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Cobalt(II), Cobalt(III) and Nickel(II) Complexes of some Tetradentate Pyridyl Phthalazines

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Abstract

Cobalt(II), cobalt(III) and nickel(II) complexes of a series of tetradentate pyridyl-phthalazine ligands have been studied. Binuclear cobalt(II) and cobalt(III) derivatives are obtained from aqueous solution with the ligands PAP and PAP4Me (PAP = 1,4-di(2′-pyridyl)aminophthalazine; PAPXMe = 1,4-di(X′-methyl-2′-pyridyl)aminophthalazine), in which three ligands are bound to the binuclear centre. An X-ray study on $[(PAP)_3Co_2(OH)_2]Br_4\cdot 9H_2O$ shows a binuclear centre involving two octahedral cobalt(III) ions bridged by two hydroxides and involving one tetradentate and two bidentate ligands. Other binuclear cobalt(II) derivatives, $[(PAP4Me)Co_2X_3]$ (X = Cl, Br, I, NCS) involve just tetradentate ligand. Binuclear nickel(II) derivatives are also obtained and in one case, $[(PAP)_3Ni_2(H_2O)_2]Br_4\cdot 6H_2O$, X-ray data indicate a binuclear centre involving two bridging water molecules, a tetradentate bridging ligand and two bidentate ligands. Steric factors involving methyl substituents on the pyridine rings are important for PAP6Me, a 6-methyl derivative, and for both cobalt and nickel complexes of this ligand only mononuclear derivatives are obtained.

Introduction

Numerous binuclear transition metal complexes involving polyfunctional diazine ligands derived from phthalazines [1–19], pyridazines [2–4, 20–23], pyrazole [2] and hydrazine [24–29] have been reported in recent years. These systems involve multiple bridges, in many cases, including the diazine (N–N) bridge plus at least one bridging anionic group [5–23]. For some copper(II) complexes involving hydroxide as a bridging entity the systems are characterized by having low room-temperature magnetic moments and strong antiferromagnetic exchange between the metal centres [5, 9, 10, 12, 13, 15–17]. In other complexes involving nickel(II) and cobalt(II) centres and just phthalazine and pyridazine bridges [3, 4, 8] and in doubly bridged cobalt(II) phthalazine complexes involving halide bridges [6, 7], antiferromagnetic exchange is also observed.

Some cobalt(II) and nickel(II) complexes of the tetradentate phthalazine ligand PAP (PAP = 1,4-di(2′-pyridyl)aminophthalazine) (Fig. 1) have already been reported, involving 1:1 (nickel) and 1:2 (nickel, cobalt) ligand to metal ratios. As part of our continuing interest in systems of this sort we have examined further the cobalt and nickel coordination chemistry of PAP and also of the other related ligands PAP3Me (1,4-di(3′-methyl-2′-pyridyl)aminophthalazine), PAP4Me (1,4-di(4′-methyl-2′-pyridyl)aminophthalazine), PAP5Me (1,4-di(5′-methyl-2′-pyridyl)aminophthalazine), and PAP6Me (1,4-di(6′-methyl-2′-pyridyl)aminophthalazine). In this study we report preliminary details of an X-ray study on the complex $[(PAP)_3Co_2(OH)_2]Br_4\cdot 9H_2O$ (I), an unusual cobalt(III) complex involving one tetradentate and two bidentate ligands bound to a di-μ-hydroxo bridged binuclear centre and on a related nickel(II) complex $[(PAP)_3Ni_2(H_2O)_2]Br_4\cdot 6H_2O$ (**XIII**) involving a similar binuclear centre with bridging water molecules. These two complexes are structurally similar to the complex $[(PAP\text{-}H)_2(PAP)Co_2(OH)_2](ClO_4)_2\cdot 1.5EtOH\cdot 6.5H_2O$ (II) (PAP-H = deprotonated ligand) which was discussed briefly in an earlier paper [9]. Binuclear cobalt(II) complexes of PAP and PAP4Me, mononuclear cobalt(II) complexes of PAP6Me and a binuclear cobalt(III) complex of PAP4Me are also described, in addition to a selection of nickel(II)

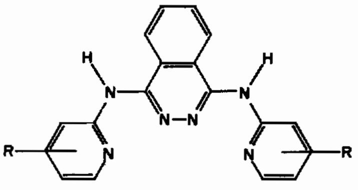

Fig. 1. PAPR (R = H, 3Me, 4Me, 5Me, 6Me).

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complexes of the ligands PAP3Me, PAP4Me, PAP5-Me and PAP6Me. Of particular interest in this group are some binuclear cobalt and nickel thiocyanate complexes, which exhibit very low energy CN stretching vibrations in the infrared (<2020 cm^{-1}) associated with single atom nitrogen bridged thiocyanate.

