and 18e-configurated Mo(III) complex.

The analogous $[Mo(Cl)(NO)(N_HS_4)]$ is obtained in methylene chloride (eq 11). It forms red crystals and shows spectroscopic properties similar to those of $[Mo(Cl)(NO)(OS_4)]$ (cf. Table VI).

The reaction according to eq 12 yields $[Mo(CO)_2(OS_4)]$, which forms orange crystals and is soluble in CH_2Cl_2 and DMSO; it

$$[MoCl_2(CO)_3(PPh_3)_2] + OS_4\text{-}Li_2 \xrightarrow[15\ h]{CH_2Cl_2} [Mo(CO)_2(OS_4)] + 2LiCl + 2PPh_3 + CO \quad (12)$$

shows two equally intense ν_{CO} bands at 1930 and 1870 cm^{-1}, indicating a cis geometry of the CO ligands.

A ruthenium complex was obtained according to eq 13.

$$[RuCl_2(PPh_3)_3] + OS_4\text{-}Li_2 \xrightarrow[reflux/2.5\ h]{THF} [Ru(PPh_3)(OS_4)] + 2LiCl + 2PPh_3 \quad (13)$$

$[Ru(PPh_3)(OS_4)]$ is easily soluble in THF, CH_2Cl_2, $CHCl_3$, and DMSO in contrast to the case for $[Ru(PPh_3)(S_5)]$, and it was characterized by spectroscopy and by elemental analysis. Table VI summarizes selected spectroscopic data of the free ligands as well as of their Mo and Ru complexes.

Conclusion

$[Fe(CO)(XS_4)]$ complexes with the novel pentadentate ligands OS_4^{2-} and $N_HS_4^{2-}$ respectively were synthesized and characterized, including X-ray structure analyses. The X donor atoms occupy positions trans to the CO ligand, resulting in different reactivities of the Fe–CO bonds. This shows that O or N donors in a coordination sphere dominated by sulfur can not only determine the reaction site of a complex but also influence markedly the degree of its reactivity. In contrast to the short Fe–CO bond of $[Fe(CO)(OS_4)]$, however, this species is the most reactive, with respect to CO substitution. The free ligands $XS_4\text{-}H_2$ or their lithium salts (X = O, NH) show good ligating properties and yield the new complexes $[Mo(Cl)(NO)(XS_4)]$, $[Mo(CO)_2(OS_4)]$, and $[Ru(PPh_3)(OS_4)]$. The NH function in $[Fe(CO)(N_HS_4)]$ renders possible the synthesis of the alkyl derivative $[Fe(CO)(N_{Me}S_4)]$ and potentially of a whole series of N_RS_4 complexes.

Acknowledgment. These investigations were supported by the Deutsche Forschungsgemeinschaft, by the Fonds der Chemischen Industrie, by the Dr. Otto Röhm Gedächtnisstiftung, and by the donation of $RuCl_3{\cdot}xH_2O$ by Degussa AG, Hanau, West Germany. We gratefully acknowledge this support.

Registry No. $[MoCl_3(NO)(CH_3CN)_2]$, 65060-56-2; $[Fe(CO)(OS_4)]$, 116888-20-1; $[Fe(CO)(N_HS_4)]$, 116888-21-2; $[Fe(CO)_2(S_2C_6H_4)_2]^{2-}$, 66350-60-5; $Fe(OS_4)$, 116888-22-3; $[Fe(PMe_3)(OS_4)]$, 116888-23-4; $[Fe(PMe_3)(N_HS_4)]$, 116888-24-5; $[Fe(N_2H_4)(N_HS_4)]$, 116888-25-6; $[Fe(CO)(N_{Me}S_4)]$, 116888-26-7; $OS_4\text{-}H_2$, 116888-31-4; $N_HS_4\text{-}H_2$, 116888-30-3; $[Mo(NO)(Cl)(OS_4)]$, 116888-27-8; $[Mo(NO)(Cl)(N_HS_4)]$, 116888-28-9; $[Mo(CO)_2(OS_4)]$, 116926-19-3; $[MoCl_2(CO)_3(PPh_3)_2]$, 17250-39-4; $[Ru(PPh_3)(OS_4)]$, 116888-29-0; $[RuCl_2(PPh_3)_3]$, 15529-49-4; bis(2-bromoethyl) ether, 5414-19-7; bis(2-bromoethyl) amine, 3890-99-1; *o*-benzenedithiol, 17534-15-5.

Supplementary Material Available: Listings of crystallographic data and data collection parameters, anisotropic thermal parameters, all bond distances and bond angles, and fractional coordinates of hydrogen atoms (9 pages); listings of F_o and F_c values (34 pages). Ordering information is given on any current masthead page. Further details of the X-ray crystal structure analyses have been deposited with the Fachinformationszentrum Energie, Physik, Mathematik, D-7514 Eggenstein-Leopoldshafen 2, West Germany, and can be obtained by quoting Deposition No. CSD-52957, the authors' names, and the reference.

Contribution from the Department of Chemistry, Memorial University of Newfoundland, St. John's, Newfoundland, Canada A1B 3X7, and Chemistry Division, National Research Council, Ottawa, Canada K1A 0R6

Binuclear Nickel(II) and Cobalt(II) Complexes of Sexadentate (N_6) Phthalazine Ligands. Crystal and Molecular Structures of [μ-1,4-Bis((6-methylpyridine-2-carboxaldimino)amino)phthalazine-N^4,N^3,μ-N^1,μ-N^{1A},N^{3A},N^{4A}](μ-chloro)tetraaquodicobalt(II) Trichloride-4.3-Water, $Co_2C_{22}H_{28}Cl_4N_8O_4{\cdot}4.3H_2O$, and [$\mu$-1,4-Bis((6-methylpyridine-2-carboxaldimino)amino)phthalazine-N^4,N^3,μ-N^1,μ-N^{1A},N^{3A},N^{4A}](μ-chloro)tetraaquodinickel(II) Trichloride-4.6-Water, $Ni_2C_{22}H_{28}Cl_4N_8O_4{\cdot}4.6H_2O$[†]

Tao Wen,[1a] Laurence K. Thompson,*[1a] Florence L. Lee,[1b] and Eric J. Gabe[1b]

Received April 22, 1988

The ligand 1,4-bis((6-methylpyridine-2-carboxaldimino)amino)phthalazine (PHP6Me) forms binuclear cobalt(II) and nickel(II) complexes, $[M_2(PHP6Me)X(H_2O)_4]X_3$·solvent (M = Co, Ni; X = Cl, Br), involving six-coordinate metal centers bridged by the phthalazine diazine (N_2) group and a halogen. Other binuclear (1:1) derivatives $[Ni_2(APHP)_2]X_4{\cdot}4H_2O$ (X = NO_3, BF_4) (APHP = 1,4-bis((pyrid-2-ylacetaldimino)amino)phthalazine) involve two six-coordinate metal centers sandwiched between adjacent sexadentate ligands. All the complexes exhibit antiferromagnetic exchange between the metal centers with the 1:1 nickel derivatives being very weakly coupled. The crystal and molecular structures of $[Co_2(PHP6Me)Cl(H_2O)_4]Cl_3{\cdot}4.3H_2O$ (I) and $[Ni_2(PHP6Me)Cl(H_2O)_4]Cl_3{\cdot}4.6H_2O$ (III) are reported. I crystallized in the trigonal system, space group $P3_121$, with a = 17.1624 (14) Å, c = 10.2358 (7) Å, and three formula units per unit cell. III crystallized in the trigonal system, space group $P3_221$, with a = 17.1237 (4) Å, c = 10.213 60 (20) Å, and three formula units per unit cell. Refinement by full-matrix least squares gave final residuals of R = 0.040 and R_w = 0.043 for I and R = 0.049 and R_w = 0.054 for III. Very large metal-metal separations are observed in these systems with Co–Co = 3.712 Å (I) and Ni–Ni = 3.678 Å (III). All the complexes exhibit very intense metal-to-ligand charge-transfer absorptions (ϵ > 10 000 L mol^{-1} cm^{-1}) in the visible region (19 000–20 200 cm^{-1}).

