Binuclear Nickel(II) and Cobalt(II) Complexes of the Novel Binucleating Ligand 3,6-Bis(1′-pyrazolyl)pyridazine. Crystal and Molecular Structure and Magnetism of Bis[μ-3,6-bis(1′-pyrazolyl)pyridazine-$N^1(Ni^1)N^{2'}(Ni^1)N^2(Ni^2)N^{2''}(Ni^2)$]-bis[diaquanickel(II)] Tetrachloride Dihydrate†

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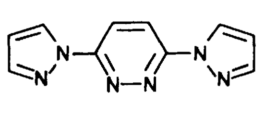
Reaction of the ligand 3,6-bis(1′-pyrazolyl)pyridazine (ppd) with nickel(II) and cobalt(II) salts produces binuclear derivatives in which the two pseudo-octahedral metal centres are bound simultaneously between two adjacent ligands in a doubly bridged structure. The complex $[Ni_2(ppd)_2(H_2O)_4]Cl_4\cdot2H_2O$ (**1**) crystallizes in the triclinic space group $P\bar{1}$ with a = 7.133 9(7), b = 10.331 0(6), c = 10.820 9(5) Å, α = 85.503(4), β = 89.939(6), γ = 75.479(6)°, and Z = 1. Refinement based on 4 505 unique reflections gave R = 0.0353. The binuclear cation $[Ni_2(ppd)_2(H_2O)_4]^{4+}$ is essentially planar with in-plane Ni–N distances of 2.130(2), 2.035(2), 2.059(2), and 2.121(2) Å, axial Ni–O distances of 2.044(2) and 2.048(2) Å, and N–Ni–N angles of 98.6(1), 77.8(1), 77.9(1), and 105.8(1)°. Variable-temperature magnetic susceptibility measurements on (**1**) indicate significant antiferromagnetic exchange between the nickel(II) centres with $-J$ = 14.8 cm⁻¹. Analogous cobalt(II) compounds are also produced and in one case, $[Co_2(ppd)_2(OH)(H_2O)_2][ClO_4]_3\cdot1.5H_2O$, a triply bridged structure is proposed involving an additional hydroxide bridge.

Binuclear complexes of polyfunctional diazine ligands involving substituted phthalazines,[1–20] pyridazines,[1,3,4,21–26] pyrazoles,[3] triazoles,[27] and hydrazines[28–33] have binuclear centres in which the metal atoms are invariably antiferromagnetically coupled *via* a superexchange mechanism. In copper(II) complexes of some quadridentate phthalazines where, in addition to the diazine bridge, a hydroxide group also bridges the two metal centres, exchange integrals fall in the range $-2J$ = 200—800 cm⁻¹ with a linear relationship between $-2J$ and Cu–O–Cu angle for systems with $d_{x^2-y^2}$ copper ion ground states.[15,18,19] Although various hydroxy-bridged binuclear copper complexes of quadridentate pyridazines have been reported, no exchange studies have been carried out.[21–26]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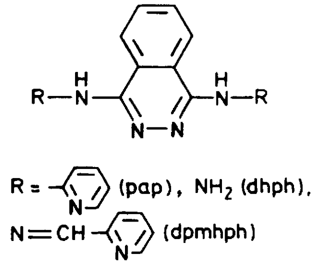
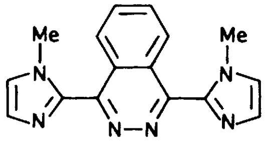
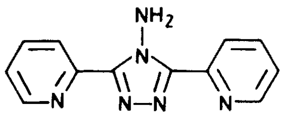




mip



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In general, the copper(II) phthalazine and pyridazine complexes are binuclear 2:1 (metal:ligand) derivatives while for cobalt(II) and nickel(II) systems both 2:1 and 1:1 binuclear derivatives are observed. *X*-Ray data on nickel diazine complexes are limited to reports of the structure of $[Ni(dhph)(H_2O)_2]_2Cl_4\cdot2H_2O$ (dhph = 1,4-dihydrazinophthalazine),[2] $[Ni_2(dpmhph)Cl(H_2O)_4]Cl_3\cdot2H_2O$ [dpmhph = 1,4-di(2′-pyridylmethylenehydrazino)phthalazine],[6] $[Ni_2(abpt)_2Cl_2(H_2O)_2]Cl_2\cdot4H_2O$ [abpt = 4-amino-3,5-bis(pyridin-2′-yl)-1,2,4-triazole],[27] and a most unusual 2:3 derivative $[Ni_2(pap)_3(H_2O)_2]Br_4\cdot6H_2O$ [pap = 1,4-di(2′-pyridylamino)phthalazine].[34]

This paper deals with some aspects of the nickel(II) and cobalt(II) co-ordination chemistry of the ligand ppd [3,6-bis(1′-pyrazolyl)pyridazine] and the nickel co-ordination chemistry of mip [1,4-di(1′-methyl-2′-imidazolyl)phthalazine]. The structural details of the complex $[Ni_2(ppd)_2(H_2O)_4]Cl_4\cdot2H_2O$ (**1**), the first documented example of a binuclear nickel pyridazine complex, are reported.

Experimental

Starting Materials.—The ligand ppd was prepared as described previously[35] or by a literature procedure[36] and mip as described previously.[19] Metal salts were used as the commercially available hexahydrates except for $Ni(NCS)_2$ which was prepared metathetically.

