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Synthesis and Relation between Magnetic and Structural Properties of a Series of Monomeric and Dimeric Nickel(II) Complexes. Crystal and Molecular Structures of Bis(2,2′-biquinolyl)di-μ-chloro-dinickel(II), (2,2′-Biquinolyl)dibromonickel(II), Bis(2,9-dimethyl-1,10-phenanthroline)di-μ-chloro-dinickel(II), Bis(2,9-dimethyl-1,10-phenanthroline)di-μ-bromo-dinickel(II), and (2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline)diiodonickel(II)

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A series of nickel(II) complexes has been synthesized with halogen and substituted phenanthroline or bipyridyl ligands. The relation between the magnetic and structural properties of the complexes has been investigated, and the crystal and molecular structures of five of them have been determined by single-crystal x-ray diffraction, using counter methods. It appears that the chloro complexes form only dimeric antiferromagnetic molecules containing five-coordinated nickel(II) atoms and that the bromo complexes can form either dimeric antiferromagnetic or pseudotetrahedral, monomeric normal paramagnetic molecules, while the iodo complexes appear to form four-coordinated paramagnetic monomers. Steric factors can weaken the bridging bonds between the halves of the dimeric molecules or prevent the dimerization which results from a drive to attain five-coordination about the nickel(II) atom. The ligand environment about the nickel atom is distorted tetrahedral in the monomeric complexes and may be regarded as either distorted square pyramidal or distorted trigonal bipyramidal in the dimers. Crystal data for bis(2,2′-biquinolyl)di-μ-chloro-dinickel(II), $[Ni(biq)Cl_2]_2$: $Ni_2Cl_4N_4C_{36}H_{24}$, space group $P\bar{1}$, $Z = 1$, $a = 9.521$ (4) Å, $b = 9.570$ (3) Å, $c = 11.226$ (3) Å, $\alpha = 95.23$ (3)°, $\beta = 117.43$ (4)°, $\gamma = 112.73$ (3)°, $V = 791$ Å^3, $R = 2.6\%$, 1977 reflections. Crystal data for (2,2′-biquinolyl)dibromonickel(II), $Ni(biq)Br_2$: $NiBr_2N_2C_{18}H_{12}$, space group $P2_1/c$, $Z = 4$, $a = 7.929$ (3) Å, $b = 12.432$ (6) Å, $c = 17.158$ (6) Å, $\beta = 102.90$ (3)°, $V = 1649$ Å^3, $R = 3.1\%$, 1621 reflections. Crystal data for (2,9-dimethyl-1,10-phenanthroline)di-μ-chloro-dinickel(II), $[Ni(dmp)Cl_2]_2$: $Ni_2Cl_4N_4C_{28}H_{24}$, space group $P\bar{1}$, $Z = 1$, $a = 9.090$ (1) Å, $b = 9.287$ (2) Å, $c = 10.327$ (2) Å, $\alpha = 100.28$ (2)°, $\beta = 113.19$ (1)°, $\gamma = 111.24$ (2)°, $V = 692$ Å^3, $R = 3.6\%$, 2083 reflections. Crystal data for (2,9-dimethyl-1,10-phenanthroline)-di-μ-bromo-dinickel(II), $[Ni(dmp)Br_2]_2$: $Ni_2Br_4N_4C_{28}H_{24}$, space group $P\bar{1}$, $Z = 1$, $a = 7.891$ (2) Å, $b = 10.259$ (3) Å, $c = 10.319$ (4) Å, $\alpha = 100.48$ (3)°, $\beta = 116.49$ (2)°, $\gamma = 99.56$ (1)°, $V = 706$ Å^3, $R = 4.2\%$, 2244 reflections. Crystal data for (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline)diiodonickel(II), $Ni(bc)I_2$: $NiI_2N_2C_{26}H_{20}$, space group $P2_1/c$, $Z = 4$, $a = 12.873$ (6) Å, $b = 23.248$ (7) Å, $c = 8.310$ (5) Å, $\beta = 101.56$ (4)°, $V = 2436$ Å^3, $R = 3.8\%$, 2270 reflections.

Introduction

Ring-substituted ligands of the phenanthroline and bipyridyl type have been shown to form monomeric and dimeric complexes with nickel(II) and manganese(II) halides,[1-4] though only one such nickel complex has so far been reported.[5] When the halide, X, is Cl, chlorine-bridged dimers $[MLX_2]_2$, containing five-coordinated nickel or manganese,[2] are formed. The manganese(II) complexes can be hydrated to form five-coordinated species of the type $[MnLX_2(H_2O)]$ which contain no metal–halogen bridging but do tend to form polymeric hydrogen-bridged chains.[3,4] When the halide is Br the (anhydrous) manganese(II) complexes studied to date are discrete monomers. We show here that the nickel(II) complexes are halide-bridged dimers with X = Cl, while both bridged and unbridged species form when X = Br depending on the experimental conditions. Only monomeric complexes appear to form with X = I. The dimeric manganese complexes display intramolecular ferromagnetic interactions,[2,4] but we find that halogen bridging in the nickel complexes leads to antiferromagnetic interactions for X = Cl or Br, despite a similarity between the geometries of the dimeric nickel and manganese complexes. The only nickel complex of this type previously studied by x-ray diffraction was reported to have equal Ni–Cl bridging bonds,[5] but we find all the dimeric complexes to be bridged by two unequal Ni–X bonds.

Experimental Section

Syntheses. (a) $[Ni(Biq)Cl_2]_2$ and $Ni(biq)Br_2$. A 1-mmol amount of ligand was dissolved in warm benzene and a solution containing 1.1 mmol of the appropriate nickel halide dissolved in 1:1 methanol triethoxymethane was added. The precipitate which formed immediately was filtered off and recrystallized from nitrobenzene (with a small amount of TEOF added). The crystals used in the x-ray study were grown by slow evaporation of the nitrobenzene solution.

(b) $[Ni(dmp)Cl_2]_2$, $[Ni(dmp)Br_2]_2$, and $Ni(bc)I_2$. A 1-mmol amount of ligand was dissolved in a minimum of chloroform with 10 mL of TEOF added and this solution was treated with 1.1 mmol of the appropriate nickel halide dissolved in methanol/triethoxymethane solution. The complexes were obtained in crystalline form by evaporation of this solution and recrystallization by slow evaporation in air from chloroform with some triethoxymethane added to remove water.

Crystal densities were measured by flotation in aqueous potassium iodide containing a small amount of detergent as wetting agent.

Crystal data for bis(2,2′-biquinolyl)di-μ-chloro-dinickel(II), $[Ni(biq)Cl_2]_2$: $Ni_2Cl_4N_4C_{36}H_{24}$, yellow-green crystal, mol wt 772,

space group $P\bar{1}$, $Z = 1$, $a = 9.521$ (4) Å, $b = 9.570$ (3) Å, $c = 11.226$ (3) Å, $\alpha = 95.23$ (3)°, $\beta = 117.43$ (4)°, $\gamma = 112.73$ (3)°, $V = 791$ Å^3, μ(Mo Kα) = 15.6 cm^{-1}, ρ_{calcd} = 1.62 g cm^{-3}, ρ_{obsd} = 1.65 g cm^{-3}; crystal dimensions (distances of faces in mm from centroid) ($\bar{1}$01) 0.07, (10$\bar{1}$) 0.07, (010) 0.15, (0$\bar{1}$0) 0.15, (0$\bar{1}$1) 0.10, (01$\bar{1}$) 0.10; maximum, minimum transmission coefficient = 0.86, 0.68, respectively.

Crystal data for (2,2′-biquinolyl)dibromonickel(II), Ni(biq)Br$_2$: $NiBr_2N_2C_{18}H_{12}$, red crystal, mol wt 475, space group $P2_1/c$, $Z = 4$, $a = 7.929$ (3) Å, $b = 12.432$ (6) Å, $c = 17.158$ (6) Å, $\beta = 102.90$ (3)°, $V = 1649$ Å^3, μ(Mo Kα) = 63.1 cm^{-1}, ρ_{calcd} = 1.91 g cm^{-3}, ρ_{obsd} = 1.91 g cm^{-3}; crystal dimensions (in mm from centroid) (100) 0.02, ($\bar{1}$00) 0.02, (010) 0.14, (0$\bar{1}$0) 0.14, (001) 0.08, (00$\bar{1}$) 0.08; maximum, minimum transmission coefficient = 0.86, 0.41 respectively.

Crystal data for (2,9-dimethyl-1,10-phenanthroline)di-μ-chloro-dinickel(II), [Ni(dmp)Cl$_2$]$_2$: $Ni_2Cl_4N_4C_{28}H_{24}$, yellow-green crystal, space group $P\bar{1}$, $Z = 1$, $a = 9.090$ (1) Å, $b = 9.287$ (2) Å, $c = 10.327$ (2) Å, $\alpha = 100.28$ (2)°, $\beta = 113.19$ (1)°, $\gamma = 111.24$ (2)°, $V = 692$ Å^3, μ(Mo Kα) = 17.75 cm^{-1}, ρ_{calcd} = 1.63 g cm^{-3}, ρ_{obsd} = 1.60 g cm^{-3}; crystal dimensions (in mm from centroid) (100) 0.10, ($\bar{1}$00) 0.10, (010) 0.085, (0$\bar{1}$0) 0.085, (011) 0.09, (0$\bar{1}\bar{1}$) 0.09, (01$\bar{1}$) 0.10, (0$\bar{1}$1) 0.10; maximum, minimum transmission coefficients = 0.88, 0.83, respectively.

Crystal data for (2,9-dimethyl-1,10-phenanthroline)di-μ-bromo-dinickel(II), [Ni(dmp)Br$_2$]$_2$: $Ni_2Br_4N_4C_{28}H_{24}$, reddish yellow crystal, space group $P\bar{1}$, $Z = 1$, $a = 7.891$ (2) Å, $b = 10.259$ (3) Å, $c = 10.319$ (4) Å, $\alpha = 100.48$ (3)°, $\beta = 116.49$ (2)°, $\gamma = 99.56$ (1)°, $V = 706$ Å^3, μ(Mo Kα) = 74.4 cm^{-1}, ρ_{calcd} = 2.03 g cm^{-3}, ρ_{obsd} = 1.99 g cm^{-3}; crystal dimensions (in mm from centroid) (1$\bar{1}$0) 0.295, ($\bar{1}$10) 0.295, (01$\bar{1}$) 0.10, (0$\bar{1}$1) 0.10, (001) 0.16, (00$\bar{1}$) 0.16; maximum, minimum transmission coefficients = 0.44, 0.14, respectively.

Crystal data for (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline)diiodonickel(II) [diiodo(bathocuproine)nickel(II)], Ni(bc)I$_2$: $NiI_2N_2C_{26}H_{20}$, space group $P2_1/c$, $Z = 4$, $a = 12.873$ (6) Å, $b = 23.248$ (7) Å, $c = 8.310$ (5) Å, $\beta = 101.56$ (4)°, $V = 2436$ Å^3, μ(Mo Kα) = 33.9 cm^{-1}, ρ_{calcd} = 1.84 g cm^{-3}, ρ_{obsd} = 1.81 g cm^{-3}; crystal dimensions (in mm from centroid) (110) 0.09, ($\bar{1}\bar{1}$0) 0.09, (1$\bar{1}$0) 0.09, ($\bar{1}$10) 0.09, (010) 0.095, (0$\bar{1}$0) 0.095, (011) 0.18, (0$\bar{1}\bar{1}$) 0.18, (01$\bar{1}$) 0.185, (0$\bar{1}$1) 0.185; maximum, minimum transmission coefficients = 0.69, 0.66, respectively.

