Transition Metal Chemistry of Quinuclidinone-Containing Ligands. IV. Crystal Structure of *trans*-2-(2'-Quinolyl)methylene-3-quinuclidinonedichloronickel(II), a Five-Coordinate Binuclear Complex[1]

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The crystal and molecular structure of the complex of nickel(II) chloride with *trans*-2-(2'-quinolyl)methylene-3-quinucli-dinone, Qnqn, has been determined using three-dimensional X-ray diffraction techniques, from 2122 independent reflections (above 2.5σ) collected on a four-circle diffractometer. The yellow crystals are triclinic, space group $P\bar{1}$, with (nonconventional) unit cell parameters $a = 9.041$ (3) Å, $b = 15.345$ (6) Å, $c = 8.622$ (7) Å, $\alpha = 42.93$ (3)°, $\beta = 90.16$ (3)°, $\gamma = 79.96$ (2)°, and $V = 788.3$ (9) Å³. The structure was solved by using Patterson and Fourier techniques and refined by full-matrix least-squares procedures. All nonhydrogen atoms were refined with anisotropic thermal parameters and all hydrogen atoms were located by electron difference methods; the resulting conventional R factor is 2.6%. There is one dimeric molecule, [Ni(Qnqn)Cl$_2$]$_2$, per unit cell with $\rho_{exptl} = 1.66$ (2) g/cm³ and $\rho_{calcd} = 1.659$ (3) g/cm³. The complex is binuclear, containing two nickel(II) ions, each with square-pyramidal coordination, with two slightly asymmetric bridging chloride ions (Ni–Cl distance 2.408 (2) and 2.422 (2) Å) in equatorial sites. The Ni–Ni nonbonded distance is 3.652 (1) Å. The two remaining equatorial coordination sites on each nickel ion are occupied by a terminal chloride ion (Ni–Cl distance, 2.296 (2) Å) and by the quinolyl nitrogen (Ni–N distance 2.047 (3) Å) atom. The apical coordination position is occupied by the quinuclidinone nitrogen (Ni–N distance 2.067 (2) Å) atom. The nickel ion is 0.40 Å above the basal plane of the square pyramid. The entire molecule is centrosymmetric. The bonding is discussed and compared with the bonding in other five-coordinate nickel complexes.

Introduction

During an investigation[2] of the complexes formed with several divalent first-row transition metal complexes and the ligand *trans*-2-(2'-quinolyl)methylene-3-quinuclidinone,
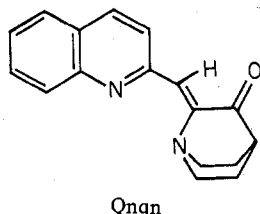
Qnqn

Qnqn, it was found that two isomeric (yellow and violet) complexes of stoichiometry Ni(Qnqn)Cl$_2$ could be isolated. A detailed spectral and magnetic study[1] of the violet complex indicated that it was pseudotetrahedral in coordination geometry. A similar study[1] of the spectral and magnetic properties of the yellow complex revealed that it was most likely a binuclear complex; but the spectral results obtained could not distinguish unambiguously among a five-coordinate square-pyramidal geometry, a five-coordinate trigonal-bi-pyramidal geometry, and a six-coordinate octahedral geometry. An additional study[3] of the thermal properties of the two isomers revealed that the isomers could be intercon-verted by a unique temperature-dependent structural transformation.

In order to determine more clearly the coordination geometry of the yellow isomer and to gain a better understanding of its unique thermal properties, we have undertaken a three-dimensional single-crystal X-ray diffraction study of the yellow isomer. The results of this study are presented in this paper.

Experimental Section

Preparation. The nickel chloride complex of Qnqn was prepared as described previously.[1] The single crystals were grown by the slow evaporation in a desiccator of a methylene chloride solution of the complex. After about 1 week a crop of single crystals of approximately 0.3–0.5 mm in their largest dimension resulted. An attempt to grow the crystals by evaporation outside a desiccator resulted in the initial formation of small yellow crystals. These, however, turned green, presumably from the addition of water, as evaporation continued. The dry yellow crystals, obtained by evaporation under anhydrous conditions, were found, nevertheless, to be unaffected by atmospheric moisture for a period of up to 3 months and hence no precautions were taken to protect the mounted crystals from the atmosphere. The crystals obtained were found to have identical spectral and thermal properties when compared with the powdered samples.[1,3]

Crystal Data. The crystal used for X-ray work was of approximate dimensions 0.1 × 0.3 × 0.6 mm and was mounted with its long dimension, c^*, approximately coincident with the spindle axis. The crystal was aligned using precession techniques. Zero- and first-order precession photographs obtained using Zr-filtered Mo Kα radiation yielded approximate unit cell parameters and indicated that the crystal was triclinic with either a $P\bar{1}$ or a $P1$ space group. The crystal was then transferred to a Picker four-circle automatic diffractometer, and the reflections were carefully centered using a narrow vertical slit in front of the counter and a takeoff angle of 0.8°. Twenty-three selected reflections of moderate to high intensity were then manually centered using Mo Kα radiation (λ 0.7107 Å) and the results were refined by a least-squares procedure[4] to obtain accurate unit cell parameters. For the triclinic crystal the nonconventional[5] unit cell parameters are $a = 9.041$ (3) Å, $b = 15.345$ (6) Å, $c = 8.622$ (7) Å, $\alpha = 42.93$ (3)°, $\beta = 90.16$ (3)°, $\gamma = 79.96$ (2)°, and $V = 788.3$ (9) Å³. The density calculated, assuming a dimer with stoichiometry [Ni-

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(1) Part III: G. J. Long and D. L. Coffen, *Inorg. Chem.*, **13**, 270 (1974).

(2) D. L. Coffen and T. E. McEntee, Jr., *J. Org. Chem.*, **35**, 503 (1970).

