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Binuclear Complexes. Synthesis and Characterization of the Binuclear Ligand 1,4-Dihydrazinophthalazine Bis(2′-pyridinecarboxaldimine) and the Nickel Complex μ-Chloro-tetraaqua[1,4-dihydrazinophthalazine bis(2′-pyridinecarboxaldimine)]dinickel(II) Chloride Dihydrate

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Received September 10, 1976 AIC606775

The synthesis and characterization by x-ray diffraction techniques of a binuclear ligand and its corresponding dinickel complex are described. The ligand dhphpy, 1,4-dihydrazinophthalazine bis(2′-pyridinecarboxaldimine), is formed by the reaction of pyridinecarboxaldehyde with the 1,4-dihydrazinophthalazine, dhph, in the presence of the Ni(II) ion. The protonated ligand $H_2dhphpy(NO_3)_2{\cdot}2H_2O$ (I) forms monoclinic crystals with unit cell dimensions of $a = 20.480$ (3), $b = 11.166$ (2), and $c = 10.704$ (2) Å with $\beta = 102.99$ (2)°. The space group is $C2/c$ and, with 4 molecules per cell, the ligand I lies on a twofold axis. The structure was solved by direct methods and refined to an R value of 0.050. The dinickel complex II also forms monoclinic crystals (green) with the space group $C/2c$. With 8 dinuclear units per cell, no symmetry is required; however, there is in essence a twofold axis in the complex. The unit cell dimensions are $a = 15.016$ (6), $b = 15.527$ (6), and $c = 28.704$ (17) Å with $\beta = 115.78$ (3)°. The final R was 0.048. The main differences between the ligand I and the dinickel complex II are the angles in the "hydrazone arms" which change slightly after complex formation. The magnetic moment in solution of the dinickel complex is 2.74 μ_B, slightly lower than the spin-only value. Since the cations are well separated in the crystal and presumably in solution, the lowering of the moment must represent a nickel–nickel interaction. Both the ligand I and the dinickel complex II (excluding the axial water molecules) are remarkably planar and show extensive delocalization. Therefore, the preparation of binuclear ligands from dhph and various aldehydes appears to be virtually limitless.

Introduction

Multidentate ligands which incorporate two metal atoms are useful in studying the magnetic interactions between metal ions. The binuclear complexes themselves are of interest as models of metalloenzymes and in applications to catalysis. Ligands which yield binuclear complexes are not common[2] and have generally involved either substituted diformylphenols,[3–5] heptatriones,[6,7] or 1,4-dihydrazinophthalazine[8,9] although a few other examples are known.[10,11] However, in the majority of cases the bridging groups are determined by the geometry of the ligand and cannot be altered. Therefore, we decided to prepare a binuclear ligand where only the bridging atom was undefined and could presumably be varied.

The reaction of 1,4-dihydrazinophthalazine with appropriate aldehydes should yield hydrazones with six donor atoms arranged in a manner which would favor the formation of bi-

Table I. Crystal Data for $H_2dhphpy(NO_3)_2 \cdot 2H_2O$ (I) and $[Ni_2Cl(H_2O)_4dhphpy]Cl_3 \cdot 2H_2O$ (II)

	Compd I	Compd II
Crystal system	Monoclinic	Monoclinic
Space group	*C*2/*c*	*C*2/*c*
a, Å	20.480 (3)	15.016 (6)
b, Å	11.166 (2)	15.527 (7)
c, Å	10.704 (2)	28.704 (17)
β, deg	102.99 (2)	115.78 (3)
Vol, Å^3	2385.0 (8)	6027 (5)
Mol wt	530.46	735.73
Z	4	8
ρ(calcd), g/cm^3	1.477	1.622
ρ(measd), g/cm^3	1.47	1.63
Crystal size, mm^3	0.34 × 0.31 × 0.18	0.29 × 0.30 × 0.14
Radiation used	Mo K*α*	Mo K*α*
μ, cm^{-1}	1.3	18.1
μr	0.04	0.5
2*θ* range, deg	0–45	0–45
No. of unique reflections	1573	3981
No. of "reliable" reflections	1093	2959

Table II. Scheme of Refinement for $H_2dhphpy(NO_3)_2 \cdot 2H_2O$ (I) and $[Ni_2Cl(H_2O)_4dhphpy]Cl_3 \cdot 2H_2O$ (II)[a]

	Compd I	Compd II
R index with all nonhydrogen atoms from Fourier synthesis	0.32	0.21
Refinement with isotropic thermal parameters	3 cycles	3 cycles
R index	0.134	0.090
Refinement with anisotropic thermal parameters	3 cycles	3 cycles[b]
R index	0.076	0.062
Refinement with hydrogen atoms included isotropically but not refined		6 cycles[b]
R index		0.048
Refinement with hydrogen atoms refined isotropically	6 cycles[b]	
R index	0.050	
F_{low} for weighting scheme	8.0	32.0
F_{high} for weighting scheme	22.0	86.0

[a] The *R* index is $\Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. [b] The block-diagonal approximation to the full matrix was used.

nuclear complexes. The bridging site would be undefined and appeared (judging from molecular models) to be able to accommodate a variety of small molecules and ions. Furthermore, the well-known deprotonation reactions of hydrazones[12] suggested that both neutral and anionic ligands could be prepared. Finally, a number of extensions of the system could be envisioned by using a variety of aldehydes and ketones. Therefore, we prepared the ligand 1,4-dihydrazinophthalazine bis(2′-pyridinecarboxaldimine), henceforth dhphpy, by the reaction of 2-pyridinecarboxaldehyde with the 1,4-dihydrazinophthalazine and determined the crystal structure of the diprotonated form, 1,4-dihydrazinophthalazine bis(2′-pyridiniumcarboxaldimine) nitrate dihydrate, I. The dinickel complex of the neutral ligand, *μ*-chloro-tetraaqua-[1-4-dihydrazinophthalazine bis(2′-pyridinecarboxaldimine)]dinickel(II) chloride dihydrate, II, has also been prepared and characterized by an x-ray crystal structure study. The present report gives the details of these studies.

Experimental Section

The 1,4-dihydrazinophthalazine (henceforth dhph) was purchased from K & K Laboratories or Pfaltz & Bauer, Inc. The 2-pyridinecarboxaldehyde was obtained from Aldrich Chemical Co., Inc. All other materials were the usual reagent grade chemicals.

