$(CO)_4$, 62264-13-5; $[Ph_2PCH_2PPh(i\text{-}Pr)]Mo(CO)_4$, 62264-10-2; $[Ph_2PCH_2PPh_2]Mo(CO)_4$, 26743-81-7; $[Ph_2PCH_2P(t\text{-}Bu)_2]W(CO)_4$, 74525-16-9; $[Ph_2PCH_2P(i\text{-}Pr)_2]W(CO)_4$, 62264-14-6; $[Ph_2PCH_2PPh(i\text{-}Pr)]W(CO)_4$, 62264-11-3; $[Ph_2PCH_2PPh_2]W(CO)_4$, 41830-14-2; $[Ph_2P(S)CH_2P(i\text{-}Pr)_2]Cr(CO)_4$, 62264-23-7; $[Ph_2P(S)CH_2PPh(i\text{-}Pr)]Cr(CO)_4$, 62263-99-4; $[Ph_2P(S)CH_2PPh_2]Cr(CO)_4$, 62264-01-1; $[Ph_2P(S)CH_2P(i\text{-}Pr)_2]Mo(CO)_4$, 62264-22-6; $[Ph_2P(S)CH_2PPh(i\text{-}Pr)]Mo(CO)_4$, 62264-28-2; $[Ph_2P(S)CH_2PPh_2]Mo(CO)_4$, 54340-52-2; $[Ph_2P(S)CH_2P(i\text{-}Pr)_2]W(CO)_4$, 62264-21-5; $[Ph_2P(S)CH_2PPh(i\text{-}Pr)]W(CO)_4$, 62264-27-1; $[Ph_2P(S)CH_2PPh_2]W(CO)_4$, 62264-00-0; $Ph_2P(S)CH_2P(i\text{-}Pr)_2$, 54006-31-4; $Ph_2P(S)CH_2PPh(i\text{-}Pr)$, 54006-27-8; $Ph_2P(S)CH_2PPh_2$, 54006-28-9.

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Structure and Magnetic Properties of the Ferromagnetically Coupled Nickel Dimer $(C_3H_6N_2H_6)_2[Ni_2Cl_8(H_2O)_2]$

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The crystal structure of dimeric $(C_3H_6N_2H_6)_2[Ni_2Cl_8(H_2O)_2]$ $[(PDANiCl_4{\cdot}H_2O)_2]$ has been determined at room temperature. Crystal data are as follows: $C2/c$; $Z = 4$; $a = 18.892\ (8)$ Å, $b = 7.354\ (2)$ Å, $c = 19.009\ (9)$ Å; $\beta = 129.15\ (3)°$; $R = 0.055$ for 2314 reflections. The salt consists of symmetrical bibridged chloride dimers, with bridging Ni–Cl distances of 2.430 and 2.459 Å. The Ni–Cl–Ni bridging angle is 95.05°. Each Ni atom has a distorted octahedral Cl_5OH_2 coordination sphere. The water molecules are trans axial within each dimer. Powder susceptibility data, determined between 2 and 240 K, show the existence of ferromagnetic exchange between Ni centers. The magnetic parameters determined are $J/k = 11.7$ K, $D/k = -4.9$ K, $z'J'/k = -0.76$ K, and $g = 2.297$. The existence of ferromagnetic coupling is consistent with predictions of modern superexchange arguments, in particular with the presence of octahedral coordination and a bridging angle near 90°.

Introduction

Magnetic exchange interactions between metal ions in binuclear transition-metal salts continue to be a subject of wide interest, with particular emphasis on determining magnetic–structural correlations. These correlations are manifestations of rather intricate details of the nature of the interactions between the unpaired electrons in the magnetic orbitals of the metal atoms. Thus, their elucidation and understanding present fundamental experimental and theoretical challenges to inorganic and theoretical chemists. In addition, the understanding of these relations is of considerable practical importance in the area of solid-state physics for the design and synthesis of new low-dimensional magnetic systems with specific types of magnetic properties.

A prime example of this type of magnetic–structural correlation has been the linear relationship found between the exchange constant, J, and the bridging Cu–O–Cu angle in bibridged copper dimers containing symmetric Cu–OH–Cu bridges.[1] Theoretical arguments predict that the exchange energy should be dependent upon such a geometrical variation. It has been shown by Hay, Thibeault, and Hoffmann[2] for two spin $^1/_2$ ions that $2J$ (the singlet–triplet energy separation) can be expressed by the combination of two terms

$$2J = 2K_{ab} - 2(\epsilon_1 - \epsilon_2)^2/(J_{aa} - J_{bb}) \qquad (1)$$

where the exchange and Coulomb integrals are slowly varying functions of the molecular parameters and ϵ_1 and ϵ_2 are the energies of the molecular orbitals formed from the magnetic orbitals on the two metal ions. The first term gives a ferromagnetic contribution; the second gives an antiferromagnetic contribution. Semiempirical techniques were used to show that $\epsilon_1 - \epsilon_2$ was 0 (e.g., the antiferromagnetic contribution was zero) at an angle slightly larger than 90°. This copper series was particularly straightforward because of the simplicity of the system: a single half-filled d orbital ($d_{x^2-y^2}$), planar coordination geometry, lack of axial perturbation. Hence, the only structural parameter of magnetic significance was the bridging Cu–O–Cuangle (or, alternatively, the Cu–Cu distance since the Cu–O distances are essentially constant).