Introduction

The study of the coordination chemistry of the ligand 1,4-dihydrazinophthalazine (DHPH) and its derivatives has been somewhat limited and includes binuclear nickel(II)[2,3] cobalt(II),[4] and molybdenum(IV)[5] complexes of DHPH, a binuclear nickel(II)

---

* To whom correspondence should be addressed.

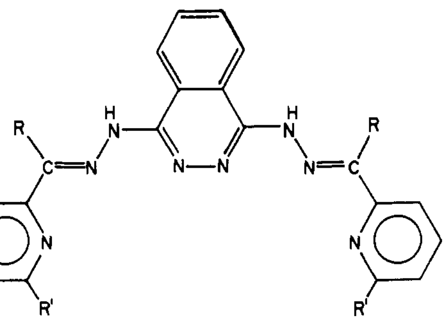
[†] This paper is assigned NRCC Contribution No. 29514.

(1) (a) Memorial University of Newfoundland. (b) National Research Council.

(2) Andrew, J. E.; Blake, A. B. *J. Chem. Soc. A* **1969**, 1408.

(3) Ball, P. W.; Blake, A. B. *J. Chem. Soc. A* **1969**, 1415.

0020-1669/88/1327-4190$01.50/0 © 1988 American Chemical Society



PHP6Me (R = H , R' = Me) ; APHP (R = CH_3 , R' = H)

Figure 1. Structures of the binucleating phthalazine ligands.

complex of the Schiff base derived from DHPH and pyridine-2-carboxaldehyde,[6] binuclear copper(II)[7] and molybdenum[8] complexes of the Schiff base ligand derived by condensation of DHPH with salicylaldehyde, binuclear copper(II) complexes of the Schiff base ligands derived by condensation of DHPH with 1-methylimidazole-2-carboxaldehyde, pyridine-2-carboxaldehyde,[7] and 2-acetylpyridine,[9] and binuclear cobalt(II)[10] and nickel(II)[11] complexes of the macrocyclic ligand derived by condensation of DHPH with acetone.

Very few structures of binuclear complexes of ligands of this sort have been reported. A dimolybdenum complex of DHPH involves two six-coordinate, formally Mo(IV) ions bridged equatorially by the phthalazine diazine group and an oxygen and axially by two bidentate molybdates (Mo–Mo = 3.47 Å).[5] The dinickel(II) complex $[Ni(DHPH)(H_2O)_2]_2Cl_4{\cdot}2H_2O$ involves two planar tetradentate ligands sandwiching two six-coordinate nickel(II) centers with axially bound water molecules (Ni–Ni = 3.79 Å).[2] The binuclear nickel(II) complex of the ligand 1,4-bis((pyridine-2-carboxaldimino)amino)phthalazine (PHP) (Figure 1), $[Ni_2(PHP)Cl(H_2O)_4]Cl_3{\cdot}2H_2O$, involves two pseudooctahedral nickel(II) centers bound to an essentially planar sexadentate ligand with a diazine (N_2) and a chlorine bridge linking the two metal centers (Ni–Ni = 3.60 Å).[6] The only binuclear copper(II) complex, $[Cu_2(APHP\text{-}H)(OH)(H_2O)_2](ClO_4)_2{\cdot}H_2O$ (APHP = 1,4-bis((pyrid-2-ylacetaldimino)amino)phthalazine) (Figure 1), consists of two square-pyramidal copper(II) centers bound to the sexadentate ligand and bridged by the diazine group and a hydroxide.[9] In general, reduced room-temperature magnetic moments indicate antiferromagnetic exchange between the metal centers in systems of this sort,[6,11] and variable-temperature magnetic studies have revealed relatively weak exchange between the nickel(II)[3] and cobalt(II)[4] centers in complexes of DHPH, while for binuclear copper(II) complexes involving hydroxide bridges a very large antiferromagnetic exchange is observed ($-2J$ > 980 cm^{-1}).[9]

In this report we describe the structures of the binuclear complexes $[Co_2(PHP6Me)Cl(H_2O)_4]Cl_3{\cdot}4.3H_2O$ (I) and $[Ni(PHP6Me)Cl(H_2O)_4]Cl_3{\cdot}4.6H_2O$ (III) and variable-temperature magnetic studies on these and related nickel(II) and cobalt(II) derivatives. These complexes have pseudooctahedral metal centers separated by 3.712 Å (Co–Co) and 3.678 Å (Ni–Ni), M–Cl–M bridge angles of 100.6° (Co) and 101.6° (Ni), short metal-oxygen (H_2O) contacts (<2.1 Å) and relatively long metal–chlorine separations (Co–Cl = 2.413 Å; Ni–Cl = 2.374 Å). All the complexes exhibit very intense (ϵ > 10 000 L mol^{-1} cm^{-1}) visible absorptions (19 000–20 200 cm^{-1}) associated with metal-to-ligand charge transfer.

Experimental Section

Synthesis of Ligands and Complexes. The ligand APHP was prepared as reported previously.[9] PHP6Me was prepared in a similar manner and obtained as orange crystals of the dihydrate $C_{22}H_{20}N_8{\cdot}2H_2O$.[12]

$[Co_2(PHP6Me)Cl(H_2O)_4]Cl_3{\cdot}4.3H_2O$ (I). $CoCl_2{\cdot}6H_2O$ (0.50 g, 2.1 mmol) was dissolved in water (5 mL) and added to a solution of PHP6Me (0.40 g, 1.0 mmol) in refluxing methanol (30 mL), and the mixture was refluxed for 2 h. The solution was filtered hot and allowed to stand at room temperature. Reddish brown crystals formed, which were isolated by decanting the mother liquor and carefully washing the product with a methanol/ether mixture. Anal. Calcd for $[Co_2(C_{22}H_{20}N_8)Cl(H_2O)_4]Cl_3{\cdot}4.3H_2O$: C, 32.79; H, 4.55; N, 13.91; Cl, 17.62. Found: C, 32.81; H, 4.64; N, 13.79; Cl, 16.86. Complexes II–IV were prepared in a similar manner. Anal. Calcd for $[Ni_2(C_{22}H_{20}N_8)Cl(H_2O)_4]Cl_3{\cdot}4.6H_2O$ (III): C, 32.66; H, 4.58; N, 13.85; Cl, 17.55. Found: C, 32.62; H, 4.57; N, 13.72; Cl, 17.09. Anal. Calcd for $[Ni_2(C_{22}H_{20}N_8)Br(H_2O)_4]Br_3{\cdot}H_2O{\cdot}0.5CH_3OH$ (IV): C, 28.75; H, 3.41; N, 11.93. Found: C, 28.76; H, 3.48, N, 11.90. Anal. Calcd for $[Co_2(C_{22}H_{20}N_8)Br(H_2O)_4]Br_3{\cdot}3H_2O$ (II): C, 27.52; H, 3.75; N, 11.67. Found: C, 27.55; H, 3.67; N, 11.54. The cobalt(II) complexes showed no oxidation instability in solution, unlike cobalt(II) derivatives of DHPH,[4] and so no precaution was taken to exclude air during the preparation of I and II.

$[Ni_2(APHP)_2](NO_3)_4{\cdot}4H_2O$ (VI). $Ni(NO_3)_2{\cdot}6H_2O$ (0.70 g, 2.4 mmol) was dissolved in methanol (25 mL) and added to a solution of APHP (0.40 g, 1.0 mmol) in refluxing methanol (50 mL). The mixture was refluxed for 3 h, cooled, and filtered and the volume reduced to 20 mL. Green-brown crystals were obtained when this mixture was allowed to stand in the refrigerator. The product was filtered off, washed with a methanol/ether mixture, and dried under vacuum. Anal. Calcd for $[Ni_2(C_{22}H_{20}N_8)_2](NO_3)_4{\cdot}4H_2O$: C, 42.94; H, 3.90; N, 22.78. Found: C, 43.19; H, 3.71; N, 22.80. V was prepared in a similar manner. Anal. Calcd for $[Ni_2(C_{22}H_{20}N_8)_2](BF_4)_4{\cdot}4H_2O$ (V): C, 39.74; H, 3.61; N, 16.86; Ni, 8.87. Found: C, 39.84; H, 3.53; N, 16.98; Ni 8.65.

