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Transition Metal Chemistry of Quinuclidinone-Containing Ligands. II. Spectral and Magnetic Properties of Some Transition Metal Complexes Containing 2-(*N*-Morpholinylmethyl)-3-quinuclidinone and Related Ligands[1]

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Complexes of cobalt(II), nickel(II), and iron(II) halides with the title compound were prepared by adding the appropriate metal salt to the ligand in alcoholic solutions. The complexes have pseudotetrahedral microsymmetry around the central metal ion as indicated by their spectral and magnetic properties; the coordination sphere contains one bidentate nitrogen-bonded ligand and two halide atoms. Ligand field band assignments, metal–halide stretching frequencies, and magnetic susceptibility data are given for each of the complexes. The cobalt(II) and nickel(II) perchlorate complexes of the title compound were also prepared, and each contains two bidentate ligands which provide a tetrahedral ligand field that is stronger than for the halide complexes. It is suggested that the apparent preference of the ligand for one-to-one metal-to-ligand coordination and the consequent tetrahedral structures result from a combination of the size of the quinuclidine group and the rigidity of the five-membered chelate ring formed by the coordinated ligand. In addition to these pseudotetrahedral complexes, an octahedral nickel chloride complex which apparently contains bridging chloride ligands is reported. A cobaltous thiocyanate complex is also found to have an octahedral structure in the solid state and a tetrahedral structure in solution.

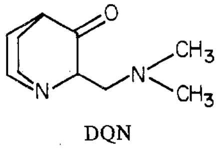
Introduction

As a part of an investigation of ligands which produce tetrahedral or distorted tetrahedral complexes with transition metal ions, we examined the coordinating ability of several potentially bidentate 2-(*N*-aminomethyl)-3-quinuclidinone ligands.

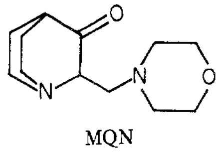
The study of the transition metal complexes which contain quinuclidinone and its derivatives has to date been limited. Yoke and his coworkers studied complexes involving quinuclidine and $AgNO_3$,[2] $CuCl_2$,[3] and $Cu(C_2H_3O_2)_2$.[4] The $CuCl_2\cdot$Quin and $CoCl_2\cdot$2Quin complexes (where Quin represents quinuclidine were reported[3] stable and magnetically normal and the cobalt was found to have an electronic spectrum typical of pseudotetrahedral coordination. The copper acetate complex $Cu(C_2H_3O_2)_2\cdot$Quin shows the antiferromagnetic behavior typically found in the dimeric copper(II) acetate systems.[5] Clark and Natile[6] prepared five- and six-coordinate vanadium(III) and chromium(III) halide complexes with quinuclidine. Complexes of the type $VX_3\cdot$2Quin (where X represents Cl or Br) were found to have trans trigonal-bipyramidal structures. Both $CrCl_3\cdot$3Quin and $CrCl_3\cdot$2Quin were prepared; the former was found to have an octahedral structure and the latter a trans bipyramidal structure. The five-coordinate compound $CrBr_3\cdot$Quin was the only isolable adduct found for chromium(III) bromide. The electron spin resonance spectra of one-to-one adducts of copper(II) bis(acetylacetonate) and copper(II) bis(hexafluoroacetylacetonate) with pyridine and quinuclidine have been examined.[7] A series of positive transition metal complexes containing the quinuclidinium ion was reported by Quagliano, *et al.*[8]

The only complexes with a bidentate quinuclidine-containing ligand appear to be those of Coffen and McEntee,[1] who reported several cobalt(II), nickel(II), and copper(II) complexes containing *trans*-2-(2′-quinolyl)methylene-3-quinuclidinone and its 6-methoxy derivative.

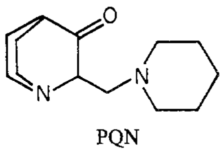
This paper reports the preparation and properties of several transition metal complexes containing the new ligands 2-(*N*-morpholinylmethyl)-3-quinuclidinone (MQN), 2-(*N*-dimethylaminomethyl)-3-quinuclidinone (DQN), and 2-(*N*-piperidinylmethyl)-3-quinuclidinone (PQN). Fisher–Hirschfelder models of MQN indicate a bulky, rigid structure which has considerable steric hindrance at the two nitrogen coordination sites. We anticipated that these ligands would coordinate through both nitrogen atoms to form complexes of the type MLX_2 in which L is the bidentate ligand, and X is a halide or pseudohalide. In view of the rigid five-membered ring which could be formed with the central metal ion and the steric factors present in these ligands, we further expected tetrahedral



DQN



MQN



PQN

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coordination. The evidence presented below substantiated these expectations in most cases.