Another series which has received considerable study, recently, has been the bibridged nickel chloride dimers.[4] Structurally, the dimers may contain either five-coordinate Ni^{2+} ions such as the $Ni_2Cl_8^{2-}$ ion in $[HN(C_2H_4)_3NCH_3]_2Ni_2Cl_8$[3a] or six-coordinate Ni^{2+} ions such as the $Ni_2(en)_4Cl_2$ ion in $[Ni_2(en)_4Cl_2]Cl_2$.[3b] The dimers with square-pyramidal coordination are generally antiferromagnetic, while the trigonal-bipyramidal or six-coordinate systems are ferromagnetic.[4] Theoretically, the expression for the exchange energy now becomes eq 2 where m is the number of unpaired electrons

$$2J = (1/m^2)\sum_{i=1}^{m}\sum_{j=1}^{m}K_{ij} - (1/m^2)\sum_{i=1}^{m}(\epsilon_{2i} - \epsilon_{2i-1})^2/(J_{ai,ai} - J_{ai,bi}) \qquad (2)$$

on each metal ion, the first sum runs over all m^2 combinations of electron i on metal a and electron j on metal b, and the second sum is over all distinct pairs of MO's formed from equivalent pairs of localized orbitals on the two metal sites. Again, the first term gives a ferromagnetic contribution; the second, an antiferromagnetic interaction. For Ni^{2+}, the localized orbitals are essentially metal d_{z^2} and $d_{x^2-y^2}$ orbitals. Because of the axially symmetric nature of the d_{z^2} orbital, the difference in energy between the MO's formed from that pair will be quite insensitive to small geometrical changes for octahedral or square-pyramidal complexes. Thus, the antiferromagnetic contributions in eq 2 will be dominated by the $d_{x^2-y^2}$ orbital contributions just as for the Cu^{2+} dimers but reduced

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(1) V. H. Crawford, H. Wayne Richardson, J. R. Wasson, D. J. Hodgson, and W. E. Hatfield, *Inorg. Chem.*, **15**, 2107 (1976).

(2) P. J. Hay, J. C. Thibeault, and R. Hoffmann, *J. Am. Chem. Soc.*, **97**, 4884 (1975).

(3) (a) F. K. Ross and G. D. Stucky, *J. Am. Chem. Soc.*, **92**, 4538 (1970). (b) A. P. Ginsberg, R. L. Martin, R. W. Brookes, and R. C. Sherwood, *Inorg. Chem.*, **11**, 2884 (1972).

(4) J. C. Jansen, H. Van Koningsveld, J. A. C. van Ooijen, and J. Reedijk, *Inorg. Chem.*, **19**, 170 (1980).

0020-1669/81/1320-2521$01.25/0

Table I. Crystal Data for $(C_3H_6N_2H_6)_2[Ni_2Cl_8(H_2O)_2]$

formula	$Ni_2Cl_8O_2N_4C_6H_{28}$	V	2048 Å^3
fw	589.36	Z	4
a	18.892 (8) Å	d(obsd)	1.92 (4) g/cm^3
b	7.354 (2) Å	d(calcd)	1.91 g/cm^3
c	19.009 (9) Å	space group	$C2/c$
β	129.15 (3)°	μ(Mo Kα)	28.6 cm^{-1}

by a factor of 4. The large number of structural parameters which affects the superexchange mechanism has precluded the clear identification of the relevant magnetic–structural correlations. Thus, continued study of these systems is in order so that the relevant magneto-structural relationships can be delineated.

In this paper, the crystal structure and magnetic susceptibility of a new nickel chloride salt is reported, that of bis(1,3-propylenediammonium) di-μ-chloro-hexachlorodiaquodinickelate(II) $[(Cu_3H_6N_2H_6)_2[Ni_2Cl_8(H_2O)_2]]$. The formation of a hydrate for the Ni(II) salt is in contrast to the anhydrous materials formed from the divalent transition-metal ions Mn(II),[5] Fe(II),[5] and Cu(II).[6] The presence of the water molecules of hydration, if coordinated to the metal ion, clearly precluded the formation of the two-dimensional layer structure assumed by the anhydrous salts. This prompted us to proceed with the structural and magnetic investigations reported here in order to determine the influence of the additional ligand.

Experimental Section

Compound Preparation and Analysis. The compound was prepared by slow evaporation at 35 °C of an equimolar solution of 1,3-propylenediamine dihydrochloride and anhydrous nickel(II) chloride in concentrated hydrochloric acid. Anal. Calcd: Ni, 19.9; Cl, 48.1; C, 12.2; N, 9.51; O, 5.43; H, 4.79. Found: Ni, 19.5; Cl, 48.1; C, 12.3; N, 9.43; H, 4.89.

Collection and Reduction of Intensity Data. The crystal used for data collection had dimensions of 0.18 × 0.18 × 0.22 mm^3. Transmission factors ranged from 0.61 to 0.65. Precession photographs taken with Mo Kα radiation showed systematic absences when $h + k = 2n + 1$, implying C centering. Additional absences were seen in the $h0l$ ($l = 2n + 1$) reflections, implying the presence of a c glide plane perpendicular to the b axis. Thus the space group is either Cc or $C2/c$. Lattice constants were determined from 12 accurately centered high-angle reflections (λ(Mo Kα) = 0.71069 Å).

A total of 2314 reflections was collected between 5° and 55° with the use of θ–2θ scan with a scan width of 1.8° (20 steps/deg, 2.5 s/step) with background measured before and after each scan (20-s counting time). Standard deviations in F_o^2 were calculated by $[\sigma(F_o^2)]^2 = \mathrm{TC} - \mathrm{BG} + (0.03F_o^2)^2$ where TC = total counts, BG = time corrected background counts, and $F_o = \mathrm{TC} - \mathrm{BG}$. Three standard reflections monitored during data collection showed no systematic variations with time.