C, H, and N analyses were carried out by Canadian Microanalytical Service, Vancouver, Canada.

Magnetic Measurements. Room-temperature magnetic moments were measured by the Faraday method on a Cahn 7600 Faraday magnetic susceptibility system. Variable-temperature magnetic susceptibility data were obtained in the range 5–300 K by using an Oxford Instruments superconducting Faraday magnetic susceptibility system with a Sartorius 4432 mircobalance. A main solenoid field of 1.5 T and a gradient field of 10 T m^{-1} were employed. Susceptibility data are corrected for diamagnetism (Pascal corrections), for temperature-independent paramagnetism, and for the presence of monomer impurity (nickel complexes only). $HgCo(NCS)_4$ was used as a calibration standard.

Infrared and Electronic Spectra. Infrared spectra were obtained by using a Perkin Elmer 283 instrument and electronic spectra with a Cary 17 instrument.

Crystallographic Data Collection and Refinement of the Structures. $[Co_2(PHP6Me)Cl(H_2O)_4]Cl_3{\cdot}4.3H_2O$ (I). Crystals of I are red-brown. The diffraction intensities of an approximately 0.20 × 0.20 × 0.20 mm crystal were collected with graphite-monochromatized Mo Kα radiation by using the $\theta/2\theta$ scan technique with profile analysis[13] to $2\theta_{max}$ = 49.9° on a Picker four-circle diffractometer. A total of 5337 reflections were measured, of which 3097 were unique and 2204 reflections were considered significant with $I_{net} > 2.5\sigma(I_{net})$. Lorentz and polarization factors were applied, but no correction was made for absorption. The cell parameters were obtained by the least-squares refinement of the setting angles of 62 reflections with 2θ in the range 45–50° (λ(Mo Kα_1) = 0.709 30 Å).

The structure was solved by direct methods using MULTAN[14] and refined by full-matrix least-squares methods to final residuals of R = 0.040 and R_w = 0.043 for the significant data (0.075 and 0.086 for all data) with unit weights. The H atoms of the H_2O molecules and of the methyl group were located from a difference map. All H atoms were refined isotropically and the calculated H atoms were fixed at their calculated thermal parameter values because one refined to a negative value. Crystal data are given in Table I, and final atomic positional parameters and equivalent isotropic temperature factors are listed in Table II. All calculations were performed with the NRCVAX system of programs.[15]

---

(4) Ball, P. W.; Blake, A. B. *J. Chem. Soc., Dalton Trans.* **1974**, 852.

(5) Attanasio, D.; Fares, V.; Imperatori, P. *J. Chem. Soc., Chem. Commun.* **1986**, 1476.

(6) Sullivan, D. A.; Palenik, G. J. *Inorg. Chem.* **1977**, *16*, 1127.

(7) Robichaud, P.; Thompson, L. K. *Inorg. Chim. Acta* **1984**, *85*, 137.

(8) Attanasio, D.; Dessy, G.; Fares, V. *Inorg. Chim. Acta* **1985**, *104*, 99.

(9) Thompson, L. K.; Mandal, S. K.; Gabe, E. J.; Charland, J.-P. *J. Chem. Soc., Chem. Commun.* **1986**, 1537.

(10) van der Putten, A.; Elzing, A.; Visscher, W.; Barendrecht, E. *J. Chem. Soc., Chem. Commun.* **1986**, 477.

(11) Rosen, W. *Inorg. Chem.* **1971**, *10*, 1832.

(12) Mp: 160 °C. Yield: 40%. Anal. Calcd for $C_{22}H_{20}N_8{\cdot}2H_2O$: C, 61.11; H, 5.55; N, 25.93. Found: C, 60.93; H, 5.57; N, 25.62.

(13) Grant, D. F.; Gabe, E. J. *J. Appl. Crystallogr.* **1978**, *11*, 114.

(14) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr.* **1971**, *A27*, 368.

Table I. Crystallographic Data for $[Co_2(PHP6Me)Cl(H_2O)_4]Cl_3 \cdot 4.3H_2O$ (I) and $[Ni_2(PHP6Me)Cl(H_2O)_4]Cl_3 \cdot 4.6H_2O$ (III)

(a) Compound I	
chem formula:	$T = 22$ °C
$Co_2C_{22}H_{28}Cl_4N_8O_4 \cdot 4.3H_2O$	$\lambda = 0.70930$ Å
$a = 17.1624$ (14) Å	$\rho_{calcd} = 1.53$ g cm^{-3}
$c = 10.2358$ (7) Å	$\mu = 1.31$ mm^{-1}
$V = 2611.01$ Å^3	$R = 0.040$
$Z = 3$	$R_w = 0.043$
fw: 805.65	
space group $P3_121$	
(b) Compound III	
chemical formula:	$T = 22$ °C
$Ni_2C_{22}H_{28}Cl_4N_8O_4 \cdot 4.6H_2O$	$\lambda = 1.54056$ Å
$a = 17.1237$ (4) Å	$\rho_{calcd} = 1.56$ g cm^{-3}
$c = 10.21360$ (20) Å	$\mu = 4.73$ mm^{-1}
$V = 2593.61$ Å^3	$R = 0.049$
$Z = 3$	$R_w = 0.054$
fw: 810.58	
space group $P3_221$	

Table II. Final Atomic Positional Parameters and Equivalent Isotropic Debye–Waller Temperature Factors (Esd's) for $[Co_2(PHP6Me)Cl(H_2O)_4]Cl_3 \cdot 4.3H_2O$ (I)

atom	*x*	*y*	*z*	B_{iso}, Å^2
Co	0.62300 (6)	0.74759 (5)	0.98773 (8)	2.41 (4)
Cl(1)	0.77515 (12)	0.77515 (0)	1.00000 (0)	2.99 (9)
Cl(2)	0.56512 (11)	0.22334 (11)	0.99536 (18)	3.86 (9)
Cl(0)	0.8031 (3)	0.7867 (3)	0.6370 (4)	6.88 (24)
O(1)	0.6363 (3)	0.7568 (4)	0.7877 (4)	4.40 (31)
O(2)	0.6225 (3)	0.7486 (3)	1.1919 (4)	3.65 (25)
O(3)	0.4934 (4)	0.2370 (4)	0.7132 (6)	5.33 (32)
N(1)	0.5574 (3)	0.6034 (3)	0.9937 (5)	2.34 (24)
N(2)	0.4295 (3)	0.6115 (3)	0.9733 (5)	2.65 (28)
N(3)	0.4856 (3)	0.7016 (3)	0.9787 (5)	2.53 (25)
N(4)	0.6131 (3)	0.8719 (3)	0.9926 (5)	2.88 (28)
C(1)	0.2775 (4)	0.3232 (4)	0.9953 (7)	3.19 (33)
C(2)	0.3217 (4)	0.4140 (4)	0.9895 (6)	2.70 (32)
C(3)	0.4157 (4)	0.4624 (4)	0.9938 (6)	2.16 (28)
C(4)	0.4697 (4)	0.5593 (4)	0.9894 (5)	2.07 (26)
C(5)	0.4577 (5)	0.7571 (5)	0.9797 (7)	3.22 (36)
C(6)	0.5270 (5)	0.8521 (4)	0.9863 (6)	2.77 (33)
C(7)	0.5023 (5)	0.9178 (5)	0.9886 (7)	3.68 (42)
C(8)	0.5707 (6)	1.0084 (5)	0.9996 (7)	4.60 (50)
C(9)	0.6573 (5)	1.0261 (5)	1.0065 (7)	3.67 (14)
C(10)	0.6769 (5)	0.9583 (4)	1.0028 (7)	3.55 (38)
C(11)	0.7721 (6)	0.9778 (5)	1.0115 (9)	5.30 (49)
O(4)	0.0341 (17)	0.0341 (0)	0.0000 (0)	10.11 (56)
O(5)	0.9475 (18)	0.9388 (19)	0.7652 (29)	14.66 (56)
H(1)	0.227 (4)	0.301 (4)	0.998 (6)	4 (0)
H(2)	0.295 (4)	0.441 (4)	0.982 (6)	4 (0)
H(5)	0.387 (5)	0.729 (5)	0.970 (6)	4 (0)
H(7)	0.460 (5)	0.906 (5)	0.991 (6)	5 (0)
H(8)	0.561 (5)	1.039 (5)	0.996 (7)	6 (0)
H(9)	0.712 (4)	1.096 (4)	1.024 (7)	5 (0)
H(N2)	0.388 (4)	0.590 (4)	0.989 (6)	3 (0)
H(11A)	0.819 (5)	1.046 (5)	1.005 (7)	6 (0)
H(11B)	0.783 (4)	0.960 (4)	0.949 (6)	4 (0)
H(11C)	0.788 (6)	0.964 (6)	1.082 (8)	8 (0)
H(101)	0.605 (4)	0.760 (4)	0.737 (5)	3 (0)
H(201)	0.684 (7)	0.753 (6)	0.740 (9)	10 (0)
H(102)	0.666 (5)	0.754 (5)	1.254 (7)	6 (0)
H(202)	0.583 (3)	0.729 (4)	1.242 (5)	2 (1)
H(103)	0.528 (4)	0.296 (5)	0.687 (7)	4 (0)
H(203)	0.505 (5)	0.230 (5)	0.783 (7)	6 (0)