For each crystal, the Enraf-Nonius program SEARCH was used to obtain 15 accurately centered reflections which were then used in the program INDEX to obtain approximate cell dimensions and an orientation matrix for data collection. Refined cell dimensions and their estimated standard deviations were obtained from least-squares refinement of 28 accurately centered reflections. The mosaicity of each crystal was examined by the ω-scan technique and judged to be satisfactory.

Collection and Refinement of Data. Diffraction data were collected at 292 °C on an Enraf-Nonius four-circle CAD-4 diffractometer controlled by a PDP8/M computer, using Mo Kα radiation from a highly oriented graphite crystal monochromator. The θ–2θ scan technique was used to record the intensities for all nonequivalent reflections for which $1° > 2\theta > 46°$ for [Ni(biq)Cl$_2$]$_2$ and Ni(biq)Br$_2$, $1° > 2\theta > 44°$ for Ni(bc)I$_2$, and $1° > 2\theta > 50°$ for [Ni(dmp)Cl$_2$]$_2$ and [Ni(dmp)Br$_2$]$_2$. Scan widths (SW) were calculated from the formula SW = $A + B \tan\theta$ where A is estimated from the mosaicity of the crystal and B allows for the increase in width of peak due to Kα_1–Kα_2 splitting. The values of A and B were respectively 0.60° and 0.30° for [Ni(biq)Cl$_2$]$_2$, [Ni(dmp)Br$_2$]$_2$, Ni(bc)I$_2$, and Ni(biq)Br$_2$ and 0.50° and 0.30° for [Ni(dmp)Cl$_2$]$_2$. The calculated scan angle is extended at each side by 25% for background determination (BG1 and BG2). The net count is then calculated as NC = TOT – 2(BG1 + BG2) where TOT is the integrated peak intensity. Reflection data were considered insignificant if intensities registered less than 5 counts above background on a rapid prescan, such reflections being rejected automatically by the computer.

The intensities of four standard reflections, monitored for each crystal at 100 reflection intervals, showed no greater fluctuations during the data collection than those expected from Poisson statistics. The raw intensity data were corrected for Lorentz–polarization effects (including the polarization effect of the crystal monochromator) and then for absorption. After the intensities of equivalent reflections were averaged, the data were reduced to 2205 independent intensities for [Ni(biq)Cl$_2$]$_2$, 2253 for Ni(biq)Br$_2$, 2338 for [Ni(dmp)Cl$_2$]$_2$, 2412 for [Ni(dmp)Br$_2$]$_2$ and for Ni(bc)I$_2$, of which 2094, 1621, 2083, 2244, and 2270, respectively, had $F_o^2 > 3\sigma(F_o^2)$, where $\sigma(F_o^2)$ was estimated from counting statistics.[6] These data were used in the final refinement of the structural parameters.

Solution and Refinement of the Structures. In each case the nickel and halogen and, in the case of the chloro complexes, the ligand nitrogen atoms were located from a three-dimensional Patterson synthesis.

Full-matrix least-squares refinement was based on F, and the function minimized was $\sum w(|F_o| - |F_c|)^2$. The weights w were then taken as $[2F_o/\sigma(F_o^2)]^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. The atomic scattering factors for nonhydrogen atoms were taken from Cromer and Waber,[7] and those for hydrogen, from Stewart et al.[8] The effects of anomalous dispersion for all nonhydrogen atoms were included in F_c using the values of Cromer and Ibers[9] for $\Delta f'$ and $\Delta f''$. Agreement factors are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = \sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2$. To minimize computer time, the initial calculations were carried out on the first 1000 reflections collected. The intensity data were phased sufficiently well by the "heavy" atom positions determined from the Patterson calculation to permit location of the remaining nonhydrogen atoms by difference Fourier syntheses. After full-matrix least-squares refinement, the models converged with R = 8.3, 7.9, 9.1, 8.0, and 10.9 for [Ni(biq)Cl$_2$]$_2$, Ni(biq)Br$_2$, [Ni(dmp)Cl$_2$]$_2$, [Ni(dmp)Br$_2$]$_2$, and Ni(bc)I$_2$. The remaining diffraction data were added to the calculation and anisotropic temperature factors were introduced for all nonhydrogen atoms. In each case, Fourier difference syntheses indicated the presence of hydrogen atoms in the expected positions, except that the methyl hydrogen atoms in Ni(bc)I$_2$ evidenced positional disorder. Except for the Ni(bc)I$_2$ methyl groups, the hydrogen atoms were included in the calculation for one cycle of full-matrix least-squares refinement and thereafter held fixed; the thermal parameters for the methyl hydrogens in [Ni(dmp)Br$_2$]$_2$ were not varied. The models converged with R = 2.6, R_w = 3.4% for [Ni(biq)Cl$_2$]$_2$, R = 3.1, R_w = 3.2% for Ni(biq)Br$_2$, R = 3.6, R_w = 5.0% for [Ni(dmp)Cl$_2$]$_2$, R = 4.2, R_w = 4.5% for [Ni(dmp)Br$_2$]$_2$, and R = 3.8, R_w = 4.2% for Ni(bc)I$_2$; the error in an observation of unit weight is 1.86, 1.70, 2.71, 3.19, and 3.10 for the five compounds, respectively. A structure factor calculation with all observed and unobserved reflections included (no refinement) gave R = 2.9, 4.6, 4.0, 4.4, and 4.7% for [Ni(biq)Cl$_2$]$_2$, Ni(biq)Br$_2$, [Ni(dmp)Cl$_2$]$_2$, [Ni(dmp)Br$_2$]$_2$, and Ni(bc)I$_2$, respectively; on this basis it was decided that careful measurement of reflections rejected automatically during data collection would not significantly improve the results. A final Fourier difference function was featureless. Tables of the observed structure factors are available.[10] The principal programs used are as described previously.[11]

Results and Discussion

Final positional and thermal parameters for the complexes [Ni(biq)Cl$_2$]$_2$, Ni(biq)Br$_2$, [Ni(dmp)Cl$_2$]$_2$, [Ni(dmp)Br$_2$]$_2$, and Ni(bc)I$_2$ are given in Table I. Tables II and III contain the bond lengths and angles. The digits in parentheses in the tables are the estimated standard deviations in the least significant figures quoted and were derived from the inverse matrix in the course of least-squares refinement calculations. Figures 1–5 are stereoscopic pair views of the [Ni(biq)Cl$_2$]$_2$, Ni(biq)Br$_2$, [Ni(dmp)Cl$_2$]$_2$, [Ni(dmp)Br$_2$]$_2$, and Ni(bc)I$_2$ molecules, respectively, while Figures 6–8 show the molecular packing in some of the unit cells. The other packing diagrams are available,[10] as are tables of selected least-squares planes and the closest intermolecular distances. The atomic numbering is uniform for analogous molecular fragments and conforms to standard nomenclature. Therefore the complete labeling is shown only for [Ni(biq)Cl$_2$]$_2$ and [Ni(dmp)Cl$_2$]$_2$ in the figures.

[Ni(biq)Cl$_2$]$_2$ consists of discrete dimeric molecules (Figures 1 and 6), the closest intermolecular contact (3.37 Å) being between quinolyl carbon atoms of adjacent molecules. The halves of the dimeric molecule are related by the crystallographically imposed center of symmetry. The bridging chlorine atoms differ significantly in their distances from the nickel atom (2.372 (1), 2.400 (1) Å). This observation contrasts with equal distances, within experimental error, reported[5] for the related complex [Ni(dmp)Cl$_2$]$_2$·2CHCl$_3$. The asymmetry of

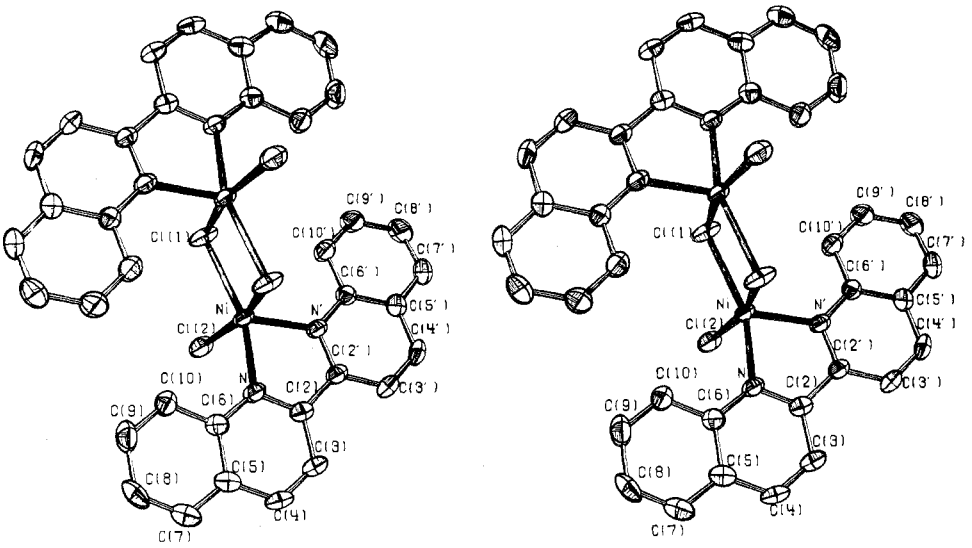

Figure 1. Stereoscopic pair view of $[Ni(biq)Cl_2]_2$.

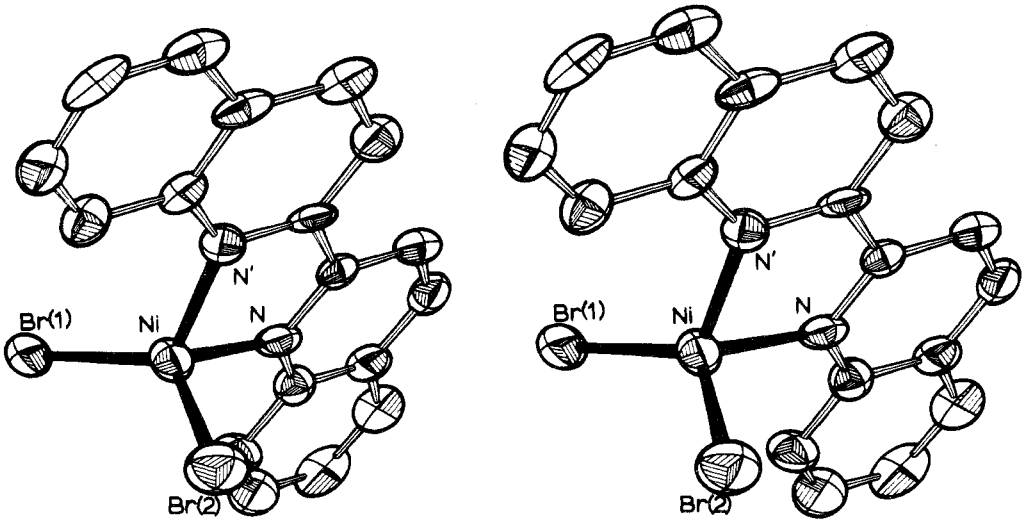

Figure 2. Stereoscopic pair view of $Ni(biq)Br_2$.

