Substituted Phenols as Ligands. Part 7.[1] *X*-Ray Crystal-structure Analysis of Bis(2-methoxy-4-nitrophenolato)bis(pyridine)nickel(II) and the Electronic and Magnetic Properties of the Isomorphous Bis(2-methoxy-4-nitrophenolato)bis(pyridine)cobalt(II)

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Crystals of the title nickel(II) complex are triclinic with a = 9.642(1), b = 10.793(1), c = 12.622(1) Å, α = 85.28(1), β = 69.22(1), γ = 87.76(1)°, Z = 2, and space group $P\bar{1}$. The structure has been determined by direct methods, with Cu-K_α diffractometer data, and refined by full-matrix least squares to R 0.039 for 3 475 reflections. Both methoxy- and phenolic oxygen atoms co-ordinate to the metal and, together with the nitrogen atoms from the pyridine molecules, give the nickel atoms six-co-ordination. The *d–d* electronic spectrum is that expected for a six-co-ordinate complex with $m3m$ (O_h) symmetry, in spite of the long Ni–O(CH$_3$) bonds, but for the isomorphous cobalt(II) complex the effect of the low symmetry is observed. Similarly, the effective magnetic moments indicate deviations from regular stereochemistry for the cobalt(II) complex but not for the nickel(II) analogue.

PREVIOUS work in this series has shown that 2-alkoxyphenols can act as ligands, and a number of copper(II) complexes containing substituted phenolate ligands have been reported as adducts of nitrogen bases.[2] However, the role of the 2-alkoxy-substituents was not clearly understood. The *X*-ray crystallographic analyses of three copper(II) 2-methoxyphenolates have been carried out.[1-3] In each case, the phenolates were found to act as bidentate ligands. The Cu–O(CH$_3$) distances were much longer than either the Cu–O(phenolate) or the Cu–N bonds (Table 3). Based on structures of copper(II) complexes alone, it was not possible to decide if the long Cu–O(CH$_3$) distances were caused by an intrinsic weakness of the ether oxygen atom as a donor, by a Jahn–Teller distortion, by steric hindrance (although this was slight), or by a combination of these factors.

The structure determination of bis(2-methoxy-4-nitrophenolato)bis(pyridine)nickel(II), [Ni(mnp)$_2$(py)$_2$], has helped to resolve this problem.

EXPERIMENTAL

Samples of [Ni(mnp)$_2$(py)$_2$] crystallise from ethanol as dark green prisms. Unit-cell and space-group data were obtained from Weissenberg and precession photographs, and a Delauny reduction indicated that a primitive reduced cell had been correctly chosen. Accurate unit-cell dimensions were obtained by a weighted (w = tan θ) least-squares fit to the θ values of 19 reflections with resolvable α_1–α_2 doublets (38 measurements), measured on a Siemens four-circle diffractometer (A.E.D.), using nickel-filtered Cu-K_α radiation.

Crystal Data.—$C_{24}H_{22}N_4NiO_8$, M = 553.17, Triclinic, a = 9.642(1), b = 10.793(1), c = 12.622(1) Å, α = 85.28(1), β = 69.22(1), γ = 87.76(1)°, U = 1 223.9(5) Å^3, D_c = 1.507, Z = 2, D_m = 1.49 g cm^{-3} (by flotation in aqueous potassium iodide), $F(000)$ = 572, μ(Cu-K_α) = 15.0 cm^{-1}, space group $P\bar{1}$. A crystal of dimensions 0.25 × 0.2 × 0.1 mm, parallel to *a*, *b*, and *c* respectively, was selected for the intensity measurements. The intensities of 4 154 symmetry-independent reflections with $(\sin\theta)/\lambda \leqslant 0.60$ were measured on the diffractometer (equipped with a scintillation counter and pulse-height discriminator), using the five-value measurement technique.[4] A reference reflection, monitored after every 20 data reflections, gave no indication of crystal decomposition.

Each intensity was assigned a variance, $\sigma^2(I)$, based on the counting statistics. A total of 679 reflections was classified as ' unobserved ', using the criterion $I/\sigma(I) \leqslant 2.58$. The intensities were corrected for Lorentz and polarisation effects but not for absorption.