Synthesis of $[Ni_2(ppd)_2(H_2O)_4]Cl_4\cdot2H_2O$ (**1**).—A solution of ppd (0.50 g, 2.4 mmol) in warm acetonitrile (100 cm³) was added to a solution of $NiCl_2\cdot6H_2O$ (2.5 g, 10 mmol) in warm

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† *Supplementary data available* (No. SUP 56387, 6 pp.): H-atom co-ordinates, H-bridge distances, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Non-S.I. unit employed: $\chi_{\text{c.g.s.u.}} = \frac{10^6}{4\pi}\chi_{\text{S.I.}}$

Table 1. Analytical* and i.r. data for the complexes

Complex	Colour	Analysis (%)*				ν/cm^{-1}
		C	H	N	M	
(**1**) $[Ni_2(ppd)_2(H_2O)_4]Cl_4\cdot2H_2O$	Lavender	30.6	3.4	21.0	14.4	
		(30.3)	(3.5)	(21.2)	(14.8)	
(**2**) $[Ni_2(ppd)_2(H_2O)_4]Br_4$	Lavender	25.9	2.5	17.95	12.4	
		(25.7)	(2.6)	(18.0)	(12.6)	
(**3**) $[Ni_2(ppd)_2(H_2O)_4][NO_3]_4$	Lavender	27.75	2.8	26.1	13.3	1 760 ($\nu_1 + \nu_4$, NO_3^-)
		(27.9)	(2.8)	(26.0)	(13.6)	
(**4**) $[Ni_2(ppd)_2(H_2O)_4][ClO_4]_4\cdot H_2O$	Lavender	23.4	2.2	16.2	10.9	1 080 (ClO_4^-)
		(23.3)	(2.5)	(16.3)	(11.4)	
(**5**) $[Ni(ppd)_2Br_2]$	Olive green	37.3	2.5	26.15	9.0	215 (Ni-Br)
		(37.0)	(2.5)	(25.9)	(9.1)	
(**6**) $[Ni(ppd)_2(NCS)_2]\cdot2.5H_2O$	Lavender	40.8	2.7	30.5	9.0	2 086 (NCS^-)
		(41.0)	(3.3)	(30.4)	(9.1)	
(**7**) $[Ni(mip)_2(H_2O)_2]Br_2\cdot3H_2O$	Yellow	43.5	3.7	19.0	6.5	
		(43.2)	(4.3)	(18.9)	(6.6)	
(**8**) $[Ni(mip)_2(H_2O)_2][NO_3]_2$	Yellow	48.0	3.5	24.0	7.6	1 740 ($\nu_1 + \nu_4$, NO_3^-)
		(48.1)	(4.0)	(24.5)	(7.4)	
(**9**) $[Ni(mip)_2(H_2O)_2][ClO_4]_2\cdot H_2O$	Yellow	42.9	3.3	18.6	6.6	1 090 (ClO_4^-)
		(43.1)	(3.8)	(18.8)	(6.4)	
(**10**) $[Co_2(ppd)_2(H_2O)_4]Cl_4\cdot2.5H_2O$	Orange	29.8	3.7	21.0	14.6	
		(30.0)	(3.6)	(21.0)	(14.7)	
(**11**) $[Co_2(ppd)_2(H_2O)_4]Br_4$	Orange	26.0	2.7	18.2	12.8	
		(25.7)	(2.6)	(18.0)	(12.6)	
(**12**) $[Co_2(ppd)_2(OH)(H_2O)_2][ClO_4]_3\cdot1.5H_2O$	Orange	26.1	2.6	18.2	12.9	3 600 (sh) (OH^-)
		(26.1)	(2.6)	(18.3)	(12.8)	

* Required values are given in parentheses.

water (50 cm^3) and the mixture heated on a steam-bath until lavender crystals appeared. After standing for several hours the product was filtered off, washed with acetonitrile and diethyl ether and dried *in vacuo* at room temperature.

The compounds $[Ni_2(ppd)_2(H_2O)_4]Br_4$ (**2**), $[Ni_2(ppd)_2(H_2O)_4][NO_3]_4$ (**3**), $[Ni_2(ppd)_2(H_2O)_4][ClO_4]_4\cdot H_2O$ (**4**), $[Co_2(ppd)_2(H_2O)_4]Cl_4\cdot2.5H_2O$ (**10**), and $[Co_2(ppd)_2(H_2O)_4]Br_4$ (**11**) were prepared similarly. $[Ni(ppd)_2Br_2]$ (**5**) and $[Ni(ppd)_2(NCS)_2]\cdot2.5H_2O$ (**6**) were prepared by the same general method but with a minimal volume of water and $[Co_2(ppd)_2(OH)(H_2O)_2][ClO_4]_3\cdot1.5H_2O$ (**12**) was prepared by raising the pH of the reaction mixture, produced by the same general method, from 3.5 to 6.5 using aqueous NaOH. In some cases unreacted ligand was observed to crystallize from the reaction mixture but could be made to redissolve by addition of acetonitrile with further heating. The cobalt complexes appeared to be unaffected by the presence of air and no precautions were taken to exclude it.

Synthesis of $[Ni(mip)_2(H_2O)_2][NO_3]_2$ (**8**).—Warm solutions of mip (0.40 g, 1.4 mmol) in methanol (50 cm^3) and $Ni(NO_3)_2\cdot6H_2O$ (2.0 g, 6.9 mmol) in methanol (50 cm^3) were mixed and a small amount of water added to dissolve a pale green precipitate which formed initially. Reduction in volume on a steam-bath led to the formation of a yellow powder, which was isolated by filtration, washed with ether and dried *in vacuo* at room temperature. The compounds $[Ni(mip)_2(H_2O)_2]Br_2\cdot3H_2O$ (**7**) and $[Ni(mip)_2(H_2O)_2][ClO_4]_2\cdot H_2O$ (**9**) were prepared similarly.