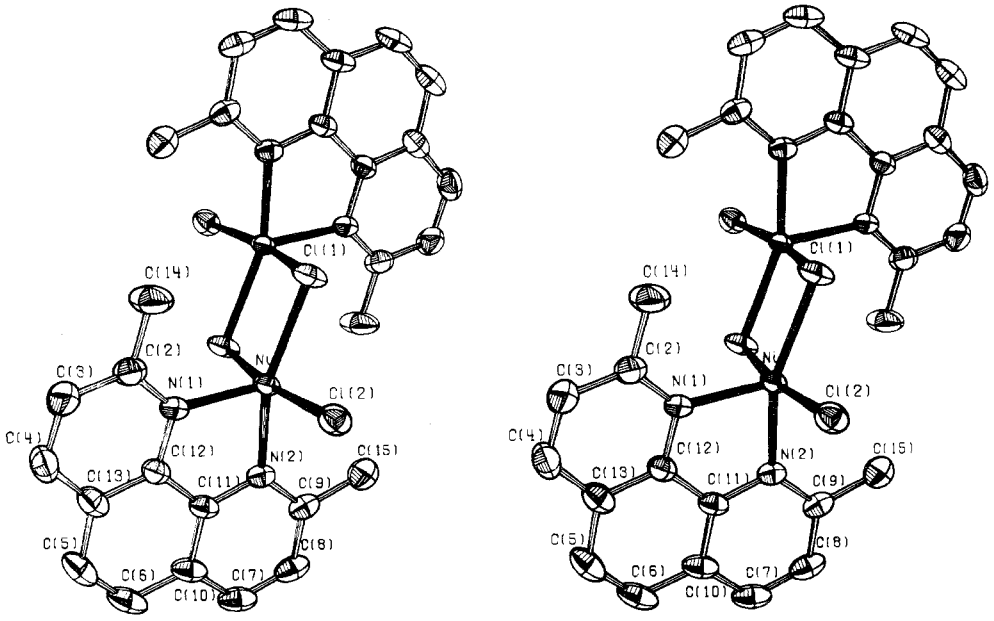

Figure 3. Stereoscopic pair view of $[Ni(dmp)Cl_2]_2$.

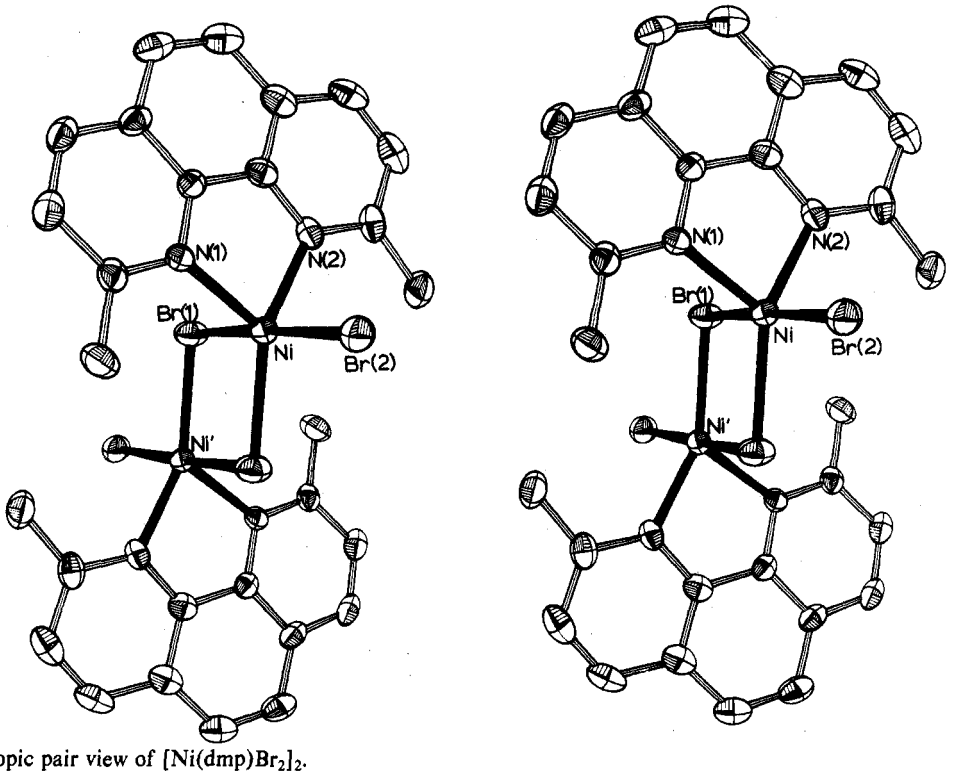

Figure 4. Stereoscopic pair view of $[Ni(dmp)Br_2]_2$.

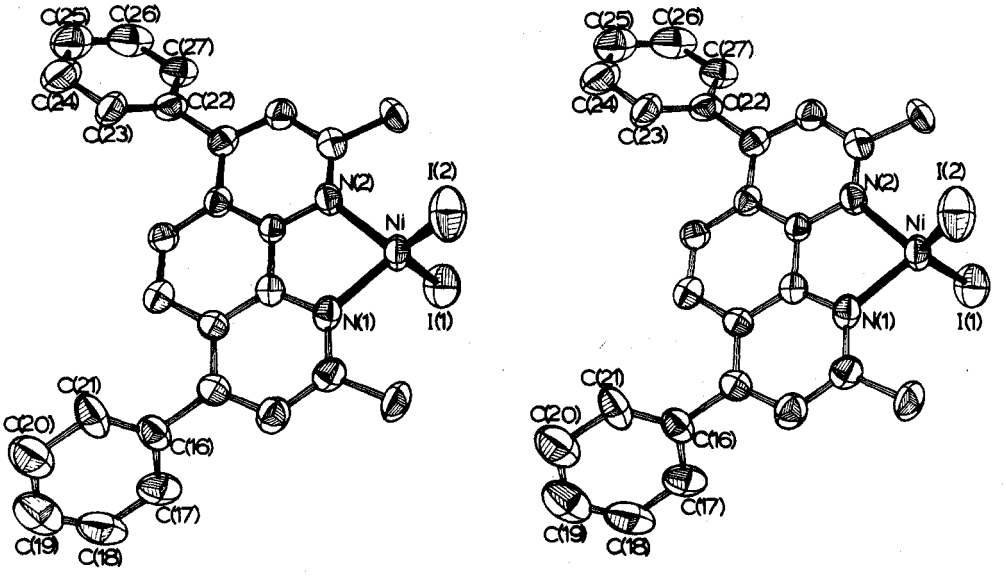

Figure 5. Stereoscopic pair view of $Ni(bc)I_2$.

the bridging is much greater than in the related complex $[Mn(biq)Cl_2]_2$ (2.543 (1), 2.539 (1) Å).[4] The nonbridging chlorine atom is joined to the metal by a much shorter bond (2.306 Å).

Each nickel(II) atom is in a distorted trigonal-bipyramidal ligand environment, 0.10 Å from the equatorial plane NN′Cl(1). The distortions of the trigonal bipyramid are indicated by the unequal bond lengths in the equatorial plane between Ni and N, N′, Cl(1) and along the axis Ni to Cl(1′), Cl(2). The distortions are even more dramatically indicated by the unequal bond angles of 157.6, 121.2, and 80.4° for Cl(1)–Ni–N, Cl(1)–Ni–N′, and N–Ni–N′ (pure trigonal-bipyramidal geometry requires 120° for each) and the nonlinearity (164.0°) of the Cl(2)–Ni–Cl(1′) axis between the apices. The dimeric molecule is formed from the monomeric trigonal-bipyramidal fragments by joining one apex of each one to an equatorial point of the other. The geometry about the metal atom may also be regarded as a distorted square pyramid with a slightly lengthened (2.042 (2) vs. 2.034 (1) Å) Ni–N bond to the off-center apex of the pyramid. The nickel atom is located 0.37 Å above the approximately planar base of the pyramid, Cl(1)–Cl(1′)–Cl(2)–N. In this case the dimeric molecule consists of the two distorted square pyramids joined along an edge of the base. The Ni–Ni separation is 3.565 Å and the Ni–Cl–Ni bridging angle is 96.7°, compared with 3.887 (1) Å and 99.8° for the equivalent quantities in the analogous complex $[Mn(biq)Cl_2]_2$.[2]

The quinolyl fragment of biq having the longer Ni–N bond is distorted from planarity, as indicated by an angle of 4.6° between the pyridyl and phenyl groups. The quinolyl fragment has a C–H bond (from C(10′)) pointing toward the Ni_2Cl_2 bridge (nearest Cl(1)), a feature not shown by the other quinolyl group. Distortions from planarity were also observed in the quinolyl groups of $[Mn(biq)Cl_2]_2$ and were attributed

Table I. Positional and Thermal Parameters[a] and Their Estimated Standard Deviations