Structure Determination and Refinement.—An $N(Z)$ test established the space group as $P\bar{1}$. The structure was solved by direct methods using the SHEL-X suite of

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[1] Part 6, M. F. C. Ladd and D. C. Povey, *J. Cryst. Mol. Struct.*, 1976, **6**, 205.

[2] J. I. Bullock, R. J. Hobson, and D. C. Povey, *J.C.S. Dalton*, 1974, 2037.

[3] R. J. Hobson, M. F. C. Ladd, and D. C. Povey, *J. Cryst. Mol. Struct.*, 1973, **3**, 377.

[4] W. Hoppe, *Angew. Chem.*, 1965, **77**, 484.

crystallographic programs:[5] 574 reflections with $|E| \geqslant 1.40$ were used in the sign-determining procedure. The structure was solved automatically by the program, the whole molecule being revealed in the E map having the highest figure of merit. Positional and isotropic thermal parameters and an overall scale factor, all refined by full-matrix least squares, reduced the conventional R factor from 0.20 to 0.12, the quantity minimised being $\Sigma w(|F_o| - |F_c|)^2$ with $w = 1$. Two further cycles of least squares, now with anisotropic thermal parameters, gave R 0.074.

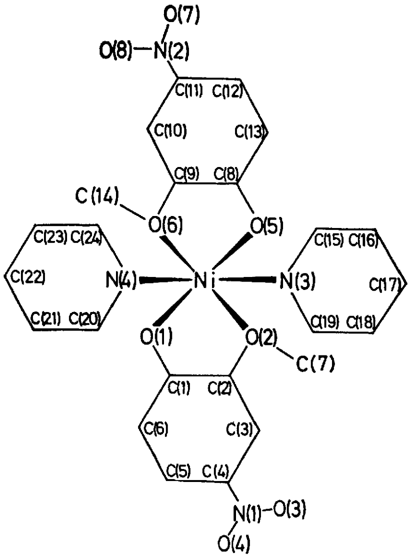

FIGURE 1 Numbering scheme for [Ni(mnp)$_2$(py)$_2$]

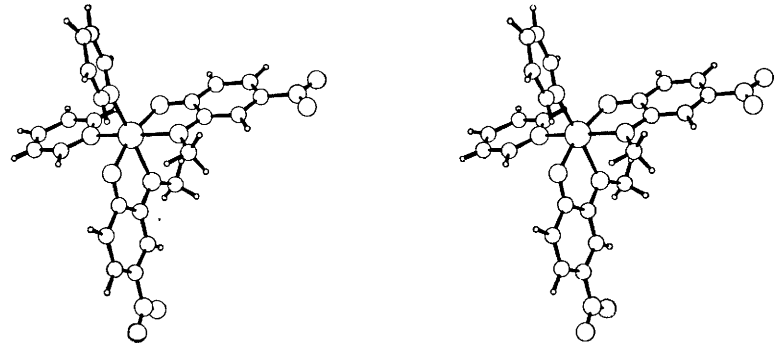

FIGURE 2 Stereoscopic view of [Ni(mnp)$_2$(py)$_2$]

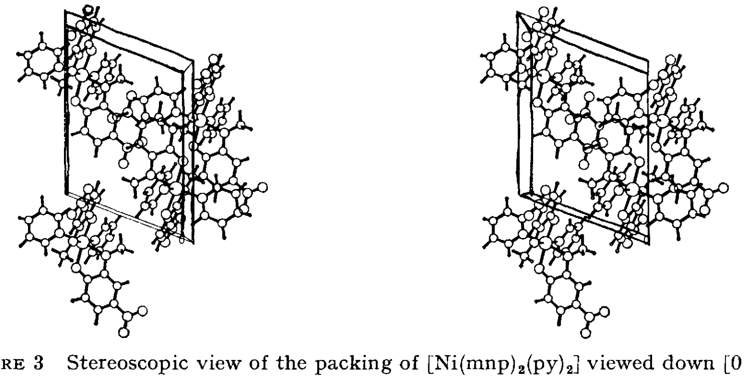

FIGURE 3 Stereoscopic view of the packing of [Ni(mnp)$_2$(py)$_2$] viewed down [010]

A three-dimensional difference-Fourier map revealed the positions of all the hydrogen atoms except those of the methyl groups; these atomic co-ordinates were obtained by calculation, assuming a minimum-energy conformation for the methyl group. At this point, a weighting scheme ($w = 1$ if $A \geqslant |F_o|$; otherwise, $w = (A/|F_o|)^2$ with $A = 25$) was applied to the data and judged to be satisfactory by the usual criteria. Six further cycles of least-squares refinement, including the hydrogen atoms and a dispersion correction applied to the nickel atom, reduced R to 0.039. The hydrogen atoms were not refined and were allocated isotropic temperature factors 0.5 Å^2 higher than the equivalent isotropic temperature factors of the atoms to which they were bonded. In the final cycle of refinement, no parameter shift was greater than 0.2σ and the refinement was, therefore, terminated at R 0.039.