(3) G. J. Long, G. L. Bertrand, D. Noel, S. H. Wu, K. G. Mayhan, and D. L. Coffen, submitted for publication in *Inorg. Chem.*

(4) All calculations were preformed on the IBM 360/65 computer of the University of Missouri—Columbia Computer Research Center using the following programs: S. L. Lawton, TRACERA, Delauney reduction program; W. C. Hamilton, SORTH, sorting program; W. C. Hamilton and J. A. Ibers, NUPIK, Picker input program; W. C. Hamilton, HORSE, general adsorption program; R. Doedens and J. A. Ibers, NUCLS, least-squares program; a modification of W. Busing and H. Levy's program; A. Zalkin, FORDAP, Fourier program; W. Busing and H. Levy, ORFFE, function and error program; C. Johnson, ORTEP, thermal ellipsoid plot program; local data processing programs.

(5) All subsequent work was performed using this nonconventional unit cell. A Delauney reduction using TRACERA indicated that the conventional unit cell was triclinic. The conventional cell indices and fractional coordinates can be obtained by using the following 3 × 3 matrix: −1, 0, 0; 0, −1, 1; 0, 0, 1.

Table I. Final Positional and Anisotropic Thermal ($\times 10^4$) Parameters for Nonhydrogen Atoms[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	0.00620 (3)	0.13604 (3)	0.19211 (5)	69.9 (6)	39.3 (4)	146 (1)	−13.1 (3)	0.4 (5)	−51.8 (6)
Cl(1)	0.07367 (8)	−0.10208 (6)	0.5017 (1)	117 (1)	44.2 (7)	161 (2)	−14.2 (6)	6 (1)	−59 (1)
Cl(2)	0.16129 (8)	0.14338 (7)	−0.0268 (1)	101 (1)	69.4 (8)	249 (3)	−24.4 (7)	48 (1)	−100 (1)
N(1)	0.0221 (2)	0.3232 (2)	0.0004 (4)	89 (3)	52 (2)	177 (7)	−26 (2)	28 (4)	−76 (4)
N(2)	−0.2048 (2)	0.1876 (2)	0.0179 (4)	75 (3)	43 (2)	169 (7)	−13 (2)	4 (4)	−63 (3)
O	−0.4084 (2)	0.4415 (2)	−0.5693 (3)	121 (3)	89 (2)	190 (7)	−8 (2)	−20 (4)	−92 (4)
C(1)	−0.1839 (3)	0.4207 (3)	−0.3057 (4)	89 (4)	49 (3)	153 (8)	−7 (3)	11 (4)	−60 (4)
C(2)	−0.0624 (3)	0.4305 (2)	−0.2102 (4)	96 (4)	42 (3)	153 (8)	−20 (3)	34 (4)	−59 (4)
C(3)	−0.0374 (3)	0.5568 (3)	−0.3550 (5)	135 (5)	53 (3)	217 (10)	−36 (3)	72 (5)	−81 (5)
C(4)	0.0763 (4)	0.5729 (3)	−0.2807 (5)	157 (5)	67 (3)	285 (11)	−63 (3)	119 (6)	−113 (5)
C(5)	0.2927 (4)	0.4705 (4)	0.0241 (6)	155 (5)	136 (5)	375 (14)	−100 (4)	137 (7)	−198 (7)
C(6)	0.3820 (4)	0.3609 (4)	0.2336 (7)	157 (6)	194 (6)	403 (15)	−115 (5)	118 (8)	−247 (9)
C(7)	0.3547 (4)	0.2359 (4)	0.3690 (6)	130 (5)	156 (5)	295 (12)	−72 (4)	44 (6)	−166 (7)
C(8)	0.2365 (4)	0.2245 (3)	0.2910 (5)	114 (5)	98 (4)	234 (10)	−42 (3)	18 (5)	−112 (6)
C(9)	0.1401 (3)	0.3374 (3)	0.0750 (5)	94 (4)	73 (3)	221 (9)	−43 (3)	56 (5)	−107 (5)
C(10)	0.1696 (3)	0.4627 (3)	−0.0634 (5)	123 (4)	86 (3)	273 (11)	−63 (3)	100 (6)	−135 (6)
C(11)	−0.2432 (3)	0.3224 (3)	−0.2178 (4)	72 (3)	50 (3)	154 (8)	−2 (3)	−4 (4)	−64 (4)
C(12)	−0.3777 (3)	0.3481 (3)	−0.3598 (5)	81 (4)	68 (3)	208 (10)	4 (3)	−11 (4)	−96 (5)
C(13)	−0.4636 (3)	0.2431 (3)	−0.2082 (5)	78 (4)	73 (3)	260 (10)	−13 (3)	−12 (5)	−105 (5)
C(14)	−0.3545 (3)	0.1155 (3)	−0.1047 (6)	91 (4)	84 (3)	364 (13)	−1 (3)	−47 (6)	−134 (6)
C(15)	−0.1978 (3)	0.0950 (3)	0.0025 (5)	97 (4)	64 (3)	307 (11)	−3 (3)	−42 (5)	−116 (5)
C(16)	−0.4899 (3)	0.2238 (3)	−0.0097 (5)	76 (4)	87 (3)	238 (10)	−23 (3)	11 (5)	95 (5)
C(17)	−0.3362 (3)	0.1772 (3)	0.1346 (5)	79 (4)	77 (3)	179 (9)	−24 (3)	16 (5)	−76 (5)

[a] The anisotropic temperature factors ($\times 10^4$) are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

(Qnqn)Cl$_2$]$_2$, C$_{34}$H$_{32}$Cl$_4$N$_4$Ni$_2$O$_2$, mol wt 787.86, and $Z = 1$, is 1.659 (3) g/cm^3. The density measured by flotation in a CCl$_4$–CBr$_4$ solution is 1.66 (2) g/cm^3.

Data Collection. The X-ray intensity data were obtained on the same crystal using a variable nonsymmetric 2θ scan with a scan rate of 1.0°/min. This scan was made from 0.50° below the 2θ setting for Kα_1 (λ 0.70926 A) to 0.55° above the 2θ setting for Kα_2 (λ 0.71354 A). The intensities of 3075 reflections were measured out to a 2θ angle of 48°. The diffracted Mo Kα radiation was filtered through 1 mil of niobium foil in front of a 3 mm $\times$ 3 mm receiving aperture at a takeoff angle of 2.0°. The background radiation level was measured for 20 sec at the 2θ angles corresponding to the beginning and the end of the scan. Calibrated copper attenuators were used to prevent the count rate at the detector from exceeding about 10^4 counts/sec. A recorder was used to monitor the shape of the scan peaks. Three standard reflections were measured at approximately 3-hr intervals in order to detect any drift in the instrument operating parameters and any degradation of the crystal with time. No significant change in the intensity of the standard reflections was observed during the 8 days required to collect the intensity data.