Solution and Refinement of Structure. The Ni position was found by direct methods (MULTAN)[7] which also showed the compound to be centric. The space group is thus $C2/c$. The Cl positions were deduced from a three-dimensional Patterson function. A subsequent Fourier synthesis yielded O, N, and C positions. The carbon backbone on the 1,3-propylenediammonium ion is disordered. Full-matrix least-squares refinement (based on F_o) of the nonhydrogen atom positions yielded final R values of $R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.062$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.056$ for all reflections where $w = 1/[\sigma(F_o)]^2$. Atomic scattering factors were taken from Cromer and Waber[8a] for nonhydrogen atoms and from Stewart et al.[8b] for hydrogen atoms. Computer programs used were part of a local program library.[7] A table of observed and calculated structure factors is available as supplementary material.

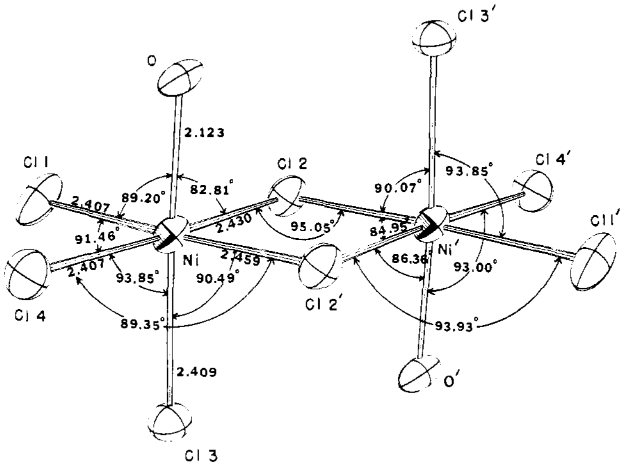

Figure 1. The dimeric unit of $[PDANiCl_4 \cdot H_2O]_2$.

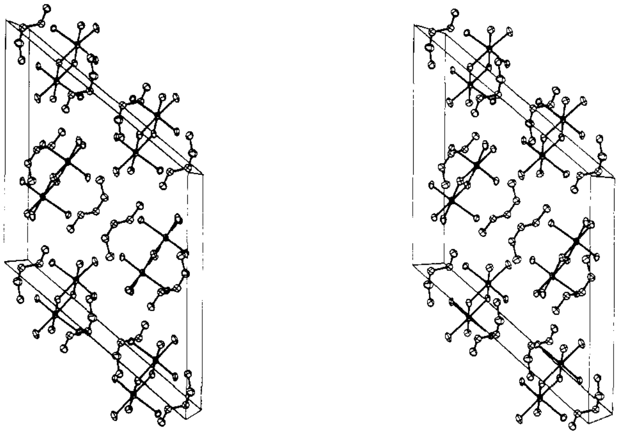

Figure 2. Stereoview of the contents of the unit cell for $(C_3H_6N_2H_6)_2[Ni_2Cl_8(H_2O)_2]$.

Magnetic Susceptibility Measurements. Powder susceptibility measurements on a 160-mg sample were performed with a PAR vibrating-sample magnetometer[9] with the use of a calibrated carbon glass resistance thermometer.[10] The data were collected between 2 and 240 K in a magnetic field of 0.5 T, a value at which the M vs. H curve was still linear at 4.2 K. Corrections were made, per mole of Ni atoms, for diamagnetism (−153 × 10^{-6} emu/mol) and the temperature independent paramagnetism (TIP) of the Ni^{2+} ions (+100 × 10^{-6} emu/mol).

Results and Discussion

Final parameters and thermal parameters are given in Table II. Tables III and IV give pertinent bond distances and angles, respectively. Figures 1 and 2 show the dimeric unit and a stereoscopic view of the unit cell, respectively.

The structure consists of anionic $[Ni_2Cl_8(H_2O)_2]^{4-}$ units and 1,3-propylenediammonium cations. The N–Cl distances (Table III) indicate the presence of hydrogen bonding between the cations and anions, forming a three-dimensional network consistent with the hardness of the crystals.

Each nickel atom (Figure 1) has a distorted octahedral configuration with five chloride and one water ligand. The cis L–Ni–L angles range from 82.8 (1) to 93.9 (1)° while trans

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(5) R. D. Willett and E. F. Riedel, *Chem. Phys.*, **8**, 112 (1975).

(6) D. W. Phelps, D. B. Losee, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, **15**, 3147 (1976).

(7) The computer programs used are part of a local crystallographic program library which contains modified versions of the following: Busing, Martin, and Levy's ORFLS least-squares program; Hubbard, Quicksall, and Jacobson's ALFF Fourier program; the function and error program, ORFFE, by Busing, Martin, and Levy; Johnson's ORTEP program for crystallographic illustrations; the absorption correction subroutine ORABS by Wehe, Busing, and Levy; direct methods program, MULTAN, by Main, et al.

(8) (a) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965). (b) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(9) C. P. Landee, S. A. Roberts, and R. D. Willett, *J. Chem. Phys.*, **68**, 4574 (1978).

(10) Available Lake Shore Cryotronics, 64 East Walnut St., Westerville, Ohio 43081.