Analyses.—Carbon, H, and N analyses were carried out by the Canadian Microanalytical Service, Vancouver, Canada. Metal analyses were carried out by atomic absorption spectroscopy using a Varian Techtron AA5 instrument on solutions obtained by digestion of the samples in aqua-regia. Results are in Table 1.

Spectra and Magnetic Measurements.—Infrared spectra were recorded using Nujol mulls in the range 4 000—200 cm^{-1} with a Perkin-Elmer 283 spectrometer, while ligand field spectra were recorded by the mull transmittance technique in the range 300—1 500 nm using a Cary 17 spectrometer. Magnetic moments were measured at room temperature by the Faraday method using a Cahn model 7600 Faraday magnetic susceptibility system. Variable-temperature magnetic susceptibility data were obtained in the range 6—300 K using an SHE SQUID magnetometer.

Crystal Structure Determination.—Crystal data for (**1**). $C_{20}H_{28}Cl_4N_{12}Ni_2O_6$, $M = 791.71$, triclinic, space group $P\bar{1}$, $a = 7.133\,9(7)$, $b = 10.331\,0(6)$, $c = 10.820\,9(5)$ Å, $\alpha = 85.503(6)$, $\beta = 89.939(6)$, $\gamma = 75.479(6)°$, $U = 769.51$ Å^3, $Z = 1$, $D_c = 1.71$ Mg m^{-3}, $F(000) = 404$, $\mu(\text{Mo-}K_\alpha) = 1.62$ mm^{-1}, $\lambda(\text{Mo-}K_\alpha) = 0.709\,30$ Å.

Data collection and structure refinement. The diffraction intensities of a crystal of dimensions *ca.* 0.3 × 0.2 × 0.15 mm were collected with graphite-monochromatized Mo-K_α radiation using the $\theta/2\theta$ scanning technique with profile analysis[37] to $2\theta_{max.} = 60°$. A total of 4 703 reflections were measured, of which 4 505 were unique and 3 758 were considered significant with $I > 2.5\sigma(I)$. Lorentz and polarization factors were applied and absorption corrections were calculated. The cell parameters were obtained by least-squares refinement of the setting angles of 36 reflections with $2\theta > 55°$.

The structure was solved by Patterson and heavy-atom techniques and refined by full-matrix least-squares methods to final residuals of $R = 0.0353$ and $R' = 0.0339$ for the significant data (0.0452 and 0.0341 for all data) with unit weights (hydrogen-atom positions were calculated but not refined). The final atomic positional parameters are listed in Table 2. All calculations were performed with the NRC PDP-8e system of programs,[38] adapted for the VAX computer. Scattering factors were taken from International Tables.[39]

Table 2. Atomic fractional parameters for $[Ni_2(ppd)_2(H_2O)_4]Cl_4{\cdot}2H_2O$ (1) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ni(1)	0.888 52(5)	0.138 88(3)	0.111 31(3)	N(5)	0.815 7(3)	0.387 46(19)	−0.041 26(19)
Cl(1)	0.511 54(11)	0.113 44(7)	−0.206 78(6)	N(6)	0.807 8(3)	0.344 68(20)	0.080 08(19)
Cl(2)	1.170 60(14)	0.328 42(7)	0.368 61(7)	C(1)	0.706 0(5)	0.195 8(3)	0.375 7(3)
O(1)	1.161 7(3)	0.150 23(18)	0.156 45(17)	C(2)	0.684 2(5)	0.116 3(3)	0.482 8(3)
O(2)	0.616 6(3)	0.126 86(18)	0.062 30(17)	C(3)	0.777 2(4)	−0.011 7(3)	0.459 85(24)
O(3A)	0.409(3)	0.480 7(20)	0.562 8(15)	C(4)	0.943 9(4)	−0.108 23(25)	0.273 51(22)
O(3B)	0.397 0(14)	0.417 2(17)	0.607 6(13)	C(5)	1.000 2(4)	−0.241 7(3)	0.326 19(24)
O(3C)	0.263 2(21)	0.506 5(10)	0.555 2(8)	C(6)	0.916 2(4)	0.336 6(3)	−0.250 88(25)
N(1)	0.807 5(3)	0.123 19(20)	0.291 12(19)	C(7)	0.893 5(4)	0.294 21(24)	−0.126 61(23)
N(2)	0.852 0(3)	−0.004 98(20)	0.344 24(18)	C(8)	0.755 9(4)	0.524 0(3)	−0.058 7(3)
N(3)	1.026 2(3)	0.072 32(19)	−0.156 67(18)	C(9)	0.710 3(4)	0.568 4(3)	0.054 8(3)
N(4)	0.945 2(3)	0.167 66(19)	−0.080 02(18)	C(10)	0.744 7(4)	0.454 5(3)	0.138 6(3)

Table 3. Interatomic distances (Å) and angles (°) for $[Ni_2(ppd)_2(H_2O)_4]Cl_4{\cdot}2H_2O$ (1) with estimated standard deviations in parentheses