Data Reduction. The observed integrated intensities were corrected for background radiation and Lorentz–polarization effects and were assigned standard deviations using the methods of Corfield, *et al.*[6] In order to determine whether the crystal was of space group $P1$ or $P\bar{1}$, the intensities of all Friedel pairs were measured out to a 2θ angle of 25° yielding 422 observed reflections. A comparison of the Friedel pairs resulted in an agreement factor of approximately 1.5% indicating that the crystal was centrosymmetric and had space group $P\bar{1}$. Above a 2θ of 25°, only reflections of negative l values were measured. The dimensions of the crystal and the indices of the faces were determined by optical goniometric and microscopic techniques. All reflection intensities were corrected for absorption, the correction ranging from 0.75 to 0.87. Of the 3075 measured intensities, 2235 independent data points were obtained of which 2122 had intensities greater than 2.5σ, where $\sigma = [\sigma^2_{\text{counting}} + (0.03F_o{}^2)^2]^{1/2}$.

Structure Determination and Refinement. A straightforward interpretation of the Patterson map located the positions of the nickel and two chloride atoms. Full-matrix least-squares refinement of the positions of these atoms, minimizing the function $\Sigma w(|F_o|^2 - |kF_c|^2)^2$, converged with $R_1 = \Sigma(||F_o|^2 - |kF_c|^2|)/\Sigma|F_o|^2 = 0.609$ and $R_2 = [\Sigma w(|F_o|^2 + |kF_c|^2)^2/\Sigma w(|F_o|^2)^2]^{1/2} = 2.76$. In these expressions, the weight w is defined as $1/\sigma^2$, where σ is defined above. A subsequent three-dimensional Fourier synthesis was used to locate all the remaining nonhydrogen atoms. Three subsequent cycles of isotropic refinement of all nonhydrogen atoms gave $R_1 = 0.135$ and $R_2 = 0.239$. Two cycles of refinement of the nickel and chlorine atoms (anisotropically) and the remaining nonhydrogen atoms (isotropically), including extinction and anomalous dispersion corrections, resulted in $R_1 = 0.091$ and $R_2 = 0.180$. The nonhydrogen

scattering factors[7] and the anomalous dispersion factors[8] were taken from the values presented by Ibers. Extinction corrections were made using the method of Zachariasen ($\chi = 1.9$ (2) $\times 10^{-7}$).[9] Hydrogen scattering factors were taken from the work of Stewart, *et al.*[10] Two subsequent cycles with all nonhydrogen atoms refined anisotropically, led to $R_1 = 0.070$ and $R_2 = 0.138$. A difference Fourier synthesis based on this refinement indicated 16 peaks of electron density which corresponded to the 16 chemically expected hydrogen ions. Two final refinement cycles, refining all nonhydrogen atoms anisotropically and including the 16 hydrogen atoms ($B = 6.0$–7.0 A^2), led to $R_1 = 0.038$ and $R_2 = 0.077$. In the last cycle of refinement, the shifts in the parameters were all less than $^1/_2\sigma$. The final standard deviation of an observation of unit weight was 1.87. An attempt to refine the positions of the hydrogen atoms did not result in any significant improvement in R_1 and R_2. The final, conventional agreement factor, $R = \Sigma(||F_o| - |kF_c||)/\Sigma|F_o|$, was 0.026.

The observed and calculated structure factors ($\times 10$) are available.[11] The final position and anisotropic thermal parameters for nonhydrogen atoms are listed[12] in Table I and the final position parameters for the hydrogen atoms are listed in Table II.

Results and Discussion

The results of the structural analysis indicate that the molecule exists as a dimer. The structure of the molecule, the numbering scheme, and the bond distances in angstroms are shown in Figure 1. The dimer is centrosymmetric about a point in the plane of and equidistant from each of the two nickel and chlorine atoms. A stereoscopic view of the dimeric molecule is presented in Figure 2. The molecule is binuclear, containing two nickel atoms with approximately square-pyramidal coordination. The two coordination spheres are joined by two bridging chloride ions. The details of the coordination sphere are presented in Figure 3. The intramolecular bond distances in angstroms are given in Table III and the intramolecular bond angles in degrees are given in Table IV. The C–H bond distances ranged from 0.90 to 1.12 Å with an average value of 1.00 Å. The equations

(6) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

(7) J. A. Ibers in "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962, p 202, Table 3.3.1A.

(8) J. A. Ibers, ref 7, p 215, Table 3.3.2C.

(9) W. H. Zachariasen, *Acta Crystallogr.*, **16**, 1139 (1963).

(10) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(11) See paragraph at end of paper regarding supplementary material.

(12) Numbers in parentheses here and elsewhere in this paper indicate estimated standard deviations in the least significant digits.

Table II. Final Positional Parameters for Hydrogen Atoms

Atom	x	y	z
HC(1)	−0.235	0.510	−0.470
HC(3)	−0.100	0.635	−0.510
HC(4)	0.100	0.660	−0.380
HC(5)	0.305	0.570	−0.100
HC(6)	0.455	0.375	0.285
HC(7)	0.430	0.155	0.530
HC(8)	0.210	0.130	0.380
HC(13)	−0.570	0.270	−0.315
HC(14)	−0.340	0.135	−0.230
HC(14)	−0.415	0.045	0.015
HC(15)	−0.120	0.120	−0.105
HC(15)	−0.160	0.010	0.160
HC(16)	−0.540	0.155	0.080
HC(16)	−0.550	0.305	−0.070
HC(17)	−0.325	0.225	0.165
HC(17)	−0.310	0.090	0.285

Table III. Intramolecular Bond Distances (Å)