Table II. Atomic Positional Parameters and Thermal Parameters

atom	*x*	*y*	*z*	*U*(1,1) [*U*, Å^2]	*U*(2,2)	*U*(3,3)	*U*(1,2)	*U*(1,3)	*U*(2,3)
Ni	0.68747 (3)	−0.71110 (7)	0.38054 (3)	0.0174 (3)	0.0217 (3)	0.0227 (3)	0.0014 (2)	0.0099 (2)	−0.0007 (2)
Cl(1)	0.63478 (7)	−0.4612 (2)	0.28215 (8)	0.0312 (5)	0.0336 (6)	0.0340 (6)	0.0102 (4)	0.0196 (5)	0.0106 (5)
Cl(2)	0.76776 (7)	−0.5290 (1)	0.51769 (7)	0.0270 (5)	0.0209 (5)	0.0299 (5)	−0.0051 (4)	0.0141 (4)	−0.0031 (4)
Cl(3)	0.82592 (7)	−0.7402 (2)	0.40005 (7)	0.0253 (5)	0.0328 (6)	0.0345 (5)	0.0043 (4)	0.0199 (4)	0.0031 (5)
Cl(4)	0.60281 (8)	−0.9150 (2)	0.25298 (8)	0.0277 (5)	0.0405 (7)	0.0331 (6)	0.0028 (5)	0.0077 (5)	−0.0146 (5)
O	0.5767 (2)	−0.6766 (5)	0.3818 (2)	0.018 (1)	0.037 (2)	0.033 (2)	−0.001 (1)	0.012 (1)	−0.003 (1)
N(1)	0.7095 (3)	−0.6487 (6)	0.1814 (3)	0.035 (2)	0.038 (2)	0.031 (2)	−0.004 (2)	0.016 (2)	−0.007 (2)
C(1A)	0.6645 (7)	−0.756 (1)	0.0950 (7)	[0.035 (2)]					
C(1B)	0.6210 (7)	−0.732 (1)	0.1033 (7)	[0.039 (2)]					
C(2A)	0.5707 (6)	−0.690 (1)	0.0183 (6)	[0.033 (2)]					
C(2B)	0.6248 (6)	−0.716 (1)	0.0252 (6)	[0.035 (2)]					
C(3)	0.5355 (4)	−0.8005 (9)	0.9359 (4)	0.056 (3)	0.059 (4)	0.037 (3)	−0.019 (2)	0.029 (3)	−0.012 (3)
N(2)	0.5573 (3)	−0.7591 (7)	0.8758 (3)	0.041 (2)	0.059 (3)	0.048 (2)	0.017 (2)	0.030 (2)	0.022 (2)
H(1)	0.4051	−0.7136	0.0624	[0.0887]					
H(2)	0.4370	−0.5630	0.1250	[0.0887]					

Table III. Interatomic Distances (Å)[a]

Ni–O	2.123 (3)	O–H(1)	0.927 (3)
Ni–Cl(1)	2.407 (1)	O–H(2)	0.860 (3)
Ni–Cl(2)	2.430 (2)	O–Cl(3′)	3.367 (4)[a]
Ni–Cl(2′)	2.459 (1)[a]	N(1)–Cl(3′)	3.250 (5)[b]
Ni–Cl(3)	2.409 (2)	N(1)–Cl(3)	3.322 (4)
Ni–Cl(4)	2.407 (2)	N(1)–Cl(1)	3.345 (4)
Ni–Ni	3.606 (2)[a]	N(1)–Cl(4′)	3.391 (4)[b]
N(1)–C(1A)	1.512 (11)	N(1)–Cl(1′)	3.393 (4)[c]
N(1)–C(1B)	1.500 (11)	N(2)–Cl(2′)	3.244 (4)[d]
C(1A)–C(1B)	0.947 (12)	N(2)–Cl(1′)	3.291 (4)[e]
C(1A)–C(2A)	1.499 (13)	N(2)–Cl(1″)	3.315 (4)[f]
C(1B)–C(2B)	1.535 (14)	N(2)–Cl(4′)	3.398 (5)[g]
C(2A)–C(2B)	0.965 (12)		
C(2A)–C(3)	1.498 (11)		
C(2B)–C(3)	1.580 (11)		
C(3)–N(2)	1.471 (7)		

[a] Primed atom position transformed by (a) $2-x, -1-y, 1-z$, (b) $2-x, 1+y, {}^1/_2-z$, (c) $2-x, y, {}^1/_2-z$, (d) $2-x, y, {}^3/_2-z$, (e) ${}^3/_2-x, -{}^1/_2-y, 1-z$, (f) ${}^1/_2+x, -{}^1/_2-y, {}^1/_2+z$, and (g) ${}^3/_2-x, -{}^3/_2-y, 1-z$.

Table IV. Interatomic Angles (Deg)[a]