(a) $[Ni(biq)Cl_2]_2$

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni	0.11090 (3)	−0.02308 (3)	0.16913 (3)	0.00799 (3)	0.00946 (3)	0.00514 (3)	0.00861 (5)	0.00364 (4)	0.00029 (5)
Cl(1)	−0.17145 (8)	−0.16772 (7)	−0.05090 (6)	0.01047 (8)	0.01267 (8)	0.00674 (6)	0.0057 (1)	0.0026 (1)	0.0058 (1)
Cl(2)	−0.00544 (7)	−0.18466 (7)	0.27646 (6)	0.01121 (8)	0.01316 (8)	0.00764 (5)	0.0087 (1)	0.0074 (1)	0.0065 (1)
N	0.3068 (2)	0.1538 (2)	0.3595 (2)	0.0095 (2)	0.0094 (2)	0.0057 (2)	0.0088 (4)	0.0059 (3)	0.0039 (3)
N′	0.3247 (2)	−0.0572 (2)	0.2077 (2)	0.0103 (2)	0.0096 (2)	0.0055 (2)	0.0100 (3)	0.0061 (3)	0.0037 (3)
C(2)	0.4670 (3)	0.1610 (3)	0.4168 (2)	0.0105 (3)	0.0087 (3)	0.0060 (2)	0.0078 (4)	0.0075 (3)	0.0051 (4)
C(3)	0.6144 (3)	0.2658 (3)	0.5546 (2)	0.0099 (3)	0.0107 (3)	0.0067 (2)	0.0079 (5)	0.0046 (4)	0.0038 (5)
C(4)	0.5917 (3)	0.3646 (3)	0.6309 (2)	0.0125 (3)	0.0105 (3)	0.0056 (2)	0.0065 (5)	0.0044 (4)	0.0029 (5)
C(5)	0.4240 (3)	0.3623 (3)	0.5728 (2)	0.0141 (3)	0.0083 (3)	0.0064 (2)	0.0077 (5)	0.0094 (4)	0.0041 (4)
C(6)	0.2815 (3)	0.2539 (3)	0.4340 (2)	0.0125 (3)	0.0089 (3)	0.0068 (2)	0.0093 (4)	0.0097 (4)	0.0048 (4)
C(7)	0.3895 (3)	0.4606 (3)	0.6455 (3)	0.0210 (4)	0.0111 (3)	0.0082 (2)	0.0137 (5)	0.0146 (4)	0.0037 (5)
C(8)	0.2252 (3)	0.4522 (3)	0.5832 (3)	0.0240 (4)	0.0140 (3)	0.0120 (2)	0.0218 (5)	0.0224 (4)	0.0067 (5)
C(9)	0.0862 (3)	0.3466 (3)	0.4448 (3)	0.0163 (3)	0.0150 (4)	0.0129 (3)	0.0176 (5)	0.0167 (4)	0.0077 (5)
C(10)	0.1122 (3)	0.2493 (3)	0.3709 (3)	0.0125 (3)	0.0122 (3)	0.0086 (2)	0.0119 (5)	0.0088 (4)	0.0032 (5)
C(2′)	0.4806 (3)	0.0493 (3)	0.3273 (2)	0.0094 (3)	0.0098 (3)	0.0060 (2)	0.0085 (4)	0.0060 (3)	0.0047 (4)
C(3′)	0.6457 (3)	0.0533 (3)	0.3664 (3)	0.0091 (3)	0.0133 (3)	0.0084 (2)	0.0089 (5)	0.0060 (4)	0.0042 (5)
C(4′)	0.6506 (3)	−0.0516 (3)	0.2810 (3)	0.0106 (3)	0.0155 (3)	0.0105 (2)	0.0145 (5)	0.0113 (4)	0.0068 (5)
C(5′)	0.4896 (3)	−0.1674 (3)	0.1554 (2)	0.0128 (3)	0.0130 (3)	0.0088 (2)	0.0149 (4)	0.0119 (4)	0.0073 (5)
C(6′)	0.3261 (3)	−0.1688 (3)	0.1220 (2)	0.0120 (3)	0.0110 (3)	0.0066 (2)	0.0131 (4)	0.0085 (4)	0.0047 (4)
C(7′)	0.4836 (3)	−0.2865 (3)	0.0662 (3)	0.0172 (3)	0.0179 (4)	0.0114 (3)	0.0230 (5)	0.0169 (4)	0.0077 (5)
C(8′)	0.3220 (3)	−0.4041 (3)	−0.0475 (3)	0.0212 (4)	0.0171 (4)	0.0105 (3)	0.0229 (5)	0.0152 (4)	0.0017 (5)
C(9′)	0.1624 (3)	−0.4048 (3)	−0.0782 (3)	0.0169 (4)	0.0159 (4)	0.0093 (3)	0.0164 (5)	0.0061 (5)	−0.0036 (6)
C(10′)	0.1610 (3)	−0.2905 (3)	0.0019 (3)	0.0124 (3)	0.0145 (3)	0.0087 (3)	0.0141 (5)	0.0065 (4)	−0.0008 (5)

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
H(3)	0.724 (3)	0.272 (3)	0.590 (2)	3.5 (7)	H(3′)	0.751 (3)	0.133 (3)	0.443 (3)	4.9 (8)
H(4)	0.684 (3)	0.437 (3)	0.720 (2)	3.1 (6)	H(4′)	0.756 (3)	−0.046 (3)	0.297 (3)	5.2 (8)
H(7)	0.476 (3)	0.528 (3)	0.728 (2)	3.8 (7)	H(7′)	0.584 (3)	−0.283 (3)	0.081 (3)	4.8 (8)
H(8)	0.207 (3)	0.514 (3)	0.637 (3)	5.3 (8)	H(8′)	0.317 (3)	−0.474 (3)	−0.105 (3)	5.1 (8)
H(9)	−0.022 (3)	0.334 (3)	0.405 (3)	4.8 (8)	H(9′)	0.061 (3)	−0.483 (3)	−0.148 (3)	4.3 (7)
H(10)	0.025 (3)	0.185 (3)	0.285 (3)	3.7 (7)	H(10)	0.056 (3)	−0.293 (3)	−0.015 (3)	4.0 (7)

(b) $Ni(biq)Br_2$

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Br1	0.1942 (1)	0.15815 (6)	0.73825 (3)	0.0224 (1)	0.00860 (6)	0.00219 (2)	0.0064 (2)	0.00090 (9)	−0.00015 (6)
Br2	−0.2879 (1)	0.30416 (6)	0.66759 (4)	0.0215 (1)	0.00814 (6)	0.00404 (2)	0.0026 (2)	0.00755 (9)	−0.00017 (7)
Ni	−0.0314 (1)	0.23197 (6)	0.64175 (4)	0.0168 (1)	0.00540 (6)	0.00174 (2)	−0.0025 (2)	0.0026 (1)	0.00006 (6)
N	0.0669 (6)	0.3256 (4)	0.5679 (2)	0.0113 (9)	0.0045 (4)	0.0021 (2)	−0.000 (1)	0.0021 (6)	−0.0001 (4)
N′	−0.1079 (6)	0.1429 (4)	0.5430 (2)	0.0108 (9)	0.0048 (4)	0.0019 (1)	0.000 (1)	0.0015 (6)	0.0002 (4)
C(2)	0.0210 (7)	0.2923 (5)	0.4917 (3)	0.012 (1)	0.0046 (4)	0.0020 (2)	0.006 (1)	0.0034 (7)	0.0013 (5)
C(3)	0.0789 (8)	0.3470 (5)	0.4302 (3)	0.015 (1)	0.0048 (4)	0.0023 (2)	0.000 (1)	0.0047 (8)	0.0002 (5)
C(4)	0.1829 (8)	0.4344 (5)	0.4487 (3)	0.014 (1)	0.0055 (5)	0.0028 (2)	0.006 (1)	0.0062 (8)	0.0028 (5)
C(5)	0.2355 (7)	0.4712 (5)	0.5287 (3)	0.011 (1)	0.0043 (4)	0.0029 (2)	0.002 (1)	0.0040 (8)	0.0010 (5)
C(6)	0.1721 (7)	0.4126 (5)	0.5879 (3)	0.010 (1)	0.0045 (4)	0.0023 (2)	0.000 (1)	0.0010 (8)	0.0013 (5)
C(7)	0.3438 (8)	0.5597 (5)	0.5508 (3)	0.011 (1)	0.0060 (5)	0.0041 (2)	−0.002 (1)	0.0041 (9)	0.0003 (6)
C(8)	0.3870 (9)	0.5917 (5)	0.6285 (4)	0.014 (1)	0.0056 (5)	0.0051 (3)	−0.005 (2)	0.0012 (11)	−0.0001 (7)
C(9)	0.3233 (9)	0.5347 (6)	0.6873 (4)	0.017 (1)	0.0075 (6)	0.0035 (2)	−0.006 (2)	−0.0014 (10)	−0.0001 (7)
C(10)	0.2185 (8)	0.4481 (5)	0.6671 (3)	0.016 (1)	0.0066 (5)	0.0027 (2)	−0.004 (2)	0.0023 (9)	0.0014 (6)
C(2′)	−0.0859 (7)	0.1948 (5)	0.4776 (3)	0.011 (1)	0.0040 (4)	0.0023 (2)	0.001 (1)	0.0037 (7)	−0.0003 (5)
C(3′)	−0.1591 (8)	0.1545 (5)	0.4008 (3)	0.017 (1)	0.0054 (5)	0.0021 (2)	−0.000 (1)	0.0038 (8)	−0.0002 (5)
C(4′)	−0.2496 (8)	0.0620 (5)	0.3932 (3)	0.015 (1)	0.0055 (5)	0.0028 (2)	0.001 (1)	0.0015 (9)	−0.0028 (5)
C(5′)	−0.2705 (7)	0.0037 (5)	0.4601 (3)	0.010 (1)	0.0041 (4)	0.0031 (2)	0.001 (1)	0.0020 (8)	−0.0010 (5)
C(6′)	−0.1959 (7)	0.0472 (4)	0.5363 (3)	0.010 (1)	0.0036 (4)	0.0026 (2)	0.001 (1)	0.0014 (8)	−0.0005 (5)
C(7′)	−0.3608 (8)	−0.0949 (5)	0.4559 (3)	0.013 (1)	0.0055 (5)	0.0037 (2)	0.002 (1)	0.0013 (9)	−0.0020 (6)
C(8′)	−0.3766 (8)	−0.1471 (5)	0.5238 (4)	0.012 (1)	0.0039 (4)	0.0052 (3)	0.002 (1)	0.0038 (9)	0.0010 (6)
C(9′)	−0.3006 (8)	−0.1030 (5)	0.5998 (3)	0.015 (1)	0.0053 (5)	0.0038 (2)	−0.001 (1)	0.0033 (9)	0.0015 (6)
C(10′)	−0.2129 (8)	−0.0081 (5)	0.6059 (3)	0.014 (1)	0.0058 (5)	0.0026 (2)	−0.000 (1)	0.0018 (8)	0.0010 (6)

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
H(3)	0.033 (7)	0.307 (5)	0.376 (3)	5.0 (14)	H(3′)	−0.137 (6)	0.200 (4)	0.355 (2)	2.6 (11)
H(4)	0.222 (6)	0.476 (4)	0.411 (2)	2.4 (11)	H(4′)	−0.306 (5)	0.034 (3)	0.345 (2)	1.7 (10)
H(7)	0.392 (8)	0.592 (5)	0.511 (3)	6.3 (17)	H(7′)	−0.424 (6)	−0.126 (4)	0.403 (3)	3.4 (12)
H(8)	0.469 (7)	0.651 (5)	0.642 (3)	5.4 (15)	H(8′)	−0.432 (7)	−0.213 (4)	0.522 (3)	4.2 (14)
H(9)	0.371 (7)	0.562 (4)	0.739 (3)	4.5 (14)	H(9′)	−0.315 (7)	−0.142 (5)	0.650 (3)	5.6 (16)
H(10)	0.183 (5)	0.414 (3)	0.702 (2)	1.4 (8)	H(10′)	−0.160 (6)	0.019 (4)	0.655 (2)	2.0 (11)

(c) $[Ni(dmp)Cl_2]_2$

Atom	x		z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni	0.07860 (4)	0.18420 (4)	0.15525 (4)	0.01081 (4)	0.00893 (4)	0.00528 (3)	0.01037 (7)	0.00961 (6)	0.00491 (7)
Cl(2)	0.3263 (1)	0.4469 (1)	0.26631 (9)	0.0140 (1)	0.0095 (1)	0.00997 (8)	0.0085 (2)	0.0135 (1)	0.0044 (2)
Cl(1)	0.1359 (1)	0.1095 (1)	−0.04558 (8)	0.0167 (1)	0.0099 (1)	0.00846 (7)	0.0074 (2)	0.0177 (1)	0.0035 (1)

Table I (*Continued*)