The atomic-scattering factors and dispersion corrections were taken from ref. 6. The numbering scheme used is shown in Figure 1, a stereoscopic view of the molecule in Figure 2, and the final positional parameters are listed in Table 1. Observed and calculated structure factors and thermal parameters are in Supplementary Publication No. SUP 22134 (36 pp.).[*]

RESULTS AND DISCUSSION

X-Ray Crystal Structure.—The two molecules of the unit cell lie in general positions. A stereoscopic view

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[*] For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue.

[5] G. M. Sheldrick, SHEL-X Crystallographic Programs, personal communication, 1976.

[6] 'International Tables for X-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

of the packing within the unit cell is shown in Figure 3. Bond lengths and angles are given in Table 2.

TABLE 1

Final positional parameters with estimated standard deviations in parentheses

Atom	x	y	z
Ni	−0.126 1(1)	0.171 1(0)	−0.264 5(0)
O(1)	−0.203 0(2)	0.206 7(2)	−0.101 0(1)
O(2)	−0.047 1(2)	0.357 7(2)	−0.273 5(1)
O(3)	−0.180 8(3)	0.725 7(2)	0.074 8(2)
O(4)	−0.045 5(3)	0.760 4(2)	−0.102 5(2)
O(5)	−0.070 0(2)	0.177 6(2)	−0.433 8(1)
O(6)	−0.320 6(2)	0.259 6(2)	−0.288 2(2)
O(7)	−0.626 4(2)	0.386 6(2)	−0.530 3(2)
O(8)	−0.468 8(3)	0.391 5(2)	−0.701 5(2)
N(1)	−0.121 7(3)	0.691 6(2)	−0.021 9(3)
N(2)	−0.500 5(3)	0.368 4(2)	−0.598 7(2)
N(3)	0.074 1(2)	0.096 2(2)	−0.365 9(2)
N(4)	−0.230 3(2)	0.000 6(2)	−0.233 6(2)
C(1)	−0.184 4(3)	0.319 9(2)	−0.079 5(2)
C(2)	−0.102 1(3)	0.407 2(2)	−0.169 2(2)
C(3)	−0.081 9(3)	0.527 5(2)	−0.151 3(2)
C(4)	−0.144 5(3)	0.564 8(2)	−0.041 3(2)
C(5)	−0.224 0(3)	0.484 3(3)	0.049 2(2)
C(6)	−0.243 6(3)	0.363 2(3)	0.029 3(2)
C(7)	0.029 6(5)	0.435 9(3)	−0.370 5(3)
C(8)	−0.169 1(3)	0.221 8(2)	−0.474 7(2)
C(9)	−0.308 9(3)	0.267 3(2)	−0.400 7(2)
C(10)	−0.416 6(3)	0.313 1(2)	−0.439 9(2)
C(11)	−0.387 8(3)	0.318 4(2)	−0.556 4(2)
C(12)	−0.254 1(3)	0.277 9(2)	−0.632 4(2)
C(13)	−0.147 7(3)	0.228 9(2)	−0.591 2(2)
C(14)	−0.449 2(4)	0.311 4(4)	−0.208 0(2)
C(15)	0.197 3(3)	0.111 4(3)	−0.357 3(3)
C(16)	0.333 4(4)	0.065 1(4)	−0.358 9(4)
C(17)	0.343 4(4)	0.000 4(3)	−0.264 0(4)
C(18)	0.217 6(4)	−0.018 1(3)	−0.170 1(3)
C(19)	0.085 8(4)	0.032 3(3)	−0.174 2(2)
C(20)	−0.319 5(4)	−0.038 5(3)	−0.129 4(2)
C(21)	−0.386 0(4)	−0.152 1(3)	−0.105 4(3)
C(22)	−0.359 2(4)	−0.231 2(3)	−0.189 8(3)
C(23)	−0.268 6(4)	−0.192 1(3)	−0.297 4(3)
C(24)	−0.206 5(3)	−0.075 6(3)	−0.316 4(2)
H(3)	−0.033	0.589	−0.219
H(5)	−0.258	0.511	0.131
H(6)	−0.300	0.311	0.094
H(71)	−0.040	0.507	−0.381
H(72)	0.117	0.474	−0.361
H(73)	0.062	0.389	−0.440
H(10)	−0.504	0.339	−0.394
H(12)	−0.238	0.289	−0.719
H(13)	−0.042	0.196	−0.641
H(141)	−0.457	0.404	−0.229
H(142)	−0.541	0.271	−0.208
H(143)	−0.444	0.301	−0.130
H(15)	0.188	0.161	−0.422
H(16)	0.408	0.089	−0.434
H(17)	0.425	−0.054	−0.272
H(18)	0.229	−0.064	−0.094
H(19)	−0.008	0.018	−0.100
H(20)	−0.325	0.018	−0.075
H(21)	−0.450	−0.193	−0.031
H(22)	−0.396	−0.314	−0.172
H(23)	−0.250	−0.246	−0.350
H(24)	−0.146	−0.046	−0.397