Ni–Ni	3.652 (1)	C(3)–C(4)	1.361 (4)
Ni–Cl(1)	2.408 (2)	C(4)–C(10)	1.398 (5)
Ni–Cl(1)	2.422 (2)	C(5)–C(10)	1.416 (4)
Ni–Cl(2)	2.296 (2)	C(5)–C(6)	1.352 (5)
Ni–N(1)	2.047 (3)	C(6)–C(7)	1.409 (5)
Ni–N(2)	2.067 (2)	C(7)–C(8)	1.367 (4)
O–C(12)	1.211 (3)	C(8)–C(9)	1.410 (4)
N(1)–C(2)	1.336 (4)	C(9)–C(10)	1.417 (4)
N(1)–C(9)	1.375 (3)	C(11)–C(12)	1.505 (4)
N(2)–C(11)	1.459 (4)	C(12)–C(13)	1.502 (4)
N(2)–C(15)	1.511 (4)	C(13)–C(14)	1.542 (4)
N(2)–C(17)	1.508 (4)	C(13)–C(16)	1.534 (4)
C(1)–C(2)	1.468 (4)	C(14)–C(15)	1.546 (4)
C(1)–C(11)	1.320 (4)	C(16)–C(17)	1.533 (4)
C(2)–C(3)	1.405 (4)		

Table IV. Bond Angles (deg)

Cl(1)–Ni–Cl(1)	81.78 (6)	C(3)–C(4)–C(10)	119.4 (3)
Cl(1)–Ni–Cl(2)	92.07 (6)	C(6)–C(5)–C(10)	121.0 (3)
Cl(1)–Ni–Cl(2)	160.55 (6)	C(5)–C(6)–C(7)	120.4 (3)
Cl(1)–Ni–N(1)	91.79 (8)	C(6)–C(7)–C(8)	120.3 (3)
Cl(1)–Ni–N(1)	158.00 (7)	C(7)–C(8)–C(9)	120.5 (3)
Cl(1)–Ni–N(2)	99.60 (8)	N(1)–C(9)–C(8)	119.3 (2)
Cl(1)–Ni–N(2)	104.15 (8)	N(1)–C(9)–C(10)	121.4 (3)
Cl(2)–Ni–N(1)	87.08 (7)	C(8)–C(9)–C(10)	119.2 (3)
Cl(2)–Ni–N(2)	99.80 (9)	C(4)–C(10)–C(5)	122.9 (3)
N(1)–Ni–N(2)	97.65 (9)	C(4)–C(10)–C(9)	118.5 (3)
Ni–Cl(1)–Ni	98.23 (5)	C(5)–C(10)–C(9)	118.6 (3)
Ni–N(1)–C(2)	122.6 (2)	N(2)–C(11)–C(1)	127.9 (2)
Ni–N(1)–C(9)	118.4 (2)	N(2)–C(11)–C(12)	112.2 (2)
C(2)–N(1)–C(9)	118.2 (2)	C(1)–C(11)–C(12)	119.6 (2)
Ni–N(2)–C(11)	112.9 (2)	O–C(12)–C(11)	123.0 (3)
Ni–N(2)–C(15)	107.2 (1)	O–C(12)–C(13)	125.9 (3)
Ni–N(2)–C(17)	114.2 (2)	C(11)–C(12)–C(13)	111.1 (2)
C(11)–N(2)–C(15)	107.7 (2)	C(12)–C(13)–C(14)	105.5 (2)
C(11)–N(2)–C(17)	106.2 (2)	C(12)–C(13)–C(16)	107.7 (2)
C(15)–N(2)–C(17)	108.4 (2)	C(14)–C(13)–C(16)	108.2 (3)
C(2)–C(1)–C(11)	133.0 (2)	C(13)–C(14)–C(15)	109.0 (3)
N(1)–C(2)–C(1)	120.9 (2)	N(2)–C(15)–C(14)	111.9 (2)
N(1)–C(2)–C(3)	122.7 (3)	C(13)–C(16)–C(17)	110.1 (2)
C(1)–C(2)–C(3)	116.4 (2)	N(2)–C(17)–C(16)	111.5 (2)
C(2)–C(3)–C(4)	119.8 (3)	Ni–N(2)–C(13)	175.8 (2)

for several least-squares planes through selected sets of atoms in the molecule are presented in Table V[11] along with the deviations of these atoms from the least-squares plane and the values for several of the dihedral angles contained in the molecule. The root-mean-square thermal displacements in angstroms along the directions of the principal axes are presented in Table VI. All intermolecular contacts of less than 3.8 Å are listed in Table VII.[11] The shortest inter-molecular contact observed is between O and C(12) (3.078 Å) and is only slightly less than the van der Waals distance. None of the intermolecular contacts suggest any unusual interactions.
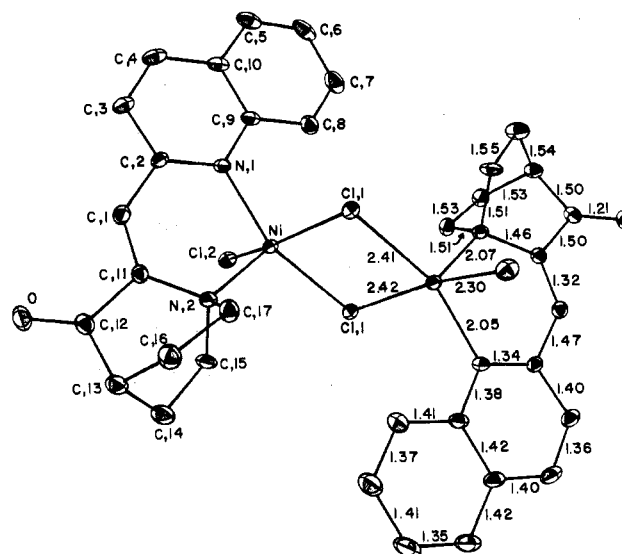

Figure 1. A perspective drawing of the molecular structure of [Ni(Qnqn)Cl₂]₂ including bond distances.

