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Transition Metal Chemistry of Quinuclidinone-Containing Ligands. III. Electronic and Structural Properties of Several Transition Metal Complexes Containing *trans*-2-(2′-Quinolyl)methylene-3-quinuclidinone[1]

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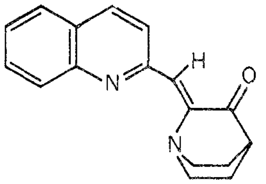
The complexes of the title ligand, Qnqn, with iron(II), cobalt(II), nickel(II), and copper(II) chloride and nickel(II) bromide have been prepared and characterized utilizing analytical, spectral, and magnetic techniques. In each case the compounds are found to be pseudotetrahedral in structure and to have $M(Qnqn)X_2$ stoichiometry; the coordination sphere contains the two halide ions and the two Qnqn nitrogen donor atoms. Two isomeric complexes may be obtained with Qnqn and nickel(II) chloride. The yellow isomer is dimeric, $[Ni(Qnqn)Cl_2]_2$, with square-pyramidal coordination about the two nickel ions and the two bridging chloride ions between them. The violet isomer is pseudotetrahedral in structure. These two nickel isomers undergo a unique solid-state structural interconversion from the yellow isomer to the violet isomer at high temperature (*ca.* 230°) and from the violet isomer to the yellow isomer at low temperature (−78°).

Introduction

Although primary, secondary, tertiary, and aromatic amine transition metal complexes have been studied extensively,[2-4] the complexes formed by ligands containing the quinuclidine moiety, which is a tertiary, bicyclic amine, have received relatively little attention. Coffen and McEntee have reported[5] on the preparation and some of the properties of several transition metal complexes of *trans*-2-(2′-quinolyl)methylene-3-quinuclidinone, Qnqn, and its 6-methoxy derivative.



Qnqn

Dickinson and Long[1] have described the structural and magnetic properties of several transition metal complexes formed by 2-(*N*-morpholinylmethyl)-3-quinuclidinone and some related ligands. Because their paper reviews some of the previous reports regarding complexes of the quinuclidine group, the reports will not be reviewed again here.

The purpose of this paper is to report on the electronic, spectral, and magnetic properties of several complexes containing Qnqn. In particular, a new binuclear five-coordinate, nickel complex, which has rather unique thermal properties, is described. Subsequent papers will be concerned with the X-ray structure of the binuclear nickel complex,[6] its thermal properties,[7] and the X-ray structure of the cobalt complex.[8]

Experimental Section

Materials. The compound 3-quinuclidinone was obtained from the Aldrich Chemical Co., Inc., and used as received. The metal salts were used as received without recrystallization.

***trans*-2-(2′-Quinolyl)methylene-3-quinuclidinone.** This ligand, Qnqn, which was prepared by a previously described method,[5] is a fine, yellow, crystalline powder. It has shown no tendency to decompose during the period of years in which it has been stored in a desiccator. *Anal.* Calcd for $C_{17}H_{16}N_2O$: C, 77.25; H, 6.10; N, 10.60. Found: C, 77.46; H, 6.10; N, 10.52.

$Fe(Qnqn)Cl_2$. A solution of 3.88 g (0.0195 mol) of $FeCl_2 \cdot 4H_2O$ in 70 ml of deoxygenated absolute methanol was prepared and kept under a stream of N_2 gas. The solution should be pale green; a yellowish color is an indication that oxidation to iron(III) has occurred. A solution of 3.06 g (0.0195 mol) of Qnqn in 100 ml of 95% ethanol was prepared by heating while bubbling a rapid stream of N_2 gas through the solution. The iron chloride was then added slowly under a stream of N_2 gas to the solution of Qnqn. A dull green color formed immediately, and a precipitate formed within minutes. The mixture was allowed to stand for about 0.5 hr under N_2, then brought to a boil, and filtered hot *via* suction through a sintered-glass filter under N_2 gas. The precipitate was dried in an Abderhalden drying apparatus under vacuum at 76° for 0.5 hr. After drying, 3.99 g (54%) of a dull, dark green, crystalline material resulted. *Anal.* Calcd for $FeC_{17}H_{16}N_2OCl_2$: C, 52.21; H, 4.12; N, 7.16. Found: C, 52.24; H, 3.97; N, 6.76.

$Co(Qnqn)Cl_2$. This compound was prepared by a previously described method.[5] The green, crystalline product is stable when stored in a desiccator. *Anal.* Calcd for $CoC_{17}H_{16}N_2OCl_2$: C, 51.80; H, 4.09; N, 7.11. Found: C, 51.60; H, 4.22; N, 7.10.

Violet $Ni(Qnqn)Cl_2$. A solution of 2.64 g of Qnqn in 200 ml of 1-butanol was heated to boiling in a 1-l. erlenmeyer flask. A large flask is essential. At the same time, a solution of 2.38 g of $NiCl_2 \cdot 6H_2O$ in 25 ml of 95% ethanol was heated to boiling. The two flasks were lifted from the hot plate, and the nickel chloride solution was quickly poured into the Qnqn solution. Vigorous spattering accompanied the mixing. Instantly after mixing, the flask was chilled by swirling it vigorously in an ice bath. The complex precipitated as a fine, violet, crystalline material which was filtered, washed with 1-butanol (not ethanol) and dried in an Abderhalden drying apparatus under vacuum at 76° for 0.5 hr. It is essential that the violet precipitate be dried immediately after filtration. If allowed to stand overnight without drying completely, the precipitate changes color and becomes partially yellow. The violet material when completely dry is stable when stored in a desiccator (see Results and Discussion). The yield was 3.28 g. *Anal.* Calcd for $NiC_{17}H_{16}N_2OCl_2$: C, 51.83; H, 4.09; N, 7.11. Found: C, 52.05; H, 4.21; N, 7.20.

Yellow $[Ni(Qnqn)Cl_2]_2$. This compound was prepared by dissolving the violet $Ni(Qnqn)Cl_2$ complex in a sufficient amount of methylene chloride to give a clear violet solution. Rotary evaporation of this solution to dryness yielded a yellow, crystalline material. This solid was dried in an Abderhalden drying apparatus under vacuum at 76° for 0.5 hr. This material was found to be stable when stored in a desiccator. The yield was essentially 100%. *Anal.* Calcd for $NiC_{17}H_{16}N_2OCl_2$: C, 51.83; H, 4.09; N, 7.11. Found: C, 52.01; H, 4.14; N, 6.98.

$Ni(Qnqn)Br_2$. The preparation of this complex is very similar to the preparation of violet $Ni(Qnqn)Cl_2$ described above. The proce-

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(1) Part II: R. C. Dickinson and G. J. Long, *Inorg. Chem.*, 13, 262 (1974).

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dure, which was used, resulted in a light violet crystalline material which is stable when stored in a desiccator. *Anal.* Calcd for $NiC_{17}H_{16}N_2OBr_2$: C, 42.29; H, 3.34; N, 5.80. Found: C, 42.52; H, 3.48; N, 5.66.

$Cu(Qnqn)Cl_2$. This complex was prepared with the method used by Coffen and McEntee.[5] The gold, crystalline solid is stable when stored in a desiccator. *Anal.* Calcd for $CuC_{17}H_{16}N_2OCl_2$: C, 51.20; H, 4.04; N, 7.03. Found: C, 51.03; H, 3.96; N, 6.90.