Experimental Section

Preparation of Ligands. The ligand 2-(*N*-morpholinylmethyl)-3-quinuclidinone (MQN) has been briefly described in the chemical literature.[9] Rather than purify the product by distillation as previously suggested,[9] we found that the oily reaction product can be purified by recrystallizing it from boiling acetone.

A solution of 20 g of 3-quinuclidinone hydrochloride in 32 ml of ethanol and 20 ml of distilled water was mixed with a solution of 5.2 g of NaOH in 25 ml of distilled water. The mixture was refluxed momentarily to free the bicyclic amine, and after cooling, 12.6 g of morpholine and 11.7 g of 37 wt % aqueous formaldehyde were added. This mixture was refluxed gently for 1 hr and then heated with stirring at 70° for 17 additional hr. An amber-colored oil resulted when the solvents were removed by evaporation at reduced pressure. The oil was dissolved in methanol and dried several days over anhydrous Na_2SO_4. After removing the methanol, dry diethyl ether was mixed with oil to precipitate the unused portion of the bicyclic amine along with some tar-like by-products. Removal of the ether left either a yellowish solid or oil which was recrystallized from boiling acetone. The pure ligand was a white, crystalline solid, which melted at 101.5–102.7° (uncor). The yield was about 70% of the theoretical value. *Anal.* Calcd for $C_{12}H_{20}N_2O_2$: C, 64.26; H, 8.98; N, 12.48. Found: C, 64.17; H, 8.93; N, 12.25.

The ν(C=O) vibrational band for MQN in a KBr matrix was found at 1710 cm^{-1}, and the $n \rightarrow \pi^*$ transition associated with the ketone group was observed at 31,200 cm^{-1} in a mull and at 31,000 cm^{-1} in an acetonitrile solution (ϵ_M 62). The C–O–C asymmetric stretching mode is found generally as a strong band between 1140 and 1085 cm^{-1}.[10] The infrared spectrum of MQN produced bands at 1112 and 1150 cm^{-1}. The band at 1150 cm^{-1} decreased in intensity upon complexation, and we presume that the strong band at 1112 cm^{-1} is associated with the C–O–C functional group. The proton magnetic resonance spectra of 3-quinuclidinone and morpholine showed chemical shifts for CH_2 groups that are in the same general ranges. As a result, the spectrum of MQN is complicated because the chemical shifts cannot be clearly resolved. More details regarding the spectral properties of this compound have been presented elsewhere.[11]

The complex 2-(*N*-piperidinylmethyl)-3-quinuclidinone (PQN) was prepared with methods already described in the literature.[9] 2-(*N*-Dimethylaminomethyl)-3-quinuclidinone was prepared[9] and distilled under vacuum to obtain the starting material 2-methylene-3-quinuclidinone. This material was dissolved in anhydrous methanol and mixed with an equimolar quantity of piperidine, which had been distilled and stored over solid NaOH in a refrigerator. The reaction mixture was stirred for 8 days, at the end of which time, the solvents were removed by evaporating them at a reduced pressure. The residue was an amber-colored oil. The oil was dissolved in diethyl ether and dried over anhydrous K_2CO_3 for 24 hr. The ether was removed, and the resulting oil was pumped on for 2 days to remove traces of solvent. *Anal.* Calcd for $C_{13}H_{22}N_2O$: C, 70.23; H, 9.98; N, 12.60. Found:[12] C, 66.52; H, 9.65; N, 8.79.

The complex 2-(*N*-dimethylaminomethyl)-3-quinuclidinone (DQN) was prepared with described methods,[9] and 2-methylene-3-quinuclidinone was obtained in the same manner as for PQN and was dissolved in methanol. An excess of 40 wt % aqueous dimethylamine was added. The mixture was stirred for 8 days, and the product purified in the same manner as for PQN. *Anal.* Calcd for $C_{10}H_{18}N_2O$: C, 65.90; H, 9.96; N, 15.37. Found:[12] C, 64.02; H, 9.61; N, 14.28.

