry axis in [Ni(mbp)] (space group *Pncb*) requires statistical disorder in the $-[CH_2]_3-NH-[CH_2]_3-$ chain with equal distribution on either side of the two-fold axis.[1] Thus, only one of the two symmetry-equivalent positions of the disordered nitrogen atom is used in Figure 8 since, in any given [Ni(mbp)] molecule, only one of the nitrogen positions (and not the mean of the two) must be occupied. It is clear from the distances and angles in Figures 6—8 that the metal environments in the zinc complexes may be described as distorted trigonal bipyramidal, while the copper and nickel complexes show both square pyramidal and trigonal bipyramidal geometries. A more detailed comparison of

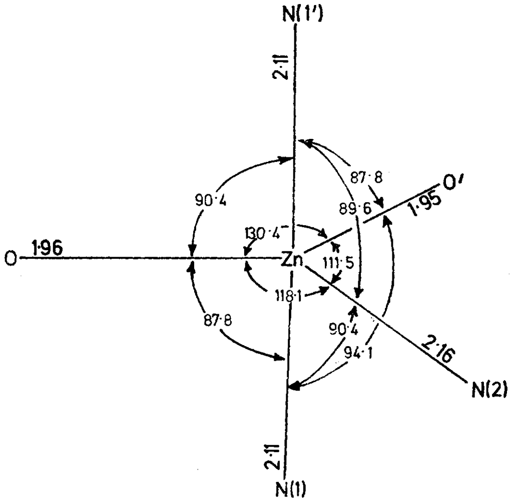

FIGURE 5 Co-ordination about Zn in [Zn(cbp)]·H_2O

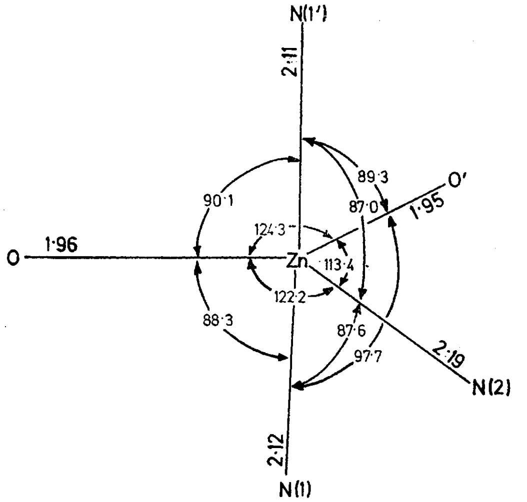

FIGURE 6 Co-ordination about Zn in [Zn(mpb)]·H_2O

the peripheral parts of the zinc complexes is given in Table 5, in the form of least-squares planes, and interplanar angles and atom-to-plane distances. Analogous interplanar angles in [Cu(mbp)] and [Ni(mbp)] are given for comparison.

The one elongated Cu–N bond gives the [Cu(mbp)] complex some features of a distorted square pyramidal or even a distorted planar configuration. The elongation cannot be dismissed as a steric requirement of the ligand, since it does not occur in the nickel analogue. This striking difference between these two compounds suggests that the regular five-co-ordinated environment is less favoured for such ligands in d^9 complexes than in d^8. Otherwise the differences between the molecular geometries of the two complexes is minimal. The shorter mean metal-to-ligand bond distance in [Ni(mbp)] implies a greater ligand-field strength in the d^8 than in the d^9 complex. The marked differences between the metal environments of [Ni(mbp)] and [Cu(mbp)] on the one hand and the d^{10} zinc complexes on the other, can be

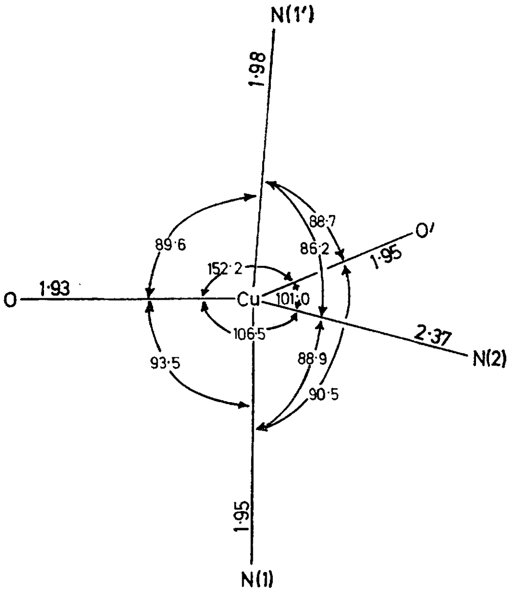

FIGURE 7 Co-ordination about Cu in [Cu(mbp)]