Experimental

$[(PAP)_3Co_2(OH)_2]Br_4\cdot 9H_2O$ (I)

$(PAP)Co_2Br_3$ [6] (0.500 g, 0.740 mmol) was dissolved in water (50 ml) and the solution stirred for 24 h in air, during which time the solution became dark brown in colour. The volume of the solution was reduced by half and it was allowed to stand for several days. Dark brown crystals of **I** formed which were filtered, washed sparingly with a cold ethanol/water mixture and dried briefly under vacuum.

$[(PAP)(PAP\text{-}H)_2Co_2(OH)_2](ClO_4)_2\cdot 1.5EtOH\cdot 6.5H_2O$ (II)

PAP (1.00 g, 3.18 mmol) was added to a solution of $Co(ClO_4)_2\cdot 6H_2O$ (2.33 g, 6.36 mmol) dissolved in water (100 ml) and the mixture stirred with warming in air. The ligand dissolved and the solution became dark brown in colour. A brown solid formed on cooling which was filtered and recrystallized from ethanol/H_2O (80/20) to give chunky dark brown cubic crystals of **II**.

$[(PAP)_3Co_2(H_2O)_2](ClO_4)_4\cdot 6H_2O$ (III)

PAP (1.00 g, 3.18 mmol) was added to a degassed solution of $CoBr_2\cdot 6H_2O$ (1.04 g, 3.18 mmol) in water (100 ml) and the mixture refluxed under nitrogen until the ligand dissolved. The orange solution was filtered and saturated aqueous sodium perchlorate added to precipitate a pale orange crystalline product. The crystals were filtered under nitrogen, washed with degassed water and dried under vacuum. **IV** was prepared in a similar manner using cobalt nitrate.

$[(PAP4Me)Co_2Cl_3]\cdot 2H_2O$ (V)

$CoCl_2\cdot 6H_2O$ (1.65 g, 6.93 mmol) was dissolved in methanol (50 ml), PAP4Me (1.00 g, 2.92 mmol) dissolved in methanol (50 ml) added and the mixture refluxed for 1 h. The green solution was cooled and its volume reduced to produce green crystals. The product was filtered, washed with cold methanol and dried under vacuum. **VI**, **VII** and **VIII** were prepared in a similar manner using acetonitrile as solvent.

$[(PAP4Me)_3Co_2(OH)_2](ClO_4)_4\cdot 6H_2O$ (IX)

$Co(ClO_4)_4\cdot 6H_2O$ (1.07 g, 2.90 mmol) was dissolved in methanol (5 ml), PAP4Me (1.00 g, 2.92 mmol) dissolved in methanol (50 ml) added and the mixture refluxed in air for 1 h. The solution, which was originally a light pink-orange in colour, became dark brown rapidly. The reaction mixture was filtered after standing for one week to remove a yellow solid (identified as $[PAP4MeH_2](ClO_4)_2\cdot 0.5H_2O$. *Anal.* calcd: C 43.5, H 3.80, N 15.2; found: C 43.5, H 3.69, N 15.2). On reduction in volume a dark red-brown crystalline solid formed, which was filtered and recrystallised from methanol containing triethylorthoformate (90/10).

$(PAP6Me)CoCl_2\cdot 2H_2O$ (X)

$CoCl_2\cdot 6H_2O$ (1.40 g, 5.88 mmol) was dissolved in hot degassed methanol (40 ml) and mixed with a solution of PAP6Me (1.00 g, 2.92 mmol) in hot degassed methanol (60 ml) and the mixture stirred under nitrogen. A green precipitate formed, which was filtered, washed with degassed methanol and dried under vacuum. **XI** was prepared in a similar manner while **XII** was prepared similarly in acetonitrile.

$[(PAP)_3Ni_2(H_2O)_2]Br_4\cdot 6H_2O$ (XIII)

$NiBr_2\cdot 3H_2O$ (0.900 g, 3.30 mmol) was dissolved in water (50 ml) and PAP (1.00 g, 3.18 mmol) added. The mixture was stirred with warming for a few minutes until the ligand dissolved and the dark blue solution filtered. The volume of the solution was reduced until crystallization just commenced giving purple-blue crystals. This product was filtered off and the mother liquor reduced in volume further until a greyish-green solid was obtained. These products, which have been reported previously [8] correspond to binuclear derivatives of the form $(PAP)_2Ni_2(H_2O)_nBr_4$. A third crop of purple-grey crystals was obtained from the mother liquor, which on recrystallization from water gave a purple crystalline material (**XIII**).

$(PAP3Me)Ni(NO_3)_2\cdot 2.5H_2O$ (XIV)

$Ni(NO_3)_2\cdot 6H_2O$ (2.00 g, 6.87 mmol) was dissolved in methanol (50 ml), PAP3Me (0.40 g, 1.2 mmol) added and the mixture refluxed with the formation of a green solution. On cooling moss green crystals formed which were filtered, washed with a methanol/ether mixture and dried *in vacuo*. Complexes **XV–XIX** were prepared in a similar manner.

