Structures and Properties of the Copper(II) and Nickel(II) Complexes of *NN'*-Bis[(2-hydroxy-5-methylphenyl)phenylmethylene]-4-azaheptane-1,7-diamine and Related Compounds: Direct Comparison of d^8 and d^9 Analogues

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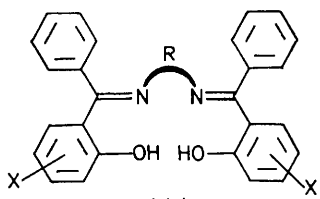
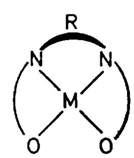
The nickel(II), copper(II), and zinc(II) complexes of the quinquedentate ligands mbp and cbp, derived from the Schiff-base condensation of 3,3'-iminobis(propylamine) with 2-hydroxy-5-methylbenzophenone (mbp) and 5-chloro-2-hydroxybenzophenone (cbp), have been investigated by magnetic, spectroscopic, and *X*-ray crystallographic techniques and shown to be five-co-ordinate monomers, the Cu compounds having normal magnetic moments while the Ni complexes are high spin. The e.s.r. spectra of the Cu complexes show ligand hyperfine splitting for two of the three nitrogen donor atoms, in agreement with *X*-ray structural observations for [Cu(mbp)]. The metal environments are approximately distorted trigonal bipyramids, but the Cu complex has one elongated Cu–N bond, which suggests distorted square pyramidal geometry, and a weaker ligand-field than for the Ni complex. Failure to observe ligand hyperfine contribution by this nitrogen to the e.s.r. spectrum of [Cu(cbp)], in either frozen chloroform or solid solution in the (isomorphous) Zn^{II} analogue, can be rationalised by the assumption that the Cu complex has essentially the same structure in the Zn lattice as in the pure Cu complex and in chloroform solution.

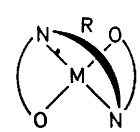
Crystal structures for [Cu(mbp)] and [Ni(mbp)] were determined by the heavy-atom method from counter data, and refined by full-matrix least-squares: [Cu(mbp)], space group $P\bar{1}$, $Z = 2$, $a = 10{\cdot}073(2)$, $b = 12{\cdot}438(3)$, $c = 13{\cdot}080(3)$ Å, $\alpha = 73{\cdot}89(2)$, $\beta = 67{\cdot}54(1)$, $\gamma = 86{\cdot}99(2)°$, R 6·3%, 2569 reflections; [Ni(mbp)], space group *Pcnb*, $Z = 4$, $a = 16{\cdot}927(2)$, $b = 24{\cdot}232(2)$, $c = 7{\cdot}1562(7)$ Å, $\alpha = \beta = \gamma = 90°$, R 6·1%, 1271 reflections. The Zn^{II} complex [Zn(cbp)] is isomorphous with [Cu(mbp)].

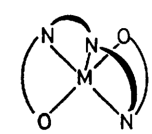
THE Schiff bases, (1), formed by condensation of 2-hydroxybenzophenones with various α,ω-diamines $R(NH_2)_2$, can act as quadridentate ligands to form monomeric complexes with copper- and nickel-(II), even if R is a very long chain.[1,2] Comparison with other Schiff-base complexes[3-5] suggests that as R increases, the ligand configuration will alter from *cis* (2) to *trans* (3). The point where this configurational


(1)

change occurs will depend on the flexibility of the ligand itself and on the metal bound to it. These compounds are frequently difficult to crystallise, and are sometimes even amorphous, possibly owing to the considerable


(2)


(3)


(4)

disorder that is possible when R is a long flexible chain, so that direct *X*-ray structural investigations have not been possible. If the chain R contains a donor atom capable of co-ordinating to the metal, as in (4), R is restricted to fewer positional possibilities. Complexes of type (4) will provide approximate models for the distortions in the ligand when R is a little too short to permit the *trans*-configuration, though the donor atom in R will produce some additional strains. The effect

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[2] G. M. Mockler and E. Sinn, unpublished work.
[3] B. O. West, in 'New Pathways in Inorganic Chemistry,' eds. E. V. Ebsworth, A. Maddock, and A. G. Sharp, Cambridge University Press, Cambridge, 1968.
[4] H. A. Goodwin, in 'Chelating Agents and Metal Chelates,' eds. F. D. Dwyer and D. P. Mellor, Academic Press, New York, 1964.
[5] R. H. Holm, G. W. Everett, jun., and A. Chakravorty, *Progr. Inorg. Chem.*, 1966, **7**, 83.

of altering the metal atom M bonded to identical quinquedentate ligands can also be observed directly in complexes of type (4). The structures and other properties of two such complexes, with R = $-[CH_2]_3\cdot NH\cdot [CH_2]_3-$, X = 5-Me, and M = Ni or Cu, are reported here.

Complexes of type (4), with salicylaldehydes in place of benzophenones have been reported previously,[6-9] and, for M = Ni and R = $-[CH_2]_3\cdot NH\cdot [CH_2]_3-$ and $-[CH_2]_3\cdot N(Me)\cdot [CH_2]_3-$, a five-co-ordinated structure has been observed.[9] For M = Cu, R = $-[CH_2]_3\cdot NH\cdot [CH_2]_3-$, an anomalous magnetic moment was observed [6] suggesting a di- or poly-meric structure, though i.r. data [7] suggest a five-co-ordinated copper environment which would make a polymeric structure unlikely. From a spectroscopic study of related quinquedentate complexes, Lane and Taylor noted that assignment of even gross stereochemical features is very difficult from electronic spectral data.[8] The results presented here indicate that e.s.r. spectra can give more specific information, but the most reliable technique is crystallography, and this may not be much more difficult with relatively small molecules (the present complexes have 40 non-hydrogen atoms).