Scattering factors were taken from ref 16. Anisotropic thermal parameters (Table SI) and a listing of structure factors (Table SII) are included as supplementary material.

$[Ni_2(PHP6Me)Cl(H_2O)_4]Cl_3 \cdot 4.6H_2O$ (III). Crystals of III are green. The diffraction intensities of an approximately 0.15 × 0.15 × 0.20 mm crystal were collected with graphite-monochromatized Cu Kα radiation and the use of the $\theta/2\theta$ scan technique with profile analysis[13] to $2\theta_{max} = 110.0°$ on a Nonius diffractometer. A total of 2288 reflections were measured, of which 2124 were considered unique and 1992 reflections were considered significant with $I_{net} > 2.5\sigma(I_{net})$. Lorentz and polarization factors were applied, but no correction was made for absorption. The cell parameters were obtained by the least-squares refinement of the setting angles of 45 reflections with 2θ in the range 90.0–96.0° (λ(Cu Kα) = 1.54056 Å).

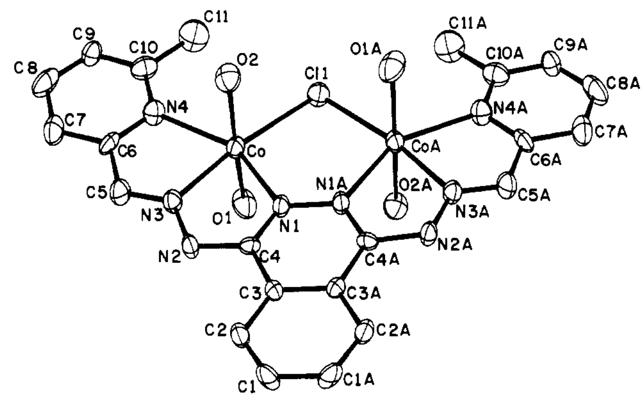


Figure 2. Structural representation of $[Co_2(PHP6Me)Cl(H_2O)_4]^{3+}$ (I^{3+}) with hydrogen atoms omitted (40% probability thermal ellipsoids).

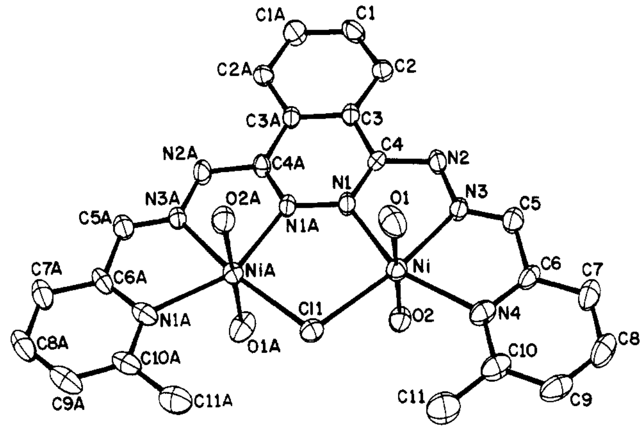


Figure 3. Structural representation of $[Ni_2(PHP6Me)Cl(H_2O)_4]^{3+}$ (III^{3+}) with hydrogen atoms omitted (40% probability thermal ellipsoids).

The structure was solved by direct methods using MULTAN[14] and refined by full-matrix least-squares methods to final residuals of $R = 0.049$ and $R_w = 0.054$ for the significant data (0.054 and 0.070 for all data) with unit weights. The H atoms of the methyl groups were located from a difference map, but attempts to locate the H atoms of the water molecules were not successful. All H atoms were refined isotropically. Crystal data are given in Table I, and final atomic positional parameters and equivalent isotropic temperature factors are listed in Table III. All calculations were performed with the NRCVAX system of programs,[15] and scattering factors were taken from ref 16. Anisotropic thermal parameters (Table SIII) and a listing of structure factors (Table SIV) are included as supplementary material.

Some disorder was observed in both structures, and an atomic site with a scattering power of approximately 13 electrons (ClO) is considered as a disordered site occupied by half a Cl atom and half an O atom. The scattering factor of the "Cl–O" atom was taken as a composite scattering factor derived from the average of the scattering factors of the Cl and O atoms.

Results and Discussion

Description of the Structures of $[Co_2(PHP6Me)Cl(H_2O)_4]Cl_3 \cdot 4.3H_2O$ (I) and $[Ni_2(PHP6Me)Cl(H_2O)_4]Cl_3 \cdot 4.6H_2O$ (III). The structure of I is shown in Figure 2, and interatomic distances and angles relevant to the cobalt coordination spheres are given in Table IV. The structure of III is shown in Figure 3, and interatomic distances and angles relevant to the nickel coordination spheres are given in Table V. Both structures are essentially the same with a 2-fold rotational axis bisecting the molecule through the chlorine bridge and the phthalazine group. Both molecules have an almost flat ligand binding each metal center via three nitrogen donor atoms, with the two metals bridged by the

---

(15) Gabe, E. J.; Lee, F. L.; LePage, Y. *Crystallographic Computing III*; Sheldrick, G., Kruger, C., Goddard, R., Eds.; Clarendon: Oxford, England, 1985; p 187.

(16) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol IV, Table 2.2B, p 99.