Table VI. Root-Mean-Square Thermal Displacements (Å) along the Directions of the Principal Axes

Atom	Minimum	Median	Maximum
Ni	0.141 (1)	0.1480 (8)	0.1868 (7)
Cl(1)	0.151 (1)	0.172 (1)	0.219 (1)
Cl(2)	0.182 (3)	0.187 (4)	0.216 (1)
N(1)	0.139 (5)	0.172 (4)	0.188 (3)
N(2)	0.143 (5)	0.158 (4)	0.189 (3)
O	0.159 (4)	0.231 (3)	0.240 (3)
C(1)	0.155 (4)	0.175 (5)	0.195 (4)
C(2)	0.143 (5)	0.160 (4)	0.196 (4)
C(3)	0.153 (5)	0.178 (4)	0.239 (4)
C(4)	0.144 (6)	0.181 (5)	0.270 (4)
C(5)	0.154 (6)	0.188 (5)	0.299 (5)
C(6)	0.151 (6)	0.208 (5)	0.335 (5)
C(7)	0.171 (5)	0.218 (5)	0.306 (5)
C(8)	0.167 (5)	0.207 (4)	0.248 (4)
C(9)	0.140 (6)	0.167 (4)	0.214 (4)
C(10)	0.141 (7)	0.162 (5)	0.250 (4)
C(11)	0.147 (5)	0.164 (5)	0.188 (4)
C(12)	0.159 (5)	0.164 (5)	0.220 (4)
C(13)	0.153 (5)	0.189 (5)	0.229 (4)
C(14)	0.159 (5)	0.196 (5)	0.283 (4)
C(15)	0.132 (7)	0.171 (4)	0.265 (4)
C(16)	0.166 (5)	0.202 (4)	0.240 (5)
C(17)	0.168 (5)	0.177 (4)	0.227 (5)

Following the first report of an X-ray structure of a high-spin five-coordinate nickel(II) complex by Sacconi, *et al.*,[13] there have been many reports on the structures of monomeric trigonal-bipyramidal, square-pyramidal, and intermediate-geometry five-coordinate nickel(II) complexes. Several excellent review articles[14–17] have described in detail the structural and electronic properties of the Ni(II) ion in these geometries. There are, however, relatively few reports of polynuclear five-coordinate nickel(II) complexes. Bennett, *et al.*,[18] have reported the crystal structure of such a tetra-nuclear nickel complex. Two structures have been reported[19,20] of trinuclear nickel complexes containing five-

(13) L. Sacconi, P. L. Orioli, and M. DiVaira, *J. Amer. Chem. Soc.*, **87**, 2059 (1965); **88**, 4383 (1966).
(14) L. Sacconi, *Transition Metal Chem.*, **4**, 199 (1968).
(15) M. Ciampolini, *Struct. Bonding (Berlin)*, **6**, 52 (1969).
(16) J. S. Wood, *Progr. Inorg. Chem.*, **16**, 227 (1972).
(17) L. Sacconi, *Coord. Chem. Rev.*, **8**, 35 (1972).
(18) M. J. Bennett, F. A. Cotton, and B. H. C. Winquist, *J. Amer. Chem. Soc.*, **89**, 5366 (1967).
(19) M. Bonamico, G. Dessy, and V. Fares, *Chem. Commun.*, 324 (1969).
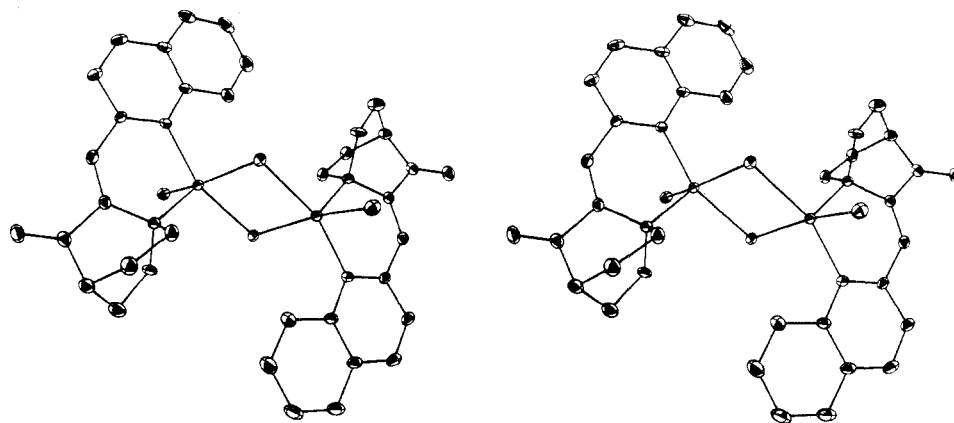(20) C. H. Wei and L. F. Dahl, *Inorg. Chem.*, **9**, 1878 (1970).

Figure 2. A stereoscopic view of the [Ni(Qnqn)Cl$_2$]$_2$ molecule.

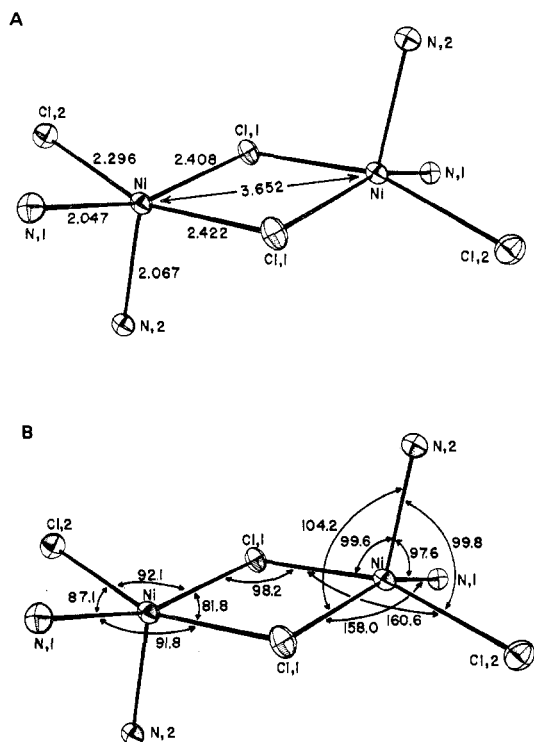**Figure 3.** A perspective view of the coordination sphere of [Ni(Qnqn)Cl$_2$]$_2$ with bond distances in angstroms given in A and bond angles in degrees given in B.

coordinate nickel. Several crystal structures of binuclear five-coordinate nickel complexes have appeared in the literature.[21-27] There have been two papers dealing with binuclear five-coordinate nickel structures which are closely related to the structure reported herein. One of these reports is by Ross and Stucky[28] on the X-ray structure of bis(*N*-methyl-*N'*-diazabicyclo[2.2.2]octonium) di-μ-chloro-hexachlorodi-