Physical Measurements. The infrared and electronic spectra and magnetic susceptibilities were measured as described previously.[1]

The Mossbauer results were obtained as described previously.[9] The error limits for the reported Mossbauer parameters are less than or equal to ±0.02 mm/sec, as calculated from the variance of the final computer iteration using the standard PARLOR program.[10]

A Siemanns Crystalflex IV X-ray diffractometer with a copper tube and a nickel filter was used to obtain X-ray powder diffraction patterns. The differential thermal gravimetric results were obtained by using a Mettler thermal analyzer.

Carbon, hydrogen, and nitrogen elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. 37921.

Results and Discussion

The X-ray powder diffraction patterns for each of the compounds under study were measured and compared for any indications of isomorphism. The results indicate that the iron and cobalt complexes have essentially identical powder patterns. Hence they are probably isostructural and have slightly different unit cell parameters. The infrared absorption spectrum of the ligand and of each of its complexes shows a strong band which can be attributed to the carbonyl stretching vibration.[11] In the ligand, this band is found at 1710 cm^{-1}; in the complexes, this band occurs in a range between 1720 and 1728 cm^{-1}. The small shift to higher frequencies is indicative of the noncoordination of the keto group with the metal.[12-14] From 400 to 4000 cm^{-1}, the infrared spectra of the complexes are very similar and resemble the spectrum of the free ligand. Below 400 cm^{-1}, metal-ligand vibrational bands are observed. These are described below.

$Fe(Qnqn)Cl_2$. The X-ray powder pattern suggests that $Fe(Qnqn)Cl_2$ is structurally similar to its cobalt analog whose single-crystal structure reveals tetrahedral coordination. This coordination geometry is further verified by its spectral and magnetic properties. The Mossbauer spectral parameters and the magnetic properties of this iron compound are presented in Tables I and II. A plot of the Mossbauer spectrum at liquid nitrogen temperature is shown in Figure 1. The electronic absorption spectrum of this complex is shown in Figure 2, and the band positions and assignments based on a distorted tetrahedral structure are included in Table III.

Table I. Mossbauer Spectral Parameters for $Fe(Qnqn)Cl_2$

T, °K	ΔE_Q, mm/sec	δ,[a] mm/sec	Γ_1,[b] mm/sec	Γ_2,[b] mm/sec
78	3.12	0.93	0.224	0.230
195	2.97	0.87	0.223	0.218
300	2.75	0.81	0.223	0.206

[a] Relative to natural iron foil. [b] Full width at half-maximum for low-velocity line, Γ_1, and high-velocity line, Γ_2.

Table II. Magnetic Susceptibility Data

Compd	T, °K	$10^6\chi_M'$, cgsu	μ_{eff}, BM
$Fe(Qnqn)Cl_2$	101.5	31,980	5.10
Mol wt 391.07	145.0	22,990	5.17
$\chi_M^c = 213$ cgsu	197.5	17,250	5.22
	254.5	13,540	5.25
	294.0	11,820	5.27
$Co(Qnqn)Cl_2$	100.0	22,940	4.28
Mol wt 394.15	112.0	19,450	4.32
$\chi_M^c = 213$ cgsu	150.5	15,740	4.35
	174.5	13,770	4.38
	199.0	12,250	4.42
	222.0	11,050	4.43
	246.5	10,010	4.44
	275.0	9,035	4.46
	294.5	8,451	4.46
Yellow $[Ni(Qnqn)Cl_2]_2$	101.5	11,160	3.00
Mol wt 393.93/Ni	139.0	8,540	3.08
$\chi_M^c = 213$ cgsu	170.5	7,130	3.12
	208.5	5,961	3.15
	256.5	4,960	3.19
	294.5	4,361	3.21
Violet $Ni(Qnqn)Cl_2$	294.5	4,998	3.43[a]
Mol wt 393.93	101.5	12,320	3.16
$\chi_M^c = 213$ cgsu	146.5	8,968	3.24
	183.0	7,331	3.28
	229.5	5,938	3.30
	271.0	5,142	3.34
	293.0	4,752	3.34[b]
$Ni(Qnqn)Br_2$	105.9	12,480	3.25
Mol wt 482.83	179.2	7,800	3.34
$\chi_M^c = 235$ cgsu	297.0	4,879	3.40
$Cu(Qnqn)Cl_2$	120.0	3,533	1.84
Mol wt 398.76	176.0	2,541	1.89
$\chi_M^c = 214$ cgsu	216.5	2,074	1.90
	295.0	1,545	1.91

[a] Before cooling. [b] After cooling.

There are two papers which deal in detail with the spectral properties of iron(II) complexes of the type reported on here. Edwards, *et al.*,[15] studied in detail the Mossbauer spectral properties of several tetrahedral iron(II) compounds. Burbridge and Goodgame[16] studied the various spectral and magnetic properties of several iron(II) halide complexes with quinoline. The room-temperature Mossbauer chemical isomer shift, δ, relative to iron foil is found to lie in the range of 0.96–1.06 mm/sec for several, octahedral, high-spin iron(II) chloride complexes containing nitrogen donor atoms.[16-19] The observed values for pseudotetrahedral complexes of the same type lie in the range of 0.80–0.91 mm/sec.[1,16] The smaller isomer shifts for the tetrahedral complexes can be attributed to the increased covalency of the tetrahedral complexes as compared with that of the octahedral complexes.[15] Hence, the observed room-temperature δ value for $Fe(Qnqn)Cl_2$ is indicative of pseudotetrahedral coordination. The large increase in δ with decreasing temperature (see Table I) can be attributed to a second-order Doppler shift and is indicative of a relatively low Debye temperature for this complex. The observed quadrupole splitting, ΔE_Q, is reasonable for pseudotetrahedral coordination, and the temperature dependence of the values reported in Table I is very

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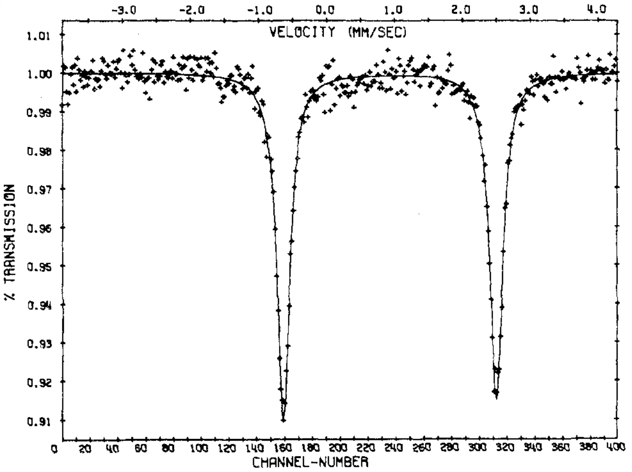

Figure 1. Mossbauer effect spectrum of $Fe(Qnqn)Cl_2$ at 78°K.