EXPERIMENTAL

Preparation of Complexes.—*NN'-Bis*[(2-*hydroxy*-5-*methylphenyl*)*phenylmethylene*]-4-*azaheptane*-1,7-*diaminato*(2—)-*copper*(II), [Cu(mbp)]. The following procedure was typical for the various metal complexes, the appropriate metal acetate being used. The ligand (an oil) was prepared, but not isolated, by heating under reflux 2-hydroxy-5-methylbenzophenone (0·2 mmol) and 3,3'-iminobis(propylamine) (0·1 mmol) in methanol for ½ h. This solution was added to copper(II) acetate monohydrate (0·05 mmol) dissolved or suspended in methanol, when a dark green crystalline precipitate was formed. Crystals were grown from dichloromethane by slow evaporation (Found: C, 69·2; H, 6·4; Cu, 10·7; N, 7·4%. Calc. for $C_{34}H_{35}CuN_3O_2$: C, 70·26; H, 6·07; Cu, 10·93; N, 7·23%); m.p. 248 °C, *M* (mass spec.) 580. Diffraction data were collected on a rectangular prismatic crystal at a scan rate 2° min^{-1}, scan range 2·5°, maximum 2θ (Cu-K_α) 120°; 2182 independent intensities were recorded of which 1271 were significantly above background [having $I > 3\sigma(I)$]. The crystal used was atypical in that it was the only one of several apparently identically shaped crystals which was single.

[Ni(mbp)]. This complex was formed as a brown crystalline precipitate. Crystals were grown by slow evaporation from chloroform–benzene 1 : 1 (Found: C, 70·9; H, 6·2; N, 7·1; Ni, 10·4%. Calc. for $C_{34}H_{35}N_3NiO_2$: C, 70·85; H, 6·12; N, 7·29; Ni, 10·19%); m.p. >300 °C, *M* (mass spec.) 575. Diffraction data were collected on a fragment from a larger crystal at a scan rate 2° min^{-1}, scan range 2·9°, maximum 2θ (Mo-K_α) 60°; 4236 independent intensities were recorded of which 2569 were significantly above background [having $I > 3\sigma(I)$].

The complexes [Zn(mbp)], [Co(mbp)], [Cu(cbp)], [Ni(cbp)], [Co(cbp)], and [Zn(cbp)] were prepared similarly. *M* (Mass spec.): [Zn(mbp)] 581, [Co(mbp)] 576, [Cu(cbp)] 620, [Ni(cbp)] 615, [Co(cbp)] 616, and [Zn(cbp)] 621. The zinc complex [Zn(cbp)] is important because of the similarity of its cell constants to those of [Cu(mbp)]; the properties of the other complexes will be reported in detail elsewhere. For e.s.r. measurements, the [Zn(cbp)] complex is a suitable diamagnetic diluent for copper(II) species having the [Cu(mbp)] structure, and crystal data for the zinc complex are given in Table 1.

Densities were determined by flotation in aqueous potassium iodide, m.p.s on a Fisher–Johns apparatus.

X-Band e.s.r. spectra of the Cu complex were run on a Varian V 4502 spectrometer equipped with a Hewlett–Packard X532B frequency meter. The magnetic field was measured with a Varian F 8 fluxmeter and a Hewlett–Packard 5246L frequency counter.

Collection and Reduction of Intensity Data.—Diffraction data for both [Cu(mbp)] and [Ni(mbp)] were collected on a Picker four-circle diffractometer, controlled by an XDS Σ2 computer as described previously.[10] Background intensities were measured as a function of θ in 30 steps and used to calculate the background for each reflection during data collection. The intensities of two standard reflections for each compound, monitored at regular intervals, were relatively constant throughout collection. Lattice constants (Table 1) were determined from least-squares

TABLE 1

Crystallographic data (distances in Å, angles in °)

Compound	[Cu(mbp)]	[Ni(mbp)]	[Zn(cbp)]
Space group	$P\bar{1}$	*Pncb*	$P\bar{1}$
a	10·073(2)	16·927(2)	10·099(1)
b	12·438(3)	24·232(2)	12·500(2)
c	13·080(3)	7·1562(7)	13·261(4)
α	73·89(2)	90	74·57(3)
β	67·54(1)	90	68·06(1)
γ	86·99(2)	90	86·67(2)
Z	2	4	2
No. of crystal faces	7	7	
μ/mm^3	0·015	0·014	
Max. trans. coeff.	0·902	0·795	
Min. trans. coeff.	0·850	0·468	
μ/cm^{-1}	8·10	12·83	
$D_m/g\ cm^{-3}$	1·32	1·32	
$D_c/g\ cm^{-3}$	1·329	1·304	

refinement of preliminary values obtained from precession photographs against the observed values of ±2θ for (31 for Cu complex; 16 for Ni) strong general reflections measured on the diffractometer. Intensity data [1271 for Ni, 2569 for Cu] were corrected for Lorentz and polarisation effects and then for absorption by use of Gaussian integration.[11] Grid sizes of 6 × 8 × 8 for Cu and 8 × 8 × 8 for Ni were used. Estimated standard deviations throughout this paper are usually derived from the inverse matrix in the course of normal least-squares refinement calculations.

Structure Determination and Refinement.—[Ni(mbp)]. A standard Patterson map calculated from all the data enabled location of the nickel atoms on a two-fold axial special position, introducing extra symmetry into the model. However, the choice of one oxygen atom peak off the two-fold axis was sufficient to phase the data correctly

[6] M. Calvin and C. H. Barkelew, *J. Amer. Chem. Soc.*, 1946, **68**, 2267.

[7] L. Sacconi and I. Bertini, *J. Amer. Chem. Soc.*, 1966, **88**, 5180.

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[9] M. Di Vaira, P. L. Orioli, and L. Sacconi, *Inorg. Chem.*, 1971, **10**, 553; M. Seleborg, S. L. Holt, and B. Post, *ibid.*, p. 1501.

[10] R. F. Bryan, P. T. Greene, P. F. Stockley, and E. W. Wilson, *Inorg. Chem.*, 1971, **10**, 1468.

[11] Absorption program DIFABS, adapted for Xerox Σ2 computer from the DATAPH program of P. Coppens.

and the remaining non-hydrogen atoms were found from three-dimensional Fourier syntheses. All atoms were unambiguously located with the exception of the $-[CH_2]_3\cdot N-$ group which evidenced disorder. Block-diagonal least-squares refinement with all atoms anisotropic reduced R to 6·84%. At this point, apparent disorder was observed in the positions of C(16) and N(2). Introduction of half-atoms for C(16) and N(2) reduced R from 6·84 to 6·40% and Hamilton's test [12] confirmed that this was significant. The structure was then refined by the CRYLSQ program of *X*-Ray '72 [13] and the eight phenyl hydrogens inserted as fixed atoms in calculated positions, assuming C–H 1·00 Å along the bisectors of C–C–C angles, with isotropic temperature factors of 3·0. Further refinement gave R 6·1% (R' 9·3%).