The nickel atoms are six-co-ordinate but, unlike the other complexes which have been examined, the methoxy-groups are in a *cis* conformation. The methoxy-oxygen atoms and the pyridine nitrogen atoms form a square-planar arrangement about nickel with a distorted-octahedral configuration being completed by the phenolic oxygen atoms (Figure 4). No Jahn–Teller distortion is expected, and, although the methoxy-groups are held in this *cis* conformation, there is no steric hindrance between either themselves or other groups. There are no H • • • H contacts less than 2.6 Å between neighbouring methoxy-groups.

TABLE 2

Bond distances (Å) and angles (°), with estimated standard deviations in parentheses

Ni–O(1)	1 995(2)	Ni–O(2)	2.161(2)
Ni–N(3)	2.059(2)	Ni–N(4)	2.072(2)
Ni–O(5)	2.006(2)	Ni–O(6)	2.176(2)
O(1)–C(1)	1.305(3)	O(2)–C(2)	1.378(3)
O(2)–C(2)	1.413(4)	C(1)–C(2)	1.430(3)
C(2)–C(3)	1.369(4)	C(3)–H(3)	1.02
C(3)–C(4)	1.391(4)	C(4)–N(1)	1.448(4)
N(1)–O(3)	1.231(4)	N(1)–O(4)	1.230(3)
C(4)–C(5)	1.384(4)	C(5)–H(5)	1.03
C(5)–C(6)	1.383(4)	C(6)–H(6)	0.96
C(6)–C(1)	1.399(4)	C(7)–H(71)	1.02
C(7)–H(72)	1.00	C(7)–H(73)	0.99
O(5)–C(8)	1.297(4)	O(6)–C(9)	1.379(3)
O(6)–C(14)	1.423(3)	C(8)–C(9)	1.436(3)
C(9)–C(10)	1.362(4)	C(10)–H(10)	0.89
C(10)–C(11)	1.393(4)	C(11)–N(2)	1.441(4)
N(2)–O(7)	1.234(3)	N(2)–O(8)	1.229(3)
C(11)–C(12)	1.385(3)	C(12)–H(12)	1.04
C(12)–C(13)	1.377(4)	C(13)–H(13)	1.05
C(13)–C(8)	1.406(4)	C(14)–H(141)	1.01
C(14)–H(142)	1.00	C(14)–H(143)	1.00
N(3)–C(15)	1.335(3)	C(15)–H(15)	0.97
C(15)–C(16)	1.380(5)	C(16)–H(16)	0.99
C(16)–C(17)	1.368(6)	C(17)–H(17)	0.94
C(17)–C(18)	1.369(5)	C(18)–H(18)	1.09
C(18)–C(19)	1.380(5)	C(19)–H(19)	1.05
C(19)–N(3)	1.334(4)		
N(4)–C(20)	1.335(3)	C(20)–H(20)	0.94
C(20)–C(21)	1.368(5)	C(21)–H(21)	1.00
C(21)–C(22)	1.367(5)	C(22)–H(22)	0.96
C(22)–C(23)	1.371(4)	C(23)–H(23)	0.89