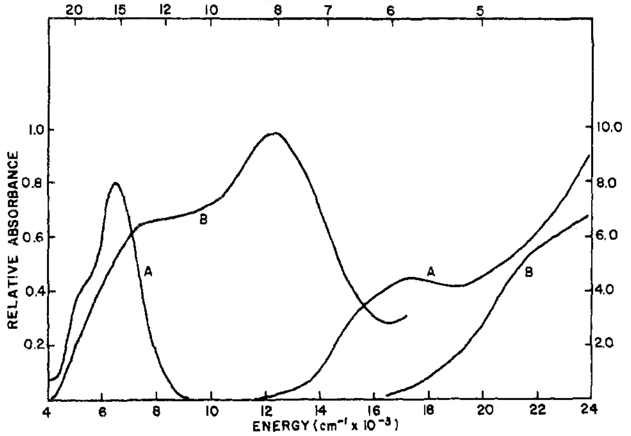

Figure 2. Electronic spectrum of $Fe(Qnqn)Cl_2$ (A) and $Cu(Qnqn)Cl_2$ (B).

similar to that observed in $Fe(quin)_2Cl_2$.[20] The temperature dependence of ΔE_Q may be related to the splitting of the ^5E ground state of the tetrahedral iron(II) ion by the lower symmetry components of the ligand field.[15,20] Here, the reduced symmetry removes the degeneracy of the d_{z^2} and $d_{x^2-y^2}$ orbitals. The observed temperature dependence is consistent with a splitting of these orbitals of the order of 500 cm^{-1} in $Fe(Qnqn)Cl_2$. However, a more precise value of the ground-state splitting cannot be determined because of the paucity of data points.

The room-temperature value of the magnetic moment for $Fe(Qnqn)Cl_2$, 5.26, is characteristic of high-spin iron(II) and agrees well with values reported for several similar tetrahedral complexes.[16] The small decrease in magnetic moment with temperature is to be expected of the ^5E ground state of the tetrahedral iron(II) ion. Because the iron complex is isostructural with the cobalt, its molecular symmetry is very similar to C_s. The cobalt complex itself contains nearly mirror symmetry.[8] If ones considers only the iron coordinated atoms, it is seen that the coordination sphere is close to C_{2v} symmetry. In this symmetry, the excited $^5T_2$ term can be split into three terms ($^5A_1$, $^5B_1$, and $^5B_2$), and the three d-d bands can be expected to be in the near-infrared spectrum of the complex, corresponding to the transitions to each of these states. Unfortunately, the near-infrared spectrum of $Fe(Qnqn)Cl_2$ contains only a single band at 5200 cm^{-1} that has a low-energy shoulder (Figure 1). This spectrum is however very similar to several related complexes of iron(II) also believed to have C_{2v} coordination symmetry.[16] As a result, the observed low-intensity bands are assigned to the ^5E to $^5T_2$ transition.

Table III. Electronic Spectral Data for the Pseudotetrahedral Complexes

Compd	Solvent	Spectral band,[a] cm^{-1}	Assignment
$Fe(Qnqn)Cl_2$	Mull	5,200 sh 6,500	$^5E \rightarrow {}^5T$
		17,700	Charge transfer
		28,600	Intraligand
$Co(Qnqn)Cl_2$	Mull	4,400	$^4A_2 \rightarrow {}^4T_2$
		6,600 7,940 10,200	$^4A_2 \rightarrow {}^4T_1(F)$
		15,600 16,130 sh 17,330	$^4A_2 \rightarrow {}^4T_1(P)$
		18,380 19,640	Spin forbidden
Violet $Ni(Qnqn)Cl_2$	Mull	7,770	$^3T_1(F) \rightarrow {}^3T_2(F)$[b]
		10,500	$^3T_1(F) \rightarrow {}^3A_2(F)$
		11,530 11,900	Spin forbidden
		15,400 sh	
		19,000	$^3T_1(F) \rightarrow {}^3T_1(P)$
$Ni(Qnqn)Br_2$	Mull	7,700	$^3T_1(F) \rightarrow {}^3T_2(F)$[b]
		10,420	$^3T_1(F) \rightarrow {}^3A_2(F)$
		11,110 11,430	Spin forbidden
		15,400 sh	
		18,180	$^3T_1(F) \rightarrow {}^3T_1(P)$
	CH_2Cl_2	7,600 (15)	$^3T_1(F) \rightarrow {}^3T_2(F)$[b]
		10,300 (75)	$^3T_1(F) \rightarrow {}^3A_2(F)$
		11,490 (63) 15,400 sh	Spin forbidden
		18,660 (194)	$^3T_1(F) \rightarrow {}^3T_1(P)$

[a] Molar extinction coefficients given in parentheses. All data at *ca.* room temperature. [b] This transition is actually to one of the components of the $^3T_2(F)$ state (see text).

The far-infrared spectrum of $Fe(Qnqn)Cl_2$ and the pure ligand Qnqn are presented in Figure 3. The iron complex exhibits two strong bands at 315 and 357 cm^{-1}. A tetrahedral complex with C_{2v} coordination symmetry is expected to show four infrared-active metal-ligand bands; two are associated in this case with the metal-chloride bonds and two with the metal-nitrogen bonds.[21] The bands at 315 and 357 cm^{-1} are assigned to the ν_{FeCl} vibrations in agreement with a great deal of data reported for related metal-chlorine vibrational bands in pseudotetrahedral complexes.[22]

$Co(Qnqn)Cl_2$. A single-crystal X-ray structural analysis of this compound[8] has revealed a pseudotetrahedral coordination geometry for the cobalt(II) ion. The two Co-Cl bond distances are essentially the same (2.219 and 2.227 Å). The cobalt to quinuclidinone nitrogen bond is 2.064 Å, while the cobalt to quinoline nitrogen bond is 2.014 Å. As noted above and elsewhere,[8] the molecule very nearly contains a mirror plane of symmetry through the ligand which bisects the Cl-Co-Cl angle; hence, it is close to C_s in molecular symmetry. The symmetry of the coordinated atoms resembles C_{2v} symmetry, and the spectral properties of the compound can be discussed in terms of this coordination symmetry.

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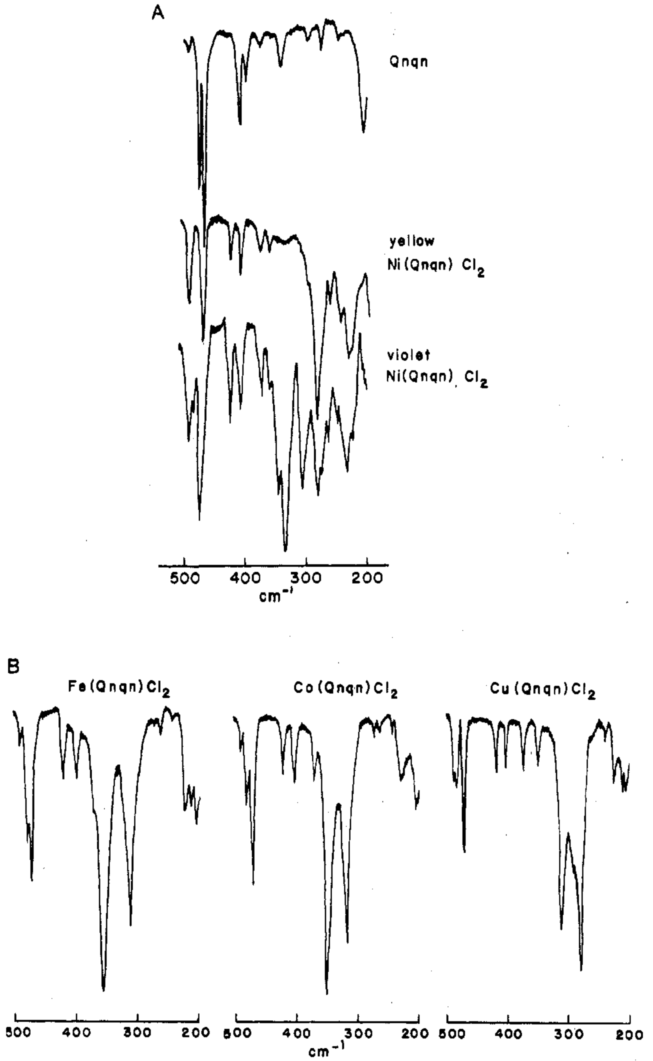

Figure 3. Far-infrared spectrum of Qnqn and its metal(II) chloride complexes.