Table III. Final Atomic Positional Parameters and Equivalent Isotropic Debye–Waller Temperature Factors (Esd's) for $[Ni_2(PHP6Me)Cl(H_2O)_4]Cl_3 \cdot 4.6H_2O$ (III)

atom	*x*	*y*	*z*	B_{iso}, Å
Ni	0.37939 (9)	0.25555 (10)	0.00972 (12)	2.52 (7)
Cl(1)	0.22983 (17)	0.22983 (0)	0.00000 (0)	2.96 (12)
Cl(2)	0.43231 (15)	0.77582 (15)	0.00470 (22)	3.83 (12)
Cl(0)	0.1987 (3)	0.2148 (3)	0.3606 (5)	6.8 (3)
O(1)	0.3690 (4)	0.2500 (5)	0.2121 (5)	4.3 (4)
O(2)	0.3812 (4)	0.2536 (4)	−0.1947 (5)	3.3 (3)
O(3)	0.5044 (5)	0.7652 (5)	0.2885 (7)	5.7 (4)
N(1)	0.4418 (4)	0.3962 (4)	0.0042 (6)	2.4 (4)
N(2)	0.5696 (5)	0.3870 (5)	0.0225 (8)	2.9 (5)
N(3)	0.5133 (5)	0.2971 (5)	0.0209 (6)	2.4 (4)
N(4)	0.3814 (5)	0.1284 (5)	0.0086 (7)	3.1 (5)
C(1)	0.7228 (6)	0.6761 (7)	0.0026 (10)	3.4 (5)
C(2)	0.6780 (5)	0.5839 (6)	0.0096 (8)	2.6 (5)
C(3)	0.5835 (6)	0.5371 (6)	0.0055 (7)	2.3 (4)
C(4)	0.5293 (6)	0.4399 (6)	0.0110 (7)	2.3 (4)
C(5)	0.5388 (7)	0.2406 (6)	0.0185 (9)	3.1 (5)
C(6)	0.4670 (6)	0.1449 (5)	0.0146 (7)	2.8 (5)
C(7)	0.4883 (8)	0.0770 (7)	0.0086 (10)	3.8 (6)
C(8)	0.4195 (9)	−0.0111 (7)	0.0019 (10)	4.3 (7)
C(9)	0.3325 (9)	−0.0282 (7)	−0.0060 (10)	4.4 (7)
C(10)	0.3158 (7)	0.0427 (6)	−0.0004 (9)	3.7 (6)
C(11)	0.2213 (9)	0.0255 (10)	−0.0106 (16)	5.4 (8)
O(4)	0.9665 (24)	0.9665 (0)	1.0000 (0)	14.3 (12)
O(5)	0.9398 (26)	0.9905 (26)	0.8995 (37)	19.4 (13)
H(1)	0.766 (7)	0.693 (7)	0.025 (10)	4 (0)
H(2)	0.717 (6)	0.556 (6)	0.019 (7)	3 (0)
H(5)	0.611 (7)	0.258 (7)	0.023 (8)	4 (0)
H(7)	0.554 (7)	0.095 (7)	0.010 (9)	5 (0)
H(8)	0.426 (8)	−0.055 (8)	−0.019 (11)	6 (0)
H(9)	0.273 (7)	−0.089 (7)	−0.019 (9)	5 (0)
H(N2)	0.613 (7)	0.406 (7)	0.022 (10)	4 (0)
H(11A)	0.196 (9)	−0.038 (10)	0.011 (12)	8 (4)
H(11B)	0.207 (8)	0.050 (7)	0.065 (10)	6 (3)
H(11C)	0.214 (8)	0.037 (8)	−0.088 (12)	8 (4)

Table IV. Interatomic Distances (Å) and Angles (deg) Relevant to the Cobalt Coordination Spheres in $[Co_2(PHP6Me)Cl(H_2O)_4]Cl_3 \cdot 4.3H_2O$ (I)

Co–CoA	3.7121 (16)	Co–N(1)	2.147 (4)
Co–Cl(1)	2.4131 (16)	Co–N(3)	2.082 (5)
Co–O(1)	2.057 (4)	Co–N(4)	2.223 (5)
Co–O(2)	2.090 (4)		

Cl(1)–Co–O(1)	88.21 (14)	O(1)–Co–N(4)	90.44 (20)
Cl(1)–Co–O(2)	87.41 (13)	O(2)–Co–N(1)	88.83 (19)
Cl(1)–Co–N(1)	96.71 (13)	O(2)–Co–N(3)	92.24 (19)
Cl(1)–Co–N(3)	170.62 (14)	O(2)–Co–N(4)	88.10 (19)
Cl(1)–Co–N(4)	113.90 (14)	N(1)–Co–N(3)	73.91 (18)
O(1)–Co–O(2)	174.37 (20)	N(1)–Co–N(4)	149.05 (18)
O(1)–Co–N(1)	95.20 (20)	N(3)–Co–N(4)	75.45 (19)
O(1)–Co–N(3)	92.66 (20)	Co–Cl(1)–CoA	100.56 (8)

Table V. Interatomic Distances (Å) and Angles (deg) Relevant to the Nickel Coordination Spheres in $[Ni_2(PHP6Me)Cl(H_2O)_4]Cl_3 \cdot 4.6H_2O$ (III)

Ni–NiA	3.6784 (27)	Ni–N(1)	2.091 (7)
Ni–Cl(1)	2.3738 (23)	Ni–N(3)	2.036 (7)
Ni–O(1)	2.072 (5)	Ni–N(4)	2.194 (8)
Ni–O(2)	2.088 (5)		

Cl(1)–Ni–O(1)	88.45 (16)	O(1)–Ni–N(4)	90.2 (3)
Cl(1)–Ni–O(2)	88.76 (15)	O(2)–Ni–N(1)	89.35 (23)
Cl(1)–Ni–N(1)	95.45 (19)	O(2)–Ni–N(3)	92.21 (24)
Cl(1)–Ni–N(3)	171.57 (21)	O(2)–Ni–N(4)	88.36 (23)
Cl(1)–Ni–N(4)	111.48 (22)	N(1)–Ni–N(3)	76.2 (3)
O(1)–Ni–O(2)	176.15 (24)	N(1)–Ni–N(4)	152.9 (3)
O(1)–Ni–N(1)	93.6 (3)	N(3)–Ni–N(4)	76.9 (3)
O(1)–Ni–N(3)	90.94 (25)	Ni–Cl(1)–Ni	101.57 (12)

phthalazine diazine nitrogen pair and a chlorine atom. The metal octahedra are completed, in both cases, by axially coordinated water molecules. For I the in-plane cobalt–ligand distances involve one normal contact (Co–N(3) = 2.082 Å) and much longer separations (Co–N(1) = 2.147 Å; Co–N(4) = 2.223 Å) to the other nitrogen donor groups and to the chlorine bridge (Co–Cl(1) = 2.413 Å). The axial water molecules are bound quite tightly (Co–O(1) = 2.057 Å; Co–O(2) = 2.090 Å). The two cobalt(II) centers are separated by a large distance (3.712 Å) with a chlorine bridge angle of 100.56°. The cobalt octahedra are severely distorted with major in-plane deformations caused by the juxtaposition of the two five-membered chelate rings generated by N(1), N(3), and N(4). The angles N(4)–Co–N(3) (75.5°), N(3)–Co–N(1) (73.9°), and N(4)–Co–N(1) (149.1°) illustrate dramatically this equatorial compression toward these three groups. For III a similar situation prevails, but somewhat shorter distances exist within the octahedral nickel coordination sphere, as would be expected, and a shorter metal–metal separation (3.678 Å) is found.

Structural comparisons can only be made between I and III and the two previously published structural analogues, $[Ni_2(PHP)Cl(H_2O)_4]Cl_3 \cdot 2H_2O$[6] and $[Cu_2(APHP\text{-}H)(OH)(H_2O)_2](ClO_4)_2 \cdot H_2O$.[9] The major difference between the ligands PHP6Me and PHP involves the presence of a 6-methyl group on the pendant pyridine rings in the former. The effect of a bulky constituent in this ring position, close to the pyridine nitrogen donor center, has been shown in a series of pyridylphthalazine copper complexes to have a dramatic effect on the dimensions of the binuclear center. Complexes of the ligand PAP (PAP = 1,4-bis(pyrid-2-ylamino)phthalazine), $[Cu_2(PAP)(OH)X_3] \cdot 1.5H_2O$ (X = Cl, Br), have copper–copper separations around 3.0 Å,[17,18] while for the system $[Cu_2(PAP6Me)(OH)Cl_3] \cdot 3H_2O$ (PAP6Me = 1,4-bis((6-methylpyrid-2-yl)amino)phthalazine), which involves a similar 6-methyl substituent on the peripheral pyridine rings, a much larger copper–copper separation (3.137 (2) Å) is found.[19] The complex $[Ni_2(PHP)Cl(H_2O)_4]Cl_3 \cdot 2H_2O$ has a nickel–nickel separation of 3.603 Å, much shorter than that observed for I and III, and this difference is associated with the absence of the 6-methyl substituent on the pyridine rings in this ligand. Although the ligand APHP has a methyl group bound to the azomethine carbon center and no methyl substituent on the pyridine ring, the copper–copper separation in the complex $[Cu_2(APHP\text{-}H)(OH)(H_2O)_2](ClO_4)_2 \cdot H_2O$ (3.295 (2) Å) is much shorter than metal–metal distances for the other complexes. This can be attributed mainly to the presence of a hydroxide bridge, rather than a chlorine bridge. However in other respects this complex is similar to the nickel and cobalt derivatives.