Preparations. 1,4-Dihydrazinophthalazine Bis(2′-pyridiniumcarboxaldimine) Nitrate Dihydrate, $H_2dhphpy(NO_3)_2 \cdot H_2O$, I. To a solution of 2.0 mmol of $Ni(NO_3)_2 \cdot 6H_2O$ and 2.5 mmol of 2-pyridinecarboxaldehyde in 10.0 mL of warm water was added 1.0 mmol of dhph in 20.0 mL of warm water. Concentrated nitric acid was added dropwise until the pH was less than 1. Upon cooling, a red-orange product formed which was recrystallized from water. The red-orange plates of I decomposed at ~123 °C. Anal. Calcd for $C_{20}H_{22}N_{10}O_8$: C, 45.29; H, 4.18; N, 26.40. Found: C, 45.36; H, 4.18; N, 26.10.

$[Ni_2Cl(H_2O)_4dhphpy]Cl_3 \cdot 2H_2O$. A solution of 0.50 mmol of dhph in 40 mL of absolute ethanol was added to a solution containing 1.0 mmol of $NiCl_2 \cdot 6H_2O$ and 1.0 mmol of 2-pyridinecarboxaldehyde in 40 mL of absolute ethanol. Upon slow evaporation in air (almost to dryness), olive green crystals of II were deposited. The crystals decomposed vigorously at 345 °C. Anal. Calcd for $Ni_2C_{20}H_{28}N_8O_6Cl_4$: C, 32.65; H, 3.84; N, 15.23. Found: C, 32.39; H, 3.84; N, 15.22.

Magnetic Measurement. The magnetic moment of II at 31 °C was determined by NMR techniques.[13] The average of five measurements on a single sample was 2.74 μ_B/nickel atom.

Data Collection and Reduction. Preliminary precession photographs were taken of both compounds to determine the space groups and approximate until cell dimensions. A different crystal was then used for the precise determination of lattice constants and the measurement of the intensity data. The pertinent crystal data are given in Table I together with other details of the data collection. The general details of the data collection have been reported previously.[12] The variations

Table III. Final Positional and Thermal Parameters of the Nonhydrogen Atoms in $H_2dhphpy(NO_3)_2 \cdot 2H_2O$, I[a]

Atom	*x*	*y*	*z*	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	378 (2)	3536 (3)	1603 (3)	21 (1)	80 (4)	76 (4)	0 (3)	6 (3)	−6 (6)
C(2)	181 (2)	2379 (3)	2019 (3)	21 (1)	71 (3)	83 (4)	−1 (3)	5 (3)	8 (6)
C(3)	354 (2)	1293 (3)	1534 (3)	33 (1)	74 (4)	110 (4)	3 (3)	36 (4)	−14 (7)
C(4)	172 (2)	240 (3)	2015 (4)	39 (2)	73 (4)	140 (5)	−2 (4)	43 (4)	−13 (7)
C(10)	1382 (2)	4771 (3)	−289 (3)	24 (1)	97 (4)	86 (4)	−1 (3)	27 (3)	−11 (6)
C(11)	1579 (2)	5947 (3)	−658 (3)	20 (1)	86 (4)	91 (4)	−7 (3)	9 (3)	0 (6)
C(12)	1968 (2)	6072 (4)	−1546 (4)	27 (1)	113 (4)	108 (4)	−8 (4)	35 (4)	2 (7)
C(13)	2116 (2)	7214 (4)	−1912 (4)	30 (1)	142 (5)	119 (5)	−13 (4)	43 (4)	36 (8)
C(14)	1883 (2)	8189 (4)	−1367 (4)	30 (1)	114 (5)	148 (5)	−15 (4)	31 (4)	44 (8)
C(15)	1521 (2)	8013 (3)	−457 (4)	28 (1)	92 (4)	140 (5)	−9 (4)	23 (4)	8 (8)
N(1)	200 (1)	4549 (2)	2064 (2)	23 (1)	77 (3)	89 (3)	4 (3)	25 (2)	−7 (5)
N(2)	783 (1)	3597 (2)	753 (3)	30 (1)	77 (3)	99 (3)	−9 (3)	36 (3)	−6 (5)
N(3)	972 (1)	4712 (2)	448 (2)	25 (1)	73 (3)	95 (3)	−4 (3)	25 (3)	1 (5)
N(10)	1368 (1)	6918 (3)	−123 (3)	27 (1)	81 (3)	111 (3)	−5 (3)	23 (3)	7 (5)
N(20)	1628 (2)	1394 (3)	−781 (4)	68 (2)	93 (4)	223 (6)	33 (4)	148 (5)	9 (7)
O(1)	565 (2)	6955 (3)	1629 (3)	53 (1)	113 (3)	162 (4)	14 (3)	62 (3)	−50 (6)
O(20)	1843 (2)	1108 (4)	−1701 (5)	114 (2)	169 (5)	445 (9)	15 (5)	355 (8)	−29 (10)
O(21)	1086 (2)	1953 (3)	−974 (3)	58 (1)	123 (3)	151 (4)	34 (3)	76 (4)	−26 (6)
O(22)	1861 (2)	1062 (4)	290 (4)	89 (2)	284 (7)	285 (7)	127 (6)	56 (6)	109 (11)

[a] All values are ×10^4 with the estimated standard deviations in parentheses. The temperature factor is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

Table IV. Final Hydrogen Atom Parameters in $H_2dhphpy(NO_3)_2 \cdot 2H_2O$, I[a]

Atom [bonded to]	Distance, Å	x	y	z	B, Å^2
H(1) [O(1)]	0.78 (5)	57 (3)	629 (4)	185 (5)	12.4 (1.5)
H(2) [O(1)]	0.88 (4)	80 (2)	737 (4)	228 (4)	10.1 (1.3)
H(3) [C(3)]	1.00 (3)	61 (2)	129 (3)	84 (3)	6.2 (0.9)
H(4) [C(4)]	1.01 (4)	33 (2)	−54 (4)	171 (3)	8.0 (1.1)
H(10) [C(10)]	1.05 (4)	157 (2)	402 (3)	−68 (3)	6.5 (1.0)
H(12) [C(12)]	1.02 (3)	212 (2)	533 (3)	−196 (3)	5.7 (0.9)
H(13) [C(13)]	0.99 (4)	235 (2)	734 (4)	−262 (4)	9.4 (1.3)
H(14) [C(14)]	0.91 (4)	200 (2)	895 (4)	−152 (4)	7.9 (1.1)
H(15) [C(15)]	1.00 (4)	136 (2)	870 (3)	−1 (3)	6.6 (1.0)
H(N2) [N(2)]	0.95 (4)	85 (2)	293 (4)	26 (4)	9.4 (1.2)
H(py) [N(10)]	1.21 (6)	105 (3)	682 (5)	69 (5)	15.9 (1.8)

[a] The hydrogen atom is given followed by the atom to which it is bonded in brackets, the corresponding bond distance, the positional parameters ($\times 10^3$), and the isotropic thermal parameter. The estimated standard deviations are given in parentheses.