The magnetic properties of the cobalt complex are included in Table II. As has been noted by several authors,[23-25] the magnetic moments of Co(II) compounds are sensitive to the magnitude of the ligand field strength, Dq, and as a result, tetrahedral cobalt complexes usually have significantly smaller magnetic moments than octahedral cobalt complexes. The room-temperature moment of 4.46 BM for $Co(Qnqn)Cl_2$ falls in the range expected[25] (4.4-4.7 BM) for pseudotetrahedral cobalt complexes with a $^4A_2$ ground state. Because this ion has an orbitally nondegenerate ground state, the small observed temperature dependence of μ_{eff} is reasonable.

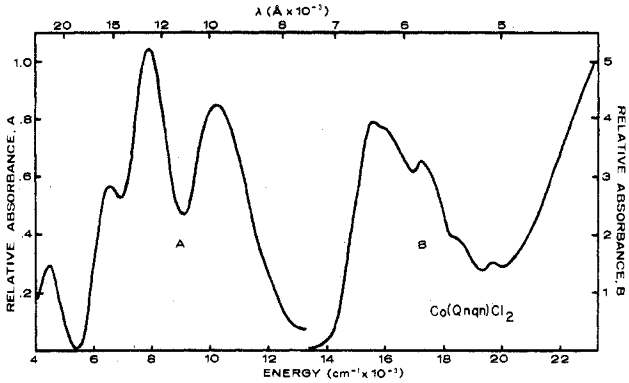

Figure 4. Electronic spectrum of $Co(Qnqn)Cl_2$.

The electronic spectrum of $Co(Qnqn)Cl_2$ is shown in Figure 4, and specific bands and assignments are included in Table III. The spectral properties of distorted, tetrahedral bis(amine)cobalt halides have been studied in detail by several groups.[23,26,27] As is usually observed for T_d cobalt, the spectrum of $Co(Qnqn)Cl_2$ shows two sets of strong bands, one between 6000 and 11,000 cm^{-1}, which we have assigned to components of the ν_2 $^4A_2 \rightarrow {}^4T_1(F)$ transition, and another between *ca.* 14,000 and 18,000 cm^{-1}, which we have assigned to components of the ν_3 $^4A_2 \rightarrow {}^4T_1(P)$ transition. In addition to these relatively intense spin-allowed transitions, $Co(Qnqn)Cl_2$ also exhibits a moderately intense band at 4400 cm^{-1} and two weak bands between 18,000 and 20,000 cm^{-1}. We have assigned the 4400-cm^{-1} band to the ν_1 $^4A_2 \rightarrow {}^4T_2$ transition. A similar low-energy band in $Co(quin)_2Cl_2$ has been observed and similarly assigned by Goodgame and Goodgame.[26] This assignment in solution has been subsequently questioned by Lever and Nelson[27] and attributed to amine combination or overtone bands. We, however, believe that our assignment of ν_1 is correct because no similar band is observed at *ca.* 4400 cm^{-1} in either the iron or copper compound. The ligand itself does exhibit weak, sharp overtone bands at 4400, 4360, and 4270 cm^{-1}; however, these bands are very narrow and an order of magnitude less intense than the band observed at 4400 cm^{-1} in $Co(Qnqn)Cl_2$. The ν_1 transition would, however, be expected to be weaker than ν_2 and ν_3, because in T_d symmetry, ν_1 is electric dipole forbidden and becomes only partially allowed in C_{2v} symmetry. Because the ν_1 transition corresponds to $10Dq$, the value of Dq based upon ν_1 is 440 cm^{-1}. The values of Dq and B can also be calculated by using the assignments of ν_2 and ν_3 as described by Konig.[28] By using this approach and taking the values of ν_2 and ν_3 as the center of the bands at half-maximum (8800 and 16,500 cm^{-1}, respectively), the crystal field parameters can be calculated as $Dq = 520$ cm^{-1}, $B = 640$ cm^{-1}, and $\beta = 0.57$. The discrepancy between the two Dq values is no doubt a result of the observed structure in each of these bands and the arbitrary choice of values for ν_2 and ν_3.

Both Lever and Nelson[27] and Goodgame and Goodgame[26] have discussed the origin of the structure observed in both ν_2 and ν_3. As the symmetry about the cobalt ion is reduced from true T_d to C_{2v}, the orbital degeneracy of the $^4T_1$ state is removed. This removal yields the $^4A_2$, $^4B_1$, and $^4B_2$ states. It is now fairly well accepted[26,27,29-31] that the structure observed in ν_2 and ν_3 in CoL_2X_2 type complexes results from a reduced-symmetry ligand field rather than from spin-orbit coupling. In general, it is found that ν_2 is more sensitive than ν_3 to reduced-symmetry ligand field components and that the line width of the components of ν_2 can be taken as an indication of the extent of distortion from pure tetrahedral symmetry. For $Co(Qnqn)Cl_2$, the width of the bands attributed to ν_2 at half-maximum is *ca.* 6000 cm^{-1}. This line

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width is much larger than that observed in $CoCl_4^{2-}$, Co(quin)$_2$-Cl$_2$, and related compounds[23,26,27] and indicates that Co(Qnqn)Cl$_2$ is more highly distorted than the tetrakis and bis complexes. The line width is, however, similar to that observed in a related complex of cobaltous chloride with a quinuclidinone-containing ligand.[1] Lever and Nelson[27] were able to assign each of the components of the ν_2 band in C_{2v} symmetry to transitions to the above-mentioned nondegenerate states by using the results of polarized single-crystal studies[31,32] and conclusions based upon steric hindrance. In an approach similar to theirs, we tentatively assign the band at 6600 cm^{-1} to the $^4A_2 \rightarrow {}^4B_1$ transition, the band at 7940 cm^{-1} to the $^4A_2 \rightarrow {}^4A_2$ transition, and the band at 10,200 cm^{-1} to the $^4A_2 \rightarrow {}^4B_2$ transition. Polarized single-crystal studies will be undertaken in the near future to support these assignments further.

The infrared spectrum (Figure 3) of Co(Qnqn)Cl$_2$ shows two strong bands at 321 and 350 cm^{-1} that can be attributed to the cobalt-chlorine vibrations. It is interesting to note that the splitting of the two ν(M–Cl) bands is larger in the iron complex (43 cm^{-1}) than in the cobalt complex (29 cm^{-1}) but that the average of the two bands is the same (336 cm^{-1}) for both complexes. This condition indicates that the metal-ligand bonding in the two complexes is very similar, while the iron complex is more highly distorted from tetrahedral symmetry than the cobalt complex.