Physical Measurements

Electronic spectra were recorded with a Cary 17 spectrometer and infrared spectra with a Perkin-Elmer Model 283 spectrometer. Magnetic susceptibilities were obtained at room temperature by the Faraday method using a Cahn Model #7600 Faraday Magnetic Susceptibility system, coupled to a Cahn gram electrobalance. Microanalyses were carried out

TABLE I. Analytical and Other Data.

	Compound	Found (%)				Calcd (%)			
		C	H	N	M	C	H	N	M
I	$[(PAP)_3Co_2(OH)_2]Br_4 \cdot 9H_2O$	40.91	3.60	15.87		41.13	3.94	15.99	
II	$[(PAP)(PAP\text{-}H)_2Co_2(OH)_2](ClO_4)_2 \cdot 1.5EtOH \cdot 6.5H_2O$	46.18	3.38	17.09	7.60	46.31	4.33	17.06	7.99
III	$[(PAP)_3Co_2(H_2O)_2](ClO_4)_4 \cdot 6H_2O$	40.15	3.54	15.55	7.38	40.00	3.70	15.55	7.28
IV	$[(PAP)_3Co_2(H_2O)_2](NO_3)_4 \cdot 6H_2O$	45.11	3.54	21.36	8.00	44.60	3.99	21.20	8.13
V	$[(PAP4Me)Co_2Cl_3] \cdot 2H_2O$	39.76	3.35	13.94	19.2	39.83	3.48	13.94	19.6
VI	$[(PAP4Me)Co_2Br_3] \cdot 0.5H_2O$	33.82	2.83	12.09	16.6	33.85	2.54	11.85	16.6
VII	$[(PAP4Me)Co_2I_3] \cdot H_2O$	27.74	2.05	9.30		27.97	2.21	9.79	
VIII	$[(PAP4Me)Co_2(NCS)_3]$	43.48	2.59	19.63	18.1	43.53	2.84	19.87	18.6
IX	$[(PAP4Me)_3Co_2(OH)_2](ClO_4)_4 \cdot 6H_2O$	42.83	3.72	14.94		42.75	4.04	14.96	
X	$(PAP6Me)CoCl_2 \cdot 2H_2O$	47.06	3.42	16.58		47.20	4.33	16.53	
XI	$(PAP6Me)CoBr_2 \cdot H_2O$	41.71	3.01	14.54	9.71	41.50	3.46	14.51	10.2
XII	$(PAP6Me)Co(NCS)_2 \cdot 0.25H_2O$	50.41	3.31	21.32	10.9	50.62	3.55	21.48	11.3
XIII	$[(PAP)_3Ni_2(H_2O)_2]Br_4 \cdot 6H_2O$	42.57	3.39	16.58		42.56	3.81	16.54	
XIV	$(PAP3Me)Ni(NO_3)_2 \cdot 2.5H_2O$	42.10	3.56	19.74	10.7	42.10	4.04	19.70	10.3
XV	$(PAP3Me)Ni(ClO_4)_2 \cdot 3.5H_2O$	36.52	3.35	12.52	9.00	36.22	3.77	12.68	8.90
XVI	$(PAP3Me)Ni(NCS)_2 \cdot 1.5H_2O$	48.31	3.35	20.72	10.3	48.50	3.86	20.61	10.8
XVII	$(PAP4Me)Ni(NCS)_2$	50.45	3.53	21.00	10.9	50.60	3.48	21.05	11.4
XVIII	$(PAP5Me)Ni(NCS)_2 \cdot 2H_2O$	47.72	3.34	20.15	10.4	47.70	3.97	20.20	10.6
XIX	$(PAP6Me)_2Ni(NCS)_2 \cdot 3.5H_2O$	54.70	4.59	21.10	6.42	54.68	4.66	21.26	6.37

by Canadian Microanalytical Service, Vancouver (C, H, N). Metal analyses were determined by atomic absorption with a Varian Techtron AA-5, after digestion of the samples in concentrated HNO_3 of aqua regia.

Satisfactory analytical data have been obtained for all complexes described and are reported in Table I.

Discussion

In a previous paper [6] we reported the synthesis and characterization of a series of complexes, (PAP)-Co_2X_3 (X = Cl, Br, I), which were shown to have binuclear structures in which the pseudo-tetrahedral cobalt(II) centres appear to be bridged by a phthalazine, N–N, fragment and a halogen (Fig. 2). The green complexes dissolved in water to give orange solutions which were found to be stable in the absence of air, but on stirring in air gradually turned dark brown in colour. The orange solutions were shown spectroscopically to contain pseudo-octahedral cobalt(II) species which became oxidized to cobalt(III) on exposure to air.