The Mannich reaction used to prepare these ligands is potentially reversible under certain circumstances,[13] *e.g.*, treatment with acids and distillation. In our preparation, the breakdown products would be 2-methylene-3-quinuclidinone and the respective secondary amine. The methylene group of the former was reported[9] to have an infrared absorption at 1640 cm^{-1}. After isolating, washing, and drying each of our complexes, we necessarily took care to inspect the infrared region around 1640 cm^{-1} for evidence of such decomposition. No such evidence was found in the spectra of any of these compounds.

Preparation of Metal(II) Complexes of 2-(*N*-Morpholinylmethyl)-3-quinuclidinone (MQN). Co(MQN)Cl_2. A mixture of 25 ml of ethanol and 25 ml of diethyl ether containing 0.70 g (0.003 mol) of $CoCl_2 \cdot 6H_2O$ was added dropwise with stirring to a mixture of 2.00 g (0.009 mol) of MQN dissolved in the same solvent. The precipitate, which formed immediately, was washed with ethanol and ether and air-dried. The product was a bright blue, polycrystalline solid. *Anal.* Calcd for $CoC_{12}H_{20}N_2O_2Cl_2$: C, 40.70; H, 5.60; N, 7.91. Found: C, 40.80; H, 5.74; N, 7.73.

Co(MQN)Br_2. This complex was prepared by employing the same procedure used for the corresponding $CoCl_2$ complex. The product was a dark blue, polycrystalline solid. *Anal.* Calcd for $CoC_{12}H_{20}N_2O_2Br_2$: C, 32.53; H, 4.55; N, 6.32. Found: C, 32.79; H, 4.61; N, 6.31.

Co(MQN)I_2. A 2.30-g sample of $CoI_2 \cdot 2H_2O$ (0.007 mol) was dissolved in a mixture of 25 ml of anhydrous methanol and 25 ml of anhydrous diethyl ether. This solution was added dropwise with stirring to 1.50 g of MQN (0.007 mol) dissolved in the same solvent mixture. The green crystalline product was collected by filtration and washed with fresh solvent. *Anal.* Calcd for $CoC_{12}H_{20}N_2O_2I_2$: C, 26.84; H, 3.75; N, 5.22. Found: C, 26.32; H, 3.90; N, 4.81.

Co(MQN)(NCS)$_2 \cdot C_2H_5OH$. A mixture of 1.16 g of Co(NCS)$_2$ (0.007 mol) in 50 ml of ethanol was heated to boiling and filtered. A hot solution of 1.50 g of MQN (0.007 mol) in 25 ml of ethanol was added to this hot filtrate. The solution was cooled to room temperature and filtered to remove a flocculent precipitate which had formed. About 100 ml of cyclohexane was added to the filtrate to promote crystallization. The walls of the container were scratched and, upon standing, a purple solid formed. The product was collected by vacuum filtration and was washed with ethanol and ether. After drying *in vacuo* over P_4O_{10} for several days, the product was a light purple, crystalline powder. *Anal.* Calcd for $CoC_{16}H_{26}N_4O_3S_2$: C, 43.14; H, 5.88; N, 12.58. Found: C, 43.09; H, 6.06; N, 12.61.

Ni(MQN)Cl_2. In the course of preparing the complexes of nickel(II) chloride, we found that by varying the experimental conditions we were able to prepare two complexes which have the formula Ni(MQN)Cl_2 but have dissimilar properties. The most efficacious means of obtaining the off-white and purple forms of this complex are as follows.

Purple Ni(MQN)Cl_2. A sample of $NiCl_2 \cdot 6H_2O$ (0.005 mol) was dissolved in a mixture of 50 ml of 1-butanol and 25 ml of 2,2-dimethoxypropane.[14] The solution was heated to its boiling point. A boiling solution, composed of 1.00 g of MQN (0.005 mol) in 25 ml of 1-butanol, was added in one portion to the nickel(II) chloride solution and rapidly stirred. The mixture was allowed to boil for several minutes until the purple product had formed; then it was quickly filtered. The product, which was a purple, crystalline solid, was dried *in vacuo* at 65° for several hours. *Anal.* Calcd for $NiC_{12}H_{20}N_2O_2Cl_2$: Ni, 16.58; C, 40.72; H, 5.70; N, 7.91. Found: Ni, 16.52; C, 40.45; H, 5.90; N, 7.71.