Nickel(II) Complexes. The nickel chloride complexes prepared in this study are particularly interesting because two isomers can be prepared which have unusual, interrelated thermal properties. The two isomers are referred to here as violet Ni(Qnqn)Cl$_2$ and yellow [Ni(Qnqn)Cl$_2$]$_2$. The dimeric nature of the yellow isomer has been verified by single-crystal X-ray analysis.[6] The violet isomer is believed to be distorted tetrahedrally in structure on the basis of the spectral data discussed below. The two isomers have completely different X-ray powder patterns.[7] The pattern for the violet isomer is similar to that of Co(Qnqn)Cl$_2$; however, the violet isomer is not isostructural with its cobalt analog. Attempts to date to obtain single crystals of the violet isomer have resulted in very small crystals, which are unsuitable for single-crystal X-ray work. We are currently trying to obtain suitable crystals at high temperature.

The true isomeric nature of the yellow and violet nickel complexes is demonstrated by their thermal properties which are described in detail, because they are apparently unique. These properties are presented in Scheme I.

Scheme I. Interrelated Thermal Properties of the Nickel Chloride Complexes

$$\begin{tikzcd}
\text{yellow } [\mathrm{Ni(Qnqn)Cl_2}]_2 \arrow[r, "\text{heat to}", "ca.\ 230^\circ"'] & \text{violet } \mathrm{Ni(Qnqn)Cl_2} \arrow[d, "\text{cool to room temp}"] \\
\text{yellow } [\mathrm{Ni(Qnqn)Cl_2}]_2 \arrow[u, "\text{warm to room temp}"'] & \text{violet } \mathrm{Ni(Qnqn)Cl_2} \arrow[l, "\text{cool to}"', "ca.\ 195^\circ\mathrm{K}\ (-78^\circ\mathrm{C})"]
\end{tikzcd}$$

When a sample of the yellow isomer is heated in a melting point tube (either sealed under helium or open), the color of the complex changes to violet over a narrow temperature range centered at *ca.* 230°. The resulting violet complex has an X-ray powder pattern identical with that of the violet nickel complex prepared directly. This solid-state structural transformation is also observed as an endotherm centered at 230° (accompanied by no weight loss) in the dtga pattern of the yellow complex.[7] The violet isomer shows no such endotherm, and both isomers exhibit identical dtga patterns above 230°. When single crystals of the yellow isomer are heated on the hot stage of a polarizing microscope, the color change can also be observed visually. At a temperature of *ca.* 230°,[33] individual crystals of the yellow isomer, within a time span of less than 1 sec, transform to the violet isomer. The transformation is occasionally accompanied by the rapid "jumping" of the crystals. The color change in a crystal appears to originate either on a surface or at a defect and to spread rapidly throughout the single crystal. The crystal subsequently becomes very brittle and exhibits a large number of faults and defects but retains its crystalline shape.[34] On cooling to room temperature (either quickly or slowly), the violet isomer does *not* revert back to the yellow isomer but remains violet. This would appear to indicate that the high-temperature solid-state transformation is irreversible. However, when a sample of the violet isomer is placed in a melting point tube (either open or sealed) and cooled quickly by inserting it in liquid nitrogen, the complex immediately changes color to the yellow isomer and remains yellow upon warming to room temperature. The resulting yellow isomer has an X-ray powder pattern which is identical with that of the material which is prepared by dissolving the violet isomer in methylene chloride and evaporating the solution to dryness (see Experimental Section). When a sample of the violet isomer is cooled slowly from room temperature, the color change takes place over a temperature range of about 15° that is centered at *ca.* 195°K (−78°C). It is not certain whether this temperature range is the result of a nonuniform sample temperature or of a solid-state transformation which occurs at slightly different temperatures; nonetheless, individual crystals appear to transform very quickly from violet to yellow. This color change can also be observed in the electronic spectrum of the violet complex mulled in Kel-F 90 (see below), but the transformation seems to be depressed upon mulling.

The thermal pathway described in Scheme I can be repeated up to at least six cycles with no apparent change in the compounds. The yellow and violet isomers are, however, completely stable at room temperature; no interconversion of the compounds at room temperature has been observed over a period of approximately 2 years. A study of the thermal properties of the two isomers at room temperature[7] has revealed that the transformation of the violet isomer to the yellow isomer is accompanied by a change in enthalpy, ΔH, of −2.60 ± 0.07 kcal/mol of violet isomer. Because the interrelated thermal properties of these two isomers are unique to the experience of the authors, a rationale, which is based upon the molecular structures of the isomers, is presented below.

There are many nickel complexes which are observed to exist as two different isomers. There are, however, only a few which appear to be similar to the nickel isomers reported

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(32) J. Ferguson, *J. Chem. Phys.*, 32, 528 (1960).

(33) All crystals do not appear to transform at exactly the same temperature. This condition is believed to be a result of differing thermal contact between the different crystals and the hot stage. All crystals do however transform over a temperature range of *ca.* 10° as measured for the hot stage. All transformations are abrupt and rapid.

(34) The yellow crystals exhibit only very slight dichroism with transmitted light of different polarization. The violet crystals, however, are strongly dichroic with transmitted light. In one polarization the crystals appear very dark violet, while at another polarization, they appear pale green. This indicates that long-range order in the yellow crystals is preserved during the transformation to the violet crystals. Polarized single-crystal studies of this behavior are in progress.

on here, and none of these exhibits the unusual low-temperature solid-state interconversion. Goedken, *et al.*,[35] have prepared both yellow and blue isomers of nickel(II) with the 1,1,1-trimethylhydrazinium cation and have described a high-temperature (145°) solid-state transformation of the yellow octahedral isomer to the blue tetrahedral isomer. This behavior is different from that observed in the nickel complexes reported on here, because the transformation is reversible; the blue isomer reverts to the yellow isomer on cooling to *ca.* 120°.[35] Preston and Kennard have reported on the X-ray structure of a very similar yellow, five-coordinate, binuclear nickel complex[36] and have described the properties of a tetrahedral violet isomer.[35,37] Unpublished work by the present authors indicates that these 2,9-dimethyl-1,10-phenanthroline isomeric complexes do exhibit a high-temperature conversion of the yellow isomer to the violet isomer. However, no low-temperature behavior similar to that reported herein for the Ni(Qnqn)Cl_2 isomers is observed down to liquid nitrogen temperature. A similar set of blue and yellow isomers has been reported with nickel(II) and 4-methylthiazole[38] and with 2-aminobenzothiazole.[39] In neither case was any thermal interconversion noted.

In an effort to determine how general this thermal behavior is, we have prepared the violet nickel bromide complex, Ni(Qnqn)Br_2. To date, we have not been able to prepare a corresponding yellow bromide isomer, and the violet bromide complex exhibits no unusual behavior at either high or low temperatures. The structural properties of this complex are described below and compared with the violet chloride complex. We have also prepared the 6′-methoxy derivative of Qnqn and have been able to prepare both a yellow and a violet complex with nickel chloride; however, these two isomers do not show any evidence of thermal interconversion at either high or low temperatures.[40] The properties of these complexes will be described in a future paper.

The magnetic properties of the nickel chloride complex and bromide complex are presented in Table II. Both complexes have magnetic moments at room temperature that are consistent with those expected for distorted tetrahedral nickel(II) complexes.[41,42] The small temperature dependence of μ_{eff} for the bromide complex is predicted[42] for a tetrahedral $^3T_1$ term in the presence of a low-symmetry ligand field component. The temperature dependence of μ_{eff} observed for violet Ni(Qnqn)Cl_2 is no doubt the result of the transformation to the yellow isomer at low temperature.