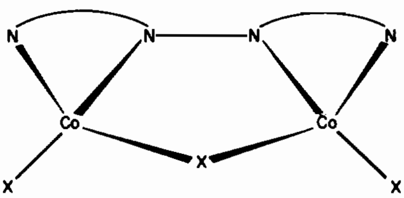


Fig. 2. Structural representation of the complexes [(PAP)-Co_2X_3] (X = Cl, Br, I).

Dark brown crystals of **I** were obtained from the dark brown solution which resulted from exposure of the orange aqueous solution of (PAP)Co_2Br_3 to air for an extended period of time. **I** has been shown to contain two cobalt(III) centres, three ligands and four bromide ions and since the compound is diamagnetic, indicating the presence of cobalt(III), the charge balance could be achieved by assuming neutral ligand and two hydroxide ions or two protonated ligands, and two oxide ions or a mixture of these two situations.

Infrared data (Table II) indicate the presence of water but no clear indication of a hydroxide bridge. However the lattice water present could broaden the O–H stretch in a hydroxide bridge due to hydrogen bonding. In the CN stretching region, associated with the heterocyclic rings, four absorptions are observed above 1600 cm^{-1}. In neutral tetradentate ligand binuclear complexes only two absorptions are normally observed in this region, while for species containing bidentate, protonated PAP up to five absorptions have been observed [8–10]. A similar situation would presumably exist for neutral bidentate PAP. In the pyridine ring breathing mode region two major absorptions are observed for **I** associated with coordinated and uncoordinated pyridine groups [5] and since the lowest energy band in this region is observed in excess of 996 cm^{-1} for uncoordinated, protonated pyridine

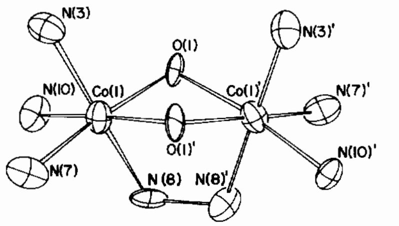
TABLE II. Infrared Data (cm^{-1}).

	Compound	
I	$[(PAP)_3Co_2(OH)_2]Br_4\cdot 9H_2O$	3500sh, 3420(OH, H_2O), 3330(NH), 1640sh, 1630, 1619, 1612(CN), 1022, 993, 990sh (pyr)
II	$[(PAP(PAP\text{-}H)_2Co_2(OH)_2](ClO_4)_2\cdot 1.5EtOH\cdot 6.5H_2O$	3540br (OH, H_2O), 3340(NH), 1633, 1626sh, 1605(CN), 1097(ClO_4^-), 1017, 990 (pyr)
III	$[(PAP)_3Co_2(H_2O)_2](ClO_4)_4\cdot 6H_2O$	3500(H_2O), 3320(NH), 1080(ClO_4^-), 1007, 992(Pyr)
IV	$[(PAP)_3Co_2(H_2O)_2](NO_3)_4\cdot 6H_2O$	3480(H_2O), 3300(NH), 1750($\nu_1 + \nu_4$ NO_3^-) 1005, 992(pyr)
V	$[(PAP4Me)Co_2Cl_3]\cdot 2H_2O$	3450sh(H_2O), 3270(NH), 1029(Pyr), 299, 272, 242(Co–Cl)
VI	$[(PAP4Me)Co_2Br_3]\cdot 0.5H_2O$	3260(NH), 1015(pyr), 241, 220(Co–Br)
VII	$[(PAP4Me)Co_2I_3]\cdot H_2O$	3500sh(H_2O), 3270(NH), 1012(Pyr)
VIII	$[(PAP4Me)Co_2(NCS)_3]$	3300(NH), 2099sh, 2058, 1969, 1934, 1903sh (NCS), 1020(pyr), 306, 290 (Co–N)
IX	$[(PAP4Me)_3Co_2(OH)_2](ClO_4)_4\cdot 6H_2O$	3620sh, 3595(OH, H_2O), 3290(NH), 1100, 1070 (ClO_4^-), 1020, 1003(pyr)
X	$(PAP6Me)CoCl_2\cdot 2H_2O$	3550(H_2O), 3340(NH), 325, 307(Co–Cl)
XI	$(PAP6Me)CoBr_2\cdot H_2O$	3550(H_2O), 3300(NH), 257, 245(Co–Br)
XII	$(PAP6Me)Co(NCS)_2\cdot 0.25H_2O$	3340(NH), 2070sh, 2050(NCS), 320, 310sh (Co–N)
XIII	$[(PAP)_3Ni_2(H_2O)_2]Br_4\cdot 6H_2O$	3450(H_2O), 3300(NH), 1012, 995(pyr)
XIV	$(PAP3Me)Ni(NO_3)_2\cdot 2.5H_2O$	1760, 1740 ($\nu_1 + \nu_4$ NO_3^-)
XV	$(PAP3Me)Ni(ClO_4)_2\cdot 3.5H_2O$	3500(H_2O), 3380(NH), 1080(ClO_4^-)
XVI	$(PAP3Me)Ni(NCS)_2\cdot 1.5H_2O$	3500(H_2O), 2093, 2070, 2020(NCS^-)
XVII	$(PAP4Me)Ni(NCS)_2$	3380(NH), 2095, 2075, 1998 (NCS^-), 273(Ni–N)
XVIII	$(PAP5Me)Ni(NCS)_2\cdot 2H_2O$	3500(H_2O), 2090, 2015(NCS^-), 280, 260 (Ni–N)
XIX	$(PAP6Me)_2Ni(NCS)_2\cdot 3.5H_2O$	3640, 3500(H_2O), 3340(NH), 2095(NCS^-), 270sh, 250(Ni–N)