Spectroscopy, Structure, and Magnetism. The infrared spectra of the ligands PHP6Me and APHP exhibit bands at 993 and 990 cm^{-1} respectively, which can be associated with pyridine ring-breathing modes of vibration, which are typically shifted to higher energy by 20–30 cm^{-1} on coordination.[17] The infrared spectra of compounds I–IV are almost identical, indicating very similar structures, and are all characterized by a pyridine ring-breathing band in excess of 1000 cm^{-1} (Table VI), indicating coordination of the pyridine residues. Other higher energy bands for these complexes are associated with coordinated water. The strong absorption at 1050 cm^{-1} for V, associated with ionic tetrafluoroborate, masks any pyridine ring-breathing vibration, but a shifted pyridine band at 1012 cm^{-1} for VI suggests coordinated pyridine. However, the general similarity of the infrared spectra of these two complexes would suggest the same structural arrangement for the binuclear cation in each case. A characteristic nitrate combination band ($\nu_1 + \nu_4$) at 1750 cm^{-1} for VI indicates the presence of ionic nitrate.[19]

The solution electronic spectra of all the complexes are characterized by low-intensity absorptions below 16 000 cm^{-1}, which can be associated with d–d transitions, and very intense visible absorptions in the range 19 000–20 200 cm^{-1}, which are clearly change transfer in origin (Table VI). Compounds I and II display near-infrared bands (6900 and 6290 cm^{-1}, respectively), which are assigned to the $\nu_1(^4T_{2g} \leftarrow {}^4T_{1g})$ transition in the pseudooc-

---

(17) Thompson, L. K.; Chacko, V. T.; Elvidge, J. A.; Lever, A. B. P.; Parish, R. V. *Can. J. Chem.* **1969**, *47*, 4141.

(18) Marongiu, G.; Lingafelter, E. C. *Acta Crystallogr.* **1982**, *B38*, 620.

(19) Lever, A. B. P.; Mantovani, E.; Ramaswamy, B. S. *Can. J. Chem.* **1971**, *49*, 1957.

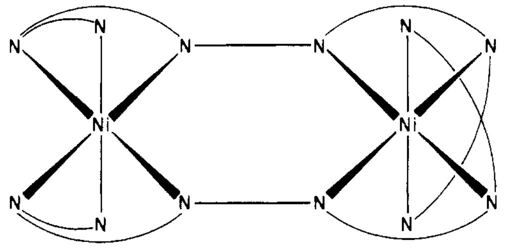


Figure 4. Proposed structure for the binuclear cation $[Ni_2(APHP)_2]^{4+}$ in V and VI.

tahedral cobalt(II) center. The difference in energy of these two bands clearly reflects the differing chromophores involved, in which the only structural difference in the two compounds would be the halogen bridge. As is typical of octahedral cobalt(II) complexes no bands could be associated with the ν_2 transition. A fairly intense shoulder at 15 400 cm^{-1} for I could perhaps be assigned to the ν_3 transition, although its high intensity is not typical of such bands, but may have arisen through "intensity stealing". Compounds III and IV each display two low-intensity, visible bands around 10 000 and 15 000 cm^{-1}, which can be associated with the $\nu_1(^3T_{2g} \leftarrow {}^3A_{2g})$ and $\nu_2(^3T_{1g} \leftarrow {}^3A_{2g})$ transitions respectively in a pseudooctahedral nickel(II) center. The low symmetry associated with the six-coordinate nickel(II) centers in III and IV is not reflected in any major splittings of these bands, and all these assignments are made on the basis of octahedral symmetry. As would be expected, ν_1 reflects the difference in chromophores for these chloro- and bromo-bridged complexes, which are otherwise assumed to be isostructural.

Compounds V and VI clearly differ from the halogen-bridged complexes I–IV in that they are 1:1 (ligand:metal) derivatives rather than 1:2 derivatives. The ν_1 transition (10*Dq* in octahedral symmetry) occurs at the same energy for both systems (12 500 cm^{-1}) but at much higher energy than the equivalent transitions for III and IV. This reflects a stronger ligand field at each nickel center and is consistent with involvement of more nitrogen donor groups at each nickel center than are present in III and IV. Only one structure of a related 1:1 nickel–phthalazine derivative has been determined for the ligand 1,4-dihydrazinophthalazine ($[Ni_2(DHPH)_2(H_2O)_4)]Cl_4{\cdot}2H_2O$),[2] and it involves two six-coordinate nickel(II) centers sandwiched between two in-plane tetradentate phthalazine ligands, with water molecules occupying the four axial ligand sites. For this complex, ν_1 was found to be 9600 cm^{-1}. A related structural arrangement seems plausible for V and VI, but this would dictate that each ligand would only behave in a tetradentate fashion, with the pyridine rings being uncoordinated, contrary to infrared evidence. Molecular models suggest that each ligand can coordinate in a sexadentate manner with the diazine and azomethine nitrogen donor centers coordinating equatorially and with the pyridine rings occupying axial sites and arranged trans to each other (Figure 4). We await structural confirmation of this arrangement, but so far crystals of these compounds have been unsuitable for X-ray analysis.

The very intense charge-transfer absorptions observed for these nickel and cobalt complexes seem to be a characteristic feature associated with ligands of this sort and are a prominent feature in the spectra of copper(II),[9] iron(II), iron(III), and manganese(II) derivatives as well.[20] The ligands in question are unsaturated derivatives with relatively low-energy π-anti-bonding orbitals, and so the electronic origin of these intense bands would reasonably be assumed to be metal → ligand in nature. Although electrochemical studies have not been carried out yet on these cobalt and nickel complexes, positive oxidation potentials (V vs SCE in DMF) have been observed for copper(II) derivatives of APHP (Cu(II) → Cu(III))[9] indicating the oxidizable nature of the copper(II) cation in such systems and supporting the metal → ligand nature of the charge-transfer transitions.

Variable-temperature magnetic studies were performed on dried, powdered samples of all the nickel compounds in the temperature range 5–300 K, and the results are summarized in Table VI. For nickel(II) binuclear complexes the crystal field splitting of the $S = 1$ ground state (*D*) is often the same order of magnitude as the electron spin-exchange integral (*J*). As a consequence a magnetic model is used which includes zero-field splitting (*D*), intradimer exchange (*J*), and also an interdimer exchange interaction parameter (zJ'). The spin Hamiltonian (eq 1) includes

$$H = -2J\hat{S}_1\cdot\hat{S}_2 - D(\hat{S}_{1z}^2 + \hat{S}_{2z}^2) - 2zJ'\hat{S}_i\langle\hat{S}_i\rangle - g_i\beta H\hat{S}_i \qquad (1)$$

these terms and the resulting magnetic susceptibility equation, $\chi(g, J, D, zJ')$, derived by Ginsberg[21] has been used to fit the magnetic data for the nickel(II) compounds under discussion. However the equation has been modified (eq 2) to account for

$$\chi_m = \chi(g,J,D,zJ')\,(1-\rho) + \frac{2g^2NB^2\rho}{3kT} + N\alpha \qquad (2)$$

monomeric impurity (ρ represents the fraction of a possible magnetically dilute mononuclear nickel(II) impurity) and temperature-independent paramagnetism ($N\alpha = 8N\beta^2/10Dq$). Nonlinear least-squares fitting of the theoretical expression 2 to

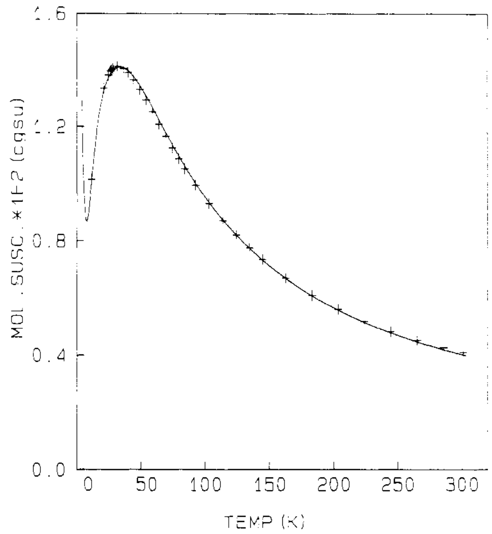


Figure 5. Magnetic susceptibility data for $[Ni_2(PHP6Me)Cl(H_2O)_4]Cl_3{\cdot}4.6H_2O$ (III). The solid line was calculated from eq 2 with $g = 2.227$ (3), $-J = 12.99$ (6) cm^{-1}, $D = 7.60$ (2) cm^{-1}, and $zJ' = 0.040$ (2) cm^{-1} (corrected for 4% paramagnetic impurity).