Table V. Final Positional and Thermal Parameters for the Nonhydrogen Atoms in $[Ni_2Cl(H_2O)_4dhphpy]Cl_3 \cdot 2H_2O$, II[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni(1)	11 817 (7)	17 289 (5)	9 891 (3)	442 (5)	273 (4)	106 (1)	−66 (8)	224 (5)	14 (4)
Ni(2)	11 346 (6)	−4 660 (5)	13 854 (3)	407 (5)	244 (3)	92 (1)	2 (8)	184 (4)	13 (4)
Cl(1)	1 046 (1)	315 (1)	650 (1)	63 (1)	31 (1)	10 (0)	−10 (2)	26 (1)	−2 (1)
Cl(2)	1 196 (2)	4 767 (1)	2 115 (1)	86 (2)	35 (1)	14 (0)	8 (2)	18 (1)	0 (1)
Cl(3)	1 297 (2)	−1 548 (1)	3 350 (1)	69 (1)	50 (1)	17 (0)	46 (2)	39 (1)	17 (1)
Cl(4)	1 288 (2)	3 725 (2)	4 540 (1)	90 (2)	72 (1)	25 (1)	−58 (3)	26 (2)	−1 (1)
O(1)	−362 (4)	1 864 (3)	639 (2)	55 (3)	42 (3)	21 (1)	3 (5)	26 (3)	6 (3)
O(2)	2 743 (4)	1 634 (3)	1 329 (2)	55 (3)	40 (2)	21 (1)	−6 (5)	29 (3)	2 (3)
O(3)	−423 (3)	−532 (3)	1 026 (2)	48 (3)	58 (3)	18 (1)	−5 (5)	23 (3)	22 (3)
O(4)	2 664 (3)	−435 (4)	1 708 (2)	48 (3)	69 (3)	12 (1)	17 (5)	14 (3)	−2 (3)
O(5)	1 626 (4)	−520 (4)	−194 (2)	54 (3)	62 (3)	17 (1)	1 (5)	26 (3)	−3 (3)
O(6)	1 072 (4)	5 047 (5)	3 678 (2)	74 (4)	111 (5)	18 (1)	1 (7)	35 (4)	−6 (4)
N(1)	1 178 (4)	1 408 (3)	1 690 (2)	50 (4)	23 (2)	11 (1)	−2 (5)	25 (3)	−1 (2)
N(2)	1 153 (4)	576 (3)	1 834 (2)	48 (4)	24 (2)	11 (1)	−1 (5)	25 (3)	1 (2)
N(3)	1 265 (4)	2 854 (3)	1 801 (2)	74 (5)	26 (2)	15 (1)	14 (6)	38 (4)	−3 (3)
N(4)	1 258 (4)	2 873 (3)	1 324 (2)	53 (4)	31 (3)	14 (1)	−12 (5)	29 (3)	3 (3)
N(5)	1 143 (4)	−469 (3)	2 395 (2)	55 (4)	25 (2)	9 (1)	1 (5)	19 (3)	1 (2)
N(6)	1 165 (4)	−1 007 (3)	2 025 (2)	45 (4)	26 (2)	11 (1)	−1 (5)	21 (3)	3 (2)
N(10)	1 234 (4)	2 554 (4)	433 (2)	54 (4)	41 (3)	14 (1)	5 (5)	33 (3)	10 (3)
N(20)	1 163 (4)	−1 776 (4)	1 227 (2)	55 (4)	32 (3)	13 (1)	13 (5)	26 (3)	0 (3)
C(1)	1 233 (5)	2 052 (4)	1 992 (3)	42 (4)	24 (3)	14 (1)	−9 (6)	26 (4)	0 (3)
C(2)	1 251 (5)	1 919 (4)	2 495 (3)	36 (4)	30 (3)	13 (1)	−11 (6)	14 (4)	−6 (3)
C(3)	1 280 (5)	2 594 (5)	2 826 (3)	50 (5)	37 (4)	14 (1)	−12 (7)	27 (4)	−10 (3)
C(4)	1 300 (5)	2 410 (5)	3 302 (3)	56 (5)	44 (4)	14 (1)	−8 (7)	26 (4)	−17 (4)
C(5)	1 288 (5)	1 559 (5)	3 450 (3)	51 (5)	55 (4)	12 (1)	−17 (7)	23 (4)	−11 (4)
C(6)	1 260 (5)	887 (4)	3 136 (2)	47 (5)	40 (4)	9 (1)	−2 (6)	18 (4)	1 (3)
C(7)	1 236 (4)	1 057 (4)	2 649 (2)	29 (4)	32 (3)	10 (1)	−8 (6)	15 (4)	−3 (3)
C(8)	1 182 (4)	394 (4)	2 288 (2)	29 (4)	28 (3)	12 (1)	−5 (6)	20 (3)	−2 (3)
C(10)	1 281 (6)	3 550 (4)	1 076 (3)	71 (6)	30 (3)	20 (2)	−7 (7)	41 (5)	7 (4)
C(11)	1 291 (5)	3 387 (5)	578 (3)	52 (5)	36 (3)	17 (1)	−3 (7)	29 (4)	7 (4)
C(12)	1 343 (6)	4 055 (5)	270 (3)	83 (7)	49 (4)	20 (2)	−19 (9)	36 (6)	19 (4)
C(13)	1 353 (7)	3 839 (6)	−202 (3)	86 (7)	68 (5)	17 (2)	−27 (10)	34 (6)	21 (5)
C(14)	1 308 (6)	2 992 (6)	−348 (3)	73 (6)	68 (5)	20 (2)	7 (9)	47 (6)	15 (5)
C(15)	1 251 (6)	2 361 (5)	−17 (3)	59 (6)	60 (5)	14 (1)	−6 (8)	27 (5)	5 (4)
C(20)	1 143 (5)	−1 829 (4)	2 053 (3)	54 (5)	29 (3)	14 (1)	0 (6)	29 (4)	6 (3)
C(21)	1 147 (5)	−2 273 (4)	1 604 (3)	48 (5)	31 (3)	14 (1)	10 (6)	25 (4)	5 (3)
C(22)	1 149 (6)	−3 175 (5)	1 577 (3)	64 (6)	32 (3)	21 (2)	6 (7)	31 (5)	3 (4)
C(23)	1 165 (6)	−3 554 (5)	1 149 (3)	77 (6)	39 (4)	21 (2)	15 (8)	33 (5)	−6 (4)
C(24)	1 204 (6)	−3 048 (5)	758 (3)	76 (6)	43 (4)	19 (2)	8 (8)	24 (5)	−13 (4)
C(25)	1 195 (5)	−2 157 (5)	812 (3)	55 (5)	39 (4)	16 (1)	2 (7)	24 (5)	−6 (4)