Ni–Cl(2)–Ni	95.05 (5)	C(1B)–C(2B)–C(3)	109.8 (7)
O–Ni–Cl(1)	89.20 (10)	C(2A)–C(3)–C(2B)	36.4 (5)
O–Ni–Cl(2)	82.81 (9)	C(2A)–C(3)–N(2)	122.9 (6)
O–Ni–Cl(2′)	86.36 (10)[a]	C(2B)–C(3)–N(2)	96.9 (5)
O–Ni–Cl(3)	172.44 (9)	C(1A)–N(1)–Cl(1)	126.9 (4)
O–Ni–Cl(4)	93.00 (9)	C(1B)–N(1)–Cl(1)	97.8 (4)
Cl(1)–Ni–Cl(2)	93.93 (5)	C(1A)–N(1)–Cl(1′)	72.5 (4)[b]
Cl(1)–Ni–Cl(2′)	175.52 (4)[a]	C(1B)–N(1)–Cl(1′)	102.4 (4)[b]
Cl(1)–Ni–Cl(3)	93.85 (4)	C(1A)–N(1)–Cl(3)	136.7 (4)
Cl(1)–Ni–Cl(4)	91.46 (5)	C(1B)–N(1)–Cl(3)	126.9 (4)
Cl(2)–Ni–Cl(2′)	84.95 (5)[a]	C(1A)–N(1)–Cl(3′)	99.2 (4)[c]
Cl(2)–Ni–Cl(3)	90.07 (5)	C(1B)–N(1)–Cl(3′)	98.1 (4)
Cl(2)–Ni–Cl(4)	173.12 (5)	C(1A)–N(1)–Cl(4′)	114.0 (4)[c]
Cl(3)–Ni–Cl(2′)	90.49 (4)[a]	C(1B)–N(1)–Cl(4′)	145.8 (4)[c]
Cl(3)–Ni–Cl(4)	93.84 (5)	C(3)–N(2)–Cl(1′)	96.8 (3)[d]
N(1)–C(1A)–C(2A)	113.3 (7)	C(3)–N(2)–Cl(1′)	161.6 (4)[e]
N(1)–C(1B)–C(2B)	102.9 (7)	C(3)–N(2)–Cl(2′)	93.6 (3)[c]
C(1A)–N(1)–C(1B)	36.6 (5)	C(3)–N(2)–Cl(4′)	81.7 (3)[f]
C(1A)–C(2A)–C(3)	108.2 (7)		

[a] Primed atom positions transformed by (a) $2-x, -1-y, 1-z$, (b) $2-x, y, {}^1/_2-z$, (c) $2-x, 1+y, {}^1/_2-z$, (d) ${}^3/_2-x, -{}^1/_2-y, 1-z$, (e) ${}^1/_2+x, -{}^1/_2-y, {}^1/_2+z$, and (f) ${}^3/_2-x, -{}^3/_2-y, 1-z$.

angles deviate as much as 8° from linearity. The Ni–O distance is 2.123 (3) Å while the terminal Ni–Cl bonds are nearly identical [2.407 (1) or 2.409 (1) Å]. The bridging Ni–Cl distances are longer [2.430 (1) and 2.459 (1) Å] and thus are significantly different from each other. The Ni–Cl(2)–Ni bridging angle is 95.05 (5)°.

The dimer sits on an inversion center; hence the Ni-Cl(2)–Ni bridging unit is planar and the water molecules are in a trans axial configuration. Although the bridging Ni–Cl distances are significantly different from a crystallographic viewpoint, the observed difference (0.029 Å) is unlikely to be significant in terms of the magnetic interactions (vide infra). The interior Cl(2)–Ni–Cl(2) angle of the bridging arrangement is 84.95 (5)°, making the intramolecular Cl(2)–Cl(2′) contact (3.301 Å) much smaller (0.1 Å or more) than other intramolecular Cl–Cl contacts. The water molecule forms one intramolecular hydrogen bond to the axial chloride ion, Cl(3), on the adjacent nickel atom [O–Cl(3) = 3.366 (4) Å], 0.24 Å shorter than the Ni–Ni distance of 3.606 Å. The bonding tilts the Ni–O bond away from the normal to the Ni_2Cl_2 plane toward Cl(3).

The presence of a disorder of the PDA cation is not at all surprising. In fact, the presence of structural phase transitions involving onset of disorder of organic cations is endemic in metal halide double salts. Thus $PDAMnCl_4$ undergoes structural phase transitions at 32 and 64 °C,[11a] while four phases exist for $(C_3H_7NH_3)_2MnCl_4$.[11b] Similarly, the cation is disordered in the high-temperature phase of $[(C_2H_5)_2NH_2]_2ZnCl_4{\cdot}xH_2O$.[11c] This, coupled with the successful refinement in *C*2/*c*, makes it likely that the correct space group is *C*2/*c* and the disorder is real. A dynamic disorder involving only the carbon backbone of the PDA ion is easy to visualize. It is a little more difficult to understand why the salt would crystallize in the space group *Cc* with two inequivalent PDA ions which differ only by the placement of two of the carbon atoms in the chain. A definitive answer would require a search for possible structure phase and characterization of transitions.

It may perhaps be of interest to compare the structure of the $Ni_2Cl_8(H_2O)_2^{4-}$ dimer to its anhydrous parent species, $Ni_2Cl_8^{4-}$, reported by Ross and Stucky.[3a] The latter centrosymmetric ion contains Ni^{2+} in a square-pyramidal coordination geometry. Several significant structural differences can be seen. In the anhydrous species, the Ni^{2+} ion lies 0.502 Å above the plane of the equatorial chloride ions. Also, the axial Ni–Cl distance is 0.126 Å shorter than that in the hydrate. The terminal Ni–Cl equatorial distances are also shorter (0.053 Å, average), but the bridging equatorial distances are longer (0.037 Å, average) in the anhydrous salt. Examining the bridging Ni_2Cl_2 linkage, the Ni–Ni distance is longer in the anhydrous salt (3.669 vs. 3.606 Å), and the bridging angle is larger (99.29 vs. 95.05°). Thus, not surprisingly, rather substantial changes in the geometrical parameters occur.

Magnetic Susceptibility Measurements. The susceptibility of a finely ground sample of crystalline $[PDANiCl_4{\cdot}H_2O]_2$ was measured between 2 and 240 K. The results are tabulated as

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(11) (a) R. Kind, S. Plesko, J. Roos, *Phys. Status Solidi A*, **47**, 233 (1978). (b) R. Blinc, M. Burgar, B. Lozar, J. Seliger, J. Slak, V. Rutar, H. Arend, and R. Kind, *J. Chem. Phys.*, **66**, 278 (1977). (c) D. R. Blomquist and R. D. Willett, *Acta Crystallogr.*, in press.