Ni(1)–Ni(1′)	3.920(1)	Ni(1)–O(2)	2.048(2)	N(2)–C(4)	1.389(3)	C(8)–N(5)	1.365(3)
Ni(1)–N(1)	2.035(2)	N(1)–C(1)	1.326(3)	C(4)–C(5)	1.410(4)	N(5)–C(7)	1.400(3)
Ni(1)–N(4)	2.121(2)	C(1)–C(2)	1.399(4)	C(5)–C(6′)	1.345(4)	C(7)–N(4)	1.325(3)
Ni(1)–N(6)	2.059(2)	C(2)–C(3)	1.364(4)	N(6)–C(10)	1.322(3)	C(7)–C(6)	1.403(4)
Ni(1)–N(3′)	2.130(2)	C(3)–N(2)	1.363(3)	C(10)–C(9)	1.399(4)	N(3)–N(4)	1.354(3)
Ni(1)–O(1)	2.044(2)	N(2)–N(1)	1.362(3)	C(9)–C(8)	1.355(4)		

O(1)–Ni(1)–O(2)	178.8(1)	N(4)–Ni(1)–N(3′)	105.8(1)	C(4)–N(2)–N(1)	118.7(2)	C(8)–N(5)–N(6)	111.1(2)
O(1)–Ni(1)–N(1)	93.8(1)	N(1)–Ni(1)–N(3′)	77.9(1)	N(2)–C(4)–N(3′)	115.8(2)	C(8)–N(5)–C(7)	129.3(2)
O(1)–Ni(1)–N(6)	89.2(1)	N(1)–Ni(1)–N(4)	174.3(1)	N(2)–C(4)–C(5)	120.7(2)	N(6)–N(5)–C(7)	119.4(2)
O(1)–Ni(1)–N(4)	90.6(1)	N(6)–Ni(1)–N(3′)	176.1(1)	C(5)–C(4)–N(3′)	123.6(2)	N(5)–C(7)–C(6)	120.7(2)
O(1)–Ni(1)–N(3′)	89.4(1)	Ni(1)–N(1)–C(1)	141.1(2)	C(4)–N(3′)–Ni(1)	113.7(2)	N(5)–C(7)–N(4)	115.0(2)
O(2)–Ni(1)–N(1)	87.4(1)	Ni(1)–N(1)–N(2)	113.8(2)	N(4′)–N(3′)–Ni(1)	126.9(2)	C(7)–N(4)–Ni(1)	114.5(2)
O(2)–Ni(1)–N(6)	90.9(1)	N(1)–C(1)–C(2)	111.6(2)	Ni(1)–N(6)–C(10)	141.4(2)	C(7)–N(4)–N(3)	118.2(2)
O(2)–Ni(1)–N(4)	88.3(1)	C(1)–C(2)–C(3)	105.4(2)	Ni(1)–N(6)–N(5)	112.9(1)	N(3)–N(4)–Ni(1)	127.3(2)
O(2)–Ni(1)–N(3′)	90.6(1)	C(2)–C(3)–N(2)	106.7(2)	N(6)–C(10)–C(9)	110.5(2)	C(7)–C(6)–C(5′)	117.2(2)
N(1)–Ni(1)–N(6)	98.6(1)	C(3)–N(2)–N(1)	111.5(2)	C(10)–C(9)–C(8)	106.5(2)	N(4)–N(3)–C(4′)	119.5(2)
N(6)–Ni(1)–N(4)	77.8(1)	C(3)–N(2)–C(4)	129.4(2)	C(9)–C(8)–N(5)	106.3(2)		

Results and Discussion

X-Ray Structure of $[Ni_2(ppd)_2(H_2O)_4]Cl_4{\cdot}2H_2O$ (1).—The structure consists of the cation $[Ni_2(ppd)_2(H_2O)_4]^{4+}$, which has a crystallographic centre of symmetry, four chloride ions and two lattice water molecules. Figure 1 represents a projection of the structure with the lattice water molecules and the chloride ions omitted for clarity. Relevant interatomic distances and angles are listed in Table 3. There are interactions between adjacent pairs of molecules along the *a* direction involving hydrogen-bonding contacts between the co-ordinated water molecules and the chloride ions. These contacts form a chain with the plane of each molecule more or less perpendicular to *a*. Each lattice water molecule is disordered between three sites [O(3A), O(3B), O(3C)] which lie in the centre of a channel parallel to *a* and there are five chloride contacts.

The cation consists of two nickel(II) centres bridged by just two diazine fragments [N(3)–N(4)] in an essentially planar dimeric arrangement of two quadridentate ligands with pyrazole nitrogens completing the equatorial co-ordination. The axial sites at the pseudo-octahedral nickel centres are occupied by water molecules. In the equatorial plane the nickel–pyrazole bond lengths are shorter than the nickel–pyridazine bond lengths by more than 0.06 Å. This is in contrast to the situation found for binuclear 1:2 (ligand:metal) copper(II) complexes of the related ligand having 3,5-dimethyl substituents on the pyrazole rings, where the copper(II)–pyrazole and copper(II)–pyridazine bond lengths were found to be comparable.[35] The nickel–oxygen bond lengths to the axial water molecules (Table 3) are significantly shorter than those reported for the related complexes $[Ni_2(abpt)_2Cl_2(H_2O)_2]Cl_2{\cdot}4H_2O$ (**13**),[27] $[Ni(dhph)(H_2O)_2]_2Cl_4{\cdot}2H_2O$ (**14**),[2] and $[Ni_2(dpmhph)Cl(H_2O)_4]Cl_3{\cdot}2H_2O$ (**15**),[6] which fall in the range 2.096—2.164 Å (Table 4).