C(23)–C(24)	1.380(4)	C(24)–H(24)	1.01
C(24)–N(5)	1.334(3)		
O(1)–Ni–O(5)	165.6(1)	O(2)–Ni–O(6)	85.8(1)
N(3)–Ni–N(4)	94.2(1)	O(1)–Ni–O(2)	78.6(1)
O(5)–Ni–O(6)	78.0(1)	O(1)–Ni–N(3)	96.2(1)
O(2)–Ni–N(3)	91.4(1)	O(5)–Ni–N(3)	94.3(1)
O(6)–Ni–N(3)	171.8(1)	O(1)–Ni–N(4)	93.6(1)
O(2)–Ni–N(4)	170.8(1)	O(5)–Ni–N(4)	95.3(1)
O(6)–Ni–N(4)	89.6(1)		
Ni–O(1)–C(1)	116.0(1)	Ni–O(2)–C(2)	111.4(1)
Ni–O(2)–C(7)	128.9(2)	Ni–O(5)–C(8)	116.7(1)
Ni–O(6)–C(9)	111.7(1)	Ni–O(6)–C(14)	130.0(2)
O(1)–C(1)–C(2)	120.3(2)	O(1)–C(1)–C(6)	123.1(2)
C(1)–C(2)–C(3)	122.6(2)	C(2)–O(2)–C(7)	118.9(2)
C(2)–C(3)–C(4)	118.0(2)	C(3)–C(4)–C(5)	122.1(3)
C(3)–C(4)–N(1)	118.1(2)	C(4)–N(1)–O(3)	118.1(2)
C(4)–N(1)–O(4)	118.8(3)	O(3)–N(1)–O(4)	123.0(3)
N(1)–C(4)–C(5)	119.7(3)	C(4)–C(5)–C(6)	119.0(3)
C(5)–C(6)–C(1)	121.8(2)	C(6)–C(1)–C(2)	116.5(2)
O(5)–C(8)–C(9)	120.4(2)	O(5)–C(8)–C(13)	123.2(2)
C(8)–C(9)–C(10)	122.3(2)	C(9)–O(6)–C(14)	118.2(2)
C(9)–C(10)–C(11)	118.3(2)	C(10)–C(11)–C(12)	122.0(3)
C(10)–C(11)–N(2)	118.7(2)	C(11)–N(2)–O(7)	118.8(2)
C(11)–N(2)–O(8)	119.2(2)	O(7)–N(2)–O(8)	122.0(3)
N(2)–C(11)–C(12)	119.3(2)	C(11)–C(12)–C(13)	119.0(2)
C(12)–C(13)–C(8)	122.0(2)	C(13)–C(8)–C(9)	116.4(3)
Ni–N(3)–C(15)	121.4(2)	Ni–N(3)–C(19)	121.0(2)
N(3)–C(15)–C(16)	122.4(3)	C(15)–C(16)–C(17)	119.3(3)
C(16)–C(17)–C(18)	119.1(4)	C(17)–C(18)–C(19)	118.4(4)
C(18)–C(19)–N(3)	123.3(3)	C(19)–N(3)–C(15)	117.6(3)
Ni–N(4)–C(20)	121.2(2)	Ni–N(4)–C(24)	121.1(2)
N(4)–C(20)–C(21)	122.7(3)	C(20)–C(21)–C(22)	119.6(3)
C(21)–C(22)–C(23)	118.4(3)	C(22)–C(23)–C(24)	119.1(3)
C(23)–C(24)–N(4)	122.5(2)	C(24)–N(4)–C(20)	117.7(2)

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[7] P. L. Orioli and M. Di Vaira, *J. Chem. Soc.* (*A*), 1968, 2078.

The Ni–O(CH_3) distance is 2.32 Å in the comparable structure [Ni(mpdo)Br_2] (Table 3), but some steric hindrance involving the bromine atoms was suspected.[7]