The value of the room-temperature magnetic moment of yellow [Ni(Qnqn)$Cl_2]_2$ is 3.21 BM per nickel ion and indicates that this five-coordinate complex contains high-spin nickel(II) ions. The high-spin configuration can be predicted on the basis of the N_2Cl_3 donor atoms,[43] and the room-temperature value is essentially the same as that reported for several similar five-coordinate nickel(II) complexes.[4,36,39,44] Because this complex is binuclear, the possibility of spin-spin coupling should be considered. The long Ni-Ni distance of 3.652 Å[6] rules out any direct Ni-Ni bonding; however, as recently discussed by Ginsberg, *et al.*,[45] magnetic exchange can be expected to occur through the bridging chloride ligands with weak ferromagnetic coupling occurring if the bridging bond angles are *ca.* 90°.[46] The observed temperature dependence in μ_{eff} for [Ni(Qnqn)$Cl_2]_2$ is small; the moment decreases slightly between room temperature and 101°K (Table II). This slight decrease in moment is not consistent with ferromagnetic coupling; however, additional lower temperature studies would be required to support any suggestion of antiferromagnetic coupling. The absence of ferromagnetic coupling may be a result of the extensive distortion of the Ni-Cl-Ni and Cl-Ni-Cl bond angles from 90°.

The electronic absorption spectra in Kel-F mulls of Ni(Qnqn)Br_2 at 300 and 23°K and violet Ni(Qnqn)Cl_2 at 300, 80, and 72°K are presented in Figures 5 and 6, respectively. The positions of the bands at room temperature and band assignments are presented in Table III. The solution spectra in CH_2Cl_2 of these compounds are very similar to the room-temperature mull spectra; the only major difference is that the two sharp peaks at *ca.* 11,500 cm^{-1} in the mull spectra are not resolved in solution. Solution spectral results (with extinction coefficients) are presented in Table III.

The electronic absorption spectra of Ni(Qnqn)Br_2 at both room temperature and low temperature and the spectrum of Ni(Qnqn)Cl_2 at room temperature are typical of pseudotetrahedral nickel complexes.[47] In fact, these spectra are essentially identical with the spectra reported for the pseudotetrahedral complexes formed with Ni(II) and *N,N,N′,N′*-tetramethyl-1,2-propylenediamine[47] and the benzaldehyde derivative of *N,N*-ethylenediamine.[48] The low-energy band at *ca.* 7700 cm^{-1} in Ni(Qnqn)Cl_2 and Ni(Qnqn)Br_2 is assigned to one of the components of the ν_1 $^3T_1(F) \rightarrow {}^3T_2(F)$ transition in tetrahedral symmetry. The requirement that this band be one of the components of the $^3T_2(F)$ state is based upon the high value of *Dq* which would result (*ca.* 770 cm^{-1}) if this band represented the complete ν_1 transition. This high a value of *Dq* would not be consistent with a tetrahedral coordination sphere containing N_2Cl_2 donor atoms.[49] The band located at *ca.* 10,500 cm^{-1} is assigned to the ν_2 $^3T_1(F) \rightarrow {}^3A_2(F)$ transition, and the band at *ca.* 18,000-19,000 cm^{-1} is assigned to the ν_3 $^3T_1(F) \rightarrow {}^3T_1(P)$ transition. Some structure is observed in ν_3 in the chloride complex and the bromide complex at low temperature (Figures 5 and 6) presumably as a result of the reduced symmetry ligand field. As has been noted previously,[50] the ν_3 band is *ca.* 10-20 times more intense than ν_2. The two sharp peaks at *ca.* 11,000-12,000 cm^{-1} are tentatively assigned to spin-forbidden transitions which are expected[49] in this region of the Ni(II) tetrahedral spectra. The very high intensity of these presumably spin-forbidden bands has been noted previously[47,50,51] and attributed to the mixing *via* spin-orbit coupling of the singlet states

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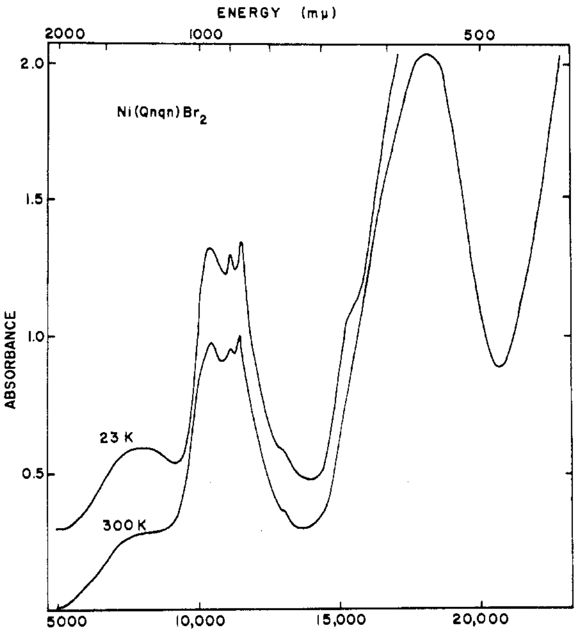

Figure 5. Electronic spectrum of Ni(Qnqn)Br$_2$ at 300 and 23°K.

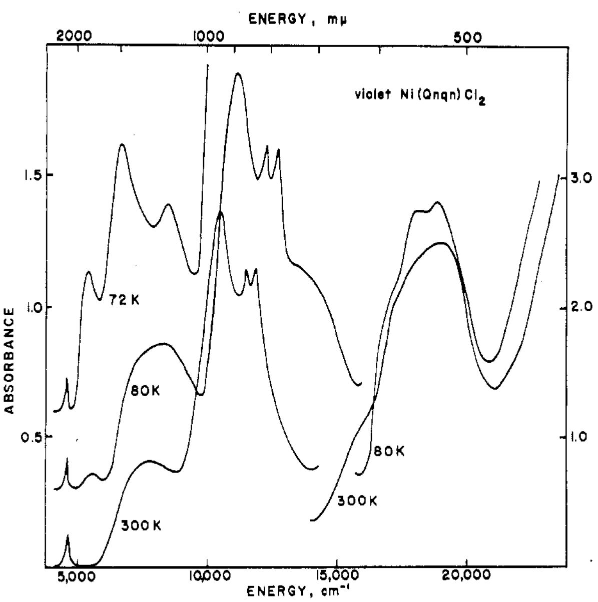

Figure 6. Electronic spectrum of violet Ni(Qnqn)Cl$_2$ at 300, 80, and 72°K.

with the nearby $^3A_2(F)$ triplet state. The large extinction coefficients included in Table III for Ni(Qnqn)Br$_2$ are reasonable for a distorted tetrahedral nickel complex. Konig's method[28] has been used to calculate the ligand field parameters at room temperature for each of these complexes: for Ni(Qnqn)Cl$_2$, $Dq = 565$ cm^{-1}, $B = 971$ cm^{-1}, and $\beta = 0.90$; for Ni(Qnqn)Br$_2$, $Dq = 552$ cm^{-1}, $B = 997$ cm^{-1}, and $\beta = 0.92$ in methylene chloride solution, and $Dq = 554$ cm^{-1}, $B = 948$ cm^{-1}, and $\beta = 0.88$ in a Kel-F mull. All of these values are typical for pseudotetrahedral nickel complexes.[49]