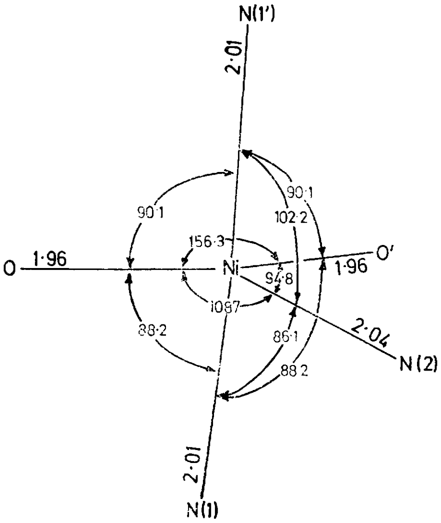

FIGURE 8 Co-ordination about Ni in [Ni(mpb)]

TABLE 5

Equations of least-squares planes in the form $AX + BY + CZ = D$; distances (Å × 10^4) of relevant atoms from the planes are given in square brackets; data for [Zn(cbp)] are given before those for [Zn(mbp)]

<table>
<tr><th>A</th><th>B</th><th>C</th><th>D</th></tr>
<tr><td colspan="4">Plane (I): Zn, O(1), N(1), C(1), C(2), C(7)</td></tr>
<tr><td>−0.8952</td><td>−0.1682</td><td>−0.4128</td><td>−3.7444</td></tr>
<tr><td>−0.3855</td><td>−0.3786</td><td>−0.8415</td><td>−12.8422</td></tr>
<tr><td colspan="4">[Zn −926, 259; O(1) 1 420, −690; N(1) 152, 308; C(1) −757, 302; C(2) −602, 462; C(4) 713, −641]</td></tr>
<tr><td colspan="4">Plane (II): Zn, O(1′), N(1′), C(1′), C(2′), C(7′)</td></tr>
<tr><td>−0.2200</td><td>−0.9754</td><td>−0.0162</td><td>−4.7089</td></tr>
<tr><td>0.3154</td><td>−0.9109</td><td>−0.2662</td><td>−8.3147</td></tr>
<tr><td colspan="4">[Zn 1 773, 737; O(1′) 2 012, −986; N(1′) 968, −251; C(1′) −1 434, 586; C(2′) −364, 338; C(7′) 592, −424]</td></tr>
<tr><td colspan="4">Plane (III): Zn, O(1), O(1′), N(2)</td></tr>
<tr><td>0.3988</td><td>0.0413</td><td>−0.9161</td><td>−1.2545</td></tr>
<tr><td>0.6771</td><td>0.3993</td><td>−0.6181</td><td>3.2702</td></tr>
<tr><td colspan="4">[Zn 189, 299; O(1) −68, −109; O(1′) −65, −101; N(2) −51, −88]</td></tr>
<tr><td colspan="4">Plane (IV): Zn, N(1), N(1′), N(2)</td></tr>
<tr><td>−0.6847</td><td>0.6963</td><td>−0.2155</td><td>1.0196</td></tr>
<tr><td>−0.6989</td><td>0.4216</td><td>−0.5778</td><td>−5.6527</td></tr>
<tr><td colspan="4">[Zn −256, 665; N(1) 128, −348; N(1′) 128, −349; N(2) 0, 31]</td></tr>
<tr><td colspan="4">Plane (V): C(1)—(6), C(14)</td></tr>
<tr><td>−0.8707</td><td>−0.0611</td><td>−0.4881</td><td>−3.1476</td></tr>
<tr><td>−0.4584</td><td>−0.2677</td><td>−0.8475</td><td>−12.7012</td></tr>
<tr><td colspan="4">[C(1) 1 228, 171; C(2) 511, −99; C(3) −68, −49; C(4) −841, 121; C(5) −603, −30; C(6) 581, −107; C(14) −808, −6]</td></tr>
<tr><td colspan="4">Plane (VI): C(8)—(13)</td></tr>
<tr><td>−0.1424</td><td>0.9813</td><td>−0.1297</td><td>5.1867</td></tr>
<tr><td>−0.7077</td><td>0.7012</td><td>−0.0864</td><td>−0.7623</td></tr>
<tr><td colspan="4">[C(8) 9, −9; C(9) 29, 5; C(10) −35, −3; C(11) 3, 3; C(12) 35, −6; C(13) −41, 9]</td></tr>
<tr><td colspan="4">Plane (V′) C(1′)–(6′), C(14′)</td></tr>
<tr><td>0.1300</td><td>0.9732</td><td>−0.1898</td><td>3.3796</td></tr>
<tr><td>0.4567</td><td>−0.8615</td><td>−0.2221</td><td>−7.0091</td></tr>
<tr><td colspan="4">[C(1′) −170, −6; C(2′) 481, 486; C(3′) −294, 74; C(4′) −138, −529; C(5′) 261, −123; C(6′) −86, −436; C(14′) −52, 536]</td></tr>
<tr><td colspan="4">Plane (VI′): C(8′)—(13′)</td></tr>
<tr><td>−0.8699</td><td>−0.0563</td><td>−0.4900</td><td>−4.8282</td></tr>
<tr><td>−0.7232</td><td>−0.1641</td><td>−0.6708</td><td>−10.4499</td></tr>
<tr><td colspan="4">[C(8′) −10, 18; C(9′) −27, 38; C(10′) 57, −88; C(11′) −49, 82; C(12′) 10, −26; C(13′) 19, −24]</td></tr>
</table>