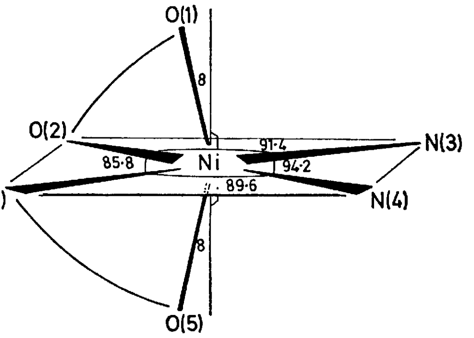

FIGURE 4 Stereochemistry about the Ni atom

TABLE 3

Summary of bond lengths for complexes of Cu^{II} and Ni^{II}

Complex [a]	Bond length/Å M–N	M–O(Ph)	M–O(CH_3)	Ref.
[Cu(mnp)$_2$(py)$_2$]	2.07	1.94	2.58, 2.46	2
[Cu(mnp)$_2$(tmen)]·2H_2O	2.05	1.93	2.57	1
[Cu(fmp)$_2$(py)$_2$]·H_2O [b]	2.04	1.94	2.41	3
	2.06	1.94	2.32	
[Ni(mnp)$_2$(py)$_2$]	2.07	2.00	2.17	c
[Ni(mpdo)Br_2] [d]	2.02 [e]		2.32	7
[Ni(mac)$_2$(OH_2)$_2$]		2.05 [e]	1.99	8
[Ni(tha)$_2$][NO_3]$_2$ [f]	2.12		2.05 [g]	9

[a] tmen = *NNN'N'*-Tetramethylethylenediamine; fmp = 4-formyl-2-methoxyphenolate; mpdo = 1-(*o*-methoxyphenyl)-2,6-diazaoctane. [b] Contains two distinct molecular types. [c] This work. [d] Five-co-ordinate. [e] Ni–O(acetate). [f] Each tha co-ordinated through nitrogen and two oxygen atoms. [g] M–O(H).

The fully aliphatic ligand, methoxyacetate,[8] gives a hydrated nickel(II) complex with a Ni–O(CH_3) bond (Table 3) about the same as or shorter than bond lengths found to sp^3-hybridised oxygen atoms carrying no negative charge, as in[9] [Ni(tha)$_2$][NO_3]$_2$ [tha = tris-(2-hydroxyethyl)amine] (Table 3), or, for example, with water as ligand.[8]

There seems to be an important difference between the donor properties of an ether oxygen atom attached to the aromatic ring and the ether oxygen atom in methoxyacetate, in that the former is the poorer donor. Thus, the longer Ni–O(CH_3) bonds in [Ni(mnp)$_2$(py)$_2$] are caused by an inherent property of the phenolate ligand. There is no significant difference between the Ni–O bond lengths for charged phenolic and carboxylic oxygen atoms. In spite of this observation, the methoxy-oxygen atoms are not co-ordinated in [Cu(mac)$_2$(imidazole)$_4$] (mac = methoxyacetate), but we have been unable to make analogous complexes of Cu^{II} and Ni^{II} with our phenols. The ether oxygen atom is not co-ordinated[8] in tetra-aquabis(phenoxyacetato)nickel(II), but we have not so far crystallised the complex [Co(mnp)$_2$(OH_2)$_4$] and the nickel(II) analogue was unobtainable.

Returning to the copper(II) phenolate complexes, we consider that the unusually long Cu–O(CH_3) bond distances arise partially as an inherent property of the ligand and partially by a Jahn–Teller distortion, and that the contribution from steric hindrance is small.

Electronic and Diffuse-reflectance Spectra and Magnetic Properties.—Notwithstanding the observed deviations from a regular six-co-ordinate stereochemistry, the electronic *d–d* absorption spectrum (Figure 5) of [Ni(mnp)$_2$(py)$_2$] corresponds to that expected for a nickel(II) ion in a weak octahedral field of O_h (*m*3*m*) symmetry. Two spin-allowed transitions were observed: ν_1, $^3T_{2g}\leftarrow{}^3A_{2g}$ (8 600 cm^{-1}); and ν_2, $^3T_{1g}(F)\leftarrow{}^3A_{2g}$ (15 600 cm^{-1}). The third [ν_3, $^3T_{1g}(P)\leftarrow{}^3A_{2g}$ (*ca.* 24 500 cm^{-1})] was obscured by ligand charge-transfer transitions. In common with many nickel(II) complexes,[10] departure from regular O_h symmetry did not cause the expected splitting of the bands, even when the spectrum was measured at low temperature, and the spectra are clearly no guide to detailed stereochemistry. As would be expected, the effective magnetic moment (B.M.) * did not vary with temperature (292.5 K, $\mu_{eff.} = 3.18$; 89.5 K, $\mu_{eff.} = 3.19$; $\theta = 0°$) and the values were within the range usually observed for six-co-ordinate nickel(II) complexes.