The electronic spectrum of violet Ni(Qnqn)Cl$_2$ at low temperature requires special comment. As noted above, violet Ni(Qnqn)Cl$_2$ undergoes a solid-state transformation to yellow [Ni(Qnqn)Cl$_2$]$_2$ at *ca.* 195°K. We had hoped to observe this transition in the mull spectrum of violet Ni(Qnqn)Cl$_2$, but several low-temperature experiments soon made it clear that the temperature of the solid-state transition was affected by the mulling process. Indeed, in all cases, the transition temperature was depressed. The transformation is however obvious and is seen in the low-temperature spectrum presented in Figure 6. At 80°K, the weak band at *ca.* 6000 cm^{-1} and the strong shoulder at *ca.* 14,000 cm^{-1} can be attributed to the presence of a small amount of yellow [Ni(Qnqn)Cl$_2$]$_2$. The low-temperature spectrum in Figure 6 should be compared with the low-temperature spectrum of yellow [Ni(Qnqn)Cl$_2$]$_2$ in Figure 7. When the temperature is reduced to 72°K, the spectrum changes drastically, and for the spectrum above 10,000 cm^{-1}, the optical density increases to such an extent that the spectrum cannot be recorded. Visually, the color of the mull changes from violet to yellow between 80 and 72°K. Because the bands between 5000 and 10,000 cm^{-1} agree with the spectrum of the yellow isomer, the low-temperature mull spectrum is consistent with the solid-state structural transformation. Several attempts to measure the transformation directly on the violet solid failed because we could not obtain a sufficiently thin film of the pure violet complex.

The low-temperature spectrum of violet Ni(Qnqn)Cl$_2$ is interesting in another respect. It should be noted that at 80°K the positions of the ν_1 and ν_2 bands and the spin-forbidden bands in Ni(Qnqn)Cl$_2$ shift to higher energy. No such shift is observed in the spectrum of Ni(Qnqn)Br$_2$ at low temperature (Figure 5). We do not believe that this shift can be attributed completely to the presence of the band of the yellow isomer at 13,000 cm^{-1} but do believe that the shift is, at least in part, a result of an increase in *Dq* with decreasing temperature. Because this possible increase in *Dq* may be a result of changes in unit cell size or bond lengths with temperature, it is discussed below.

The electronic absorption spectrum of the binuclear square-pyramidal yellow [Ni(Qnqn)Cl$_2$]$_2$ complex was measured at 310 and 23°K and is presented in Figure 7. The numerical values for the band positions are presented in Table IV. The spectral properties of square-pyramidal nickel complexes have been the subject of a good deal of recent study,[52] and several compounds have exhibited spectra similar to the one which is recorded in Figure 7.[44,53] Probably the best framework within which to describe the spectral properties of this compound is the crystal field model presented by Ciampolini.[54] This model makes use of the weak-field configuration with configuration interaction and ignores spin–orbit coupling and intermixing with 4s and 4p orbitals. The electrostatic field is considered to arise from five point dipoles of strength μ that point at the nickel from the corners of a square pyramid. The Ni-dipole distance is taken as 2.00 Å, and the energy of the different states is calculated for a given axial ligand-nickel-basal ligand angle.[54] For the yellow [Ni(Qnqn)Cl$_2$]$_2$ complex, X-ray structural data[6] indicate a highly distorted square-pyramidal geometry with an average axial ligand-nickel-basal ligand angle of 100.3°. By taking into account the highly distorted nature of the square-pyramidal ligand field and by making use of the shape, intensity, and temperature dependence of the observed bands, a reasonable but tentative assignment of the spectral bands in yellow [Ni-

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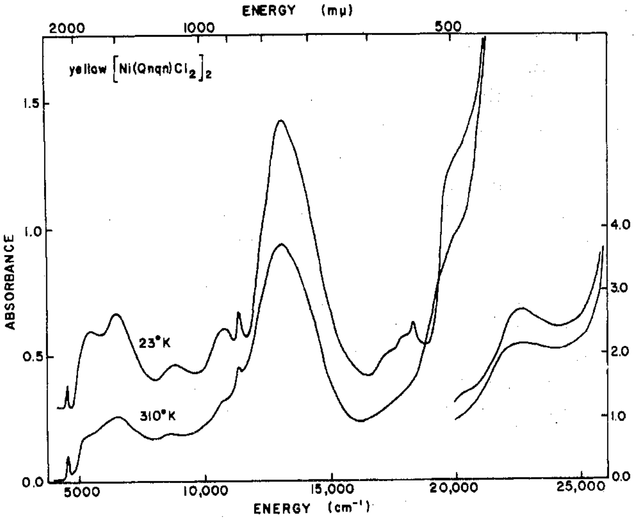

Figure 7. Electronic spectrum of yellow $[Ni(Qnqn)Cl_2]_2$ at 310 and 23°K.

Table IV. Electronic Spectrum of Yellow $[Ni(Qnqn)Cl_2]_2$

	Mull		
MeOH soln	300°K	23°K	Assignment "C_{4v}" ($\mu \simeq 4$ D)
	5,400 sh	5,490	$^3B_1 \rightarrow {}^3E(F)$ (strong)
	6,490	6,450	
	8,500 sh	8,790	$\rightarrow {}^3A_2(F)$
	10,700 sh	10,750	$\rightarrow {}^3B_2(F)$
	11,360	11,360	$\rightarrow {}^1A_1(D)$ (weak)
13,300 (3.1)	13,010	13,250	$\rightarrow {}^3E(F)$ (strong)
14,500 sh		17,240 sh	$\rightarrow {}^1E, {}^1B_1(D), {}^1A_2$ (weak)
		17,860 sh	
		18,280	
	19,600 sh	20,400 sh	$\rightarrow {}^3A_2(P)$ (weak)
	22,780	22,220	$\rightarrow {}^3E(P)$ (strong)

$(Qnqn)Cl_2]_2$ can be made. These assignments are presented in Table IV. No rigorous calculation of μ was attempted because of the highly distorted nature of the coordination symmetry; however, it should be noted that the assignments are in qualitative agreement with a value of μ of *ca.* 4 D. It is puzzling that the reduced symmetry removes the degeneracy of the low-energy $^3E(F)$ term by about 1000 cm^{-1} while the transitions to the higher energy $^3E(F)$ and $^3E(P)$ terms are unsplit. This may be an indication of a difficulty with our assignment, and plans are currently under way to study the polarized single-crystal spectrum of this complex in order to gain a better understanding of the information contained in its electronic spectrum.

We have attempted repeatedly to obtain a solution spectrum of the yellow complex with no real success. In all solvents tried to date, the complex either (1) is insoluble, or (2) dissolves to give a violet solution whose spectrum is identical with that of violet $Ni(Qnqn)Cl_2$ or (3) undergoes solvolysis to yield a spectrum quite different from that observed in the mull. The third case occurs with methanol; however, with this solvent, solvolysis is somewhat slower (requiring *ca.* 1 min), and a spectrum of this solution that is recorded in Table IV shows a band at 13,300 cm^{-1} with an extinction coefficient of 3.1 M^{-1} cm^{-1}. The shoulder at 14,500 cm^{-1} is most likely a result of the beginning of solvolysis and increases in intensity with time.