moieties [9] the ligands appear to be neutral. In the π–π^* charge transfer region of the electronic spectrum (Table III) one intense band is observed in aqueous solution at 27400 cm^{-1} supporting the presence of neutral ligand [5].

An X-ray structural investigation of I reveals a binuclear structure involving two oxygen atoms bridging the two cobalt(III) centres, a tetradentate binucleating ligand and two bidentate ligands [30] involving coordination at one pyridine and one phthalazine site only. A preliminary structural representation is shown in Fig. 3, in which the ligands themselves have been omitted for clarity. Four bromide ions and nine water molecules were located in the lattice. The stereochemistry at each cobalt centre is approximately octahedral (Table IV) with the two bridging oxygen atoms and the diazine nitrogen pair of the binucleating phthalazine ligand providing a triple bridge between the metal centres such that the two octahedra share a common edge.

Chemical and spectroscopic evidence suggests that hydroxide groups bridge the two cobalt(III) centres. This is substantiated by a comparison of the cobalt–oxygen bond lengths (Table IV) with those of binuclear cobalt(III) systems known to have hydroxide bridges. Co–O bond lengths for a number of such systems with one, two and even three hydroxide bridges fall in the range 1.88–2.01 Å [31–38]. There are no abnormal structural features associated with the uncoordinated pyridine moieties which would indicate the presence of protonated nitrogen centres, a feature which has been observed previously [9].



N(10) – N(8) – N(8)' — N(10)' represents the tetradentate ligand

Fig. 3. Molecular structural representation for the cation in $[(PAP)_3Co_2(OH)_2]Br_4\cdot 9H_2O$ (I).

TABLE III. Electronic Spectra (mull transmittance) (cm^{-1}) and Magnetic Moments.

	Compound	$^4T_{2g}(F)$	$^4T_{1g}(F)$	$^4T_{1g}(P)$	$^4T_{1g}(F)$	$\pi-\pi^*$	μ_M (BM) (room temp.)
I	$[(PAP)_3Co_2(OH)_2]Br_4 \cdot 9H_2O$	–		–		27400[a]	DIAM
II	$[(PAP)(PAP\text{-}H)_2Co_2(OH)_2](ClO_4)_2 \cdot 1.5EtOH \cdot 6.5H_2O$	–		–		26700[a]	DIAM
III	$[(PAP)_3Co_2(H_2O)_2](ClO_4)_4 \cdot 6H_2O$	10200		[20000]		28600	4.60
IV	$[(PAP)_3Co_2(H_2O)_2](NO_3)_4 \cdot 6H_2O$	10200		[22000]		28600	4.72
		$^4T_1(F)$	$^4A_2$	$^4T_1(P)$	$^4A_2$		
V	$[(PAP4Me)Co_2Cl_3] \cdot 2H_2O$	5500, 6100, 8300, 10900		14500, 14900, 16000		26700	4.28
VI	$[(PAP4Me)Co_2Br_3] \cdot 0.5H_2O$	5200, 5600, 7900, 10700		13700, 14300, 15000, 15500		27400	4.19
VII	$[(PAP4Me)Co_2I_3] \cdot H_2O$	6700, 8200, 9200		13000, 13800, 14300		28200	3.76
VIII	$[(PAP4Me)Co_2(NCS)_3]$	6760, 7600, [8300]		15900, [16900]		27800	4.13
IX	$[(PAP4Me)_3Co_2(OH)_2](ClO_4)_4 \cdot 6H_2O$	–		–			DIAM
X	$(PAP6Me)CoCl_2 \cdot 2H_2O$	6900, 8300, 11700		16700, [18200], 23500			4.41
XI	$(PAP6Me)CoBr_2 \cdot H_2O$	6760, 8160, 11400		16700, 17900, 22700			4.39
XII	$(PAP6Me)Co(NCS)_2 \cdot 0.25H_2O$	6500, 9300, 12200		16900, 18900, 22500			4.28
		$^3T_{2(g)}(F)$	$^3A_{2(g)}$	$^3T_{1g}(F)$	$^3A_{2(g)}$		
XIII	$[(PAP)_3Ni_2(H_2O)_2]Br_4 \cdot 6H_2O$	11200		17500		27200 28700[a]	3.18
XIV	$(PAP3Me)Ni(NO_3)_2 \cdot 2.5H_2O$	11200		17500		27000	3.20
XV	$(PAP3Me)Ni(ClO_4)_2 \cdot 3.5H_2O$	11400		18200		27800	3.22
XVI	$(PAP3Me)Ni(NCS)_2 \cdot 1.5H_2O$	10900		16900		28000	3.24
XVII	$(PAP4Me)Ni(NCS)_2$	10900		17900		28600	3.04
XVIII	$(PAP5Me)Ni(NCS)_2 \cdot 2H_2O$	10000, 12500		16900		–	3.14
XIX	$(PAP6Me)_2Ni(NCS)_2 \cdot 3.5H_2O$	10000		17000		–	3.11