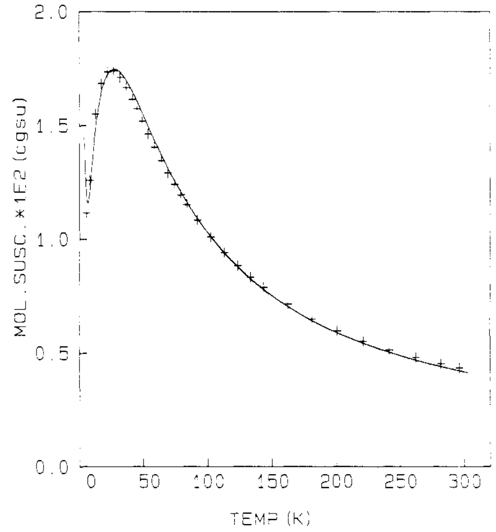


Figure 6. Magnetic susceptibility data for $[Ni_2(PHP6Me)Br(H_2O)_4]Br_3{\cdot}H_2O{\cdot}0.5CH_3OH$ (IV). The solid line was calculated from eq 2 with $g = 2.248$ (8), $-J = 10.6$ (1) cm^{-1}, $D = 10.3$ (1) cm^{-1}, and $zJ' = 0.0010$ (2) cm^{-1} (corrected for 4.2% paramagnetic impurity).

---

(20) Wen, T.; Thompson, L. K., unpublished results.

(21) Ginsberg, A. P.; Martin, R. L.; Brookes, R. W.; Sherwood, R. C. *Inorg. Chem.* **1972**, *11*, 2884.

Table VI. Electronic Spectral, Infrared, and Magnetic Data

compd	electronic spectra, cm^{-1} (ϵ)[a]	infrared bands, cm^{-1}	g [ρ][b]	*J*, cm^{-1}	*D*, cm^{-1}	*zJ'*, cm^{-1}	10^2R[c]
$[Co_2(PHP6Me)Cl(H_2O)_4]Cl_3\cdot 4.3H_2O$ (I)	6900 (49.4), 15400 (5400), 19000 (13700)	1010 (py), 3340 (H_2O)					
$[Co_2(PHP6Me)Br(H_2O)_4]Br_3\cdot 3H_2O$ (II)	6290 (44), 19000 (13800)	1010 (pyr), 3300 br sh (H_2O)					
$[Ni_2(PHP6Me)Cl(H_2O)_4]Cl_3\cdot 4.6H_2O$ (III)	9900 (36), 15400 (30), 19600 (13600), 25000 (17100)	1010 (pyr), 3330 br sh (H_2O)	2.227 (3) [0.04]	−12.99 (6)	7.60 (2)	0.040 (2)	0.9
$[Ni_2(PHP6Me)Br(H_2O)_4]Br_3\cdot H_2O\cdot 0.5CH_3OH$ (IV)	9600 (41), 15400 (33), 19600 (22600)	1007 (pyr), 3340 br sh (H_2O)	2.248 (8) [0.042]	−10.6 (1)	10.3 (1)	0.0010 (2)	2.3
$[Ni_2(APHP)_2](BF_4)_4\cdot 4H_2O$ (V)	12500 (63), 20000 (45500)	1050 (BF_4^-), 3590, 3460 (H_2O)	2.148 (2) [0]	−0.35 (1)	20.22 (2)	0.41 (1)	0.8
$[Ni_2(APHP)_2](NO_3)_4\cdot 4H_2O$ (VI)	12500 (49), 20200 (33100)	1012 (pyr), 1750 ($\nu_1 + \nu_4$, NO_3^-), 3400 br sh (H_2O)	2.127 (2) [0]	−0.34 (1)	20.5 (1)	0.30 (1)	0.7

[a] Solution in DMF (ϵ, L mol^{-1} cm^{-1}). [b] ρ = fraction of paramagnetic impurity. [c] $R = [\sum(\chi_{obs} - \chi_{calc})^2/\sum\chi_{obs}^2]^{1/2}$.

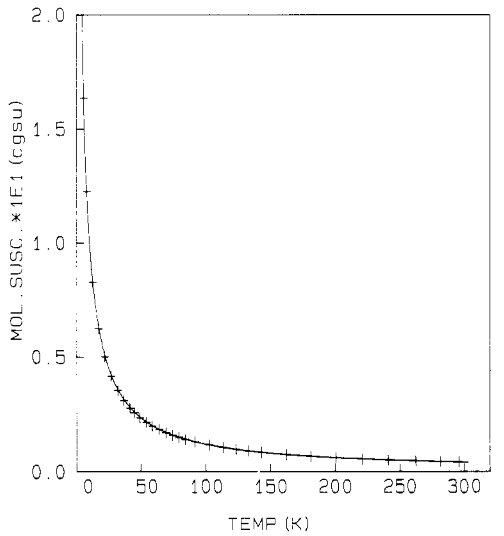


Figure 7. Magnetic susceptibility data for $[Ni_2(APHP)_2](BF_4)_4\cdot 4H_2O$ (V). The solid line was calculated from eq 2 with $g = 2.148$ (2), $-J = 0.35$ (1) cm^{-1}, $D = 20.22$ (2) cm^{-1}, and $zJ' = 0.41$ (1) cm^{-1}.

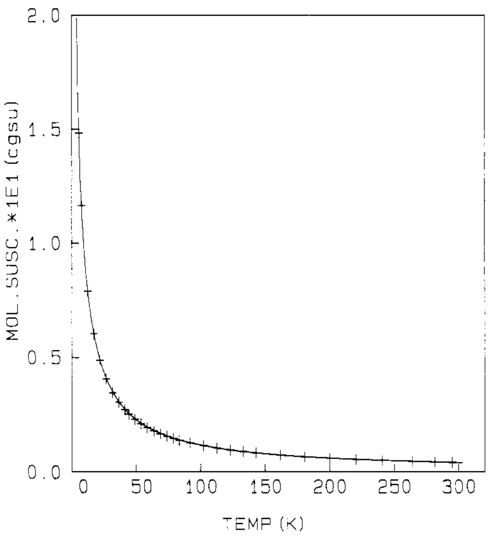


Figure 8. Magnetic susceptibility data for $[Ni_2(APHP)_2](NO_3)_4\cdot 4H_2O$ (VI). The solid line was calculated from eq 2 with $g = 2.127$ (2), $-J = 0.34$ (1) cm^{-1}, $D = 20.5$ (1) cm^{-1}, and $zJ' = 0.30$ (1) cm^{-1}.

the experimental data is illustrated in Figures 5–8 for compounds III–VI, respectively. Antiferromagnetic exchange is observed in all cases, although for compounds V and VI it is very weak. III and IV exhibit significant antiferromagnetic exchange and essentially the same *g* and *J* values are obtained for an $S = 1$ dimer fit using an isotropic model without zero-field splitting or interdimer exchange.