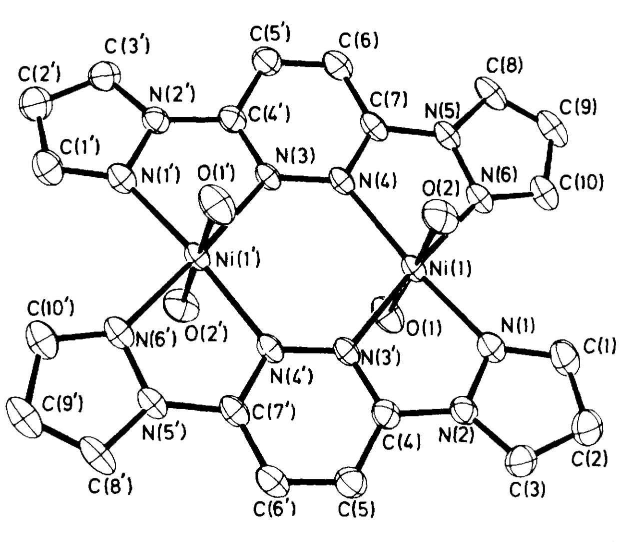
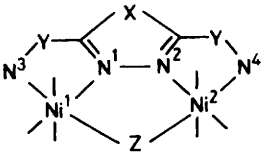


Figure 1. Projection of the structure of the cation $[Ni_2(ppd)_2(H_2O)_4]^{4+}$ with the atomic labelling scheme. Lattice water molecules, chloride ions, and hydrogen atoms have been omitted for clarity

The centrosymmetric structure of (1) may be compared with the centrosymmetric nickel complexes of the related quadri-

Table 4. Structural (distances in Å, angles in °) and magnetic comparison of (**1**) with related nickel–diazine complexes



Compound	Ni–O	N^1–N^2	Ni^1–N^1, Ni^2–N^2	Ni^1–N^3, Ni^2–N^4	Ni^1–Ni^2	Ni^1–N^1–N^2, Ni^2–N^2–N^1	N^3–Y–C, N^4–Y–C	$-J$/cm^{-1}
$[Ni_2(ppd)_2(H_2O)_4]Cl_4{\cdot}2H_2O$ (**1**) (X = C–C, Y = N, Z = N–N)	2.044 2.048	1.354	2.130, 2.121	2.035, 2.059	3.920	126.9, 127.3	118.7, 119.4	14.8
$[Ni_2(abpt)_2Cl_2(H_2O)_2]Cl_2{\cdot}4H_2O$ (**13**) (X = N, Y = C, Z = N–N)	2.096 Ni–Cl 2.427	1.354	2.013, 2.029	2.164, 2.155	4.135	132.6, 134.2	111.5, 112.1	12.5
$[Ni(dhph)(H_2O)_2]_2Cl_4{\cdot}2H_2O$ (**14**) (X = C–C, Y = NH, Z = N–N)	2.159 2.164	1.398	2.072, 2.080	2.099, 2.097	3.791	124.8, 125.6	115.8, 115.4	22.3
$[Ni_2(dpmhph)Cl(H_2O)_4]Cl_3{\cdot}2H_2O$ (**15**) (X = C–C, Y = NH, Z = Cl)	2.098 2.117 2.108 2.070	1.363	2.074, 2.061	1.999, 2.001	3.603	122.4, 123.3	115.8, 113.8	

dentate ligands abpt, (**13**), and dhph, (**14**), and also the binuclear complex of the sexidentate ligand dpmhph, (**15**). The same basic structural unit Ni_2N_4 (Table 4) exists in each case with the diazine fragment arising from pyridazine, triazole, and phthalazine residues. The two other nitrogen-donor centres are provided by pyrazole, pyridine, amine, and azomethine groups. In the diazine fragments the N^1–N^2 separation (Table 4) is comparable for (**1**), (**13**), and (**15**) (1.35—1.36 Å) but slightly longer (1.40 Å) for (**14**). Nickel–nitrogen (Ni^1–N^1, Ni^2–N^2) distances for (**13**), (**14**), and (**15**) fall in the range 2.01—2.08 Å while for (**1**) significantly longer separations are observed (2.12—2.13 Å). However, nickel–nitrogen (Ni^1–N^3, Ni^2–N^4) distances vary somewhat differently with short separations (2.00 Å) for (**15**), intermediate for (**1**) (2.035, 2.059 Å) and (**14**) (2.10 Å), and long separations (2.16 Å) for (**13**).

Nickel–nickel separations differ considerably among the four complexes [(**1**), (**13**)—(**15**)] with chelate ring size and diazine ring size being major factors in the difference. The shortest Ni–Ni distance (3.60 Å) occurs in (**15**) which involves a five-membered chelate ring, Ni_2N_2Cl, with a chlorine bridge (Table 4, Z = Cl). As would be expected, this system has the smallest angles Ni^1–N^1–N^2 and Ni^2–N^2–N^1 (122—123°), where N^1–N^2 is a phthalazine fragment (six-membered ring). Both (**14**) and (**1**) have six-membered chelate rings, Ni_2N_4, with six-membered diazine rings and, as expected, slightly larger angles Ni^1–N^1–N^2 and Ni^2–N^2–N^1 (125—127°). Ni–Ni separations are larger also but the larger separation for (**1**) is associated in part with longer Ni–N distances. For compound (**13**) the six-membered chelate ring, Ni_2N_4, is characterized by having much larger angles Ni^1–N^1–N^2 and Ni^2–N^2–N^1 (133—134°), in keeping with the geometrical requirements of the five-membered triazole ring, which leads to a much larger nickel–nickel separation (4.14 Å). In comparing these systems the individual chelate rings involving Ni^1 and Ni^2 are all five-membered and although bond-length and bond-angle differences between these rings are, in some cases, significant, the binuclear chelate ring and the diazine ring are considered to be major influences on the dimensions at the binuclear centre. Such factors are of great importance in the design of model compounds for binuclear copper protein centres where metal–metal separations, and in particular oxygen bridge angles, can be controlled by the choice of ligands with appropriate donor ring and chelate ring sizes.[18,19,35]

An *X*-ray structural study on $[Ni_2(ppd)_2(H_2O)_4]Br_4$ (**2**) (space group $P2_1/n$)[40] has revealed the same basic cation structure as (**1**) with comparable dimensions in the binuclear chelate ring and around the pseudo-octahedral metal centres.