(21) M. Bonamico, G. Dessy, and V. Fares, *Chem. Commun.*, 697 (1969).
(22) G. A. Melson, P. T. Green, and R. F. Bryan, *Inorg. Chem.*, 9, 1119 (1970).
(23) G. A. Melson, N. P. Crawford, and B. J. Geddes, *Inorg. Chem.*, 9, 1123 (1970).
(24) A. Hermann and R. M. Wing, *Inorg. Chem.*, 11, 1415 (1972).
(25) T. S. Cameron and C. K. Prout, *Acta Crystallogr., Sect. B*, 28, 2021 (1972).
(26) L. Sacconi, P. L. Orioli, and M. DiVaira, *Chem. Commun.*, 849 (1967).
(27) P. Dapporto and L. Sacconi, *Chem. Commun.*, 329 (1969); *J. Chem. Soc. A*, 618 (1970).
(28) F. K. Ross and G. D. Stucky, *J. Amer. Chem. Soc.*, 92, 4538 (1970).

nickelate(II) which contains the unusual Ni$_2$Cl$_8$$^{4-}$ anion. This anion contains two bridging chlorine atoms and two square-pyramidal nickel ions. The second report by Preston and Kennard[29] describes a nickel(II) chloride complex with 2,9-dimethyl-1,10-phenanthroline. The structure of this complex is very similar to the structure reported in this paper.

The structure of the dimeric molecule shown in Figure 1 is unusual because it contains two square pyramids sharing a common edge. The crystallographic center of inversion located midway between the two nickel atoms requires both pyramids to be identical with their apices, atom N(2) pointing in opposite directions. The Ni–Ni distance is 3.652 (1) Å which is significantly larger than the sum of the two nickel radii (2.48 Å for nickel(0) and 1.56 Å for nickel(II)) and precludes any direct Ni–Ni bonding which is consistent with the high-spin magnetic moment[1] of the molecule. The observed Ni–Ni distance is essentially the same as that observed in the structurally similar Ni$_2$Cl$_8$$^{4-}$ anion (3.669 (2) Å),[28] in the closely related complex of Ni(II) with 2,9-dimethyl-1,10-phenanthroline (3.602 (2) Å),[29] and in the octahedral binuclear complex of [(en)$_2$NiCl$_2$Ni(en)]$^{2+}$ which contains bridging chloride ions[30] (3.67 Å). The details of the bridging system for each of these related dimeric nickel complexes is summarized in Table VIII. The angles of the Ni$_2$Cl$_2$ ring are highly distorted from the true square-pyramidal angles of 90°. The Ni–Cl bond distances are slightly asymmetric; the difference, 0.014 Å, corresponds to 7 times the estimated standard deviations of the measured bond lengths. The Cl(1)–Cl(1) nonbonded distance is 3.16 Å, a value which falls in the region predicted by Ross and Stucky[28] in an extensive evaluation of the steric forces in square metal–chlorine rings. Their analysis indicated that the geometries of four-membered metal–chlorine bridged rings are determined by the Cl–Cl intra-ring nonbonded interactions. In almost all of their examples, the M–Cl–M bond angle was significantly greater than 90°. The increase was tentatively attributed to the charges associated with the metal atoms which force the metals apart opening up the M–Cl–M bridge angle until the optimum Cl–Cl nonbonded distance is obtained. The observed Ni–Cl–Ni bond angle of 98.2° is consistent with this explanation; however, it is difficult to eliminate the possibilities of packing forces and ligand steric restrictions as an explanation for the large distortion. The

(29) H. S. Preston and C. H. L. Kennard, *Chem. Commun.*, 708 (1967); *J. Chem. Soc. A*, 2682 (1969).
(30) L. K. Minacheva, A. S. Antsyshkina, and M. A. Porai-Koshits, *Zh. Strukt. Khim.*, 12, 845 (1971).

Table VIII. Structural Comparisons of Some Binuclear Nickel Complexes

Structural feature	[Ni(Qnqn)Cl$_2$]$_2$	Ni$_2$Cl$_8$$^{4-}$	[Ni-(2,9-Me$_2$phen)Cl$_2$]$_2$	[(en)$_2$-NiCl$_2$Ni(en)$_2$]$^{2+}$
Coordination geometry	Sq py	Sq py	Sq py	Oct
Ni-Ni distance, A	3.652 (1)	3.669 (2)	3.602 (2)	3.67
Cl-Cl nonbonded bridging distance, A	3.160 (2)	3.119 (2)	3.13 (1)	3.41
Ni-Cl(bridge) bond length, A	2.408 (2)	2.366 (2)	2.378 (3)	2.485
	2.422 (2)	2.449 (2)	2.394 (3)	2.522
Ni-Cl-Ni angle, deg	98.23 (5)	99.29 (6)	98.0 (1)	
Cl-Ni-Cl angle, deg	81.78 (6)	80.71 (6)	81.9 (1)	85.8 (5)
Ni-basal plane distance, A	0.40	0.5	0.39	
Reference	This work	28	29	30

Ni-Cl(1) bridging bond distances (2.415 (7) Å average) are much longer than the terminal Ni-Cl(2) bond distance (2.296 (2) Å) as would be expected for the three-center bridging chlorine bonds as compared with the two-center terminal bonds. The Ni-Cl(2) bond distance is typical of terminal nickel-chlorine bond distances.[14] A review of approximately 30 Ni-Cl bond distances reveals a range of *ca.* 2.25-2.45 Å and no distinct differences in the range for different nickel coordination geometries. The four chlorine atoms and two N(1) atoms form a least-squares plane with a maximum deviation from the plane of 0.032 Å for the two N(1) atoms. The chlorine atoms are all within ±0.006 Å of this plane. The nickel atom is 0.40 Å from this least-squares plane in the direction of the apical nitrogen atom. This nickel to basal plane distance is found to be rather typical of complexes of this type.[14]

As can be seen in Table VI, the thermal vibration of most of the lighter atoms is highly anisotropic with as much as a factor of 2 difference in the minimum and maximum ellipsoid axes. In the case of the atoms in the planar portion of the Qnqn, the vibrations seem to be generally the greatest in a direction corresponding to a twisting motion of the planar portion of the ligand about an axis perpendicular to the plane. For the remainder of the atoms, the vibration, as is generally observed, is nearly a minimum along bonds and greater perpendicular to the bonds. For the nickel atom the maximum vibration is approximately in the direction of the trans Cl(2)-Cl(1) vector while the minimum vibration is nearly perpendicular to the square plane. The vibration of the bridging chlorine Cl(1) is much more anisotropic than that of Cl(2) but the minimum vibration for both is essentially along the Ni-Cl bonds.