[a] The Ni(1) and Ni(2) values are $\times 10^5$ and the remaining values are $\times 10^4$. The estimated standard deviations are in parentheses. The temperature factor is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

in the standard reflections were ±5% for I and ±3% for II. In both cases only those reflections with I (intensity) $\geq 2.0\sigma(I)$ were considered reliable and used in the analysis. Absorption corrections were not made because of the relatively small value of μr, Table I.

Structure Determination and Refinement. The computer programs FAME, MAGIC, LINK, and SYMPL[14] were used to determine the structure of I. All 14 nonhydrogen atoms of the ligand were located in an E map. Two Fourier syntheses served to locate the remaining heavy atoms and refine the model. The model was refined by least-squares techniques (see Table II) to a final R of 0.050.

The structure of II was determined by the heavy-atom method and refined by least-squares techniques as outlined in Table II. The weighting scheme has been described previously.[12] The scattering factors were from the usual sources.[15,16]

The final parameters for the nonhydrogen atoms in I are given in Table III, with hydrogen atom parameters in Table IV. The corresponding data for II are given in Tables V and VI. The distances (Table VII) and angles (Table VIII and IX) for both I and II are presented. The observed and calculated structure factors are available.[17]

Results and Discussion

The atomic numbering and the thermal ellipsoids of the protonated ligand I and the dinickel complex II are given in Figures 1 and 2, respectively. In I the molecule lies on a

Table VI. Final Hydrogen Atom Parameters in $[Ni_2Cl(H_2O)_4(dhphpy)]Cl_3 \cdot 2H_2O$, II[a]

Atom [bonded to]	Distance, Å	x	y	z	B, Å^2
H(N3) [N(3)]	0.91	1397	3365	1972	4.6
H(N5) [N(5)]	0.97	1394	−703	2742	3.8
H(C3) [C(3)]	1.09	1271	3289	2781	4.8
H(C4) [C(4)]	1.05	1323	2949	3525	4.9
H(C5) [C(5)]	0.99	1316	1515	3799	4.8
H(C6) [C(6)]	1.02	1283	313	3312	4.2
H(10) [C(10)]	1.06	1379	4129	1286	5.0
H(12) [C(12)]	1.15	1514	4705	486	6.0
H(13) [C(13)]	1.10	1428	4364	−441	6.6
H(14) [C(14)]	1.04	1443	2797	−657	6.2
H(15) [C(15)]	1.04	1025	1751	−172	4.6
H(20) [C(20)]	1.05	998	−2168	2330	4.5
H(22) [C(22)]	1.04	1197	−3492	1907	5.3
H(23) [C(23)]	1.02	1313	−4180	1108	5.8
H(24) [C(24)]	1.17	972	−3299	337	6.4
H(25) [C(25)]	1.18	1238	−1547	576	5.4
H(1) [O(1)]	1.12	−708	1312	372	5.6
H(1′) [O(1)]	0.95	−494	2465	576	5.6
H(2) [O(2)]	0.84	3145	1240	1479	5.5
H(2′) [O(2)]	1.00	3228	2098	1520	5.5
H(3) [O(3)]	0.91	−793	−51	891	5.6
H(3′) [O(3)]	0.73	−688	−756	1149	5.6
H(4) [O(4)]	0.92	3049	−428	2060	5.4
H(4′) [O(4)]	0.85	2808	−935	1646	5.4
H(5) [O(5)]	0.86	1353	−476	14	5.7
H(5′) [O(5)]	0.90	2283	−622	−50	5.7
H(6) [O(6)]	1.15	863	4328	3630	7.4
H(6′) [O(6)]	1.13	1345	4724	4067	7.4

[a] The hydrogen atom is given followed by the atom to which it is bonded in brackets, the corresponding bond distance, the positional parameters ($\times 10^3$), and the isotropic thermal parameter.

Table VIII. Selected Angles (deg) in $H_2dhphpy(NO_3)_2 \cdot 2H_2O$[a]

N(1)–C(1)–N(2)	117.9 (3)	C(1)–C(2)–C(3)	123.1 (3)
N(1)–C(1)–C(2)	121.9 (3)	C(2′)–C(2)–C(3)	119.7 (3)
C(1)–C(2)–C(2′)	117.2 (3)	C(1)–N(1)–N(1′)	120.8 (3)
C(2)–C(3)–C(4)	119.4 (3)	C(2)–C(1)–N(2)	120.1 (3)
C(3)–C(4)–C(4′)	120.8 (4)	N(2)–N(3)–C(10)	117.2 (3)
C(1)–N(2)–N(3)	116.9 (3)	C(10)–C(11)–N(10)	118.5 (3)
N(3)–C(10)–C(11)	118.4 (3)	C(11)–C(12)–C(13)	119.0 (4)
C(10)–C(11)–C(12)	121.2 (3)	C(13)–C(14)–C(15)	119.1 (4)
C(12)–C(13)–C(14)	119.5 (4)	C(14)–C(15)–N(10)	121.5 (4)
C(15)–N(10)–C(11)	120.6 (3)	N(10)–C(11)–C(12)	120.3 (3)
N(1)···O(1)···N(10)	108.3 (1)	O(20)–N(20)–O(21)	118.1 (4)
N(20)–O(21)···N(2)	123.0 (3)	O(20)–N(20)–O(22)	123.9 (5)
O(21)–N(20)–O(22)	117.6 (4)		

[a] The estimated standard deviations are given in parentheses.

twofold axis which passes through the midpoints of the N(1)–N(1′), C(2)–C(2′), and C(4)–C(4′) bonds. In the dinickel complex II, with the exception of the Ni–Cl (bridge) bonds, there is essentially a twofold axis in the molecule. There appear to be no significant differences in the bond distances of I compared to II (see Table VII for the individual values). The major changes in going from I to II occur in the various angles in the two hydrazone "arms". The "arms" must bend slightly so that the three nitrogen atoms can coordinate to an octahedral nickel atom. The N(2)–N(3)–C(10) angle increases while the remaining ones in the "arm" decrease. The result is to align N(10) and N(1) in a more nearly linear fashion relative to the Ni atom. The ligand I appears to have some flexibility and therefore should be able to complex other metal ions.