[a] Solution in water.

TABLE IV. Interatomic Distances (Å) and Angles (deg.) (e.s.d.s) Relevant to the Cobalt Coordination Spheres in (I), $[(PAP)_3Co_2(OH)_2]Br_4 \cdot 9H_2O$. Space group $C222_1$, $R = 0.044$.

Co(1)–O(1)	1.902(7)	Co(1)–N(10)	1.956(7)
Co(1)–O(1)′	1.929(6)	Co(1)–N(8)	1.880(8)
Co(1)–N(3)	1.885(9)	Co(1)–Co(1)′	2.795(3)
Co(1)–N(7)	1.951(8)		
N(3)–Co(1)–N(7)	90.1(3)	N(7)–Co(1)–O(1)′	92.5(3)
N(3)–Co(1)–N(8)	177.4(3)	N(8)–Co(1)–N(10)	87.3(3)
N(3)–Co(1)–N(10)	91.0(4)	N(8)–Co(1)–O(1)	84.1(3)
N(3)–Co(1)–O(1)	93.5(3)	N(8)–Co(1)–O(1)′	87.6(3)
N(3)–Co(1)–O(1)′	93.1(3)	N(10)–Co(1)–O(1)	94.9(3)
N(7)–Co(1)–N(8)	92.4(3)	N(10)–Co(1)–O(1)′	173.5(3)
N(7)–Co(1)–N(10)	91.8(4)	Co(1)–O(1)–Co(1)′	93.7(3)
N(7)–Co(1)–O(1)	172.3(3)		

Structurally 1 is unusual in that the oxidation of the cobalt(II) species, $(PAP)Co_2Br_3$, by molecular oxygen in air does not produce a classical Werner type complex with a peroxo bridge [39]. This may be attributed to the fact that $(PAP)Co_2Br_3$ is already binuclear. Also a major molecular rearrangement is involved in going from a binuclear 1:2 cobalt(II) complex to a binuclear 3:2 cobalt(III) complex. The mechanism of this process is, as yet, not understood. The structure of **I** is analogous to that of compound **II**, which has been shown from analytical, spectroscopic and preliminary X-ray data [9, 40] to be a binuclear cobalt(III) derivative with the same basic structure as 1, but involving two non-coordinated perchlorate anions. Bond lengths to the oxygen bridges fall in the range 1.88–1.95 Å suggesting hydroxide bridges, with oxygen bridge angles of 92.4 and 92.5 deg. The presence of anionic ligands, as implied by the analytical data is not revealed clearly in the structure, although short axial bond lengths to phthalazine atoms of 1.84 Å (tetradentate) and 1.77 Å (bidentate) could indicate the coordination of anionic ligand sites ($R \simeq 12\%$).

The general stability of binuclear cobalt centres involving three pyridyl-phthalazine ligands is illustrated by the synthesis of compounds **III** and **IV**. These are binuclear, octahedral, cobalt(II) derivatives, as indicated by magnetic and electronic spectral data, and appear to contain neutral ligands. The charge balance would then imply that two water molecules occupy bridging positions between the cobalt centres. However, since complexes involving bidentate PAP, in which a non-coordinated nitrogen site, probably pyridine, is protonated, have π–π^* charge transfer absorptions in the range 27400–29400 cm^{-1}, it may not be possible to distinguish neutral and protonated PAP on the basis of change transfer absorption [8, 9]. The distinction between bridging water and hydroxide may have to be made using X-ray crystallography.

An analogous diamagnetic binuclear cobalt(III) derivative, **IX**, is produced on reaction of PAP4Me with cobalt perchlorate in methanol in the presence of air. The protonated ligand salt $[PAP4MeH_2](ClO_4)_2 \cdot 0.5H_2O$ is also produced in the same reaction indicating the sensitivity of the system to pH [8, 9]. The two cobalt(III) centres appear to be bridged by two hydroxides in addition to a phthalazine, as indicated by infrared and electronic spectral data.