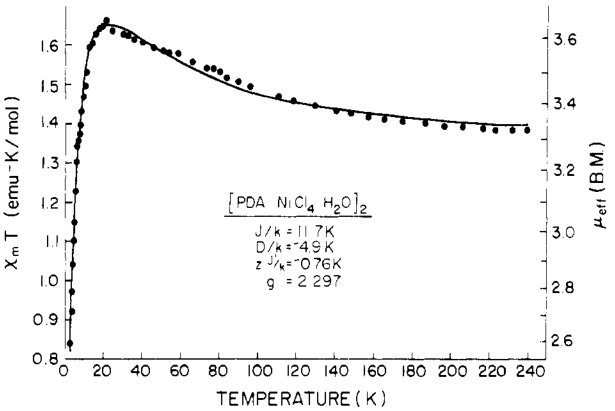

Figure 3. Molecular susceptibility times temperature ($\chi_m T$) vs. temperature for $[PDANiCl_2{\cdot}H_2O]_2$. The square of the effective moment (in Bohr magnetons) is the ordinate on the right-hand side. All data are per mole of nickel ions. The full curve represents the theoretical curve of Ginsberg et al.[3b] for $J/k = 11.7$ K, $D/k = -4.9$ K, $z'J'/k = -0.76$ K, and $g = 2.297$.

the susceptibility per mole of nickel atoms vs. temperature in Table V. The high-temperature data ($T > 140$ K) were fit to a Curie–Weiss relationship, yielding a $\Theta = +12$ K and a Curie constant of 1.318 ($g = 2.297$). The positive intercept indicates ferromagnetic interactions. The data are plotted, in Figure 3, as $\chi_m T$ vs. T, where $\chi_m T = \mu_{eff}^2/8$. $\chi_m T$ is seen to rise with decreasing temperature, signifying an increase in effective moment due to the intradimeric ferromagnetic exchange. The value of $\chi_m T$ reaches a maximum of 1.666 emu K/mol at 21 ± 1 K; the susceptibility has a maximum value of 0.284 emu/mol at 2.95 ± 0.05 K. The rapid drop off at lower temperatures indicates a depopulation into a diamagnetic ground state as well as antiferromagnetic *inter*dimer interactions. The model used to fit the data was that derived by Ginsberg et al.[11] and is based upon the spin Hamiltonian

$$\mathcal{H} = -2J\vec{S}_1\cdot\vec{S}_2 - D(S_{1z}^2 + S_{2z}^2) - g\mu_\beta\vec{H}\cdot(\vec{S}_1 + \vec{S}_2) - z'J'\vec{S}\langle\vec{S}\rangle$$

Here J is the usual *intra*dimer exchange parameter and D the zero-field splitting of the ${}^3A_2$ ground state, with a negative value corresponding to the $M_s = 0$ value lying below the $M_s = \pm 1$ doublet. Because of the interdimer contacts, it is necessary to include the mean field correction term to the Hamiltonian, parameterized by $z'J'$. Excellent agreement between observed and calculated values of $\chi_m T$ were obtained at all temperatures above 3.5 K with the parameters $J/k = 11.7$ (2) K, $D/k = -4.9$ (2) K, and $z'J' = -0.76$ (2) K. Below 3.5 K, the experimental values dropped considerably faster than the models prediction. No reasonable fit to the data could be obtained with D positive. The g value was held fixed at 2.297 as determined by the Curie–Weiss plot. These parameters are somewhat different from those appearing previously[4] for this compound due to an incorrect value initially used for the TIP corrrection. The prediction for $\chi_m T$ based upon the susceptibility equation derived by Ginsberg et al.[11] using these parameters is seen as the solid curve in Figure 3. An EPR signal was searched for at 9.3 GHz at 77 and 300 K. No signal was found, as is to be expected from the value of the zero-field splitting parameter.

In a recent paper by Reedijk and co-workers,[4] a discussion was given on the relationship between magnetic behavior and the structural parameters of five-coordinate nickel dimers, all of which are antiferromagnetic except for $[Ni(CH_2(dmpz)_2)Cl_2]_2$[4] (dmpz = 3,5-dimethylpyrazolyl). The antiferromagnetic five-coordinate dimers has square-pyramidal geometry whereas the latter compound had a geometry approaching trigonal-bypyramidal geometry. In the Discussion it was pointed out the bridging angle did not, a priori, determine the value of the exchange constant nor did the Ni–Ni or Ni–Cl distances. Earlier Butcher and Sinn[12] had pointed out a decrease in exchange constant accompanying a decrease of bridging angle.

Table V. Susceptibility per Mole of Nickel Atoms vs. Temperature for $(C_3H_6N_2H_6)_2Ni_2Cl_8(H_2O)_2$

T, K	$10^{-3}\chi_m$, emu/mol	T, K	$10^{-3}\chi_m$, emu/mol
1.904	193.1	29.72	54.8
2.245	217.4	32.02	50.7
2.565	255.5	35.63	45.4
2.711	281.3	40.01	40.2
2.950	284.2	46.04	34.6
3.278	280.9	50.9	31.2
3.523	275.6	53.8	29.4
3.903	267.0	57.9	27.3
4.29	256.2	66.3	23.5
4.70	245.7	73.7	20.9
5.42	226.6	76.9	20.1
6.27	207.3	80.2	19.1
6.79	197.3	83.6	18.2
7.12	190.6	89.9	16.8
7.69	179.0	96.3	15.5
7.99	174.7	111.2	13.2
8.63	166.7	118.9	12.3
8.88	161.9	130.0	11.1
9.43	155.7	141.9	10.1
10.41	143.6	147.7	9.65
10.61	145.0	157.7	8.99
12.64	126.1	165.7	8.51
14.27	112.5	175.4	8.03
15.76	103.6	186.8	7.50
17.57	93.5	196.2	7.09
18.60	88.5	205.7	6.76
19.71	83.6	216.6	6.40
21.04	79.2	223.3	6.20
23.60	69.3	232.1	5.96
26.23	62.4	238.4	5.80