The water molecules O(1) and O(1′) in I occupy approximately the same sites as the nickel atoms in II. There is a strong N(10)–H(py)···O(1) hydrogen bond (see Table X) which is very close to being symmetrical. The water molecule, in turn, forms a moderately strong hydrogen bond to N(1) of the ligand. The remaining hydrogen atom on O(1) forms an intermolecular hydrogen bond to O(21) of the nitrate group. The atom O(21) is an acceptor not only for the hydrogen bond from O(1) but also from N(2)–H(N2) (Figure 3). These hydrogen bonds serve to bond the ions together in the solid state.

Both I and II are remarkably planar, with the pyridine rings twisted by 3.25° in I and 3.37 and 3.67° in II. The "coordinated" water in I is 0.243 Å from the phthalazine plane while the nickel atoms lie only 0.043 and 0.040 Å from the corresponding plane in II. The bridging Cl in II lies −0.055 Å from the phthalazine plane. For all practical purposes, the two Ni atoms and the Cl atom are coplanar with the phthalazine ring. The planarity of the ligand in I and II together with a comparison of the various distances in the molecules suggests an extensively delocalized system. The

Table VII. Selected Interatomic Distances (Å) for $H_2dhphpy(NO_3)_2 \cdot 2H_2O$ and $[Ni_2Cl(H_2O)_4(dhphpy)]Cl_3 \cdot 2H_2O$[a]

(a) In the Coordination Sphere of $[Ni_2Cl(H_2O)_4(dhphpy)]Cl_3 \cdot 2H_2O$

Ni(1)–N(1)	2.074 (6)	Ni(2)–N(2)	2.061 (6)	Ni(1)–O(1)	2.098 (6)
Ni(1)–N(4)	1.999 (5)	Ni(2)–N(6)	2.001 (5)	Ni(1)–O(2)	2.117 (6)
Ni(1)–N(10)	2.074 (6)	Ni(2)–N(20)	2.089 (6)	Ni(2)–O(3)	2.108 (6)
Ni(1)–Cl(1)	2.374 (2)	Ni(2)–Cl(1)	2.387 (2)	Ni(2)–O(4)	2.070 (6)

(b) Within the Ligand

$H_2dhphpy(NO_3)_2 \cdot 2H_2O$		$[Ni_2Cl(H_2O)_4(dhphpy)]Cl_3 \cdot 2H_2O$			
N(1)–N(1′)	1.374 (4)	N(1)–N(2)	1.363 (7)		
N(1)–C(1)	1.318 (4)	N(1)–C(1)	1.302 (8)	N(2)–C(8)	1.313 (8)
C(1)–C(2)	1.454 (5)	C(1)–C(2)	1.447 (10)	C(7)–C(8)	1.439 (9)
C(2)–C(3)	1.396 (5)	C(2)–C(3)	1.402 (10)	C(6)–C(7)	1.407 (9)
C(3)–C(4)	1.369 (5)	C(3)–C(4)	1.383 (10)	C(5)–C(6)	1.368 (10)
C(2)–C(2′)	1.396 (5)	C(2)–C(7)	1.414 (9)		
C(4)–C(4′)	1.378 (6)	C(4)–C(5)	1.390 (11)		
C(1)–N(2)	1.362 (4)	C(1)–N(3)	1.370 (8)	C(8)–N(5)	1.382 (8)
N(2)–N(3)	1.366 (4)	N(3)–N(4)	1.366 (8)	N(5)–N(6)	1.364 (7)
N(3)–C(10)	1.277 (4)	N(4)–C(10)	1.278 (9)	N(6)–C(20)	1.279 (8)
C(10)–C(11)	1.454 (5)	C(10)–C(11)	1.457 (11)	C(20)–C(21)	1.464 (10)
C(11)–C(12)	1.377 (5)	C(11)–C(12)	1.388 (11)	C(21)–C(22)	1.402 (10)
C(12)–C(13)	1.387 (6)	C(12)–C(13)	1.400 (13)	C(22)–C(23)	1.370 (12)
C(13)–C(14)	1.370 (6)	C(13)–C(14)	1.373 (13)	C(23)–C(24)	1.392 (12)
C(14)–C(15)	1.364 (6)	C(14)–C(15)	1.392 (12)	C(24)–C(25)	1.393 (11)
C(15)–N(10)	1.331 (5)	C(15)–N(10)	1.339 (10)	C(25)–N(20)	1.349 (10)
N(10)–C(11)	1.343 (4)	N(10)–C(11)	1.351 (9)	N(20)–C(21)	1.339 (9)
N(20)–O(20)	1.209 (6)	Ni(1)···Ni(2)	3.603 (1)		
N(20)–O(21)	1.249 (6)				
N(20)–O(22)	1.197 (6)				