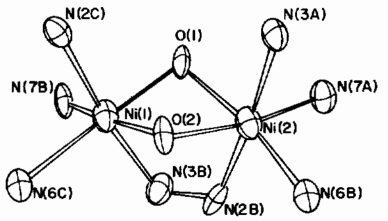
Compounds **V–VIII** are binuclear cobalt(II) species involving two metal centres bound to one ligand. Electronic spectra (Table III) indicate the presence of pseudo-tetrahedral cobalt(II) centres and magnetic moments are comparable to those found for the analogous PAP systems [6], which were shown to be weakly spin coupled via a superchange mechanism. For **V–VII** a diazine bridge and a halogen bridge are expected as the only bridge groups between the cobalt(II) centres, with infrared data for **V** and **VI** indicating the presence of both terminal and bridging halogens. The thiocyanate derivative, **VIII**, has an unusual infrared spectrum in the CN stretching region associated with the thiocyanate groups. A major absorption at 2058 cm^{-1} is associated with terminal isothiocyanate while lower energy bands in the range 1900–1970 cm^{-1}, which are most unusual, could possibly be associated with a single atom, nitrogen bridged thiocyanate. **VIII** differs from the PAP analogue, $Co_2(PAP)(NCS)_2(OH)_2$ [6], by having three thiocyanate groups. This derivative exhibited a simple CN stretching region in the infrared with just one band at 2086 cm^{-1}. CN bands around 2000 cm^{-1} and below have been observed for a few binuclear and trinuclear compounds involving N-bridging isothiocyanate ligands [41–44] and it is tempting to assign a structure to **VIII** involving one N-bridging isothiocyanate and two terminal isothiocyanates in a binuclear arrangement involving pseudo-tetrahedral cobalt(II) centres.

TABLE V. Interatomic Distances (Å) and Angles (deg.) (e.s.d.s) Relevant to the Nickel Coordination Spheres in (XIII), $[(PAP)_3Ni_2(H_2O)_2]Br_4 \cdot 6H_2O$. Space group $P2_1/C$, $R = 0.073$.

Ni(1)–O(1)	2.139(10)	Ni(2)–O(1)	2.173(11)
Ni(1)–O(2)	2.166(11)	Ni(2)–O(2)	2.143(10)
Ni(1)–N(2C)	2.056(14)	Ni(2)–N(3A)	2.014(14)
Ni(1)–N(7B)	2.070(15)	Ni(2)–N(7A)	2.084(13)
Ni(1)–N(6C)	2.119(13)	Ni(2)–N(6B)	2.082(14)
Ni(1)–N(3B)	2.075(13)	Ni(2)–N(2B)	2.084(14)
Ni(1)–Ni(2)	3.39(2)		
O(1)–Ni(1)–O(2)	79.0(4)	O(1)–Ni(2)–O(2)	78.7(4)
O(1)–Ni(1)–N(3B)	82.7(5)	O(1)–Ni(2)–N(2B)	87.5(5)
O(1)–Ni(1)–N(7B)	93.4(5)	O(1)–Ni(2)–N(6B)	171.1(5)
O(1)–Ni(1)–N(2C)	90.3(5)	O(1)–Ni(2)–N(3A)	90.0(5)
O(1)–Ni(1)–N(6C)	170.9(5)	O(1)–Ni(2)–N(7A)	91.0(5)
O(2)–Ni(1)–N(3B)	87.7(5)	O(2)–Ni(2)–N(2B)	81.2(4)
O(2)–Ni(1)–N(7B)	170.1(5)	O(2)–Ni(2)–N(6B)	93.9(5)
O(2)–Ni(1)–N(2C)	90.2(5)	O(2)–Ni(2)–N(3A)	90.8(5)
O(2)–Ni(1)–N(6C)	92.1(5)	O(2)–Ni(2)–N(7A)	169.6(5)
N(3B)–Ni(1)–N(7B)	85.2(5)	N(2B)–Ni(2)–N(6B)	86.5(5)
N(3B)–Ni(1)–N(2C)	172.9(5)	N(2B)–Ni(2)–N(3A)	172.0(5)
N(3B)–Ni(1)–N(6C)	99.1(5)	N(2B)–Ni(2)–N(7A)	99.6(5)
N(7B)–Ni(1)–N(2C)	96.1(6)	N(6B)–Ni(2)–N(3A)	95.2(6)
N(7B)–Ni(1)–N(6C)	95.7(5)	N(6B)–Ni(2)–N(7A)	96.5(5)
N(2C)–Ni(1)–N(6C)	87.8(5)	N(3A)–Ni(2)–N(7A)	88.0(5)

Complexes **X–XII**, involving PAP6Me, exhibit typical pseudo-tetrahedral d–d absorptions which are clearly not associated with ions of the type CoX_4^{2-} (X = Cl, Br, NCS). The d–d bands and infrared data, indicating the presence of two coordinated anionic groups, suggest that these complexes are mononuclear involving pseudo-tetrahedral metal centres with a bidentate ligand, coordination occurring via one phthalazine and one pyridine nitrogen only. The formation of mononuclear species may be the result of steric effects associated with the pyridine 6-methyl groups.