A final difference map showed only diffuse electron density of the magnitude expected for hydrogen atoms on the methylene chain, but these atoms were not included owing to the disorder.

[Cu(mbp)]. A standard Patterson map calculated from all data enabled location of the copper atom in a general position (R 46%) and this was sufficient to phase the data correctly. All the remaining non-hydrogen atoms were unambiguously located from a three-dimensional Fourier synthesis, and block-diagonal least-squares refinement with all the atoms anisotropic produced R 6·7, R' 7·7%. Full-matrix least-squares [13] gave R 6·8%. A

[12] W. C. Hamilton, *Acta Cryst.*, 1965, **18**, 502.

[13] '*X*-Ray '72' program system, ed. J. M. Stewart, University of Maryland Technical Report TR 192.

TABLE 2

Final positional ($\times 10^4$) and thermal * ($\times 10^3$) parameters

(*a*) For [Cu(mbp)]

Atom	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	1244·6(1·0)	3144·1(0·8)	2046·1(0·8)	32·6(0·6)	30·1(0·6)	29·9(0·6)	−4·2(0·3)	−1·9(0·4)	−0·9(0·4)
O	311(5)	4534(4)	1859(4)	32(3)	38(3)	42(3)	10(2)	−6(2)	−2(3)
O′	2564(5)	2155(4)	2570(4)	32(3)	41(3)	27(2)	12(2)	−6(2)	−5(2)
N(1)	2643(6)	3661(5)	465(5)	32(3)	30(3)	33(3)	3(2)	−12(3)	−9(3)
N(1′)	−282(6)	2560(5)	3600(5)	29(3)	29(3)	40(3)	3(2)	−13(2)	−5(3)
N(2)	131(7)	1921(7)	1462(6)	40(4)	55(5)	42(4)	−3(3)	−8(3)	−15(4)
C(1)	2254(8)	5656(6)	201(6)	31(4)	21(3)	26(3)	2(3)	−4(3)	−4(3)
C(2)	995(8)	5516(7)	1243(7)	26(4)	49(5)	34(4)	2(3)	−5(3)	−9(4)
C(3)	467(9)	6475(8)	1570(8)	38(5)	55(6)	48(5)	15(4)	−5(4)	−21(4)
C(4)	1156(9)	7515(8)	962(8)	43(5)	45(5)	47(5)	9(4)	−11(4)	−20(4)
C(5)	2405(9)	7672(7)	−42(7)	45(5)	35(5)	40(4)	−4(4)	−13(4)	−3(4)
C(6)	2909(9)	6733(7)	−412(6)	45(5)	32(4)	27(4)	1(3)	−10(3)	−6(3)
C(7)	2921(7)	4693(6)	−222(6)	29(4)	23(4)	29(4)	−3(3)	−9(3)	−1(3)
C(8)	3931(8)	4962(6)	−1463(7)	31(4)	34(4)	36(4)	2(3)	−6(3)	−10(4)
C(9)	5393(9)	5094(8)	−1766(8)	31(5)	51(5)	50(5)	−8(4)	−7(4)	−20(4)
C(10)	6342(10)	5330(7)	−2936(9)	48(5)	32(5)	67(6)	−11(4)	5(5)	−18(4)
C(11)	5804(12)	5380(8)	−3766(8)	77(8)	46(6)	35(5)	12(5)	−3(5)	−15(4)
C(12)	4331(12)	5258(9)	−3456(8)	79(7)	58(6)	39(5)	14(5)	−23(5)	−17(5)
C(13)	3393(9)	5036(7)	−2306(7)	51(5)	37(5)	35(4)	6(4)	−17(4)	−2(4)
C(14)	3170(12)	8836(8)	−691(9)	77(7)	31(5)	64(6)	−8(5)	−13(5)	−9(4)
C(15)	3347(9)	2747(6)	−18(7)	41(5)	28(4)	36(4)	9(3)	−3(3)	−23(4)
C(16)	2335(10)	2141(8)	−335(8)	62(6)	47(5)	46(5)	14(4)	−20(4)	−10(3)
C(17)	1215(10)	1332(8)	692(9)	49(5)	49(6)	67(6)	2(4)	−10(5)	−28(5)
C(1′)	1353(8)	2082(6)	4588(6)	28(4)	33(4)	33(4)	1(3)	−4(3)	−8(3)
C(2′)	2580(8)	2013(7)	3589(6)	29(4)	42(5)	24(3)	−4(3)	−6(3)	−6(3)
C(3′)	3858(8)	1718(7)	3673(7)	36(5)	44(5)	33(4)	−4(4)	−6(3)	0(4)
C(4′)	3993(8)	1619(7)	4791(7)	34(5)	45(5)	42(5)	2(3)	−19(4)	3(4)
C(5′)	2823(9)	1767(8)	5754(6)	47(5)	56(6)	24(4)	−12(4)	−9(3)	−3(4)
C(6′)	1525(9)	1963(6)	5641(6)	43(5)	30(4)	28(4)	−7(3)	−9(3)	−1(3)
C(7′)	−82(8)	2243(6)	4543(6)	35(4)	21(3)	28(4)	−5(3)	−2(3)	2(3)
C(8′)	−1349(8)	1899(7)	5698(6)	22(4)	39(4)	25(4)	2(3)	−0(3)	−5(3)
C(9′)	−1845(9)	793(7)	6207(8)	32(4)	41(5)	47(5)	−2(4)	1(4)	−13(4)
C(10′)	−3028(9)	508(7)	7260(7)	38(5)	41(5)	42(4)	−7(4)	0(4)	1(4)
C(11′)	−3676(9)	1305(8)	7772(7)	32(4)	53(6)	40(4)	−1(4)	7(4)	−5(4)
C(12′)	−3193(11)	2407(9)	7271(9)	58(6)	64(7)	55(6)	7(5)	11(5)	−29(5)
C(13′)	−2014(11)	2711(8)	6291(8)	56(6)	37(5)	49(5)	−0(4)	8(4)	−7(4)
C(14′)	3014(11)	1704(10)	6863(8)	70(7)	83(8)	47(5)	−5(6)	−33(5)	−18(5)
C(15′)	−1699(8)	2564(8)	3554(7)	26(4)	54(6)	45(5)	7(4)	−10(3)	−3(4)
C(16′)	−2043(10)	1527(9)	3293(8)	37(5)	76(7)	51(5)	11(5)	−15(4)	−9(5)
C(17′)	−758(10)	1053(8)	2514(8)	52(6)	53(6)	53(5)	−4(5)	−20(5)	−12(5)