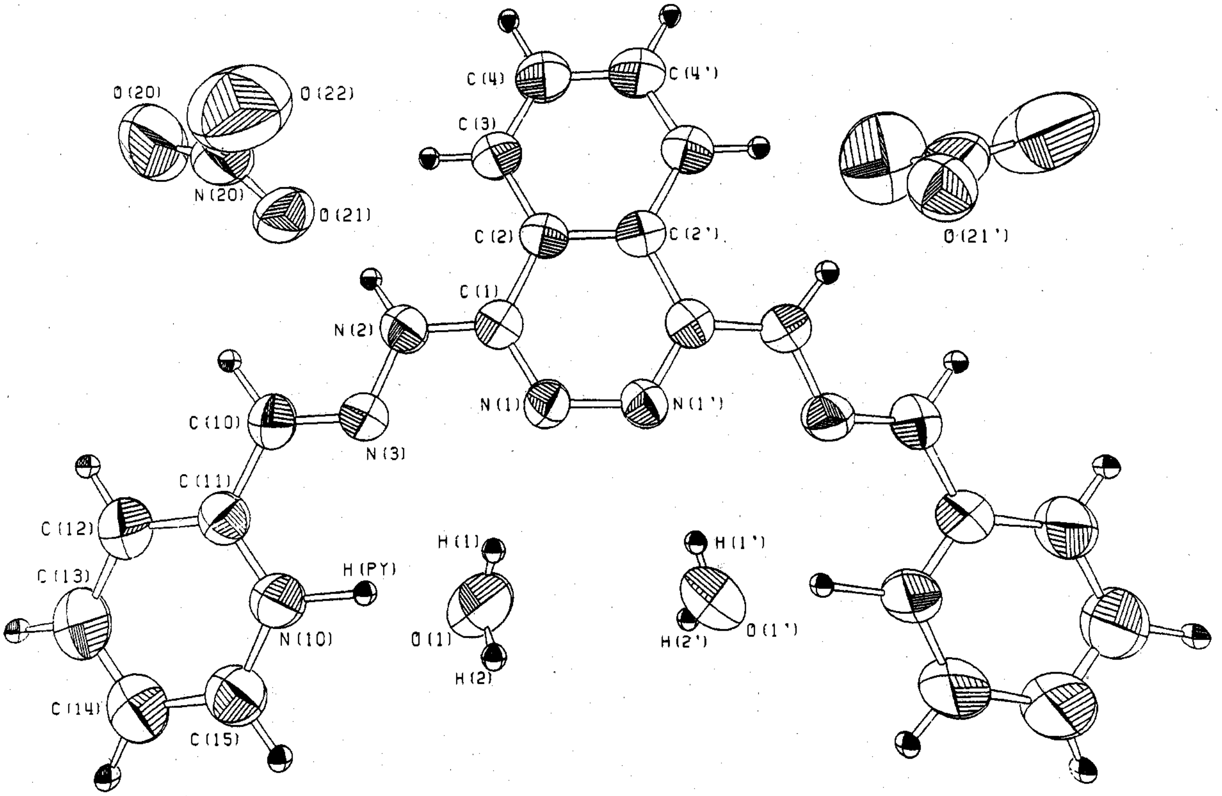

Figure 1. ORTEP drawing of 1,4-dihydrazinophthalazine bis(2′-pyridiniumcarboxaldimine) nitrate dihydrate, I, showing the atomic numbering and thermal ellipsoids. A twofold axis passes through the midpoints of the C(4)–C(4′), C(2)–C(2′), and N(1)–N(1′) bonds. The proton is located on N(10).

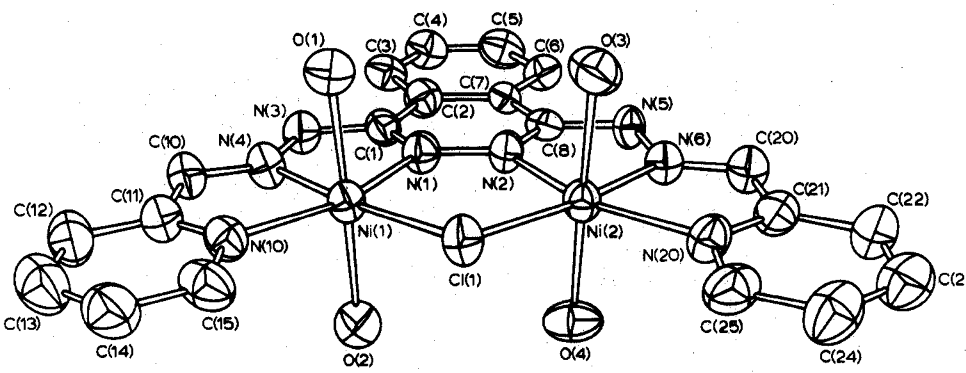

Figure 2. ORTEP drawing of μ-chloro-tetraaqua[1,4-dihydrazinophthalazine bis(2′-pyridinecarboxaldimine)]dinickel(II) cation. The chloride anions and the two water molecules have not been included for clarity.

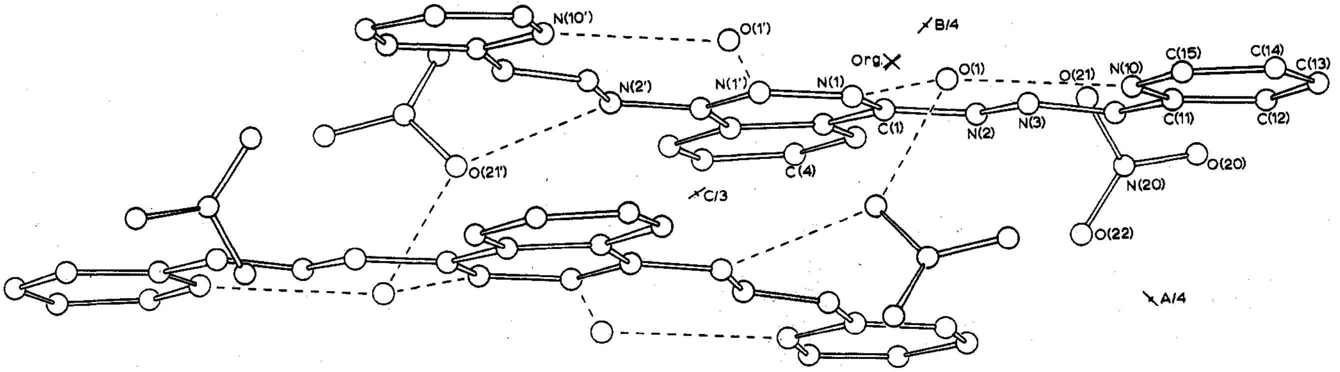

Figure 3. Packing diagram for the diprotonated species, I, showing the hydrogen bonds to the "coordinated" water molecules and nitrate anions.

delocalization can be appreciated by considering the distances in the hydrazone "arms". The C(1)–N(2) distance in I of 1.362 (4) Å and the C(1)–N(3) and C(8)–N(5) distances of 1.370 (8) and 1.382 (8) Å in II are appreciably longer than

Table IX. Selected Angles (deg) in $[Ni_2Cl(H_2O)_4(dhphpy)]Cl_3 \cdot 2H_2O$[a]