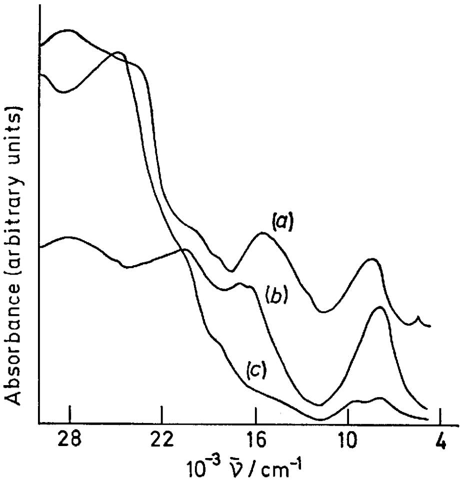

FIGURE 5 Low-temperature diffuse-reflectance of (*a*) [Ni(mnp)$_2$(py)$_2$], (*b*) [Co(mnp)$_2$(py)$_2$], and (*c*) [Co(mnp)$_2$(OH_2)$_4$]

The [Ni(mnp)$_2$(py)$_2$] and [Co(mnp)$_2$(py)$_2$] complexes are isomorphous.[11] Three spin-allowed transitions are expected for octahedral (O_h) high-spin cobalt(II) complexes which arise from transitions to $^4T_{2g}$ (ν_1), $^4A_{2g}$ (ν_2), and $^4T_{1g}(P)$ (ν_3) states from the $^4T_{1g}$ ground state. For O_h symmetry, ν_1 (*ca.* 8 000 cm^{-1}) is usually weak compared with ν_3 (*ca.* 20 000 cm^{-1}) and ν_2 is often unobserved. Unlike the case of [Ni(mnp)$_2$(py)$_2$], the structural deviations from O_h symmetry had a marked

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* Throughout this paper: 1 B.M. ≈ 9.27×10^{-24} A m^2.

[8] C. K. Prout, C. Walker, and F. J. C. Rossotti, *J. Chem. Soc.* (*A*), 1971, 556.

[9] K. Nielsen, R. G. Hazell, and S. E. Rasmussen, *Acta. Chem. Scand.*, 1972, **26**, 889.

[10] A. B. P. Lever, 'Inorganic Electronic Spectroscopy,' Elsevier, Amsterdam, 1968, 337.

[11] J. I. Bullock and R. J. Hobson, *Inorg. Chim. Acta*, 1976, **19**, 79.

effect (Figure 5) for [Co(mnp)$_2$(py)$_2$], in that ν_1 (*ca.* 8 000 cm^{-1}) and ν_2 (*ca.* 16 700 cm^{-1}) were both strong and asymmetric with the position of ν_3 masked by charge-transfer absorption. Interestingly, [Co(mnp)$_2$(OH$_2$)$_4$] has a spectrum (Figure 5) more like that expected for O_h symmetry since ν_1 is weak and ν_2 unobserved.

The low-symmetry components of the ligand field reduced the magnetic moments of [Co(mnp)$_2$(py)$_2$] to the low end of the range (4.7—5.2 B.M.) observed for six-co-ordinate high-spin cobalt(II) complexes (288 K, $\mu_{\text{eff.}} = 4.57$ B.M.; 89 K, $\mu_{\text{eff.}} = 4.42$ B.M.; $\theta = 10°$). The lowering in moment is due to the splitting of the $^4T_{1g}$ ground state of O_h symmetry which reduces the orbital contribution.

The spectrum and the magnetic properties of the cobalt(II) complex are not inconsistent with *cis*-N$_2$O$_4$ co-ordination of ligand donor atoms, but the crystallographic evidence is clearly the more certain method of assigning detailed stereochemistry even though the bond lengths and angles in the complexes of Co$^{\text{II}}$ and Ni$^{\text{II}}$ could be significantly different notwithstanding the observed isomorphism.

The magnetic moments for [Co(mnp)$_2$(OH$_2$)$_4$] (202.5 K, $\mu_{\text{eff.}} = 4.56$ B.M.; 89 K, $\mu_{\text{eff.}} = 4.47$ B.M.; $\theta = 7°$) indicate a low-symmetry field component unlike the diffuse-reflectance spectrum.

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