Atom †	X	Y	Z	Atom	X	Y	Z
H(3)	−443	6415	2273	H(3′)	4717	1581	3102
H(4)	761	8179	1262	H(4′)	4958	1432	4867
H(6)	3786	6820	−1146	H(6′)	648	2018	6328
H(9)	5797	5031	−1150	H(9′)	−1363	197	5804
H(10)	7412	5456	−3152	H(10′)	−3408	−305	7653
H(11)	6490	5526	−4585	H(11′)	−4519	1092	8536
H(12)	3930	5339	−4080	H(12′)	−3688	2999	7663
H(13)	2313	4924	−2080	H(13′)	−1656	3535	5865
H(151)	4251	3048	−725	H(151′)	−2454	2613	4319
H(152)	3639	2185	570	H(152′)	−1761	3246	2941
H(161)	1833	2731	−728	H(161′)	−2518	932	4051
H(162)	2938	1728	−902	H(162′)	−2768	1708	2915
H(171)	694	867	417	H(171′)	−153	703	2970
H(172)	1704	790	1155	H(172′)	−1111	445	2291

TABLE 2 (*Continued*)

(*b*) For [Ni(mbp)]

Atom	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni	0	2500	1393(2)	43·2(0·8)	34·1(0·8)	40·1(0·8)	−4·7(0·6)	0	0
O	9063(3)	2945(2)	832(8)	41(2)	46(3)	95(4)	−4(2)	3(3)	18(3)
N	650(3)	3193(2)	1188(8)	42(3)	41(3)	56(4)	−1(2)	−15(3)	6(3)
N(2)	9972(12)	2653(4)	4192(14)	63(7)	42(9)	37(5)	−16(11)	−3(8)	9(4)
C(1)	9776(3)	3604(3)	8908(9)	34(3)	43(3)	43(4)	7(2)	2(3)	−5(3)
C(2)	9087(4)	3278(3)	9413(11)	44(4)	34(3)	66(5)	−6(3)	−10(4)	−13(3)
C(3)	8420(4)	3349(3)	8243(12)	33(4)	63(5)	89(6)	1(3)	−7(4)	−13(4)
C(4)	8427(4)	3678(4)	6685(12)	54(4)	72(5)	70(6)	16(4)	−20(4)	−18(4)
C(5)	9092(4)	3968(3)	6179(10)	62(5)	74(5)	47(4)	21(4)	−9(4)	3(4)
C(6)	9745(4)	3933(3)	7300(10)	50(4)	51(4)	47(4)	11(3)	−5(3)	−7(3)
C(7)	495(3)	3601(2)	59(10)	40(3)	34(3)	50(4)	2(3)	−1(3)	0(3)
C(8)	1060(3)	4067(2)	9763(9)	38(3)	32(3)	43(4)	1(3)	−0(3)	5(3)
C(9)	874(4)	4593(2)	451(9)	44(4)	37(3)	47(4)	9(3)	−7(3)	6(3)
C(10)	1385(4)	5038(2)	108(10)	59(4)	33(3)	55(4)	7(3)	−6(4)	5(3)
C(11)	2067(4)	4946(3)	9086(11)	50(4)	51(4)	62(4)	−12(3)	−3(4)	17(3)
C(12)	2260(4)	4432(3)	8439(10)	47(4)	50(4)	62(5)	3(3)	16(4)	1(3)
C(13)	1750(4)	2988(3)	8760(10)	45(4)	47(4)	57(4)	4(3)	7(4)	−8(3)
C(14)	9120(3)	4342(5)	4355(14)	151(11)	144(9)	57(6)	36(8)	−12(6)	60(6)
C(15)	1381(5)	3213(3)	2340(12)	60(4)	52(4)	76(6)	−10(3)	−31(4)	23(4)
C(16′)	1313(10)	2827(7)	4200(22)	79(11)	41(8)	57(10)	−7(9)	−38(9)	21(8)
C(16″)	1203(10)	3193(7)	4181(24)	65(10)	49(9)	66(11)	−17(9)	−18(8)	11(8)
C(17)	638(7)	2733(3)	5107(12)	113(8)	61(5)	48(4)	−19(5)	−15(5)	8(4)

Atom †	X	Y	Z	Atom	X	Y	Z
H(3)	2238	4361	2702	H(10)	4108	803	−13
H(4)	2570	5274	3794	H(11)	2940	1292	855
H(6)	481	4784	403	H(12)	2912	1851	3618
H(9)	5148	775	2636	H(13)	4416	1415	4977

* Anisotropic thermal parameters in the form $T = -2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{13}klb^*c^*)$.

† All H atoms were inserted as fixed atoms before the final refinement, with U 0·0380.

difference map revealed peaks of the electron density expected for hydrogen atoms. Inclusion of non-methyl and non-amine hydrogen atoms, calculated as before for phenyl groups, and calculated at tetrahedral positions for methylene hydrogen, at the calculated positions, reduced R to 6·3% (R' 9·1%). A final difference map was featureless. A weighting scheme based on counting statistics was used in the final stages of both refinements.

Atomic scattering-factor curves were derived from ref. 14 for neutral copper, nickel, oxygen, nitrogen, and carbon atoms, those for copper and nitrogen being corrected for the effects of anomalous dispersion according to the values of ref. 15. Scattering factors for hydrogen were taken from ref. 16.

Final atomic co-ordinates and anisotropic thermal parameters with standard deviations for both structures are given in Table 2. Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 21233 (28 pp., 1 microfiche).*

Molecular diagrams were drawn by use of the program ORTEP,[17] modified slightly to make it compatible with the University of Virginia CDC6400 computer, and to produce lower case letters and other symbols.

RESULTS AND DISCUSSION

The molecular geometries and numbering systems are given in Figures 1 and 2 respectively. Both positions of each disordered atom in the nickel complex are shown. Figure 3 gives the packing in the nickel complex, again with the disordered atoms in both positions, and Figure 4 a stereoscopic view of the packing in the copper complex.

* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

[14] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.
[15] D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891.

Interatomic distances and angles for both complexes are listed in Table 3.