The structural and magnetic properties of octahedrally coordinated nickel dimers with two (pseudo)halide bridging ligands are listed in Table VI. The first four entries correspond to the present compound and the other three dichloro bridged dimers which have been studied both magnetically and crystallographically.[3b,13-19] All four are seen to have ferromagnetic intradimer interactions but with no obvious correlation of J with bridging angle. The next two entries are considered to be dichloro bridged and octahedrally coordinated, either on the basis of their resemblance to known structures,[17] $[Ni_2(en)_4Cl_2](BPh_4)_2$, or for spectral reasons,[20] $[Ni_2(dien)_2(H_2O)Cl_2]Cl_2$. Both have been studied magnetically and have ferromagnetic exchange constants of 13.7[17] and ~7 K,[21] respectively.

Substitution of bromide for chloride ions has been carried out for two of the above dimers, $[Ni_2(en)_4Br_2]Br_2$[11,13] and $[Ni(EG)_2Br_2]_2$.[18] The structure of the first dimer has been

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(12) R. J. Butcher and E. Sinn, *Inorg. Chem.*, **16**, 2334 (1977).

(13) A. S. Antsyshkina and M. A. Porai-Koshits, *Dokl. Chem.* (*Engl. Trans.*), **143** (1962); *Dokl. Akad. Nauk SSSR*, **143**, 105 (1962).

(14) K. O. Joung, C. J. O'Connor, E. Sinn, and R. L. Carlin, *Inorg. Chem.*, **18**, 804 (1979).

(15) G. A. Bottomley, L. G. Glossop, C. L. Raston, A. H. White, and A. C. Willis, *Aust. J. Chem.*, **31**, 285 (1978).

(16) Y. Journaux, O. Kahn, B. Chevalier, J. Etourneau, R. Claude, and A. Dworkin, *Chem. Phys. Lett.*, **55**, 140 (1978).

(17) Y. Journeaux and O. Kahn, *J. Chem. Soc., Dalton Trans.*, 1575 (1979).

(18) D. Knetsch and W. L. Groeneveld, *Inorg. Nucl. Chem. Lett.*, **12**, 27 (1976).

(19) B. M. Antti, *Acta Chem. Scand., Ser. A*, **A29**, 76 (1975).

(20) N. F. Curtis and H. K. J. Powell, *J. Chem. Soc. A*, 3069 (1968).

(21) E. J. Laskowski, T. R. Felthouse, D. N. Hendrickson, and G. L. Long, *Inorg. Chem.*, **15**, 2908 (1976).

Table VI. Structural and Magnetic Properties of Octahedrally Coordinated Di(pseudo)halide-Bridged Nickel Dimers

compd[a]	Ni-Cl-Ni, deg	Ni-Ni, Å	$Ni-Cl_{b_1}$, Å	$Ni-Cl_{b_2}$, Å	$J/k; D/k$, deg
$[Ni_2(en)_4Cl_2]Cl_2$[3b,14,15]					~14; (+9.4, −16)[3b]
	96.55 (1)[14]		2.471 (1)	2.561 (1)	5.0 (5); 14 (1)[b,14]
	96.6 (1)[15]		2.461 (3)	2.551 (3)	9.6 (1); −5.3 (1.1)[17]
$[Ni_2(en)_4Cl_2](ClO_4)$[15]	95.4 (1)[15]		2.461 (3)	2.512 (3)	12.8 (1); −6.1 (1.0)[17]
$[Ni_2(EG)_4Cl_2]Cl_2$[18,19]	93.03 (5)[19]	3.458 (1)	2.383 (1)	2.383 (1)	~13[18]
	92.89[d]	3.452 (1)	2.382 (1)	2.382 (1)	
$[Ni_2(H_2O)_2Cl_8](PDA)_2$[c]	95.05 (5)	3.606 (2)	2.430 (1)	2.459 (1)	11.7 (2); −4.9 (2)
$[Ni_2(en)_4Cl_2](BPh_4)_2$[17]					13.7 (1); −11.1 (1.1)[17]
$[Ni_2(dien)_2(H_2O)_2Cl_2]Cl_2$[20]					7; 26[21]
$[Ni_2(en)_4Br_2]Br_2$[3b,13]					11–12; (+9, −11)[3b]
$[Ni_2(EG)_4Br_2]Br_2$					~11.5[18]
$[Ni_2(en)_4(NCS)_2]I_2$[27]					6.5–7; (+6.8, −4.8)[3b]
$[Ni_2(tren)_2SCN_2](BPh_4)_2$					+3.5; −0.65[22]
$[Ni_2(tren)_2(SeCN)_2](BPh_4)_2$					+2.3; −0.71[22]
$[Ni_2(tren)_2(OCN)_2](BPh_4)_2$[24]					−6.3; −14.6[22]
$[Ni_2(tren)_2(N_3)_2](BPh_4)_2$[25]					−50; +9.9[23]

[a] Abbreviations: en = ethylenediamine, EG = ethylene glycol, PDA = 1,3-propylenediammonium, dien = diethylenetriamine, tren = 2,2′,2″-triaminoethylamine. [b] Magnetic measurements made below the phase transition. [c] Present work. [d] From the compilation of Jansen et al;[4] structure determined by van Ingen Schenau.[35]

found to be isomorphous to its chloride analogue,[13] though no detailed information is available. The ethylene glycol bromide compound is similarly expected to be closely analogous to its chloride-bridged counterpart. In both cases the ferromagnetic interactions are preserved under the substitution, the exchange constants being 11–12[3b] and ~11.5 K,[18] respectively.