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
N(1)	−0.1166 (3)	0.2533 (3)	0.1278 (3)	0.0119 (3)	0.0101 (3)	0.0056 (2)	0.0112 (5)	0.0090 (4)	0.0042 (5)
N(2)	0.0899 (3)	0.1956 (3)	0.3591 (3)	0.0114 (3)	0.0074 (3)	0.0058 (2)	0.0056 (5)	0.0080 (4)	0.0036 (5)
C(2)	−0.2127 (4)	0.2879 (4)	0.0133 (4)	0.0172 (5)	0.0141 (4)	0.0070 (3)	0.0190 (7)	0.0099 (6)	0.0068 (6)
C(3)	−0.3396 (5)	0.3383 (5)	0.0166 (4)	0.0169 (5)	0.0179 (5)	0.0097 (4)	0.0226 (7)	0.0095 (7)	0.0084 (8)
C(4)	−0.3692 (4)	0.3531 (4)	0.1370 (4)	0.0135 (4)	0.0143 (5)	0.0137 (4)	0.0168 (6)	0.0145 (7)	0.0076 (8)
C(5)	−0.2802 (4)	0.3426 (4)	0.3957 (4)	0.0189 (4)	0.0136 (5)	0.0151 (4)	0.0163 (7)	0.0268 (5)	0.0106 (7)
C(6)	−0.1743 (5)	0.3147 (5)	0.5127 (4)	0.0233 (5)	0.0130 (5)	0.0117 (3)	0.0135 (8)	0.0271 (5)	0.0079 (7)
C(7)	0.0726 (5)	0.2376 (4)	0.6249 (4)	0.0217 (6)	0.0113 (5)	0.0071 (3)	0.0081 (9)	0.0164 (6)	0.0063 (6)
C(8)	0.1933 (5)	0.1946 (4)	0.6097 (4)	0.0166 (6)	0.0109 (5)	0.0058 (3)	0.0057 (8)	0.0070 (7)	0.0061 (6)
C(9)	0.2027 (4)	0.1741 (4)	0.4746 (3)	0.0124 (5)	0.0080 (4)	0.0062 (3)	0.0051 (7)	0.0062 (6)	0.0051 (6)
C(10)	−0.0466 (4)	0.2634 (4)	0.5057 (3)	0.0180 (5)	0.0095 (4)	0.0077 (3)	0.0075 (7)	0.0168 (5)	0.0054 (6)
C(11)	−0.0312 (4)	0.2404 (4)	0.3746 (3)	0.0123 (4)	0.0080 (4)	0.0067 (3)	0.0062 (6)	0.0118 (5)	0.0041 (6)
C(12)	−0.1428 (4)	0.2707 (4)	0.2505 (3)	0.0110 (4)	0.0087 (4)	0.0071 (3)	0.0077 (6)	0.0104 (5)	0.0041 (6)
C(13)	−0.2675 (4)	0.3204 (4)	0.2604 (4)	0.0134 (4)	0.0098 (4)	0.0110 (3)	0.0094 (6)	0.0163 (5)	0.0059 (6)
C(14)	−0.1815 (5)	0.2698 (5)	−0.1183 (4)	0.0381 (6)	0.0331 (6)	0.0091 (4)	0.0580 (8)	0.0247 (7)	0.0214 (8)
C(15)	0.3355 (5)	0.1291 (4)	0.4557 (4)	0.0150 (5)	0.0139 (5)	0.0099 (4)	0.0139 (7)	0.0099 (7)	0.0099 (7)

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
H(3)	−0.402 (5)	0.367 (5)	−0.076 (5)	5.4 (12)	H(141)	−0.108 (5)	0.244 (5)	−0.112 (5)	5.5 (11)
H(4)	−0.449 (5)	0.387 (4)	0.136 (4)	3.5 (9)	H(142)	−0.293 (5)	0.167 (5)	−0.206 (4)	5.8 (11)
H(5)	−0.352 (5)	0.385 (4)	0.401 (4)	4.0 (10)	H(143)	−0.163 (5)	0.371 (5)	−0.151 (5)	5.6 (11)
H(6)	−0.174 (5)	0.338 (5)	0.600 (4)	4.2 (10)	H(151)	0.331 (5)	0.110 (5)	0.375 (5)	5.1 (11)
H(7)	0.070 (5)	0.248 (5)	0.709 (4)	4.5 (10)	H(152)	0.457 (5)	0.208 (5)	0.524 (5)	5.3 (11)
H(8)	0.276 (5)	0.169 (5)	0.691 (4)	4.9 (11)	H(153)	0.326 (5)	0.017 (5)	0.461 (4)	5.5 (11)

(d) $[Ni(dmp)Br_2]_2$

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Br(1)	−0.1274 (1)	0.06438 (5)	−0.14373 (5)	0.0165 (1)	0.00657 (5)	0.00574 (5)	0.0064 (2)	0.0075 (1)	0.00130 (8)
Br(2)	−0.1129 (1)	0.36632 (5)	0.10781 (5)	0.0133 (1)	0.00784 (5)	0.00784 (5)	0.0088 (1)	0.0088 (1)	0.00394 (8)
Ni	0.0215 (1)	0.16692 (6)	0.13177 (6)	0.0083 (1)	0.00592 (6)	0.00511 (6)	0.0026 (2)	0.0059 (2)	0.00078 (9)
N(1)	0.3066 (7)	0.2754 (4)	0.2742 (4)	0.0095 (9)	0.0045 (3)	0.0055 (4)	0.002 (1)	0.007 (1)	−0.0006 (6)
N(2)	0.0209 (7)	0.1689 (4)	0.3290 (4)	0.0110 (9)	0.0048 (3)	0.0077 (4)	0.004 (1)	0.011 (1)	0.0019 (6)
C(2)	0.4399 (9)	0.3312 (5)	0.2399 (5)	0.011 (1)	0.0053 (4)	0.0081 (5)	0.004 (1)	0.011 (1)	0.0010 (8)
C(3)	0.6417 (9)	0.3944 (5)	0.3580 (6)	0.010 (1)	0.0064 (5)	0.0095 (6)	0.004 (1)	0.010 (1)	0.0023 (9)
C(4)	0.6946 (9)	0.3963 (5)	0.5028 (6)	0.007 (1)	0.0063 (5)	0.0096 (6)	0.004 (1)	0.003 (1)	−0.0007 (9)
C(5)	0.5952 (10)	0.3419 (5)	0.6914 (5)	0.015 (1)	0.0071 (5)	0.0058 (5)	0.005 (2)	0.002 (2)	0.0013 (8)
C(6)	0.4507 (11)	0.2957 (5)	0.7203 (5)	0.020 (2)	0.0074 (5)	0.0058 (5)	0.007 (2)	0.007 (2)	0.0031 (8)
C(7)	0.0860 (11)	0.1944 (5)	0.6215 (5)	0.024 (1)	0.0070 (5)	0.0071 (5)	0.009 (2)	0.017 (1)	0.0056 (8)
C(8)	−0.0960 (10)	0.1391 (5)	0.5001 (6)	0.023 (1)	0.0074 (5)	0.0132 (5)	0.014 (2)	0.027 (1)	0.0100 (8)
C(9)	−0.1278 (9)	0.1235 (5)	0.3516 (6)	0.013 (1)	0.0051 (4)	0.0113 (6)	0.007 (1)	0.016 (1)	0.0046 (8)
C(10)	0.2470 (10)	0.2382 (4)	0.5993 (5)	0.019 (1)	0.0047 (4)	0.0081 (5)	0.008 (1)	0.015 (1)	0.0048 (7)
C(11)	0.2075 (9)	0.2270 (4)	0.4508 (5)	0.013 (1)	0.0041 (4)	0.0065 (5)	0.004 (1)	0.009 (1)	0.0017 (7)
C(12)	0.3581 (9)	0.2799 (4)	0.4194 (5)	0.009 (1)	0.0043 (4)	0.0059 (5)	0.005 (1)	0.005 (1)	0.0005 (7)
C(13)	0.5569 (9)	0.3406 (5)	0.5413 (5)	0.010 (1)	0.0054 (4)	0.0068 (5)	0.006 (1)	0.003 (1)	0.0013 (8)
C(14)	0.3761 (10)	0.3307 (6)	0.0809 (6)	0.016 (1)	0.0087 (6)	0.0085 (5)	−0.000 (2)	0.015 (1)	0.0006 (9)
C(15)	−0.3264 (10)	0.0579 (6)	0.2144 (6)	0.011 (1)	0.0090 (6)	0.0131 (7)	0.003 (2)	0.014 (1)	0.0047 (10)

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
H(3)	0.74 (1)	0.432 (5)	0.316 (6)	3 (2)	H(141)	0.45 (1)	0.403 (6)	0.043 (6)	5
H(4)	0.81 (1)	0.417 (6)	0.558 (7)	5 (2)	H(142)	0.22 (1)	0.356 (6)	0.039 (6)	5
H(5)	0.71 (1)	0.359 (5)	0.783 (6)	4 (2)	H(143)	0.35 (1)	0.248 (6)	0.027 (6)	5
H(6)	0.49 (1)	0.296 (5)	0.821 (6)	2 (1)	H(151)	−0.36 (1)	0.107 (6)	0.162 (6)	5
H(7)	0.10 (1)	0.183 (6)	0.704 (6)	4 (2)	H(152)	−0.31 (1)	−0.007 (6)	0.162 (6)	5
H(8)	−0.20 (1)	0.115 (6)	0.517 (7)	5 (2)	H(153)	−0.40 (1)	0.044 (6)	0.265 (6)	5

(e) $Ni(bc)I_2$

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
I(1)	0.29805 (7)	−0.03569 (4)	−0.11036 (9)	0.01232 (7)	0.00256 (2)	0.0175 (1)	0.00021 (6)	0.0047 (2)	0.00334 (8)
I(2)	0.21019 (7)	−0.03520 (3)	0.39706 (9)	0.01553 (8)	0.00202 (1)	0.0191 (1)	0.00015 (6)	0.0119 (2)	−0.00142 (8)
Ni	0.2550 (1)	−0.07926 (5)	0.1456 (1)	0.00686 (9)	0.00107 (2)	0.0158 (2)	0.00001 (9)	0.0003 (2)	−0.0003 (1)
N(1)	0.3589 (6)	−0.1428 (3)	0.1980 (8)	0.0059 (5)	0.0013 (1)	0.011 (1)	−0.0003 (5)	0.000 (1)	0.0012 (7)
N(2)	0.1553 (6)	−0.1428 (3)	0.0655 (8)	0.0060 (5)	0.0012 (1)	0.014 (1)	0.0006 (5)	0.002 (1)	0.0001 (7)
C(2)	0.4620 (7)	−0.1398 (4)	0.2632 (10)	0.0059 (7)	0.0017 (2)	0.012 (1)	−0.0006 (6)	−0.001 (2)	0.0014 (9)
C(3)	0.5254 (7)	−0.1893 (4)	0.2819 (11)	0.0048 (7)	0.0020 (2)	0.016 (2)	−0.0009 (6)	−0.001 (2)	0.0003 (10)
C(4)	0.4845 (7)	−0.2432 (4)	0.2335 (10)	0.0048 (6)	0.0016 (2)	0.014 (1)	−0.0003 (6)	0.001 (2)	−0.0006 (9)
C(5)	0.3206 (7)	−0.2973 (4)	0.0951 (11)	0.0057 (7)	0.0011 (2)	0.018 (2)	0.0003 (6)	0.004 (2)	−0.0003 (9)
C(6)	0.2162 (7)	−0.2975 (4)	0.0312 (10)	0.0052 (6)	0.0012 (2)	0.015 (1)	−0.0010 (6)	0.003 (2)	−0.0020 (8)
C(7)	0.0424 (7)	−0.2442 (4)	−0.0321 (10)	0.0058 (7)	0.0014 (2)	0.013 (1)	−0.0004 (6)	0.004 (2)	−0.0008 (9)
C(8)	−0.0046 (7)	−0.1901 (4)	−0.0434 (12)	0.0043 (6)	0.0021 (2)	0.018 (2)	−0.0006 (7)	0.001 (2)	−0.0009 (10)
C(9)	0.0514 (8)	−0.1404 (4)	0.0015 (11)	0.0065 (7)	0.0014 (2)	0.016 (2)	0.0000 (6)	0.002 (2)	−0.0008 (9)
C(10)	0.1535 (7)	−0.2467 (4)	0.0258 (10)	0.0057 (6)	0.0013 (2)	0.013 (1)	−0.0004 (6)	0.003 (2)	−0.0016 (8)
C(11)	0.2058 (7)	−0.1951 (3)	0.0784 (10)	0.0050 (6)	0.0012 (2)	0.012 (1)	−0.0004 (5)	0.005 (1)	−0.0004 (8)