The extensive twinning observed in [Ni(mbp)] may be a consequence of the conflict between the space

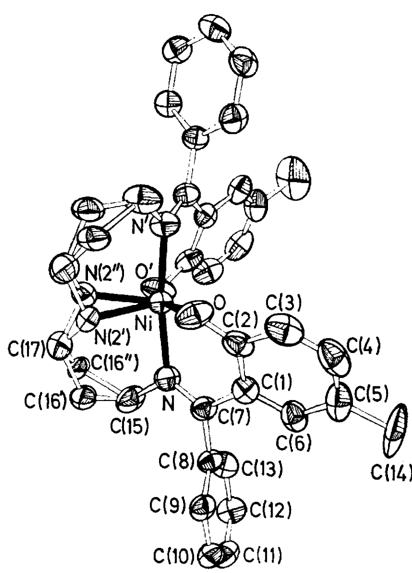

FIGURE 1 The molecule of [Ni(mbp)], showing the atom numbering system used

group which requires a crystallographic two-fold axis and the fact that the compound has no possible two-fold symmetry. The symmetry requirement can be

[16] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.
[17] C. K. Johnson, ORTEP (with overlap modifications, ORTEP 2), Report ORNL 2794, Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A., 1965.

satisfied chemically by the molecule only if the $N\cdot[CH_2]_3\cdot NH\cdot[CH_2]_3\cdot N$ chain were oxidised to form a conjugated imine group. This possibility was tested but found to be incompatible with the *X*-ray data. Our results indicate statistical packing disorder in the crystal chosen for data collection, with equal distributions of the chain R on either side of the two-fold axis. The average of the two conformations has apparent two-fold symmetry.

TABLE 3

Bond distances and angles

(*a*) For [Cu(mbp)]; equivalent dimensions in the primed portion of the ligand (see Figure 2) are given second

(*i*) Distances (Å)

Cu–O	1·925(5), 1·951(5)
Cu–N(1)	1·951(5), 1·983(5)
Cu–N(2)	2·374(10)
C(1)–C(2)	1·438(9), 1·435(9)
C(1)–C(6)	1·402(10), 1·420(13)
C(1)–C(7)	1·481(11), 1·471(12)
C(2)–O	1·317(9), 1·302(10)
C(2)–C(3)	1·389(14), 1·404(12)
C(3)–C(4)	1·374(12), 1·374(14)
C(4)–C(5)	1·403(10), 1·407(11)
C(5)–C(6)	1·385(13), 1·373(14)
C(5)–C(14)	1·531(12), 1·515(16)
C(7)–N(1)	1·319(8), 1·276(11)
C(7)–C(8)	1·501(9), 1·523(9)
C(8)–C(9)	1·377(12), 1·377(12)
C(8)–C(13)	1·383(15), 1·378(13)
C(9)–C(10)	1·416(12), 1·400(10)
C(10)–C(11)	1·374(18), 1·351(14)
C(11)–C(12)	1·384(17), 1·368(14)
C(12)–C(13)	1·393(11), 1·398(12)
C(15)–N(1)	1·472(10), 1·451(11)
C(15)–C(16)	1·534(16), 1·511(17)
C(16)–C(17)	1·517(11), 1·519(14)
C(17)–N(2)	1·493(13), 1·482(10)

(*ii*) Angles (°)

O–Cu–O′	152·2(3)	C(1)–C(7)–C(8)	116·3(6)
O–Cu–N(1)	90·5(2)	C(8)–C(7)–N(1)	122·4(7)
O–Cu–N(2)	106·5(3)	N(1)–Cu–N(1′)	174·9(3)
O–Cu–N(1′)	89·6(2)	O′–Cu–N(1)	93·5(2)
N(1)–Cu–N(2)	88·9(3)	O′–Cu–N(2)	101·0(3)
Cu–O–C(2)	124·0(5)	O′–Cu–N(1′)	88·7(2)
Cu–N(1)–C(7)	127·9(5)	N(1′)–Cu–N(2)	86·2(3)
Cu–N(1)–C(15)	113·7(4)	Cu–O′–C(2′)	121·6(5)
C(7)–N(1)–C(15)	118·1(5)	Cu–N(1′)–C(7′)	125·5(5)
Cu–N(2)–C(17)	111·7(6)	Cu–N(1′)–C(15′)	111·7(5)
C(17)–N(2)–C(17′)	107·3(7)	C(7)–N(1′)–C(15′)	122·8(6)
C(2)–C(1)–C(6)	119·1(7)	Cu–N(2)–C(17′)	107·3(7)
C(2)–C(1)–C(7)	122·2(6)	C(2′)–C(1′)–C(6′)	119·4(7)
C(6)–C(1)–C(7)	118·7(6)	C(2′)–C(1′)–C(7′)	120·9(8)
C(1)–C(2)–C(3)	117·5(7)	C(6′)–C(1′)–C(7′)	119·7(6)
C(1)–C(2)–O	122·7(8)	C(1′)–C(2′)–C(3′)	116·1(8)
C(3)–C(2)–O	119·8(6)	C(1′)–C(2′)–O′	124·8(7)
C(2)–C(3)–C(4)	121·8(7)	C(3′)–C(2′)–O′	119·0(6)
C(3)–C(4)–C(5)	121·9(9)	C(2′)–C(3′)–C(4′)	122·7(7)
C(4)–C(5)–C(6)	117·1(7)	C(3′)–C(4′)–C(5′)	121·4(8)
C(4)–C(5)–C(14)	120·9(8)	C(4′)–C(5′)–C(6′)	117·3(9)
C(6)–C(5)–C(14)	122·0(7)	C(4′)–C(5′)–C(14′)	120·4(9)
C(1)–C(6)–C(5)	122·5(6)	C(16)–C(15)–N(1)	111·4(7)
C(6′)–C(5′)–C(14′)	122·2(7)	C(15)–C(16)–C(17)	113·8(9)
C(1′)–C(6′)–C(5′)	122·6(7)	C(16)–C(17)–N(2)	122·3(8)
C(1′)–C(7′)–N(1′)	123·0(6)	C(7′)–C(8′)–C(9′)	120·6(7)
C(1′)–C(7′)–C(8′)	115·8(7)	C(7′)–C(8′)–C(13′)	119·2(7)
C(8′)–C(7′)–N(1′)	121·0(7)	C(9′)–C(8′)–C(13′)	120·1(6)
C(7)–C(8)–C(9)	120·6(9)	C(8′)–C(9′)–C(10′)	119·2(8)
C(7)–C(8)–C(13)	119·7(7)	C(9′)–C(10′)–C(11′)	120·6(8)
C(9)–C(8)–C(13)	119·6(7)	C(10′)–C(11′)–C(12′)	120·7(7)
C(8)–C(9)–C(10)	120·4(10)	C(11′)–C(12′)–C(13′)	119·8(10)
C(9)–C(10)–C(11)	119·7(9)	C(8′)–C(13′)–C(12′)	119·7(8)
C(10)–C(11)–C(12)	119·5(8)	C(16′)–C(15′)–N(1′)	112·0(7)
C(11)–C(12)–C(13)	120·9(11)	C(15′)–C(16′)–C(17′)	115·0(8)
C(8)–C(13)–C(12)	111·8(9)	C(16′)–C(17′)–N(2)	112·5(8)
C(1)–C(7)–N(1)	121·3(7)		