The apical to equatorial bonding angles about the coordination sphere are all distorted from the normal values of 90° (see Figure 3B). The average of the apical to equatorial bonding angles is 100.3°, a value comparable to that found in many five-coordinate complexes. The "bite" angle (97.6°) of the ligand, N(2)-Ni-N(1), is the smallest of these angles and the steric constraints of the ligand presumably open up the opposite N(2)-Ni-Cl(1) angle to the rather large value of 104.2°. The "bite" distance is 3.096 Å.

The values of the nickel to nitrogen bond distances are rather typical of this type of bond. An evaluation of approximately 100 nickel-nitrogen bond distances shows that a rather broad range of values is observed and no real generalization of bond distance on the basis of nitrogen type or coordination geometry is possible. The slightly shorter Ni-N(1) bond distance (2.047 (3) Å) compared with Ni-N(2) (2.067 (2) Å) may be a result of the higher percentage s character associated with the sp^2-hybridized N(1) atom relative to the sp^3-hybridized N(2) atom. A comparable value has been reported[31] for a five-coordinate Ni(II) com-

plex with a quinoline N-Ni bond distance of 2.06 (1) Å. An X-ray structure[32] of a five-coordinate Ni(II) complex containing the *N*-methyl-1,4-diazabicyclo[2.2.2]octonium ligand, which is structurally similar to the quinuclidinone moiety, reveals a Ni-N distance of 2.140 (6) Å. It is however, unfortunately, difficult to separate the effects of crystal packing and ligand constraints from the electronic factors affecting bond length and hence it is not possible to attribute the Ni-N(1) and Ni-N(2) bond length differences to electronic effects. The bonding within the ligand is consistent with normally accepted bonds in organic materials. The atoms in the quinoline group form a least-squares plane (plane 1, Table V) with the largest deviation of only 0.03 Å for C(7). The bridging carbon atoms in the quinuclidinone portion of the molecule, C(14)-C(16), have highly anisotropic thermal parameters indicating that the bridging ethylene groups have a good deal of freedom to vibrate about the N(2)-C(13) axis. Each of the three bridges in the quinuclidinone group shows a significant deviation from planarity indicating a slight twist in the bridging ethylene carbon atoms. Each ligand portion of the dimer contains an extensive nearly planar system of atoms (plane 10, Table V) including all of the atoms except the chlorine atoms and two bridging ethylene groups, C(14)-C(17).

In order to gain a better understanding of the high- and low-temperature thermal properties of the nickel complex under study,[3] it would have been beneficial to have obtained a crystal structure of the violet isomer of the nickel complex.[1] However, crystals of the violet isomer of sufficient size for X-ray work have not as yet been obtained. In view of this difficulty, we decided to determine the X-ray structure of the related cobalt complex Co(Qnqn)Cl$_2$.[33] This compound is known to be tetrahedral[1,33] and has an X-ray powder pattern similar to but not identical with that of the violet Ni(Qnqn)Cl$_2$ isomer. A comparison of the results for Co-(Qnqn)Cl$_2$ with those for yellow [Ni(Qnqn)Cl$_2$]$_2$ reveals that the ligand structures are essentially identical in each of the compounds. The only differences not involving the metal, and above 4σ, between the two structures involve the C(15)-N(2)-C(17) bond angle which is 1.2° larger in the cobalt complex and the C(13)-C(14) bond distance which is 0.025 Å longer in the nickel complex.

It appears that the open nickel coordination site is somewhat protected since the Ni to HC(8) hydrogen nonbonded distance is only 2.40 Å. The presence of this hydrogen apparently prevents the addition of a solvent molecule to the coordination sphere. It does not, however, prevent the molecule from absorbing over a period of time a water at this coordination site.[1]

(31) P. S. Shetty and Q. Fernando, *J. Amer. Chem. Soc.,* **92**, 3964 (1970).

(32) F. K. Ross and G. D. Stucky, *Inorg. Chem.,* **8**, 2734 (1969).

(33) G. J. Long and E. O. Schlemper, submitted for publication in *J. Chem. Soc., Dalton Trans.*

Supplementary Material Available. Table V, showing planes and dihedral angles, Table VII, showing intermolecular contact distances, and a listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-279.

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Mixed Thiocyanate Complexes of Platinum(II). Crystal Structure of *cis*-Thiocyanatoisothiocyanatobis(3,3-dimethylbutynyldiphenylphosphine)platinum(II)

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Mixed thiocyanate complexes of the type *cis*-Pt(NCS)(SCN)(Ph₂PC≡CR)₂ (R = Ph, Et, *i*-Pr, *t*-Bu) have been prepared and characterized. The purely N-bonded compound *cis*-Pt(NCS)₂(Ph₂PC≡C-*t*-Bu)₂ and the chloride complexes *cis*-PtCl₂-(Ph₂PC≡CR) are also described. Infrared vibrational frequencies for the coordinated CNS⁻ ion have been assigned using ¹⁵N isotopically substituted compounds. *cis*-Pt(NCS)(SCN)(Ph₂PC≡C-*t*-Bu)₂ crystallizes in space group *Pca2₁* with *a* = 18.272 (13), *b* = 13.287 (5), and *c* = 16.470 (17) Å. Observed and calculated densities are 1.47 and 1.40 g cm⁻³, respectively, for mol wt 843.9 and *Z* = 4. The structure was solved by a combination of Patterson, Fourier, and least-squares refinement techniques. The final discrepancy index for 1951 observed, independent reflections is *R* = 0.057. The platinum atom is coordinated in square-planar fashion by two phosphorus atoms of the acetylenic phosphines, a nitrogen atom of an isothiocyanate group, and a sulfur atom of a thiocyanate group. Relevant intramolecular distances include Pt–P(1) (2.275 (6) Å), Pt–P(2) (2.244 (7) Å), Pt–S(1) (2.374 (8) Å), and Pt–N(1) (2.061 (29) Å). Factors influencing the bonding mode of the thiocyanate ion in platinum(II) complexes are discussed.