The far-infrared spectra of the two nickel isomers are presented in Figure 3A along with that of the ligand. No difficulty was found in obtaining the spectrum of the yellow complex, but a good deal of difficulty was encountered in preparing either a mull or a KBr or CsI pellet of the violet complex. Upon grinding with either KBr or CsI or mulling with Nujol, the violet $Ni(Qnqn)Cl_2$ complex was visually observed to turn yellow. To avoid grinding, the violet isomer was gently mixed with finely ground CsI. This procedure yielded a pale violet mixture. Upon pressing this mixture (or a mixture with KBr) at 20,000 lb, an essentially yellow pellet was obtained. If the mixture was pressed at 2000 lb for *ca.* 30 sec, a pellet of partly violet color could be obtained. It was this type of pellet which was used to obtain the spectrum shown in Figure 3A, and the poor quality of the spectrum is a result of these problems. The spectrum of this pellet shows two lines at 310 and 340 cm^{-1}. These two lines can be attributed, by comparison with the other tetrahedral complexes, to the ν_{Ni-Cl} vibrational bands in the tetrahedral violet $Ni(Qnqn)Cl_2$ complex and the two bands at 230 and 282 cm^{-1} can be attributed to the yellow $[Ni(Qnqn)Cl_2]_2$ isomer which was formed during the preparation of the pellet. The spectrum of the yellow complex exhibits two lines at 228 and 285 cm^{-1}. In agreement with other work[22] on complexes containing bridging chlorine atoms, we assign the band at 228 cm^{-1} to the bridging nickel chlorine stretch and the band at 285 cm^{-1} to the terminal stretch. The bridging absorption band is expected to occur at lower frequencies than the terminal band because the longer nickel–chlorine three-center bonds are weaker than the shorter terminal Ni–Cl bonds. In addition, the terminal Ni–Cl vibrational band in the yellow isomer lies at a lower frequency than in the violet isomer because of the increased coordination number in the five-coordinate yellow isomer. The ratio of ν_{Ni-Cl} (bridging) to ν_{Ni-Cl}(terminal) is 0.80 and agrees well with the ratio observed in similar complexes.[22] These assignments are supported by high-pressure infrared studies and pure nickel isotope studies which will be reported elsewhere.[55]

The unusual structural transformations of the yellow and violet nickel isomers at high and low temperatures (Table IV) requires some comment. The failure of the transformation to occur at room temperature indicates that there must be some barrier present at room temperature which prevents the thermodynamically less stable violet isomer from converting to the more stable[7] yellow isomer. It appears reasonable that as the yellow isomer is heated, the vibrational energy of the dimeric molecule increases to a point where the vibrational energy is sufficient to break the two longer (2.422 Å), bridging Ni–Cl bonds (*ca.* 230°K). As this occurs, the molecule is structurally rearranged to the tetrahedral isomer. This change in Ni–Cl bond angles may also be accompanied by a significant change in the internal planarity of the ligand.[6,8] If a comparison of the tetrahedral $Co(Qnqn)Cl_2$ structure and the violet $Ni(Qnqn)Cl_2$ structure is valid, the results for the cobalt complex indicate that in the tetrahedral complex the ligand has a much higher degree of planarity than in the dimeric, square-pyramidal yellow complex (see ref 8 for specific details). These two structural changes along with entropy considerations may prevent the reverse transformation from occurring and may also provide the required energy barrier which prevents interconversion at room temperature.

As the violet tetrahedral isomer is cooled below room temperature to *ca.* 195°K, the barrier to the interconversion must be removed again. This could come about in two obvious ways. As the crystallites of the violet isomer are cooled, the unit cell volume may undergo a contraction. At the same time, the vibrational ellipsoids associated with the chlorine

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atoms may decrease in volume. Either one of these processes, or perhaps both, may account for the removal of the barrier for transformation at low temperatures. Some evidence, which has been observed (see above) in the low-temperature electronic spectrum of the violet isomer, indicates that the ligand field strength increases with decreasing temperature. This increase could be a result of a decreasing unit cell size. The observation that the transformation on cooling appears to originate either at a lattice defect or at the surface of a crystal may indicate that the barrier is more easily removed at these points and that a "cooperative effect" then occurs throughout the crystal that forces the structural change.

The dimerization must be viewed as a bona fide chemical reaction because it entails the formation of two new Ni–Cl bonds. However, the dimerization is highly anomalous in that it can be induced by cooling but not by heating. The resolution of this kinetic dilemma could be pursued along the lines of the special crystal effects associated with a solid-state reaction as described above. Alternatively, the postulation of a square-planar intermediate in the dimerization can be invoked to provide the explanation

$$\text{tetrahedral} \rightleftharpoons \text{square planar} \xrightarrow{k_2} \text{dimer}$$

If the square-planar monomer were an obligatory intermediate in the dimerization, the rate of formation of the dimer could be virtually nil at room temperature in the absence of any appreciable concentration of this isomer. However, as the sample is cooled, the tetrahedral square-planar equilibrium is well known[56] to shift in favor of the square-planar isomer and, of course, the dimerization rate can then increase exponentially as the temperature decreases.

It is interesting to speculate about the portion of the ligand which is responsible for the unusual thermal behavior. No doubt, the size and position of the quinoline portion of the ligand is closely tied to the unusual geometry observed in the yellow [Ni(Qnqn)Cl$_2$]$_2$ complex. This has been indicated by the X-ray results[6] which place one of the quinoline hydrogen atoms near the open coordination site in the yellow square-pyramidal nickel complex. Replacement of the quinoline group in the ligand with pyridine would most likely lead to rather different behavior. It would then be useful to substitute different groups in the five and six position of the pyridine ring and study the thermal properties of the resulting complexes. If the required ligands can be prepared, these studies will be undertaken.

Within our experience, this type of a structural change appears to be unique. Additional X-ray work is currently in progress, including low-temperature work, to determine more precisely the exact mechanism or structural detail which permits this unusual thermal behavior.

Cu(Qnqn)Cl$_2$. All of the properties of this complex are consistent with a highly distorted tetrahedral structure. Its magnetic properties, which are presented in Table II, indicate that the compound is paramagnetic with one unpaired electron. The very small temperature dependence observed in μ_{eff} indicates the absence of any extensive magnetic coupling between copper ions. The electronic spectrum of the copper complex is presented in Figure 2. The broad band at 12,300 cm^{-1} and the shoulder at *ca.* 8000 cm^{-1} can be assigned as d–d transitions from the ground state to the ^{2}E excited state whose orbital degeneracy has been removed by the low-symmetry ligand fields. A similar spectrum for the distorted tetrahedral copper(II) chloride complex with 2 mol of 1,2-dimethylimidazole has been reported.[57] Similar spectral results have also been obtained for the pseudotetrahedral bis(*N*-isopropylsalicylidenaminato)copper(II) complex.[58]

The infrared spectrum of the copper complex shows two bands at 293 and 315 cm^{-1}. These agree reasonably well with the metal–chlorine vibrational bands for the other tetrahedral complexes reported on here. The lower values for the copper–chlorine vibrational bands indicate somewhat weaker metal–ligand bonding in the copper complex.

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Registry No. Fe(Qnqn)Cl$_2$, 42847-00-7; Co(Qnqn)Cl$_2$, 42847-01-8; [Ni(Qnqn)Cl$_2$]$_2$, 42847-02-9; Ni(Qnqn)Cl$_2$, 42847-03-0; Ni(Qnqn)Br$_2$, 42847-04-1; Cu(Qnqn)Cl$_2$, 42847-05-2.

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