TABLE 3 (*Continued*)

(*b*) [Ni(mbp)]

(*i*) Distances

Ni–O	1·959(4)	C(5)–C(6)	1·368(10)
Ni–N	2·013(5)	C(5)–C(14)	1·591(13)
Ni–N(2)	2·038(10)	C(7)–N	1·304(8)
C(1)–C(2)	1·453(9)	C(7)–C(8)	1·494(8)
C(1)–C(6)	1·402(10)	C(8)–C(9)	1·401(8)
C(2)–O	1·298(9)	C(8)–C(13)	1·385(9)
C(2)–C(3)	1·416(10)	C(9)–C(10)	1·405(9)
C(3)–C(4)	1·371(12)	C(10)–C(11)	1·386(10)
C(4)–C(5)	1·375(11)	C(11)–C(12)	1·368(9)
C(1)–C(7)	1·470(9)	C(12)–C(13)	1·399(9)
C(15)–N	1·487(10)	C(16′)–C(17)	1·611(20)
C(15)–C(16′)	1·631(18)	C(17)–N(2′)	1·317(21)
C(15)–C(16″)	1·353(20)	C(17)–N(2″)	1·539(18)
C(16′)–C(17)	1·334(20)		

(*ii*) Angles

O–Ni–O′	156·3(3)	C(16″)–C(17)–N(2′)	113·8(10)
O–Ni–N	90·1(2)	N(2′)–C(17)–N(2″)	29·0(7)
O–Ni–N(2′)	108·7(5)	N–Ni–N′	171·7(2)
N–Ni–N(2′)	86·1(4)	O–Ni–N′	88·2(2)
N(2′)–Ni–N(2″)	21·1(4)	O–Ni–N(2″)	94·8(5)
Ni–N–C(15)	116·2(4)	N–Ni–N(2″)	102·2(4)
Ni–O–C(2)	118·5(4)	Ni–N–C(7)	124·6(4)
C(2)–C(1)–C(7)	121·5(6)	C(7)–N–C(15)	119·1(5)
C(1)–C(2)–O	123·9(6)	Ni–N(2′)–C(17)	119·7(12)
C(3)–C(2)–O	120·9(6)	Ni–N(2″)–C(17)	108·9(8)
C(3)–C(4)–C(5)	121·1(7)	C(2)–C(1)–C(6)	118·9(6)
C(4)–C(5)–C(14)	122·1(7)	C(6)–C(1)–C(7)	119·6(6)
C(1)–C(6)–C(5)	123·1(6)	C(1)–C(2)–C(3)	115·3(6)
C(1)–C(7)–N	121·2(5)	C(2)–C(3)–C(4)	123·0(7)
C(7)–C(8)–C(9)	119·6(5)	C(4)–C(5)–C(6)	118·4(7)
C(9)–C(8)–C(13)	119·9(5)	C(6)–C(5)–C(14)	119·5(7)
C(9)–C(10)–C(11)	118·8(6)	C(1)–C(7)–C(8)	116·5(5)
C(11)–C(12)–C(13)	119·9(6)	C(8)–C(7)–N	122·2(5)
C(16′)–C(15)–N	112·0(8)	C(7)–C(8)–C(13)	120·5(5)
C(16′)–C(15)–C(16″)	33·7(9)	C(8)–C(9)–C(10)	119·9(6)
C(15)–C(16′)–C(17)	123·8(13)	C(10)–C(11)–C(12)	121·6(6)
C(16′)–C(17)–N(2′)	121·0(11)	C(8)–C(13)–C(12)	119·9(6)
C(16″)–C(15)–N	110·6(9)	C(16″)–C(17)–N(2″)	130·0(9)
C(15)–C(16″)–C(17)	124·0(13)	C(16′)–C(17)–C(16″)	34·2(9)
C(16′)–C(17)–N(2″)	118·1(11)		

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

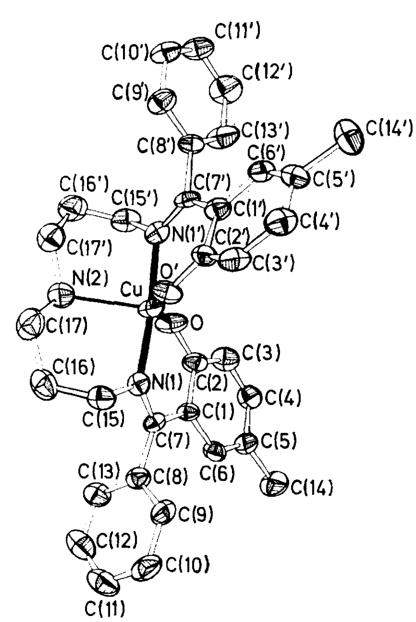

FIGURE 2 The molecule of [Cu(mbp)], showing the atom numbering system used

TABLE 4

Coefficients of least-squares planes; equations in the form $AX + BY + CZ = D$; distances (Å) of relevant atoms from the planes are given. Data for [Cu(mbp)] are given before data for [Ni(mbp)]