Table I (*Continued*)

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(12)	0.3167 (7)	−0.1950 (3)	0.1474 (9)	0.0051 (6)	0.0012 (2)	0.010 (1)	−0.0002 (6)	0.002 (1)	−0.0003 (8)
C(13)	0.3745 (7)	−0.2458 (4)	0.1608 (10)	0.0049 (6)	0.0015 (2)	0.012 (1)	0.0002 (6)	0.001 (2)	0.0011 (9)
C(14)	0.5089 (9)	−0.0808 (4)	0.3202 (14)	0.0076 (8)	0.0014 (2)	0.027 (2)	−0.0022 (7)	−0.008 (2)	−0.0016 (11)
C(15)	−0.0005 (9)	−0.0815 (4)	−0.0155 (14)	0.0067 (8)	0.0015 (2)	0.030 (2)	0.0022 (7)	−0.001 (2)	−0.0000 (12)
C(16)	0.5524 (7)	−0.2943 (4)	0.2536 (10)	0.0057 (7)	0.0016 (2)	0.013 (1)	0.0011 (6)	−0.002 (2)	0.0002 (9)
C(17)	0.6461 (8)	−0.2957 (5)	0.1970 (11)	0.0067 (8)	0.0024 (2)	0.015 (2)	−0.0005 (8)	−0.001 (2)	−0.0012 (11)
C(18)	0.7097 (8)	−0.3442 (6)	0.2151 (14)	0.0047 (7)	0.0041 (3)	0.024 (2)	0.0022 (9)	0.000 (2)	−0.0055 (14)
C(19)	0.6797 (10)	−0.3914 (5)	0.2953 (15)	0.0088 (10)	0.0027 (3)	0.029 (2)	0.0035 (8)	−0.010 (3)	−0.0067 (13)
C(20)	0.5897 (9)	−0.3911 (5)	0.3566 (15)	0.0084 (9)	0.0021 (2)	0.028 (2)	0.0016 (8)	−0.006 (3)	−0.0001 (13)
C(21)	0.5269 (9)	−0.3422 (4)	0.3343 (12)	0.0088 (9)	0.0019 (2)	0.018 (2)	0.0025 (8)	−0.000 (2)	0.0011 (11)
C(22)	−0.0251 (7)	−0.2965 (4)	−0.0729 (11)	0.0046 (6)	0.0019 (2)	0.017 (2)	−0.0007 (6)	0.002 (2)	−0.0029 (10)
C(23)	−0.0100 (8)	−0.3456 (4)	0.0225 (12)	0.0069 (7)	0.0018 (2)	0.022 (2)	−0.0021 (7)	0.008 (2)	−0.0021 (11)
C(24)	−0.0729 (9)	−0.3934 (5)	−0.0163 (15)	0.0102 (9)	0.0020 (2)	0.032 (2)	−0.0021 (8)	0.014 (2)	−0.0009 (13)
C(25)	−0.1523 (10)	−0.3935 (5)	−0.1491 (15)	0.0096 (10)	0.0027 (3)	0.034 (3)	−0.0039 (9)	0.010 (3)	−0.0087 (13)
C(26)	−0.1719 (9)	−0.3456 (6)	−0.2499 (14)	0.0074 (9)	0.0038 (3)	0.026 (2)	−0.0018 (9)	0.003 (2)	−0.0082 (14)
C(27)	−0.1073 (8)	−0.2964 (4)	−0.2112 (12)	0.0064 (8)	0.0021 (2)	0.020 (2)	−0.0005 (7)	0.002 (2)	−0.0029 (11)

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
H(3)	0.596 (6)	−0.185 (3)	0.311 (8)	3 (2)	H(20)	0.561 (8)	−0.423 (4)	0.417 (11)	7 (3)
H(5)	0.352 (6)	−0.331 (3)	0.092 (8)	2 (2)	H(21)	0.467 (7)	−0.345 (4)	0.378 (10)	6 (2)
H(6)	0.187 (6)	−0.332 (3)	0.002 (9)	3 (2)	H(23)	0.046 (7)	−0.343 (4)	0.117 (10)	6 (2)
H(8)	−0.066 (6)	−0.192 (3)	−0.082 (8)	2 (2)	H(24)	−0.053 (7)	−0.431 (4)	0.052 (10)	6 (2)
H(17)	0.665 (5)	−0.268 (3)	0.151 (8)	2 (2)	H(25)	−0.195 (7)	−0.421 (4)	−0.163 (10)	6 (2)
H(18)	0.766 (7)	−0.340 (3)	0.161 (9)	4 (2)	H(26)	−0.215 (7)	−0.342 (4)	−0.330 (10)	6 (2)
H(19)	0.736 (8)	−0.423 (4)	0.305 (11)	7 (3)	H(27)	−0.128 (6)	−0.264 (3)	−0.280 (9)	3 (2)

[a] The form of the anisotropic thermal parameter is $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$.

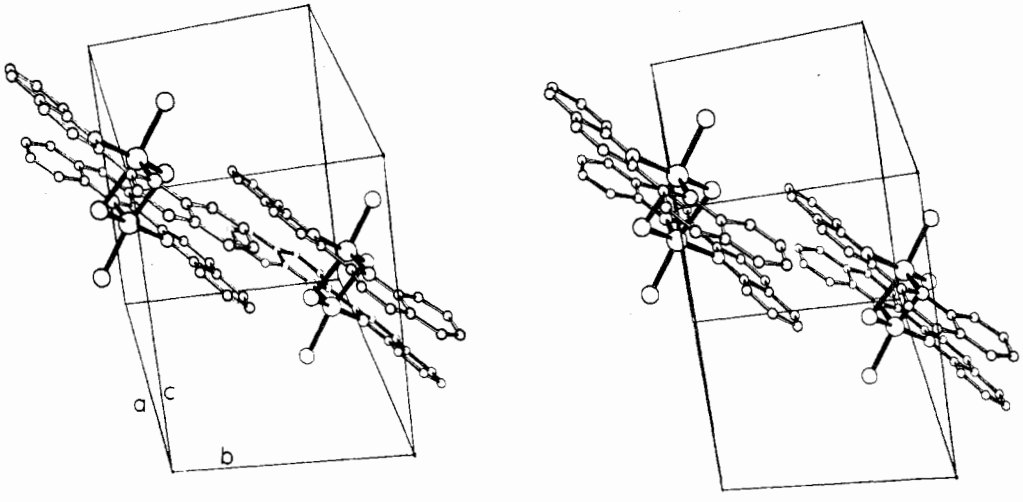

Figure 6. Molecular packing in $[Ni(biq)Cl_2]_2$.

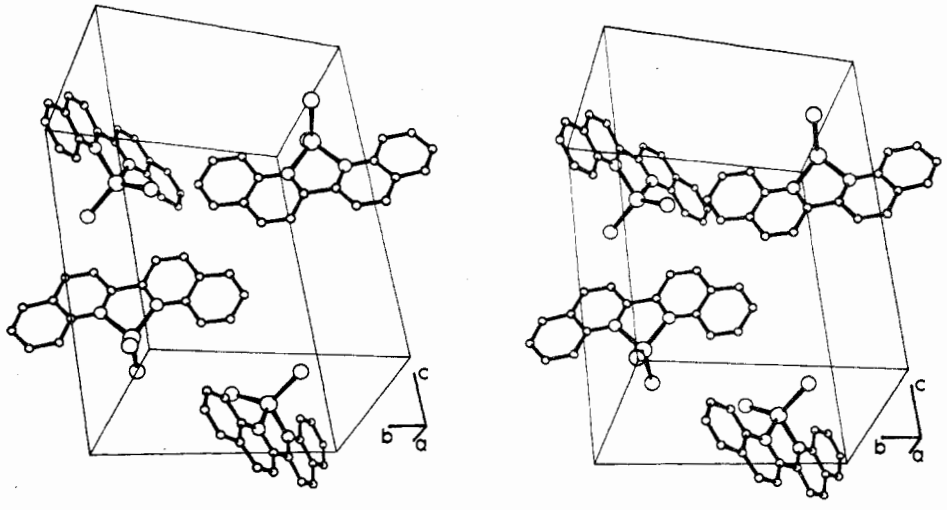

Figure 7. Molecular packing in $Ni(biq)Br_2$.

Table II. Bond Lengths (Å) for $[Ni(biq)Cl_2]_2$, $Ni(biq)Br_2$, $[Ni(dmp)Cl_2]_2$, $[Ni(dmp)Br_2]_2$, and $Ni(bc)I_2$

	$[Ni(biq)Cl_2]_2$	$Ni(biq)Br_2$		$[Ni(biq)Cl_2]_2$	$Ni(biq)Br_2$
Ni-X(1)	2.372 (1)	2.331 (1)	C(5)-C(7)	1.415 (3)	1.42 (1)
Ni-X(1′)	2.400 (1)		C(6)-C(10)	1.410 (3)	1.408 (8)
Ni-X(2)	2.306 (1)	2.351 (1)	C(7)-C(8)	1.352 (3)	1.36 (1)
Ni-N	2.034 (1)	1.991 (5)	C(8)-C(9)	1.404 (3)	1.38 (1)
Ni-N′	2.042 (2)	1.993 (5)	C(9)-C(10)	1.358 (3)	1.38 (1)
N-C(2)	1.323 (2)	1.330 (7)	C(2′)-C(3′)	1.407 (3)	1.411 (9)
N-C(6)	1.377 (2)	1.377 (8)	C(3′)-C(4′)	1.354 (3)	1.366 (9)
N′-C(2′)	1.388 (2)	1.328 (7)	C(4′)-C(5′)	1.406 (3)	1.412 (9)
N′-C(6′)	1.378 (2)	1.378 (8)	C(5′)-C(6′)	1.417 (3)	1.416 (8)
C(2)-C(3)	1.414 (3)	1.408 (9)	C(5′)-C(7′)	1.412 (3)	1.43 (1)
C(2)-C(2′)	1.483 (3)	1.494 (9)	C(6′)-C(10′)	1.412 (3)	1.399 (8)
C(3)-C(4)	1.362 (3)	1.351 (9)	C(7′)-C(8′)	1.362 (3)	1.346 (9)
C(4)-C(5)	1.409 (3)	1.394 (9)	C(8′)-C(9′)	1.392 (3)	1.39 (1)
C(5)-C(6)	1.419 (3)	1.405 (8)	C(9′)-C(10′)	1.359 (3)	1.38 (1)