Interplanar angles	(I)–(II)	(I)–(V)	(II)–(V′)	(III)–(IV)	(V)–(VI)	(V′)–(VI′)
[Zn(cbp)]	68.4	7.6	12.9	87.3	82.7	94.3
[Zn(mbp)]	63.4	7.6	9.0	87.0	77.9	92.3
[Cu(mbp)]	58.6	16.8	17.5	89.0	82.7	87.8
[Ni(mbp)]	71.8	22.0	22.0	89.0	82.3	82.3

attributed almost entirely to the *d*-electron configuration. The difference between mbp and cbp, as viewed from the metal atom, is minimal because of the remoteness of the chloro- and methyl-substituents. A slight constraint on the comparison is the hydrogen-bonded water molecule in [Zn(mbp)]·H_2O, but comparison of the two zinc complexes shows that this is negligible compared to the effect of changing the *d*-orbital configuration. The complexes exhibit a progression from trigonal bipyramidal to square pyramidal geometry in the sequence Zn $\ll$ Ni $<$ Cu.

The geometry of the zinc complexes results from a combination of lattice forces due to the specific mode of packing of the molecules in the crystals, the steric requirements of the ligands and the mutual repulsion of the electronegative donor atoms. There are no net ligand-field effects on the d^{10} configurations, and the close approach to trigonal bipyramidal geometry, presumably due mainly to donor atom repulsion, attests to the flexibility of the ligand. Further support is provided by the structure of the cobalt(III) complex [Co(cbp)-(CNS)], which approaches quite close to the octahedral ligand environment preferred by the low-spin d^6 configuration.[6]

The distortion of the nickel(II) and copper(II) complexes towards square planar geometry indicates that, as expected, the crystal-field stabilization energy (CFSE), and hence the overall crystal-field splitting, is greater in this geometry than in a trigonal bipyramid. The specific further distortion for Cu(cbp) compared with Ni(cbp), *viz.* the lengthening of the C–N bond, can be attributed to the extra electron. This bond elongation can be represented by an axial distortion operator $(l_z^2-2)\delta$ added to the crystal-field diagonalized Hamiltonian for a square pyramid. This raises the energy of $d_{x^2-y^2}$ orbital by 2δ and lowers that of d_{z^2} by 2δ (Figure 9). The net gain in CFSE is 2δ for d^9 and 0 for d^8. Thus a copper(II) complex in a square-pyramidal environment is stabilized by such axial distortion, while a nickel(II) complex is not, in agreement with the experimental observations. The e.s.r. spectra of Cu(cbp) can be rationalized in terms of this model: Healy *et al.*[1] observed ligand hyperfine splittings with the two (for this purpose equivalent) non-axial nitrogen donors, while failing to observe splittings due to the axial nitrogen, which would be expected if the unpaired electron were in the $d_{x^2-y^2}$ orbital, in the square plane of a distorted square pyramid.

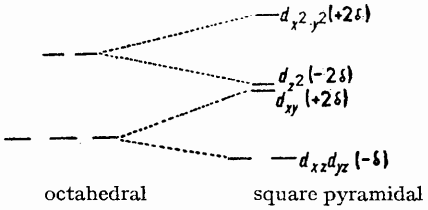

FIGURE 9 Effect of axial distortion on *d*-orbital configuration

The slight difference between the co-ordination in the two zinc complexes is presumably due to constraint of the two ligand oxygens in [Zn(mbp)]·H_2O set up by the hydrogen bonding to the water molecule.

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[6] D. P. Freyberg and E. Sinn, unpublished data.