Ferromagnetic interactions have been found for three dimers with polynuclear bridges (Table VI). In Ginsberg's original paper,[3b] the thiocyanate-bridged dimer $[Ni_2(en)_4(NCS)_2]I_2$ was found to be ferromagnetically coupled with a J/k of 6.5–7 K. In a series of investigations on tren-coordinated nickel dimers $[Ni_2(tren)_2X_2]$ (tren = 2,2′,2″-triaminotriethylamine; X = SCN, SeCN, OCN, N_3), Duggan, Hendrickson, and co-workers[22–25] found the thiocyanate- and selenocyanate-bridged dimers to be ferromagnetic with J/k's equal to 3.5 and 2.3 K,[22] respectively, while cyanate and azide dimers are antiferromagnetically coupled with exchange constants of −6.3[22] and −50 K,[23] respectively (Table VI).

Theoretical calculations have been performed on the superexchange in the Ni_2X_2 unit (X = Cl, Br) by Barraclough and Brookes.[26] They concluded the exchange was ferromagnetic for a 90° bridging angle and was quite sensitive to variations of bridging angle and distortion around the nickel ion which would mix the d orbitals. These conclusions are in accord with the experimental evidence discussed above except for the azide and cyanate dimers. It is important to note, however, that the nickel atoms in these two dimers lie significantly out of the planes formed by the bridging groups. In the azide dimer, the nickels lie 0.52 Å above and below that plane[25] while in the cyanate dimer the distance is 0.25 Å.[22] By comparison, for the $[Ni_2(en)_4(NCS)_2]I_2$ dimer, the nickels are only 0.05 Å out of the plane of the thiocyanate groups.[27] In terms of the MO description of Hay et al.,[2] Bencini and Gatteschi have recently shown that $\epsilon_2 - \epsilon_1$ increases as the metal ion is moved out of the plane,[28] thus enhancing the antiferromagnetic contributions to the exchange. In view of this and the conclusions of Barraclough and Brookes,[26] these distortions would seem to play a significant role in determining the net magnetic interaction.

The general understanding is that ferromagnetic superexchange will arise from pathways which have an orthogonal interaction. Recently Kahn and co-workers[29,30] have studied several heterobinuclear compounds for which the metal orbitals are rigorously orthogonal. Strong ferromagnetic interactions are found. For octahedral nickel dimers bridged by more complex polynuclear units such as oxalate or squarate groups,[31] biimidazolates,[32] substituted 1,3,5-triketone ligands,[33] or chloranilate groups,[34] such orthogonality is not present and the dominant magnetic interaction is invariably antiferromagnetic.

Concluding Remarks

The present study has shown $(PDA)_2[Ni_2Cl_8(H_2O)_2]$ to contain ferromagnetically coupled octahedrally coordinated dimers. In accordance with theoretical predictions, every such dimer with halide bridging is ferromagnetic. Antiferromagnetism in nickel dimers predominates only in the presence of significant deviations from octahedral coordination or non(pseudo)halide exchange paths.

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Supplementary Material Available: Listing of observed and calculated structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

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(22) D. M. Duggan and D. N. Hendrickson, *Inorg. Chem.*, **13**, 2929 (1974).
(23) D. M. Duggan and D. N. Hendrickson, *Inorg. Chem.*, **12**, 2422 (1973).
(24) D. M. Duggan and D. N. Hendrickson, *Inorg. Chem.*, **13**, 2056 (1974).
(25) C. G. Pierpont, D. N. Hendrickson, D. M. Duggan, F. Wagner, and E. K. Barefield, *Inorg. Chem.*, **14**, 604 (1975).
(26) C. G. Barraclough and R. W. Brookes, *J. Chem. Soc., Faraday Trans. 2*, 1364 (1974).
(27) A. E. Shvelashvili, M. A. Porai-Koshits, and A. S. Antsyshkina, *J. Struct. Chem.* (*Engl. Transl.*), **10**, 552 (1969).
(28) A. Bencini and D. Gatteschi, *Inorg. Chim. Acta*, **31**, 11 (1978).
(29) O. Kahn, R. Claude, and H. Coudanne, *J. Chem. Soc., Chem. Commun.*, 1012 (1978).
(30) O. Kahn, P. Tola, J. Galy, and H. Coudanne, *J. Am. Chem. Soc.*, **100**, 3931 (1978).
(31) D. M. Duggan, E. K. Barefield, and D. N. Hendrickson, *Inorg. Chem.*, **12**, 985 (1973).
(32) M. S. Haddad and D. N. Hendrickson, *Inorg. Chem.*, **17**, 2622 (1978).
(33) R. L. Lindvedt, L. L. Borer, D. P. Murtha, J. M. Kuszaj, and M. D. Glick, *Inorg. Chem.*, **13**, 18 (1974).
(34) C. G. Pierpont, L. C. Francesconi, and D. N. Hendrickson, *Inorg. Chem.*, **16**, 2367 (1977).
(35) A. D. van Ingen Schenau, Thesis, State University, Leiden, 1976.