Plane	Atoms	A	B	C	D	Distances
(I)	Cu, O, O′, N(1), N(1′)	−0·6508	−0·6909	−3·148 0	−5·6881	O −0·3161, O′ −0·3067, N(1) 0·2294, N(1′) 0·2425, Cu 0·1509, N(2) 2·5221
	Ni, O, O′, N, N′	0	0	−1·0	−0·7732	O 0·1803, O′ 0·1803, N −0·0690, N′ −0·0690, Ni −0·2227, N(2) −0·2312
(II)	Cu, O, C(1), C(2), C(7), N(1)	−0·8496	−0·2786	−0·4479	−4·2664	Cu −0·1853, O 0·2502, C(2) −0·0892, C(1) −0·1418, C(7) 0·1136, N(1) 0·0525
	Ni, O, C(1), C(2), C(7), N	−0·2583	0·5262	−0·8102	2·0708	Ni 0·3099, O −0·3432, C(2) 0·0653, C(1) 0·2402, C(7) −0·1050, N −0·1672
(II)	Cu, O′, C(1′), C(2′), C(7′), N(1′)	0·3029	0·9530	−0·0047	4·8527	Cu 0·2667, O′ −0·2768, C(2′) 0·0336, C(1′) 0·2087, C(7′) −0·0562, N(1′) 0·1760
	Ni, O′, C(1′), C(2′), C(7′), N′	0·2583	−0·5262	−0·8102	−4·3042	Ni 0·3099, O′ −0·3432, C(2′) 0·0653, (C1′), 0·2402, C(7′), −0·1050, N′ −0·1672
(IV)	Cu, O, O′, N(2)	0·3771	0·0620	−0·9241	−1·0108	Cu 0·0364, O −0·0155, O′ −0·0150, N(2) −0·0059
	Ni, O, O′, N(2)	−0·5589	−0·8207	−0·1182	−5·0562	Ni −0·0336, O 0·0137, O′ 0·0144, N(2) 0·0055
(V)	Cu, N(1), N(1′), N(2)	−0·6960	0·6838	−0·2193	0·9094	Cu −0·0150, N(1) 0·0078, N(1′) 0·0077, N(2) −0·0006
	Ni, N, N′, N(2)	0·8326	−0·5428	−0·1103	−3·3866	Ni −0·0116, N 0·0053, N′ 0·0054, N(2) 0·0008
(VI)	C(1)—(6), C(14)	−0·8374	−0·0038	−0·5466	−2·4455	C(1) −0·0032, C(2) −0·0305, C(3) 0·0135, C(4) 0·0110, C(5) 0·0068, C(6) 0·0270, C(14) −0·0246
	C(1)—(6), C(14)	−0·3255	0·7809	−0·5332	2·9340	C(1) −0·0021, C(2) 0·0418, C(3) −0·0072, C(4) −0·0029, C(5) −0·0227, C(6) −0·0277, C(7) 0·0408
(VII)	C(8)—(13)	−0·0819	0·9902	−0·1130	5·5147	C(8) 0·0006, C(9) −0·0073, C(10) 0·0142, C(11) −0·0145, C(12) 0·0077, C(13) −0·0007
	C(8)—(13)	0·4913	−0·2022	−0·8472	−1·1999	C(8) 0·0041, C(9) −0·0036, C(10) −0·0016, C(11) 0·0063, C(12) −0·0058, C(13) 0·0006
(VI)′	C(1′)—(6′), C(14′)	0·1926	0·9382	−0·2876	3·0886	C(1′) −0·0134, C(2′) 0·0652, C(3′) −0·213, C(4′) −0·0301, C(5′) −0·0066, C(6′) −0·0367, C(14′) 0·0430
(VII′)	C(8′)—(13′)	−0·8728	−0·0111	−0·4880	−4·6802	C(8′) −0·0014, C(9′) 0·0004, C(10′) 0·0010, C(11′) −0·0015, C(12′) 0·0004, C(13′) 0·0010

	(I)–(II)	(I)–(III)	(I)–(IV)	(II)–(III)	(II)–(VI)	(III)–(VI′)	(IV)–(V)	(VI)–(VII)	(VI)–(VII′)
Cu	27·6	31·3	89·9	58·6	16·8	17·5	89·0	82·7	87·8
Ni	35·9	35·9	83·2	71·8	22·0	22·0	89·6	82·3	

cannot be dismissed as a steric requirement of the ligand, since it does not occur in the nickel analogue. This striking difference between the two compounds suggests that the regular five-co-ordinated environment is less favoured for such ligands in d^9 than in d^8 complexes. Otherwise the difference between the molecular geometries of the two complexes is minimal. The shorter mean metal–ligand bond distance in [Ni(mbp)] implies a greater ligand-field strength in the d^8 than in the d^9 complex. A more detailed comparison of the peripheral parts of the molecules is given in Table 4, in the form of least squares planes, interplanar angles, and deviations of atoms from the planes.

The mass spectrum of each complex exhibited the molecular ion, and the values given in the experimental section are based on ^{63}Cu, ^{58}Ni, ^{64}Zn, ^{59}Co, ^{12}C, and ^{35}Cl. That the spectra are temperature dependent is due mainly to pyrolysis products at the relatively high temperatures (*ca.* 350—400 °C) needed to produce volatility, again indicating that the various metals form very similar complexes with the two ligands. Certain characteristic peaks can be identified unambiguously, *e.g.* the Cu, Ni, Co complexes have $M - 18$, presumably

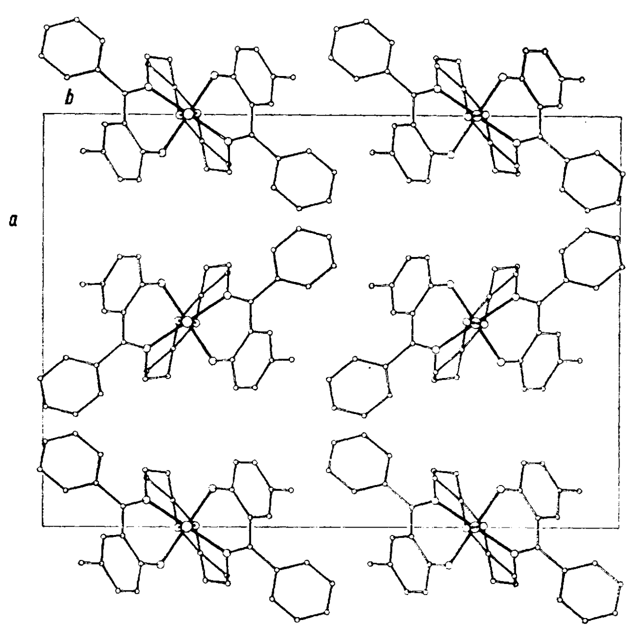

FIGURE 3 The unit cell of [Ni(mbp)] viewed down the c axis

$M - (H_2O)$, the Zn complexes have $M - 17$, the cbp complexes $MH - (Cl)$, the mbp complexes $M - 196$, 211, and the Cu and Ni complexes have $MH_2 - (Cu,Ni)$ at high temperatures. In each case, the spectra provide unique identification of the complex.