N(1)–Ni(1)–Cl(1)	98.0 (2)	N(2)–Ni(2)–Cl(1)	97.8 (2)
N(1)–Ni(1)–N(4)	76.8 (2)	N(2)–Ni(2)–N(6)	76.5 (2)
N(1)–Ni(1)–N(10)	155.7 (2)	N(2)–Ni(2)–N(20)	154.8 (2)
N(1)–Ni(1)–O(1)	91.1 (2)	N(2)–Ni(2)–O(3)	93.1 (2)
N(1)–Ni(1)–O(2)	90.3 (2)	N(2)–Ni(2)–O(4)	89.5 (2)
N(4)–Ni(1)–Cl(1)	174.6 (2)	N(6)–Ni(2)–Cl(1)	174.1 (2)
N(4)–Ni(1)–N(10)	78.9 (2)	N(6)–Ni(2)–N(20)	78.2 (2)
N(4)–Ni(1)–O(1)	87.8 (2)	N(6)–Ni(2)–O(3)	90.4 (2)
N(4)–Ni(1)–O(2)	91.1 (2)	N(6)–Ni(2)–O(4)	91.2 (2)
N(10)–Ni(1)–Cl(1)	106.3 (2)	N(20)–Ni(2)–Cl(1)	107.5 (2)
N(10)–Ni(1)–O(1)	88.5 (2)	N(20)–Ni(2)–O(3)	88.3 (2)
N(10)–Ni(1)–O(2)	89.6 (2)	N(20)–Ni(2)–O(4)	89.8 (2)
O(1)–Ni(1)–Cl(1)	90.9 (2)	O(3)–Ni(2)–Cl(1)	88.2 (2)
O(1)–Ni(1)–O(2)	178.0 (2)	O(3)–Ni(2)–O(4)	177.2 (2)
O(2)–Ni(1)–Cl(1)	90.3 (2)	O(4)–Ni(2)–Cl(1)	90.5 (2)
N(10)–C(11)–C(12)	122.2 (7)	N(20)–C(21)–C(22)	121.9 (7)
C(11)–C(12)–C(13)	117.8 (8)	C(21)–C(22)–C(23)	118.7 (7)
C(12)–C(13)–C(14)	120.3 (9)	C(22)–C(23)–C(24)	120.2 (8)
C(13)–C(14)–C(15)	118.4 (8)	C(23)–C(24)–C(25)	117.7 (8)
C(14)–C(15)–N(10)	122.3 (8)	C(24)–C(25)–N(20)	122.6 (7)
C(15)–N(10)–C(11)	119.1 (7)	C(25)–N(20)–C(21)	118.8 (6)
N(10)–C(11)–C(10)	116.2 (7)	N(20)–C(21)–C(20)	116.7 (6)
C(12)–C(11)–C(10)	121.6 (7)	C(22)–C(21)–C(20)	121.4 (7)
C(11)–C(10)–N(4)	114.7 (7)	C(21)–C(20)–N(6)	113.8 (6)
C(10)–N(4)–N(3)	125.9 (6)	C(20)–N(6)–N(5)	123.4 (6)
N(4)–N(3)–C(1)	115.8 (6)	N(6)–N(5)–C(8)	113.8 (5)
N(1)–C(1)–N(3)	115.7 (6)	N(2)–C(8)–N(5)	116.3 (6)
C(2)–C(1)–N(3)	122.7 (6)	C(7)–C(8)–N(5)	121.8 (6)
N(1)–C(1)–C(2)	121.6 (6)	N(2)–C(8)–C(7)	121.8 (6)
C(1)–N(1)–N(2)	121.8 (6)	C(8)–N(2)–N(1)	120.8 (5)
C(1)–C(2)–C(7)	116.8 (6)	C(2)–C(7)–C(8)	117.0 (6)
C(1)–C(2)–C(3)	123.5 (6)	C(6)–C(7)–C(8)	123.5 (6)
C(2)–C(3)–C(4)	119.7 (7)	C(5)–C(6)–C(7)	119.4 (6)
C(3)–C(4)–C(5)	120.1 (7)	C(4)–C(5)–C(6)	121.6 (7)
Ni(1)–N(1)–N(2)	122.4 (4)	Ni(2)–N(2)–N(1)	123.3 (4)
Ni(1)–N(1)–C(1)	115.8 (5)	Ni(2)–N(2)–C(8)	115.9 (4)
Ni(1)–N(4)–N(3)	115.9 (4)	Ni(2)–N(6)–N(5)	117.3 (4)
Ni(1)–N(4)–C(10)	118.2 (5)	Ni(2)–N(6)–C(20)	119.1 (5)
Ni(1)–N(10)–C(11)	111.9 (5)	Ni(2)–N(20)–C(21)	112.1 (5)
Ni(1)–N(10)–C(15)	128.9 (5)	Ni(2)–N(20)–C(25)	129.1 (5)
Ni(1)–Cl(1)–Ni(2)	98.4 (1)		

[a] The estimated standard deviations are given in parentheses.

a pure C=N of about 1.29 Å.[18] Similarly, the N(2)–N(3), N(3)–N(4), and N(5)–N(6) bonds in I and II are shorter than an N–N single bond.

The Ni–N distances of the phthalazine ring and pyridine rings (average 2.07 Å) are slightly longer than the distances to the hydrazone nitrogen atoms (average 2.000 Å). In the $Ni_2(dhph)_2$ complex[19] the Ni–N(phthalazine) distances were slightly shorter (average 2.076 Å) than the Ni–N(NH_2 group) distances (average 2.098 Å), essentially the reverse of our study. However, the Ni–N(phthalazine) distances in the two studies are in excellent agreement. An understanding of the differences in the two studies requires further data to differentiate between trans effects, ligand geometry constraints, or electronic differences in the donor atoms.

One interesting feature is the asymmetry in the Ni–Cl bridge distances. The Ni(1)–Cl(1) distance of 2.374 (2) Å is significantly shorter than the Ni(2)–Cl(1) distance of 2.387 (2) Å. A similar difference (2.378 (3) and 2.394 (3) Å) was reported in di-μ-chloro-*sym,trans*-(2,9-dimethyl-1,10-phenanthroline)dinickel.[20] Unfortunately, not only are there very few binuclear nickel complexes but the only reasonably accurate chloro-bridged complex was the phenanthroline case.[20] Consequently, although the data at present favor unsymmetrical Ni–Cl bridges, extrapolation from two points is risky. However, asymmetrical bridges may be a common feature of unconstrained bridging groups.[21]

The Ni–Ni distance of 3.603 (1) Å is not particularly short compared to those of other binuclear nickel complexes: 3.791 (4),[19] 3.602 (2),[20] 3.166 (3),[22] 3.706 (1),[10] 2.690 (4),[23] and 2.503 (4) Å.[24] The magnetic moment of 2.74 μ_B is very similar to the 2.82 μ_B observed in the related $Ni_2(dhph)_2$ complex,[8,19] as well as 3.18[20] and 2.75 μ_B[22] in other binuclear nickel complexes. The slight lowering of the moment from the spin-only value is not surprising but unfortunately we have no data on the variation of μ with temperature for our complex. The Ni–Ni and Ni–Cl distances and Ni–Cl–Ni angles between our study and the phenanthroline derivative[20] are very similar; consequently, the difference in the moments is somewhat puzzling. However, a comparison may not be strictly valid since the nickel atoms in the phenanthroline derivative[20] are closer to a square-pyramidal rather than to an octahedral geometry. Certainly, additional studies would be most useful in resolving some of these questions.