	$[Ni(dmp)Cl_2]_2$	$[Ni(dmp)Br_2]_2$	$Ni(bc)I_2$		$[Ni(dmp)Cl_2]_2$	$[Ni(dmp)Br_2]_2$	$Ni(bc)I_2$
Ni-X(1)	2.378 (1)	2.468 (1)	2.515 (1)	N(1)-C(2)	1.337 (3)	1.329 (3)	1.331 (6)
Ni-X(1′)	2.414 (1)	2.649 (1)		N(1)-C(12)	1.371 (3)	1.356 (3)	1.362 (6)
Ni-X(2)	2.307 (1)	2.458 (1)	2.497 (1)	N(2)-C(9)	1.335 (3)	1.323 (4)	1.338 (7)
Ni-N(1)	2.033 (2)	2.021 (2)	1.981 (4)	N(2)-C(11)	1.362 (3)	1.374 (3)	1.372 (6)
Ni-N(2)	2.049 (2)	2.034 (2)	1.983 (4)	C(2)-C(3)	1.402 (3)	1.443 (4)	1.402 (8)
C(2)-C(14)	1.488 (3)	1.485 (3)	1.535 (7)	C(12)-C(13)	1.401 (3)	1.436 (3)	1.389 (7)
C(3)-C(4)	1.366 (4)	1.355 (3)	1.388 (7)	C(16)-C(17)			1.381 (8)
C(4)-C(13)	1.409 (3)	1.389 (4)	1.425 (7)	C(16)-C(21)			1.373 (8)
C(4)-C(16)			1.464 (7)	C(17)-C(18)			1.383 (9)
C(5)-C(6)	1.352 (3)	1.338 (5)	1.342 (7)	C(18)-C(19)			1.38 (1)
C(5)-C(13)	1.432 (3)	1.436 (3)	1.435 (7)	C(19)-C(20)			1.36 (1)
C(6)-C(10)	1.426 (4)	1.455 (4)	1.425 (7)	C(20)-C(21)			1.386 (9)
C(7)-C(8)	1.348 (4)	1.349 (4)	1.391 (7)	C(22)-C(23)			1.379 (8)
C(7)-C(10)	1.411 (3)	1.405 (5)	1.416 (7)	C(22)-C(27)			1.397 (7)
C(7)-C(22)			1.493 (7)	C(23)-C(24)			1.376 (9)
C(8)-C(9)	1.415 (3)	1.411 (4)	1.375 (7)	C(24)-C(25)			1.35 (1)
C(9)-C(15)	1.481 (3)	1.496 (4)	1.517 (8)	C(25)-C(26)			1.39 (1)
C(10)-C(11)	1.402 (3)	1.399 (3)	1.402 (7)	C(26)-C(27)			1.412 (9)
C(11)-C(12)	1.436 (3)	1.416 (4)	1.428 (7)				

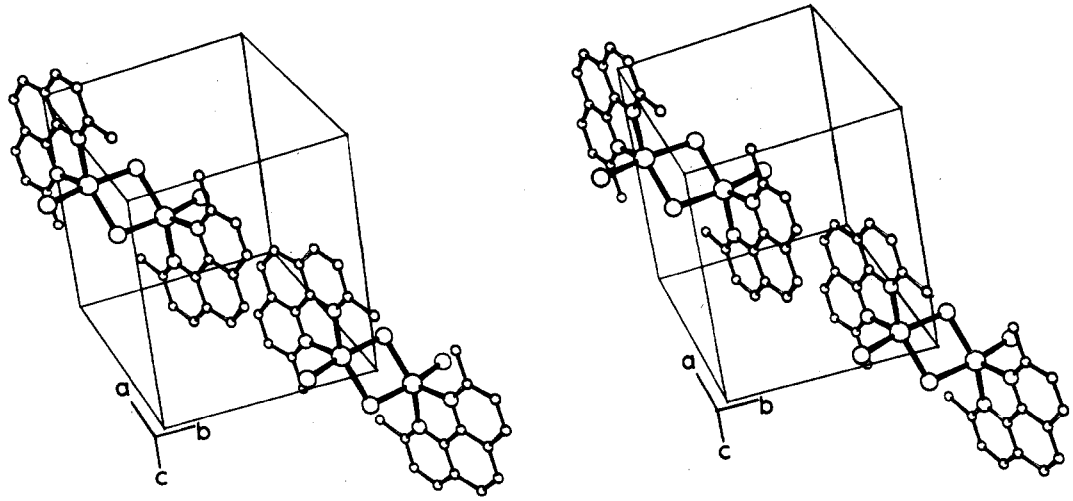

Figure 8. Molecular packing in $[Ni(dmp)Cl_2]_2$.

to intramolecular steric repulsions.[2]

Ni(biq)Br$_2$ consists of discrete monomeric molecules (Figures 2 and 7) the closest intermolecular contact (3.62 Å) being between bromine and a quinolyl carbon of an adjacent molecule. The Ni–Br bonds differ in length (2.331 (1) vs. 2.351 (1) Å) but not as much as do the bridging and nonbridging Ni–Cl bonds of $[Ni(biq)Cl_2]_2$. The two Ni–N bond lengths do not differ significantly and are shorter (1.99 Å) than in the chloro analogue. The two quinolyl fragments of the biq ligand in $Ni(biq)Br_2$ are relatively undistorted and are well clear of the bromine atoms, suggesting strongly that the distortion observed in $[Ni(biq)Cl_2]_2$ is due to steric interaction. The geometry about the metal atom is approximately tetrahedral, with distortions indicated by the unequal metal–ligand bond lengths and angles (125, 110, 116, 112, 115, and 83°) and by the deviation from 90° of the angle (84.9°) between the $NiBr_2$ plane and the NiN_2 plane.

[Ni(dmp)Cl$_2$]$_2$ consists of discrete dimeric molecules (Figures 3 and 8) the closest intermolecular approaches (>3.4 Å) being between the aromatic carbon atoms of the dmp ligands in neighboring molecules. The halves of the dimer are related by the crystallographic center of symmetry. The bridging Ni–Cl bonds are unequal (2.378 (1), 2.414 (1) Å) to about the same extent as in $[Ni(biq)Cl_2]_2$ but much more than in $[Mn(biq)Cl_2]_2$.[2] The shorter nonbridging Ni–Cl bond is equal in length to that in $[Ni(biq)Cl_2]_2$.

Table III. Bond Angles (deg) for $[Ni(biq)Cl_2]_2$, $Ni(biq)Br_2$, $[Ni(dmp)Cl_2]_2$, $[Ni(dmp)Br_2]_2$, and $Ni(bc)I_2$

	$[Ni(biq)Cl_2]_2$	$Ni(biq)Br_2$		$[Ni(biq)Cl_2]_2$	$Ni(biq)Br_2$
X(1)-Ni-X(1′)	83.32 (2)		C(6)-C(5)-C(7)	118.4 (2)	118.5 (6)
X(1)-Ni-X(2)	90.22 (2)	124.94 (4)	N-C(6)-C(5)	120.8 (2)	120.9 (6)
X(1)-Ni-N	157.55 (5)	109.5 (2)	N-C(6)-C(10)	119.4 (2)	118.4 (6)
X(1)-Ni-N′	121.17 (4)	115.5 (2)	C(5)-C(6)-C(10)	119.8 (2)	120.7 (7)
X(1′)-Ni-X(2)	164.03 (2)		C(5)-C(7)-C(8)	120.6 (2)	119.8 (7)
X(1′)-Ni-N	89.31 (5)		C(7)-C(8)-C(9)	120.5 (2)	120.9 (7)
X(1′)-Ni-N′	94.02 (5)		C(8)-C(9)-C(10)	121.1 (2)	121.7 (7)
X(2)-Ni-N	91.22 (5)	111.8 (2)	C(6)-C(10)-C(9)	119.5 (2)	118.3 (7)
X(2)-Ni-N′	101.81 (5)	104.5 (2)	N′-C(2′)-C(2)	115.5 (2)	115.1 (5)
N-Ni-N′	80.37 (6)	82.6 (2)	N′-C(2′)-C(3′)	122.2 (2)	121.7 (6)
Ni-X(1)-Ni′	96.68 (2)		C(2)-C(2′)-C(3′)	122.3 (2)	123.2 (6)
Ni-N-C(2)	114.6 (2)	113.1 (5)	C(2′)-C(3′)-C(4′)	120.0 (2)	121.3 (6)
Ni-N-C(6)	125.6 (2)	128.0 (4)	C(3′)-C(4′)-C(5′)	119.8 (2)	117.0 (6)
C(2)-N-C(6)	119.6 (6)	118.9 (6)	C(4′)-C(5′)-C(6′)	118.2 (2)	120.6 (6)
Ni-N′-C(2′)	113.7 (2)	112.7 (4)	C(4′)-C(5′)-C(7′)	122.6 (2)	122.3 (6)
Ni-N′-C(6′)	127.5 (2)	127.1 (4)	C(6′)-C(5′)-C(7′)	119.2 (2)	117.1 (6)
C(2′)-N′-C(6′)	118.7 (2)	119.7 (5)	N′-C(6′)-C(5′)	121.2 (2)	119.7 (6)
N-C(2)-C(3)	122.5 (2)	122.5 (7)	N′-C(6′)-C(10′)	119.4 (2)	118.8 (6)
N-C(2)-C(2′)	115.3 (2)	115.2 (6)	C(5′)-C(6′)-C(10′)	119.3 (2)	121.5 (7)
C(3)-C(2)-C(2′)	122.2 (2)	122.3 (6)	C(5′)-C(7′)-C(8′)	120.2 (2)	120.7 (7)
C(2)-C(3)-C(4)	118.9 (2)	118.7 (6)	C(7′)-C(8′)-C(9′)	120.0 (2)	121.4 (7)
C(3)-C(4)-C(5)	120.3 (2)	120.7 (6)	C(8′)-C(9′)-C(10′)	122.2 (2)	120.8 (7)
C(4)-C(5)-C(6)	117.9 (2)	118.3 (7)	C(6′)-C(10′)-C(9′)	119.2 (2)	118.5 (7)
C(4)-C(5)-C(7)	123.7 (2)	123.2 (7)			