Off-White Ni(MQN)Cl_2. A 1.56-g sample of $NiCl_2 \cdot 6H_2O$ (0.007 mol) was dissolved in 350 ml of boiling ethanol, and 50 ml of 2,2-dimethoxypropane added. After the solution was boiled for several minutes, it was filtered. To the boiling filtrate, a hot solution of 1.50 g of MQN (0.007 mol) in 50 ml of ethanol was added in one portion. Upon mixing, the solution changed to a deep violet color. The mixture was heated briefly and then quenched in an ice–water bath. An off-white solid formed immediately. The sample was collected by filtration, washed with ethanol and diethyl ether, and dried *in vacuo* over P_4O_{10} for several days. The product was off-white, very finely powdered, and very hygroscopic. *Anal.* Calcd for $NiC_{12}H_{20}N_2O_2Cl_2$: C, 40.72; H, 5.70; N, 7.91. Found: C, 40.52; H, 5.74; N, 7.86.

When this off-white compound was left exposed to the air for a short time, it quickly absorbed 0.25 mol of water and changed to a pale green color. *Anal.* Calcd for $NiC_{12}H_{20.5}N_2O_{2.25}Cl_2$: C, 40.21; H, 5.77; N, 7.82. Found: C, 40.02; H, 5.69; N, 7.75. This pale

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(10) N. B. Colthup, L. H. Daly, and S. E. Wiberly, "Introduction to Infrared and Raman Spectroscopy," Academic Press, New York, N. Y., 1964, Chapter 10.

(11) R. C. Dickinson, Doctoral Dissertation, University of Missouri–Rolla, 1972.

(12) We believe that the deviation in the actual elemental analyses from the calculated values is primarily the result of solvent impurities which were not removed from the oily reaction products of PQN and DQN. Small quantities of 2-methylene-3-quinuclidinone do seem to be present as judged by the presence of a weak band at 1645 cm^{-1} which may be associated with a C=CH_2 vibration. This vibration was reported to occur at 1640 cm^{-1} by Hansen and Bader.[9] Corresponding $CoCl_2$ complexes do analyze well, which suggests that the reaction products of PQN and DQN were essentially pure.

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green complex was also prepared in a number of other solvents, such as methanol, ethanol, and methyl benzoate, by mixing together solutions of MQN and nickel(II) chloride at ambient temperatures. If no special precautions were taken to remove moisture from the solvents and reactants, the resulting complexes contained random quantities of absorbed water.

Ni(MQN)Br$_2$. A sample of anhydrous NiBr$_2$ weighing 1.44 g (0.007 mol) was dissolved in a mixture of 25 ml of ethanol and 25 ml of 2,2-dimethoxypropane. The mixture was refluxed for several hours. A solution composed of 1.50 g of MQN (0.007 mol) in 25 ml of 1:1 ethanol–2,2-dimethoxypropane was also refluxed and added dropwise with stirring to the hot solution of nickel(II) bromide. Crystallization began almost immediately. After the product was collected by filtration, washed with anhydrous diethyl ether, and dried *in vacuo*, it was a deep purple, polycrystalline solid. *Anal.* Calcd for $NiC_{12}H_{20}N_2O_2Br_2$: Ni, 13.26; C, 32.54; H, 4.55; N, 6.32. Found: Ni, 13.27; C, 32.51; H, 4.63; N, 6.21.

Ni(MQN)I$_2$. A sample of $NiI_2 \cdot 6H_2O$ weighing 2.78 g (0.007 mol) was dissolved in 30 ml of 1-butanol, heated to boiling, and filtered. A hot solution of 1.50 g of MQN (0.007 mol) in 20 ml of 1-butanol was added to the hot filtrate. Crystallization occurred immediately. The mixture was cooled and filtered, and the pasty solid was added to boiling ethanol. This mixture was cooled, filtered, and washed with ethanol and diethyl ether. The product, a dark green crystalline solid, was dried for several days over P_4O_{10} *in vacuo*. *Anal.* Calcd for $NiC_{12}H_{20}N_2O_2I_2$: C, 26.84; H, 3.76; N, 5.22. Found: C, 26.74; H, 3.74; N, 5.16.