The nickel bromide complex, **XIII**, is a binuclear derivative involving three ligands bound to the binuclear nickel(II) centre and is similar to the cobalt(II) and cobalt(III) derivatives **I–IV**, **IX**. Infrared data suggest the absence of hydroxide and the presence of both coordinated and uncoordinated pyridine residues; the absorption at 995 cm^{-1} probably indicates the absence of a protonated pyridine site. Electronic spectral absorption indicates the presence of pseudo-octahedral nickel(II) centres. The magnetic moment of 3.18 BM appears to be 'normal' but is slightly less than that of the 1:1 binuclear derivative, $[(PAP)_2Ni_2(H_2O)_4]Br_4$ which was produced in the same reaction (μ(RT) = 3.30 BM). It is of interest to note that the analogous chloride complex $[(PAP)_2Ni_2(H_2O)_4]Cl_4 \cdot 3H_2O$ (μ(RT) = 3.30 BM) was shown to exhibit weak antiferromagnetic exchange ($-J$ = 3.2 cm^{-1}) [8].



N(7B)–N(3B)–N(2B)–N(6B) represents the tetradentate ligand.

Fig. 4. Molecular structural representation for the cation in $[(PAP)_3Ni_2(H_2O)_2]Br_4 \cdot 6H_2O$ (XIII).

The preliminary results of an X-ray study on **XIII** are shown in Fig. 4 [30]. Nickel–oxygen bond lengths to the oxygen bridge atoms fall in the range 2.16–2.22 Å (Table V) consistent with the presence of bridging water molecules. Published examples of binuclear nickel(II) complexes with bridging water have Ni–O bond lengths in excess of 2.13 Å [45, 46] while for hydroxo- and methoxo-bridged species Ni–O bond lengths of <2.08 Å are observed [45, 47].

Complexes **XIV**, **XV** exhibit electronic spectra typical of pseudooctahedral nickel(II). The nitrate combination bands for **XIV** suggest the presence of monodentate nitrate while for **XV** the perchlorate groups are ionic. While there is no compelling spectral and magnetic (room temperature) evidence to suggest that these complexes are binuclear, the possibility of sandwich type dimeric structures should not be excluded. The thiocyanate complex, **XVI**, is characterized by an unusual CN stretching region in the infrared, associated with thiocyanate groups. Two bands at 2093, 2070 cm^{-1} can be associated with terminal N-bonded and ionic thiocyanate respectively, but the absorption at 2020 cm^{-1} falls below the range expected for such groups and is assigned to a single nitrogen atom bridged isothiocyanate. Previous studies on the system $[(PAP)_2Ni_2(NCS)_3]$-NCS [8] revealed a νCN band at 2002 cm^{-1} which was assigned to a μ-N-isothiocyanate and these assignments have been substantiated by other reports of low energy CN stretching frequencies associated with such groups [41–44]. Structurally **XVI** is considered to be a binuclear derivative involving two tetradentate ligands bridging two octahedral nickel(II) centres with a μ-N-isothiocyanate-bridge, two terminal isothiocyanates and an ionic thiocyanate. Analogous structures are expected for **XVII** and **XVIII**, in which low energy CN stretches are again associated with μ-N-thiocyanate. The 6-methyl analogue, **XIX**, is different and is likely to be a mononuclear derivative involving two bidentate ligands and two isothiocyanate groups bound to a six-coordinate nickel(II) centre. The fact that one sharp CN(NCS) stretching band is observed is indicative of a *trans* structure. We await structural data on the thiocyanate complexes to confirm the bridging role of the thiocyanate group but so far X-ray quality crystals have eluded us.

The unusual binuclear cobalt(II), cobalt(III) and nickel(II) complexes involving three ligands with mixed functionality are unprecedented and systems of this sort have not been observed with other binucleating tetradentate diazine ligands. However binuclear copper complexes involving the same ligands are simple 1:2 (ligand:metal) derivatives. Binuclear complexes prevail with all ligands except PAP6Me, where it is clear that steric effects associated with the 6-methyl group influence the situation to such an extent that mononuclear derivatives are the norm. That such a steric effect is significant is amply demonstrated by a comparison of the Cu–O–Cu bridge angles in the complexes $[Cu_2(PAP)(OH)Cl_3]\cdot 1.5H_2O$ (100 deg.) and $[Cu_2(PAP6Me)(OH)Cl_3]\cdot 2H_2O$ (111.6 deg.) [48].

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