Spectra and Structure.—A general similarity of the i.r. spectra of compounds (**1**)—(**4**), associated with the ligand, suggests that the basic cationic structure, which prevails in (**1**) and (**2**), is also present in (**3**) and (**4**). A strong $\nu_1 + \nu_4$ nitrate combination band[41] at 1 760 cm^{-1} (Table 1) confirms the presence of ionic nitrate in (**3**) and a strong absorption at 1 080 cm^{-1} indicates ionic perchlorate in (**4**). The spectrum of (**5**) differs somewhat from those of (**1**)—(**4**), showing no bands associated with water and the appearance of a strong i.r. absorption at 215 cm^{-1}, associated with a nickel–bromine stretch, which is absent in the other compounds. The thiocyanate complex, (**6**), has an i.r. spectrum which is in general similar to that of (**5**) but with a νCN(NCS) band at 2 086 cm^{-1} indicative of terminal isothiocyanate.

The i.r. spectra of (**10**) and (**11**) are virtually identical and very similar to (**1**) and (**2**) indicating the same basic structure. Some differences are apparent in the spectrum of (**12**), including a prominent shoulder at 3 600 cm^{-1} associated with a hydroxide bridge, and a strong absorption around 1 100 cm^{-1} indicative of ionic perchlorate. The general similarity of the i.r. spectra of (**7**), (**8**), and (**9**), associated with the ligand mip, and the presence of ionic nitrate ($\nu_1 + \nu_4$ 1 740 cm^{-1})[41] for (**8**) and ionic perchlorate (ν_3 1 090 cm^{-1}) for (**9**) suggests the same basic cationic structure for these compounds involving co-ordinated water.

The ligand-field spectra (Table 5) of the binuclear nickel–ppd complexes are characterized by the appearance of two major regions of absorption (ν_1, ν_2) in the range 8 800—12 800 cm^{-1} and 15 800—19 300 cm^{-1} respectively. In all complexes except (**5**) a significant splitting of ν_1 is observed and splittings of ν_2 are observed in most cases. A tetragonal crystal field is assumed for all the complexes (**1**)—(**4**) and the suggested assignments are shown in Table 5. Structurally these complexes are assumed to have the same in-plane arrangement of four nitrogen donors about each nickel centre [*cf.* (**1**) and (**2**); see Figure 1] with water molecules as axial donor groups. These compounds have ligand-field spectra which are comparable to those of (**13**)[27] and (**14**)[2] and related systems involving the ligand dppn [3,6-di(2′-

Table 5. Electronic spectra (ν^a/cm^{-1}) and magnetic moments for the complexes

Compound	O_h: $^3A_{2g}\rightarrow$ D_{4h}: $^3B_{1g}\rightarrow{}^3E_g$	$^3T_{2g}$	$^3B_{2g}$	$^3A_{2g}$	$^3T_{1g}(F)$	^3E_g	$\mu_{eff.}{}^b$/B.M. (r.t.)
(1) $[Ni_2(ppd)_2(H_2O)_4]Cl_4\cdot2H_2O$	9 900		12 400	16 400		18 000	2.95
(2) $[Ni_2(ppd)_2(H_2O)_4]Br_4$	10 200		12 200	16 400		19 300	2.99
(3) $[Ni_2(ppd)_2(H_2O)_4][NO_3]_4$	9 800		12 000	15 800		18 000	2.97
(4) $[Ni_2(ppd)_2(H_2O)_4][ClO_4]_4\cdot H_2O$	9 800		12 800	16 400		18 200	2.98
(5) $[Ni(ppd)_2Br_2]$	8 800			16 700		18 800	3.10
(6) $[Ni(ppd)_2(NCS)_2]\cdot2.5H_2O$	10 500		11 400		17 000(sh)		3.18
(7) $[Ni(mip)_2(H_2O)_2]Br_2\cdot3H_2O$		12 000			17 900(sh)		3.19
(8) $[Ni(mip)_2(H_2O)_2][NO_3]_2$		12 300			17 700(sh)		3.25
(9) $[Ni(mip)_2(H_2O)_2][ClO_4]_2\cdot H_2O$		11 800			18 200(sh)		3.45
		O_h: $^4T_{1g}(F)\rightarrow{}^4T_{2g}(F)$			$^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$		
(10) $[Co_2(ppd)_2(H_2O)_4]Cl_4\cdot2.5H_2O$		10 700			19 600(sh)		4.25
(11) $[Co_2(ppd)_2(H_2O)_4]Br_4$		10 900			19 600(sh)		4.18
(12) $[Co_2(ppd)_2(OH)(H_2O)_2]$-$[ClO_4]_3\cdot1.5H_2O$		10 400					3.52