The variable-temperature magnetic results on the nickel complexes clearly divide the compounds into two groups. Compounds III and IV, which involve binuclear centers with a diazine and a halogen bridge, have modest exchange integrals, but the 1:1 derivatives (V, VI) are very weakly coupled with $-J < 1$ cm^{-1}. The obvious distinction between these two groups of compounds includes the halogen bridges, which clearly play an important role in the exchange process. The proposed structures for V and VI, involving two phthalazine bridges between the two nickel(II) centers (Figure 4), would perhaps be expected to generate stronger antiferromagnetic exchange, based, for example, on the magnetic properties of $[Ni_2(DHPH)_2(H_2O)_4]Cl_4\cdot 2H_2O$[3] ($-J = 22.3$ cm^{-1}). However the complex $[(PAP)_3Ni_2(H_2O)_2]Br_4\cdot 6H_2O$ (PAP = 1,4-bis(pyrid-2-ylamino)phthalazine), which involves a phthalazine (N_2) bridge and two bridging water molecules between the two pseudooctahedral (NiN_4O_2) nickel(II) centers, only exhibits weak exchange ($-J = 4.88$ (1) cm^{-1}).[22] Also the related complex $[(PAP)_2Ni_2(H_2O)_4]Cl_4\cdot 3H_2O$, which appears to involve two bridging phthalazine groups, exhibits weaker antiferromagnetic exchange ($-J = 3.2$ cm^{-1}).[23] In another related bis(diazine)-bridged system $[Ni_2(PPD)_2(H_2O)_4]Cl_4\cdot 2H_2O$[24] (PPD = 3,6-bis-

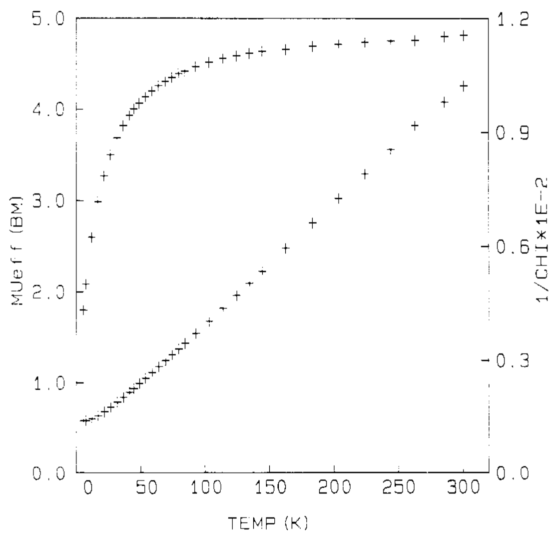


Figure 9. Magnetic data for $[Co_2(PHP6Me)Cl(H_2O)_4]Cl_3\cdot 4.3H_2O$ (I).

---

[22] Thompson, L. K., unpublished results.

[23] Doull, J. A.; Thompson, L. K. *Can. J. Chem.* **1980**, *58*, 221.

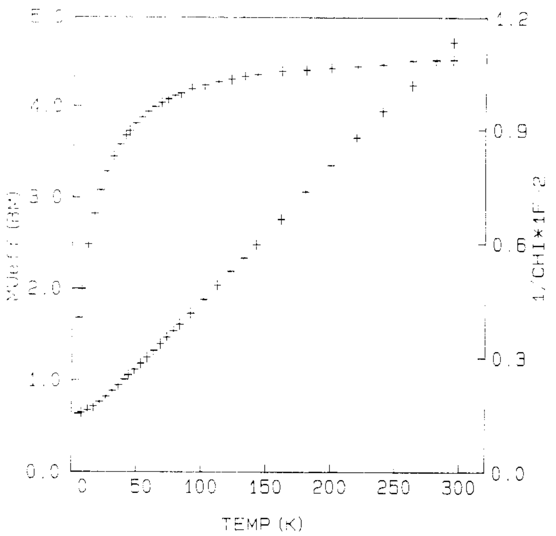


Figure 10. Magnetic data for $[Co_2(PHP6Me)Br(H_2O)_4]Br_3{\cdot}3H_2O$ (II).

(pyrazol-1-yl)pyridazine) two pseudooctahedral nickel(II) centers (NiN_4O_2) are sandwiched between the two equatorial tetradentate pyridazine ligands and the exchange ($-J$ = 14.8 (1) cm^{-1}) is much weaker than that quoted for $[Ni_2(DHPH)_2(H_2O)_4]Cl_4{\cdot}2H_2O$. It has been shown that, in general, binuclear copper(II) complexes of tetradentate phthalazine ligands exhibit weaker exchange than comparable copper(II) complexes of related pyridazine ligands, indicating the reduced superexchange capacity of the phthalazine (N_2) bridge in comparison with pyridazine (N_2)[25-27] in ligands of this sort. Such a situation could then reasonably be assumed to apply in the case of nickel systems, and so, despite the fact that the exchange for V and VI is so small, the structural proposition for these systems is not unreasonable. The weak exchange may, in part, be the result of molecular twisting at the binuclear center.

Variable-temperature magnetic data were obtained also on dried, powdered samples of the cobalt(II) complexes I and II in the temperature range 5–300 K. Plots of μ_{eff} versus temperature and $1/\chi_m$ versus temperature are illustrated in Figures 9 and 10, respectively. Both compounds obey the Curie–Weiss law above about 50 K and a linear regression of the data points in the range 50–300 K gives $\theta = -25.7$ K (I) and $\theta = -26.7$ K (II). These values are much smaller than those observed for binuclear spin-coupled cobalt(II) complexes of other diazine ligands, e.g. DHPH, DPPN (3,6-bis(pyrid-2-yl)pyridazine), and Me_2DPPN (3,6-bis-(6-methylpyrid-2-yl)pyridazine),[4] and in fact fall in the range for mononuclear octahedral cobalt(II) derivatives. However the upward curvature of the reciprocal susceptibility plots at low temperature suggests weak antiferromagnetic exchange. The susecptibility data for I and II have been fitted by using nonlinear regression to two theoretical models for spin-coupled octahedral cobalt(II) dimers: (a) the simple $s = {}^3/_2$, $s = {}^3/_2$ spin only situation for which orbital angular momentum is assumed to be quenched; (b) the extension of this model, according to Lines,[28] to include unquenched orbital angular momentum. Satisfactory fitting of the experimental data could not be obtained with either model, but for both I and II values of the intradimer coupling constant, J, were comparable with both methods. For both complexes J falls in the range −3 to −4 cm^{-1}, indicating weak antiferromagnetic exchange between the cobalt(II) centers. Further studies on these and related systems are in progress, and the results will be published elsewhere.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support for this study, including the purchase of the variable-temperature Faraday susceptometer and Dr. M. J. Newlands for graphics assistance.

Registry No. I, 116926-08-0; II, 116951-48-5; III, 116926-09-1; IV, 116926-10-4; V, 116926-13-7; VI, 116926-12-6.

Supplementary Material Available: Anisotropic thermal parameters and bond length and angle data for I (Tables SI and SV, respectively) and III (Tables SIII and SVI, respectively) (7 pages); observed and calculated structure factors for I (Table SII) and III (Table SIV) (75 pages). Ordering information is given on any current masthead page.

---

(24) Rosenberg, L.; Thompson, L. K.; Gabe, E. J.; Lee, F. L. *J. Chem. Soc., Dalton Trans.* **1986**, 625.

(25) Thompson, L. K.; Lee, F. L.; Gabe, E. J. *Inorg. Chem.* **1988**, *27*, 39.

(26) Thompson, L. K.; Mandal, S. K.; Gabe, E. J.; Lee, F. L.; Addison, A. W. *Inorg. Chem.* **1987**, *26*, 657.

(27) Mandal, S. K.; Thompson, L. K.; Newlands, M. J.; Lee, F. L.; LePage, Y.; Charland, J.-P.; Gabe, E. J. *Inorg. Chim. Acta* **1986**, *122*, 199.

(28) Lines, M. E. *J. Chem. Phys.* **1971**, *55*, 2977.