Despite the existence of a wide variety of metal thiocyanate complexes only a relatively small number contain *both* M–NCS and M–SCN linkages.[1,2] X-Ray studies have confirmed the presence of nonbridging mixed thiocyanato bonding in *cis*-Pd(NCS)(SCN)(Ph₂P(CH₂)₃NMe₂),[3] *cis*-Pd(NCS)(SCN)-(Ph₂P(CH₂)₂PPh₂),[4] and *cis*-Pd(NCS)(SCN)(Ph₂PC≡C-*t*-Bu)₂[5] while infrared spectroscopic measurements indicate probable mixed bonding modes in Pd(NCS)(SCN)[Ph₂P(*o*-C₆H₄As-Ph₂)],[6] Pd(NCS)(SCN)(Ph₂P(CH₂)₂NMe₂),[6] [M(NCS)(SCN)-(Ph₂PC≡CPPh₂)]₂ (M = Pd, Pt),[7] Pd(NCS)(SCN)L (L = 4,4'-dimethylbipyridyl),[8] and Cu(NCS)(SCN)L (L = tri-2-pyridyl-amine, phenyldi-2-pyridylamine).[9] As a continuation of our work on the novel coordinating properties of acetylenic phosphines we recently discovered[10] that the complex Pd(CNS)₂-(Ph₂PC≡C-*t*-Bu)₂ could be isolated in three isomeric forms, two

of which were *cis*-Pd(NCS)(SCN)(Ph₂PC≡C-*t*-Bu)₂ while the third, *trans*-Pd(SCN)₂(Ph₂PC≡C-*t*-Bu)₂, was an example of a hitherto unknown structural type namely a *trans*-dithio-cyanatophosphine complex of Pd(II). In an attempt to prepare and study other phosphine complexes of the transition metals containing mixed thiocyanate and purely S-bonded thiocyanate groups, in order to test current ideas on factors controlling CNS⁻ bonding,[1,3–6,10,11] the work has been extended to Pt(II) systems. This paper describes the synthesis and characterization of the complexes *cis*-Pt(CNS)₂-(Ph₂PC≡CR)₂ (R = Ph, Et, *i*-Pr, *t*-Bu) which can be isolated in the N-bonded form *cis*-Pt(NCS)₂(Ph₂PC≡CR)₂ (R = *t*-Bu) or mixed forms *cis*-Pt(NCS)(SCN)(Ph₂PC≡CR)₂. Solid-state and solution infrared measurements including assignments of CNS⁻ vibrational modes from ¹⁵N isotopic substitution studies are reported. A full three-dimensional X-ray structure determination of the complex *cis*-Pt(NCS)(SCN)-(Ph₂PC≡C-*t*-Bu)₂ has been carried out to confirm spectroscopic measurements and to provide further insight into factors influencing the bonding mode of the thiocyanate ion.

Experimental Section

The ligands Ph₂PC≡CR (R = Et, Ph, *i*-Pr, *t*-Bu) were synthesized as previously described.[12]

Preparation of Compounds. (1) PtCl₂(Ph₂PC≡CEt)₂. K₂PtCl₄ (0.5 g) dissolved in H₂O (30 ml) and ethanol (20 ml) was stirred at room temperature for 12 hr with Ph₂PC≡CEt (0.8 g). The solution was taken to dryness and the solid extracted with dichloromethane. The solution was filtered, the volume reduced to *ca.* 5 ml, and diethyl ether (20 ml) added. Yellowish white crystals of the complex were obtained on cooling. *Anal.* Calcd for PtCl₂(Ph₂PC≡CEt)₂: C, 51.75; H, 4.05. Found: C, 52.39; H, 3.75.

(1) For reviews see (a) J. L. Burmeister, *Coord. Chem. Rev.*, 1, 205 (1966); (b) J. L. Burmeister, *ibid.*, 3, 225 (1968); (c) A. H. Norbury and A. I. P. Sinha, *Quart. Rev., Chem. Soc.*, 24, 69 (1970); (d) R. A. Bailey, S. L. Kozak, T. W. Michelsen, and W. N. Mills, *Coord. Chem. Rev.*, 6, 407 (1971).

(2) We use the term "mixed thiocyanate bonding" to imply the presence of two (or more) thiocyanate groups coordinated in mono-dentate fashion but differing in their mode of attachment to the metal. Throughout the paper we represent metal–isothiocyanate bonding as M(NCS) and metal–thiocyanate bonding as M(SCN). When no specific bonding mode is implied M(CNS) is used.

(3) G. R. Clark, G. J. Palenik, and D. W. Meek, *J. Amer. Chem. Soc.*, 92, 1077 (1970); G. R. Clark and G. J. Palenik, *Inorg. Chem.*, 9, 2754 (1970).

(4) G. Beran and G. J. Palenik, *Chem. Commun.*, 1355 (1970).

(5) T. W. Ng, A. J. Carty, and G. J. Palenik, unpublished results.

(6) D. W. Meek, P. E. Nicpon, and V. I. Meek, *J. Amer. Chem. Soc.*, 92, 5351 (1970).

(7) A. J. Carty and A. Efraty, *Can. J. Chem.*, 47, 2573 (1969).

(8) I. Bertini and A. Sabatini, *Inorg. Chem.*, 5, 1025 (1966).

(9) G. L. Kulasingam and W. R. McWhinnie, *J. Chem. Soc. A*, 254 (1968).

(10) G. Beran, H. A. Patel, P. C. Chieh, and A. J. Carty, *J. Chem. Soc., Dalton Trans.*, 488 (1973).

(11) A. H. Norbury, *J. Chem. Soc. A*, 1089 (1971).

(12) A. J. Carty, N. K. Hota, T. W. Ng, H. A. Patel, and T. J. O'Connor, *Can. J. Chem.*, 49, 2706 (1971).