[a] Mull transmittance (Nujol mull), sh = shoulder. [b] $\mu_{eff.}$ for nickel is defined $\mu_{eff.} = 2.828[(\chi_m^{corr.} - N\alpha)T]^{\frac{1}{2}}$ where $\chi_m^{corr.}$ is the molar susceptibility per metal centre corrected for diamagnetic components and $N\alpha$, the temperature-independent paramagnetism (t.i.p.), is given by $8N\beta^2/10Dq$ for a system with an A_2 ground state. For cobalt a t.i.p. correction of 80 × 10^{-6} c.g.s.u. has been applied in calculating $\mu_{eff.}$.

pyridyl)pyridazine], *e.g.* $[Ni(dppn)(H_2O)_2]_2[ClO_4]_4$ **(16)**[3] (no structures reported), which all have analogous structures. The band energies and splittings of ν_1 and ν_2 compare most closely with **(16)**, a system involving a pyridazine ligand with comparable geometrical constraints and donor characteristics to ppd.

The ν_1 transition for the mononuclear bromo-complex **(5)** is not split and occurs at lower energy than the other derivatives, implying a weaker crystal field in keeping with the proposed co-ordination of bromine. The splitting of ν_2 does, however, imply the presence of a tetragonal crystal field and this complex is assumed to have a six-co-ordinate structure involving two in-plane bidentate ligands and axially bound bromines.* The mononuclear thiocyanate complex **(6)**, which clearly has co-ordinated isothiocyanate, displays a splitting of ν_1 but the higher energy absorption associated with the ν_2 transition occurs as a rather ill defined shoulder on an intense charge-transfer band. This complex is expected to have a tetragonally distorted six-co-ordinate structure, again involving two in-plane bidentate ligands and axially bound isothiocyanates.

The nickel complexes of the ligand mip are all mononuclear derivatives and within the scope of this study no binuclear complexes were obtained. Binuclear, hydroxo-bridged, copper(II) derivatives of this ligand have been described,[19] but unlike analogous copper compounds involving the ligand dppn, where the ligand is essentially planar,[21] severe twisting of the imidazole rings occurs with respect to the phthalazine plane for mip in the complex $[Cu_2(mip)(OH)Cl_3(H_2O)]\cdot H_2O$.[19] This may be attributed to steric interactions between the N-methyl groups and phthalazine hydrogen atoms on the fused benzene ring. Since binuclear 1:1 complexes, *e.g.* **(1)** and **(2)**, involve essentially planar ligands the likelihood of such a system being formed by mip is, not surprisingly, small. The electronic spectra of **(7)**, **(8)**, and **(9)** are essentially the same with ν_1 being rather asymmetric and the appearance of a shoulder (ν_2 ?) on an intense charge-transfer absorption. The minimal splitting of ν_1 may suggest tetragonally distorted six-co-ordinate centres for these complexes, rather than lower symmetry *cis*-NiN_4O_2 chromophores.

The cobalt complexes **(10)** and **(11)** exhibit a broad absorption around 11 000 cm^{-1} assigned to the $^4T_{1g}\rightarrow{}^4T_{2g}$ transition of Co^{2+} in pseudo-octahedral symmetry and a fairly sharp shoulder on an intense charge-transfer band at 19 600 cm^{-1}, which probably corresponds to the transition $^4T_{1g}\rightarrow{}^4T_{1g}(P)$. A similar assignment is made for **(12)** except that the higher energy band is hidden by charge-transfer absorption. Structurally **(10)** and **(11)** are expected to be analogous to the dimeric binuclear structures present in **(1)** and **(2)** with tetragonally distorted six-co-ordinate cobalt(II) centres and axially bound water molecules. Compound **(12)** is clearly unique, apparently involving a hydroxide bridge and a related binuclear structure is proposed for this system but with the hydroxide occupying two axial cobalt sites and water molecules at the other axial positions.

Magnetic Measurements.—Room-temperature magnetic moments for the binuclear complexes **(1)**—**(4)** fall in the range 2.95—2.99 B.M. (Table 5), somewhat less than those observed for the mononuclear derivatives **(5)** and **(6)**, with the same ligand, and the mononuclear mip derivatives **(7)**—**(9)**. This reduction in room temperature (r.t.) moment is indicative of spin-coupled systems involving antiferromagnetic exchange between the nickel(II) centres. Variable-temperature magnetic studies carried out on **(13)**[27] and **(14)**[3] and related compounds show that for the pyridazine- and phthalazine-bridged dimers values of the exchange integral ($-J$) generally fall in the range 15—25 cm^{-1}, whereas for the triazole-bridged system **(13)** a small value of 12.5 cm^{-1} was observed (Table 4).

In the present study magnetic susceptibilities were measured for **(1)** in the range 6—300 K. The susceptibility of a pair of ions in spin-triplet, orbital-singlet states for a system where exchange between nearest neighbours only is considered is given by equation (1), where $x = -J/kT$, χ_m is the susceptibility per mol of Ni and the exchange is represented by the Hamiltonian $\mathcal{H} = -2JS_1S_2$. Temperature-independent paramagnetism ($N\alpha$) has

$$\chi_m = \frac{N\beta^2g^2}{kT}\left[\frac{5 + e^{4x}}{5 + 3e^{4x} + e^{6x}}\right] + N\alpha \qquad (1)$$

been constrained to a value of 0.000 19 c.g.s.u. ($8N\beta^2/10Dq$ for A_2 ground term). Non-linear least-squares fitting of the theoretical expression (1) to the data is illustrated in Figure 2 and the results give $g = 2.11(1)$ and $-J = 14.8(1)$ cm^{-1} (corrected for 0.3% paramagnetic impurity).