The packing of the binuclear nickel complex (Figure 4) is dominated by extensive hydrogen bonding. The dimensions of the various hydrogen bonds are given in Table X. We see that the cations are well separated so that magnetic interactions between cations must be minimal. Therefore, the dhphpy ligand appears to be ideally suited for studying the magnetic interactions between two metal ions as a function of the bridging atom. Further studies are in progress.

Acknowledgment. We wish to thank the Center for Instructional and Research Activities, University of Florida, for a grant of computer time.

Table X. Hydrogen Bonds in $H_2dhphpy(NO_3)_2 \cdot 2H_2O$ and $[Ni_2Cl(H_2O)_4(dhphpy)]Cl_3 \cdot 2H_2O$

D–H···A[a]	Position of A	Distances, Å[b]			D–H···A angles, deg
		D–H	H···A	D···A	
		$H_2dhphpy(NO_3)_2 \cdot 2H_2O$			
N(2)–H(N2)···O(21)	x, y, z	0.94 (4)	1.85 (4)	2.773 (4)	163 (4)
N(10)–H(py)···O(1)	x, y, z	1.21 (6)	1.57 (6)	2.758 (4)	167 (5)
O(1)–H(1)···N(1)	x, y, z	0.78 (5)	2.12 (5)	2.855 (4)	159 (5)
O(1)–H(2)···O(21)	$x, 1-y, {}^1/_2+z$	0.88 (4)	1.98 (4)	2.824 (4)	160 (4)
		$[Ni_2Cl(H_2O)_4(dhphpy)]Cl_3 \cdot 2H_2O$			
N(3)–H(N3)···Cl(2)	x, y, z	0.91	2.26	3.119 (6)	158
N(5)–H(N5)···Cl(3)	x, y, z	0.97	2.24	3.135 (6)	153
O(1)–H(1)···O(5)	$-x, -y, -z$	1.12	1.75	2.735 (8)	144
O(1)–H(1′)···Cl(4)	$-x, y, {}^1/_2-z$	0.95	2.24	3.150 (6)	159
O(2)–H(2′)···Cl(3)	${}^1/_2-x, {}^1/_2+y, {}^1/_2-z$	1.00	2.20	3.212 (6)	152
O(3)–H(3′)···Cl(3)	$-x, y, {}^1/_2-z$	0.73	2.36	3.075 (6)	171
O(4)–H(4)···Cl(2)	${}^1/_2-x, {}^1/_2+y, {}^1/_2-z$	0.92	2.16	3.067 (5)	171
O(5)–H(5)···Cl(1)	x, y, z	0.86	2.41	3.185 (6)	151
O(5)–H(5′)···Cl(4)	${}^1/_2-x, {}^1/_2+y, {}^1/_2-z$	0.90	2.25	3.098 (6)	157
O(6)–H(6′)···Cl(4)	x, y, z	1.23	2.09	3.121 (7)	151

[a] Donor–hydrogen···acceptor. D–H is at *x, y, z*. [b] The estimated standard deviations are given in parentheses.

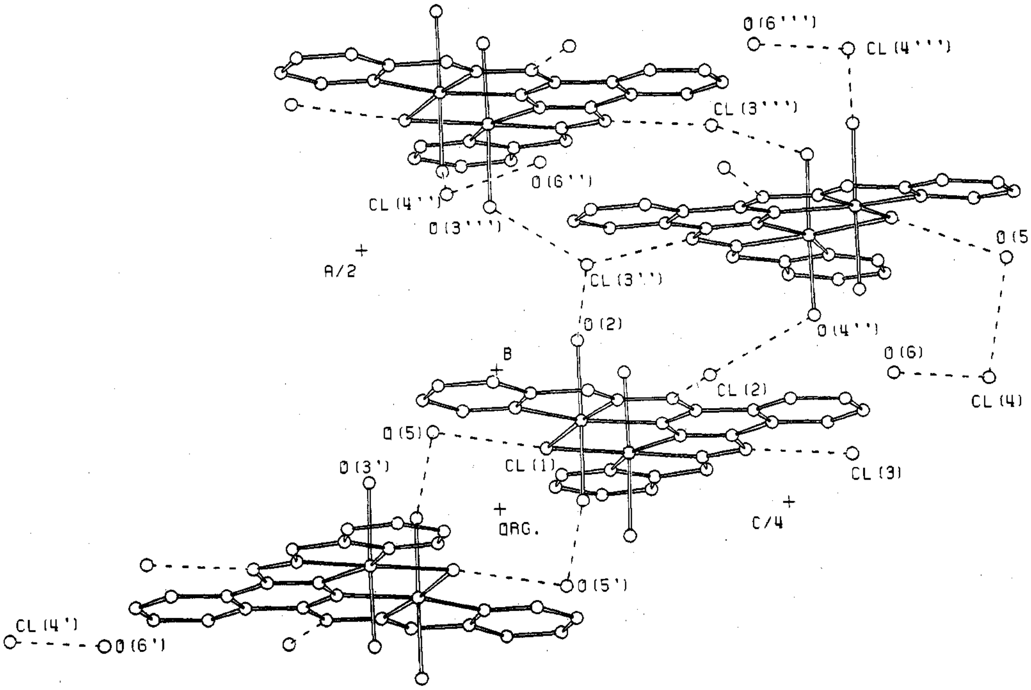

Figure 4. Packing diagram for the binuclear nickel(II) complex, II, showing the various hydrogen bonds between the ions.

Registry No. I, 61665-45-0; II, 61665-41-6; 2-pyridinecarboxaldehyde, 1121-60-4; dhph, 484-23-1.

Supplementary Material Available: Tables of least-squares planes for the various rings and the observed and calculated structures factors (24 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Abstracted in part from a dissertation submitted by D.A.S. to the Graduate School, University of Florida, in partial fulfillment of the requirements for the Ph.D. degree, Dec 1975.

(2) The diformylphenol ligands have been extensively studied by at least three different groups. Pertinent data are given in ref 3–5. The heptatriones have been studied mainly by Lintvedt[6] and Fenton.[7] The dihydrazinophthalazines have been less extensively studied and data can be found in ref 8 and 9. Finally a new binuclear complex was reported recently in ref 10.

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