Fe(MQN)Cl$_2$. A sample of $FeCl_2 \cdot 4H_2O$ weighing 4.32 g (0.022 mol) was dissolved in a deoxygenated mixture of 50 ml of anhydrous methanol and 50 ml of 2,2-dimethoxypropane. The mixture was refluxed under a nitrogen atmosphere for 12 hr. After refluxing, the mixture was diluted to 100 ml with the same mixed solvent to replenish that which was carried off in the stream of nitrogen. A 50-ml aliquot of this solution was used. To this solution, a solution composed of 2.40 g of MQN (0.011 mol) in 50 ml of a 1:1 methanol–2,2-dimethoxypropane mixture was added. The solid product was collected by filtration in an atmosphere of nitrogen and was washed with anhydrous methanol and anhydrous diethyl ether. The complex was a cream-white powder. *Anal.* Calcd for $FeC_{12}H_{20}N_2O_2Cl_2$: C, 41.06; H, 5.74; N, 7.98. Found: C, 41.36; H, 5.56; N, 7.71.

Preparation of the Cobalt(II) Chloride Complex of 2-(*N*-Piperidinylmethyl)-3-quinuclidinone (PQN), Co(PQN)Cl$_2$. About 1 g of PQN was dissolved in 35 ml of ethanol and added to a solution of cobalt(II) chloride prepared as follows. A 1.13-g sample of $CoCl_2 \cdot 6H_2O$ (0.048 mol) was dissolved in a mixture of 20 ml of ethanol and 10 ml of 2,2-dimethoxypropane, and the solution was heated at the boiling point for about 10 min and then cooled to room temperature. Upon addition of the PQN solution, a blue solid crystallized almost at once. After stirring the mixture for about 0.5 hr, the solid was collected by filtration and washed with diethyl ether. The product, which was blue and crystalline, was dried several days *in vacuo* over P_4O_{10} at room temperature. *Anal.* Calcd for $CoC_{13}H_{22}N_2OCl_2$: C, 44.34; H, 6.30; N, 7.95. Found: C, 44.13; H, 6.32; N, 7.78.

Preparation of the Cobalt(II) Chloride Complex of 2-(*N*-Dimethylaminomethyl)-3-quinuclidinone (DQN), Co(DQN)Cl$_2$. The procedure used in preparing this complex was the same as that used to prepare Co(PQN)Cl$_2$. The product was a blue, crystalline solid. *Anal.* Calcd for $CoC_{10}H_{18}N_2OCl_2$: C, 38.49; H, 5.81; N, 8.98. Found: C, 38.67; H, 6.00; N, 8.74.

Preparation of Metal(II) Perchlorates of 2-(*N*-Morpholinylmethyl)-3-quinuclidinone (MQN). The general procedure involved the dropwise addition of a solution of the metal(II) perchlorate to a solution of MQN. The solutions were composed of 0.007 mol of MQN dissolved in 50 ml of a 1:1 (by volume) ethanol–diethyl ether solution and 0.003 mol of the particular metal perchlorate was dissolved in 30 ml of the same solvent. Upon mixing, a solid formed which was collected by filtration, washed with ethanol and anhydrous ether, and air-dried.

The complex $Co(MQN)_2(ClO_4)_2$ was obtained as a purple powder. *Anal.* Calcd for $CoC_{24}H_{40}N_4O_{12}Cl_2$: C, 40.85; H, 5.72; N, 7.93. Found: C, 41.00; H, 5.90; N, 7.88.

The complex $Ni(MQN)_2(ClO_4)_2 \cdot 4H_2O$ was a dull white, powdery solid. *Anal.* Calcd for $NiC_{24}H_{48}N_4O_{16}Cl_2$: C, 37.04; H, 6.22; N, 7.20. Found: C, 37.19; H, 5.95; N, 7.01.