	$[Ni(dmp)Cl_2]_2$	$[Ni(dmp)Br_2]_2$	$Ni(bc)I_2$		$[Ni(dmp)Cl_2]_2$	$[Ni(dmp)Br_2]_2$	$Ni(bc)I_2$
X(1)-Ni-X(1′)	82.6 (1)	83.26 (1)		N(1)-C(2)-C(14)	117.7 (2)	119.1 (2)	118.1 (5)
X(1)-Ni-X(2)	91.51 (2)	94.28 (1)	132.04 (3)	C(3)-C(2)-C(14)	121.1 (2)	121.4 (3)	121.0 (5)
X(1)-Ni-N(1)	121.65 (5)	125.61 (6)	103.5 (1)	C(2)-C(3)-C(4)	120.9 (2)	120.1 (3)	122.1 (5)
X(1)-Ni-N(2)	155.41 (5)	149.79 (6)	104.7 (1)	C(3)-C(4)-C(13)	119.1 (2)	121.3 (3)	116.7 (5)
X(1′)-Ni-X(2)	168.5 (1)	173.94 (2)		C(3)-C(4)-C(16)			121.1 (5)
X(1′)-Ni-N(1)	93.4 (1)	89.05 (6)		C(13)-C(4)-C(16)	120.6 (2)	122.0 (3)	122.2 (5)
X(1′)-Ni-N(2)	89.9 (1)	86.66 (6)		C(6)-C(5)-C(13)	121.3 (2)	121.1 (2)	121.5 (5)
X(2)-Ni-N(1)	98.15 (5)	96.87 (6)	112.4 (1)	C(5)-C(6)-C(10)	120.3 (2)	119.2 (2)	121.8 (5)
X(2)-Ni-N(2)	91.51 (5)	92.81 (6)	110.1 (1)	C(8)-C(7)-C(10)			117.1 (5)
N(1)-Ni-N(2)	82.00 (7)	82.44 (8)	83.2 (2)	C(8)-C(7)-C(22)			119.7 (5)
Ni-X(1)-Ni′	97.4 (1)	96.74 (1)		C(10)-C(7)-C(22)	120.9 (2)	121.4 (3)	123.1 (5)
Ni-N(1)-C(2)	129.5 (1)	128.2 (2)	128.6 (4)	C(7)-C(8)-C(9)	120.1 (2)	120.2 (3)	123.1 (5)
Ni-N(1)-C(12)	112.1 (1)	111.2 (2)	112.8 (3)	N(2)-C(9)-C(8)	117.9 (2)	117.1 (3)	120.1 (5)
C(2)-N(1)-C(12)	118.4 (2)	120.5 (2)	118.5 (4)	N(2)-C(9)-C(15)	122.0 (2)	122.8 (3)	117.5 (5)
Ni-N(2)-C(9)	128.9 (1)	129.5 (2)	129.1 (4)	C(8)-C(9)-C(15)	124.5 (2)	124.4 (2)	122.4 (6)
Ni-N(2)-C(11)	111.9 (1)	111.0 (2)	111.7 (3)	C(6)-C(10)-C(7)	119.4 (2)	118.1 (3)	124.9 (5)
C(9)-N(2)-C(11)	119.2 (2)	119.5 (2)	119.2 (4)	C(6)-C(10)-C(11)	116.1 (2)	117.5 (3)	117.7 (5)
N(1)-C(2)-C(3)	121.2 (2)	119.5 (2)	120.8 (5)	C(7)-C(10)-C(11)			117.4 (5)
N(2)-C(11)-C(10)	123.5 (2)	122.1 (3)	122.9 (5)				
N(2)-C(11)-C(12)	117.0 (2)	116.7 (2)	116.7 (5)	C(16)-C(17)-C(18)			121.4 (6)
C(10)-C(11)-C(12)	119.4 (2)	121.2 (2)	120.3 (5)	C(17)-C(18)-C(19)			118.9 (7)
N(1)-C(12)-C(11)	117.0 (2)	118.1 (2)	115.5 (5)	C(18)-C(19)-C(20)			121.5 (7)
N(1)-C(12)-C(13)	123.1 (2)	122.3 (3)	124.0 (5)	C(19)-C(20)-C(21)			118.2 (7)
C(11)-C(12)-C(13)	119.9 (2)	119.6 (2)	120.6 (5)	C(16)-C(21)-C(20)			122.7 (7)
C(4)-C(13)-C(5)	123.3 (2)	125.9 (3)	124.1 (5)	C(7)-C(22)-C(23)			122.3 (5)
C(4)-C(13)-C(12)	117.3 (2)	116.3 (2)	118.0 (5)	C(7)-C(22)-C(27)			119.7 (5)
C(5)-C(13)-C(12)	119.4 (2)	117.9 (3)	117.9 (5)	C(23)-C(22)-C(27)			118.1 (5)
C(4)-C(16)-C(17)			121.5 (5)	C(22)-C(23)-C(24)			121.7 (6)
C(4)-C(16)-C(21)			121.2 (6)	C(23)-C(24)-C(25)			120.5 (7)
C(17)-C(16)-C(21)			117.3 (5)	C(24)-C(25)-C(26)			120.7 (7)
				C(25)-C(26)-C(27)			119.1 (6)
				C(22)-C(27)-C(26)			120.06

The metal environment may be viewed as a distorted trigonal bipyramid with the nickel atom 0.34 Å from the equatorial plane. The deviation of the Cl(2)–Ni–Cl(1′) axis from linearity (168.5°) and the deviation from 120° of the nickel ligand bond angles in the equatorial plane (155.4, 121.7, 82.0°) give a measure of the distortion from ideal trigonal-bipyramidal geometry. Although the extent of this distortion is considerable, it is significantly smaller than in $[Ni(biq)Cl_2]_2$. The dimeric molecule consists of the two distorted trigonal bipyramids with one apex of each joined to an equatorial corner of the other. The metal environment may also be regarded as distorted square pyramidal with a slightly shorter (2.033 (2) vs. 2.049 (2) Å) Ni–N bond to the off-center apex and with the nickel atom 0.34 Å above the pyramid base (Cl(1)–Cl(1′)–Cl(2)–N(2)). The dimeric molecule is then formed by joining the two square pyramids at an edge of the base. The Ni–Ni separation is 3.600 Å and the Ni–Cl–Ni bridging angle is 97.4°. As with $[Ni(biq)Cl_2]_2$, there appears to be steric interaction, albeit a less severe one, between the bridging Ni_2Cl_2 group (near the Cl(1) atom) and the organic ligands (at the C(14) methyl atom).

$[Ni(dmp)Br_2]_2$ consists of discrete dimeric molecules, the halves of which are centrosymmetrically related as in $[Ni(biq)Cl_2]_2$ and $[Ni(dmp)Cl_2]_2$ but dramatically different in detail. The closest intermolecular contacts (>3.3 Å) are between aromatic carbon atoms in neighboring molecules. The asymmetry of the bridging bonds is more than 5 times as great as in either of the chloro complexes $[Ni(biq)Cl_2]_2$ and $[Ni(dmp)Cl_2]_2$ or in the manganese(II) analogue $[Mn(biq)Cl_2]_2$;[2] the nonbridging NiBr bond is almost the same (2.458 Å) as

the shorter of the two bridging bonds. Thus one of the bridging bonds in $[Ni(dmp)Br_2]_2$ is approximately "normal" and the other one is markedly weakened. This contrasts with the observations in $[Ni(biq)Cl_2]_2$ and $[Ni(dmp)Cl_2]_2$, which have both bridging bonds weakened, though to slightly different degrees. Steric interactions between the Ni_2Br_2 bridge and the organic ligand, as in $[Ni(dmp)Cl_2]_2$, are considered to be responsible for the asymmetry of the bridging. Indeed the steric requirements of the ligands are believed to cause the differences between the bromo and chloro complexes $[Ni(dmp)Br_2]_2$, $Ni(biq)Br_2$, $[Ni(dmp)Cl_2]_2$, and $[Ni(biq)Cl_2]_2$; vide infra.

If the metal environment is regarded as distorted trigonal bipyramidal, the extent of the distortion (bond angles in equatorial plane 125.6, 149.8, 82.4°; Br(1′)–Ni–Br(2) = 173.9°) is markedly smaller than in either $[Ni(biq)Cl_2]_2$ or $[Ni(dmp)Cl_2]_2$. The nickel atom is located 0.17 Å from the equatorial plane. If the geometry about the metal atom is viewed as distorted square pyramidal, the nickel is 0.34 Å above the pyramid base (Br(1)–Br(1′)–Br(2)–N(2)), and the molecule consists of the two square pyramids joined at an edge of each of the square bases. The Ni–Ni separation is 3.826 Å and the Ni–Br–Ni bridging angle is 96.7°, in keeping with the much weaker bridging here than in the two chlorine-bridged dimers.

Ni(bc)I_2 consists of discrete monomeric molecules (Figure 5), the closest intermolecular approach (3.305 Å) being between aromatic carbon atoms in neighboring molecules. As in $Ni(biq)Br_2$, the Ni–N bonds do not differ significantly. The Ni–N bonds in both the monomeric complexes $Ni(biq)Br_2$ and $Ni(bc)I_2$ are significantly shorter than in any of the dimers. The Ni–I bonds differ in length (2.497 (1) vs. 2.515 (1) Å) but not as much as the bridging bonds in any of the dimeric complexes. The metal atom is in an approximately tetrahedral environment, with distortions from an ideal tetrahedron indicated by the unequal metal–ligand bond lengths and angles (132, 104, 105, 112, 110, and 83°) and by the deviation from 90° of the angle (88.7°) between the NiI_2 and NiN_2 planes. By the latter criterion, the distortion is slightly less in $Ni(bc)I_2$ than in $Ni(biq)Br_2$.

The ligands biq and dmp (or bc) restrict the space available to other ligands around the metal atom, due to interaction with C–H bonds (methyl carbon in dmp or bc; aromatic carbon in biq) adjacant to the nitrogen donor atoms in each case. The resulting steric constraints are similar for the two classes of ligand but slightly different due to differences in single vs. aromatic bond lengths and to phenyl vs. methyl hydrogen atom types.[12] The relative amounts of steric interaction will therefore be affected by very slight changes in the sizes and orientations of the bridging groups with respect to the organic ligand. For the present series of nickel complexes, the steric effect is greater for biq than dmp. Thus the bridging is slightly weaker in $[Ni(biq)Cl_2]_2$ than in $[Ni(dmp)Cl_2]_2$, while for the bulkier bromo complexes, a weakly bridged dimer is formed with dmp and a monomer with biq. It appears that the nickel complexes of this general type are dimeric when steric interactions permit the monomeric halves $NiLX_2$ to approach sufficiently closely. The dimerization therefore results from a drive to attain a five-coordinated ligand environment about the nickel atom, while steric factors control the strength of the bridging bonds between the monomeric units and the ability to form these bonds.

The structures for the various nickel complexes show a trend from dimeric for the chloro, sometimes dimeric and sometimes monomeric for the bromo complexes, and monomeric for the iodo complexes. The steric control of dimerization implies that this trend should be general. This is in keeping with the magnetic properties observed for these and related complexes.[13] The magnetic properties of the various complexes have been determined down to 4 K, but since completion of that work, a magnetic study on one of the complexes $[Ni(dmp)Cl_2]_2$ has been reported[14] and the results are qualitatively in agreement with ours but show some quantitative differences. Although our results were found to be reproducible, further studies are being made of the magnetic properties to determine possible causes for the differences. However, it is already possible to make general correlations between the structures and magnetic properties. In each case the known dimeric complexes exhibit antiferromagnetic interactions. All preparations of a variety of chloro complexes and some bromo complexes are found to contain predominantly antiferromagnetic material with a small proportion of paramagnetic impurity. It seems likely that the paramagnetic impurities are the monomeric form of the complexes, especially since crystal structures have shown that both monomeric and dimeric bromo complexes can exist. The iodo complexes are normally paramagnetic but with magnetic moments that decrease slightly at low temperature, suggesting either the presence of some antiferromagnetic species or perhaps long-range interactions between isolated monomeric molecules. Thus, the magnetic properties suggest that monomeric molecules form in cases (such as for iodo complexes) where large steric interactions would be expected, supporting the postulate of steric control of dimerization for such complexes in general. Comparison of the chlorine-bridged dimers of manganese and nickel indicates a decrease in the M–Cl–M bridging angle coinciding with a decrease in the magnetic exchange coupling constant J from positive to negative values.[13]

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Registry No. $[Ni(biq)Cl_2]_2$, 63180-98-3; $Ni(biq)Br_2$, 14950-13-1; $[Ni(dmp)Cl_2]_2$, 29115-92-2; $[Ni(dmp)Br_2]_2$, 63180-99-4; $Ni(bc)I_2$, 63181-00-0.

Supplementary Material Available: Tables of closest intermolecular contacts, selected least-squares planes, and structure factor amplitudes and packing diagrams for $[Ni(dmp)Br_2]_2$ and $Ni(bc)I_2$ (53 pages). Ordering information is given on any current masthead page.

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