Detailed spectral and magnetic studies down to liquid helium temperature of these and other complexes with similar ligands and various metals will be reported subsequently. An important feature is the absence of any significant magnetic exchange interactions in [Cu(mbp)] and the high-spin [Ni(mbp)], as would be expected from the separation of the metal atoms in isolated molecules in the lattice. Similarity of the solid and solution electronic spectra indicates that the structures are preserved in dichloromethane solution without detectable distortions.

The zinc complex [Zn(cbp)] has cell constants very similar to those of the triclinic [Cu(mbp)], while [Zn(mbp)] was found to be monoclinic. Thus, [Zn(cbp)] appears to be the more suitable diamagnetic diluent for an e.s.r. study of copper(II) in the [Cu(mbp)] structure. In fact, the e.s.r. spectra of [Cu(mbp)] in [Zn(mbp)] and [Cu(cbp)] in [Zn(cbp)] were found to be similar, though that of the latter was better resolved and is discussed here. The e.s.r. spectrum of [Cu(cbp)] is somewhat non-axial, indicating a deviation from a simple four-co-ordinate planar structure. This again is compatible with the observed structure. The accuracy of the average g and A^{Cu} values (Table 5) obtained for chloroform solution is limited by the slow tumbling of the rather large molecule, which leads to significant line-broadening. The anisotropic g and A values observed for frozen chloroform solution and diluted in a matrix of the isomorphous and diamagnetic [Zn(cbp)] complex, are typical of an axially elongated chromophore,[18] and compatible with the structure of Figure 2. The small differences between the values for frozen solution and matrix may be due to resolution limits especially for the solution, as much as to small structural differences. An expected moment can be derived from the e.s.r. data since the same magnetic field interactions are involved (detailed treatises have been given, *e.g.* refs. 19 and 20), and is expressed by $\mu = \bar{g}\sqrt{s(s+1)}$ where $\bar{g}^2 = \frac{1}{3}g_{\parallel}^2 + \frac{2}{3}g_{\perp}^2$ (ref. 20). Thus we have $\mu = \frac{1}{2}\sqrt{g_{\parallel}^2 + 2g_{\perp}^2}$, giving a value of 1·84 B.M., in good agreement with the observed values.[2]

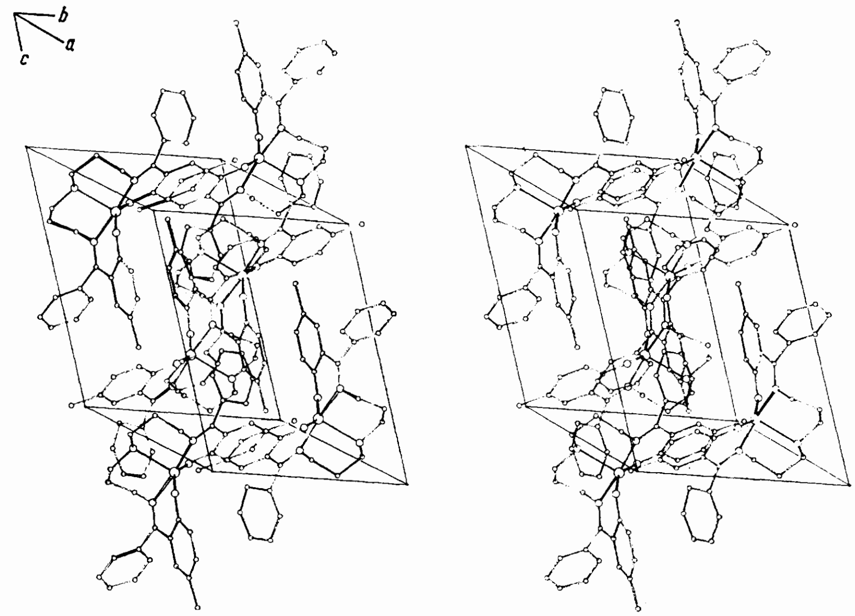

FIGURE 4 Stereodiagram of the unit cell of [Cu(mbp)]

TABLE 5

E.s.r. parameters

Medium	Temp./K	Parameters obs. from e.s.r. spectra *		
$CHCl_3$ soln.	300	g_{av} 2·13	A_{av} 64 G	$A_N \sim 10$ G
Frozen $CHCl_3$ soln.	77	$g_{\parallel}$ 2·234	$A_{\parallel}$ 131 G	A_N 12·7 G
2% in [Zn(cbp)]		$g_{\parallel}$ 2·259 $g_{\perp}$ 2·04$_5$	$A_{\parallel}$ 144 G	$A_{\perp}$ 48 G

* A^{Cu} values refer to mean for ^{63}Cu and ^{65}Cu. Resolution does not permit independent observation of the two values.

The e.s.r. parameters again suggest that the structure is closely similar in solution and diluted into [Zn(cbp)]. This makes probable a very similar structure in the Zn^{II} complexes as in the Cu^{II} complexes. However, it seems unlikely that [Zn(cbp)] will mimic the [Cu(mbp)] structure to the extent of having one very elongated metal–nitrogen bond. In fact, given the similar unit cells of [Zn(cbp)] and [Cu(mbp)], it seems likely that [Cu(cbp)] would adopt approximately the [Cu(mbp)] structure in [Zn(cbp)], and differ from its host in having the lengthened bond to the amine nitrogen. This

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[19] R. M. Golding, 'Applied Wave Mechanics,' Van Nostrand, London, 1969.

[20] B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, 1964, **6**, 37.

speculation about the structure of the zinc complex has recently been validated by the crystal structure of [Zn(cbp)], the refinement of which is near completion.[21] It is hoped that the crystal structures of [Zn(mbp)] and [Ni(cbp)] will permit a more generalised comparison of five-co-ordinate d^8, d^9, and d^{10} complexes.

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21 D. P. Freyberg, G. M. Mockler, and E. Sinn, unpublished work.