The exchange integral for **(1)** is somewhat smaller than those

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* *Note added in proof*: an *X*-ray study on **(5)** has confirmed this structure. Space group P_1, Ni–Br 2.609(1), Ni–N 2.035(2), 2.064(2) Å. E. J. Gabe and L. K. Thompson, unpublished results.

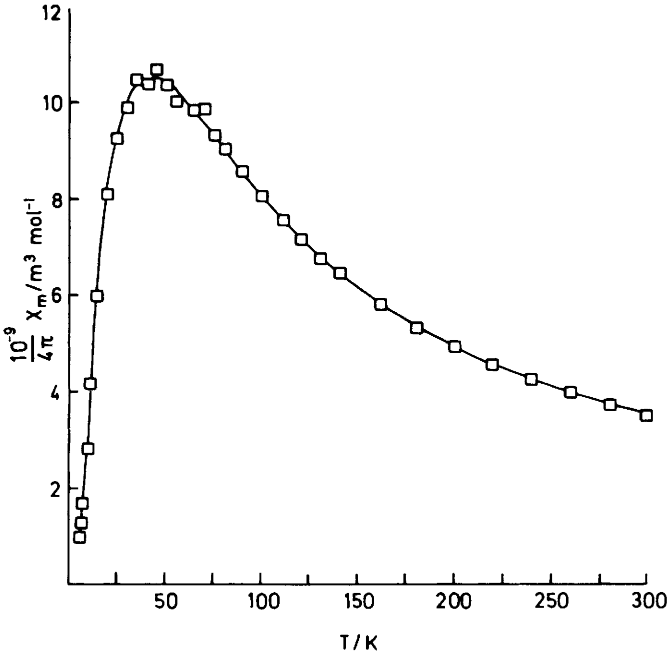

Figure 2. Molar susceptibility per metal *versus* temperature curve for $[Ni_2(ppd)_2(H_2O)_4]Cl_4 \cdot 2H_2O$. The solid line represents the least-squares fit of the data to the theoretical equation (1) corrected for 0.3% paramagnetic impurity; $-J = 14.8\ cm^{-1}$, $g = 2.11$

reported for most comparable phthalazine and pyridazine complexes[3] and slightly larger than that for the triazole complex (13)[27] (Table 4). The exchange order phthalazine > pyridazine > pyrazole has been observed elsewhere and was explained, in part, by the electron-delocalization efficiency in the π molecular orbitals of the diazine bridge itself.[3] Structural data for these systems were, however, limited to just one compound, (**14**). While other factors including σ contributions, metal–ligand bond lengths and bond angles should not be ignored in the total exchange picture, it is clear that pyridazine and phthalazine bridges are the most efficient among this group.

A comparison of metal–ligand bond lengths and bond angles involving the diazine ring N–N bridge (Table 4: Ni^1–N^1, Ni^1–N^1–N^2) in the related complexes (**1**), (**13**), and (**14**) shows that Ni–N(ring) bond lengths follow the order (**13**) (triazole) < (**14**) (phthalazine) < (**1**) (pyridazine), while Ni–N–N(ring) bond angles follow the order (**13**) > (**1**) $\simeq$ (**14**), with the large angles in (**13**) being geometrical consequences of the five-membered triazole itself. The trend in these bond lengths follows the trend in the angles N–Y–C(ring) (Table 4: N^3–Y–C) which span the range 111.5 (**13**), 115.8 (**14**), and 118.7° (**1**) and which result from the geometrical properties created by the peripheral donor groups. The shortest Ni–N(ring) distance occurs in (**13**), for which exchange is weakest, while the longest Ni–N(ring) distances occur in (**1**) for which a slightly larger exchange is observed. The strongest exchange is observed for (**14**) which has an intermediate Ni–N(ring) separation.

Assuming that the π molecular orbital pictures for a phthalazine and pyridazine diazine bridge are comparable, and different from that of a pyrazolate or 4-substituted-1,2,4-triazole bridge, then a comparison of (**1**) and (**14**) suggests that σ contributions to the overall exchange picture are significant. Despite the short Ni–N(ring) distances in (**13**) the small exchange may be a consequence of less efficient spin transfer *via* a π mechanism in the triazole ring. The Ni–N–N(ring) angles may also be a contributing factor to exchange differences but since these angles in (**1**) and (**14**) are comparable this will, perhaps, constitute a minor perturbation.

The binuclear cobalt(II) complexes (**10**) and (**11**) have magnetic moments (r.t.) which are slightly less than those observed for related complexes of the ligands dhph and dppn [*e.g.* $Co_2(dhph)_2Cl_4 \cdot 5H_2O$, $\mu_{eff.}$ (300 K) = 4.44 B.M.].[4] For these complexes, variable-temperature magnetic studies indicate weak antiferromagnetic exchange between the cobalt(II) centres, which is implied also for (**10**) and (**11**). Variable-temperature magnetic studies on the hydroxo-bridged compound $[Co_2(tren)_2(OH)][ClO_4]_3 \cdot H_2O$ (tren = 2,2′,2″-triaminotriethylamine) indicate $-J = 38\ cm^{-1}$ with a r.t. moment $\mu_{eff.} = 3.96$ B.M.[42] For (**12**), a much lower r.t. moment is observed implying stronger spin exchange and thus supporting the proposed hydroxide-bridged structure for this complex.

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