Physical Measurements. Electronic absorption spectra were recorded on a Cary 14; the solid complexes were studied in Kel-F No. 90 mulls and solution spectra were obtained by using spectral grade solvents and matched quartz cells. An Air Products and Chemicals Inc. AC-2 Cryo-Tip refrigerator was used to record the low-temperature electronic spectra of the solids. The infrared spectra in the 4000–400-cm^{-1} range were recorded in KBr on a Perkin-Elmer 337 spectrophotometer. In the 800–200-cm^{-1} range a Beckman IR-12 spectrophotometer and freshly dried CsI were used. Magnetic susceptibility measurements were obtained with a standard Gouy balance and a previously described low-temperature Faraday balance.[15] Both balances were calibrated with $CoHg(NCS)_4$, and the sample temperatures were measured with a copper–constantan thermocouple above 100°K and a platinum resistance thermometer below 100°K. All magnetic susceptibilities were measured at three different field strengths and, except as noted, were independent of field strength. The error limits for the reported magnetic moments are ±0.05 B.M.

The Mossbauer spectral results were obtained with an Austin Science Associates constant-acceleration spectrometer which has been described previously[16] and were evaluated by using the National Bureau of Standards PARLOR computer program.[17] The error limits for the Mossbauer parameters reported are less than or equal to ±0.04 mm/sec as calculated from the variance of the final computer iteration.[17] A Siemanns Crystalflex IV X-ray diffractometer with a copper tube and a nickel filter was used to obtain X-ray powder diffraction patterns.

Nickel analyses were performed in the authors' laboratory by using EDTA titrations. Carbon, hydrogen, and nitrogen elemental analyses were performed by Galbraith Laboratories.

Results and Discussion

The X-ray powder diffraction patterns for each of the new compounds have been measured and certain similarities are discussed below. The results indicate that, except where otherwise noted, the compounds are highly crystalline as opposed to amorphous or polymeric. In no instance did the X-ray powder patterns give any indication of the presence of the starting materials. In most instances, the complexes were easily recrystallized from simple solvents; however, it was found that in general, such recrystallization was not necessary and did not improve product purity. Likewise, the complexes could be recovered unchanged after solution in specific solvents such as chloroform, acetone, acetonitrile, and nitromethane. Small variations in reactant stoichiometry ratios had no effect upon the product isolated.

Cobalt(II) Halide Complexes. The complexes $Co(MQN)X_2$ (X = Cl, Br, I), $Co(PQN)Cl_2$, and $Co(DQN)Cl_2$ are air stable and are soluble in most common organic solvents but are decomposed in aqueous solutions. The X-ray powder diffraction patterns for these compounds are all dissimilar. The electronic absorption spectra of these compounds are similar to one another; band positions and assignments are presented in Table I, and the mull spectrum of $Co(MQN)Br_2$ at 25 and 280°K is depicted in Figure 1.

The relationships between electronic properties and stereochemistry of cobalt(II) complexes are well established,[18] and the spectra reported here are characteristic of pseudotetrahedral cobalt(II) ions. On the basis of this geometry, the ligand field parameter Dq and the Racah interelectronic repulsion parameter B were calculated by using the method outlined by Lever.[19] Group theoretical methods indicate that the orbital triplet in pure T_d symmetry is split in the presence of crystal fields of lower than tetrahedral symmetry.[20] The more intense components of the ν_2 and ν_3 bands in Figure 1 are presumably transitions to these levels. A similar conclusion has been reached by Lever and Nelson[21]

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Table I. Electronic Absorption Spectral Data for Cobalt(II) Halide Complexes[a]

Compd	Solvent	$^4A_2(F) \rightarrow {}^4T_1(F), \nu_2$, cm^{-1}	$^4A_2(F) \rightarrow {}^4T_1(P), \nu_3$, cm^{-1}	*Dq*, cm^{-1}	*B*, cm^{-1}
Co(MQN)Cl$_2$	Mull	5830, 7220, 9660	15,150, 15,565 sh, 17,240, 18,050 sh, 19,050 sh, w	430	695
	CHCl$_3$	5715 (25), 7145 (42), 10,000 (13)	14,705 (470), 15,015 sh, 15,750 (400), 17,390 (305), 18,050 sh, 19,050 sh, w		
Co(MQN)Br$_2$	Mull[b]	5715, 6895, 9435	14,925, 16,395, 17,545 sh, 18,520 sh	410	685
	Mull[c]	5680, 6950, 9430	10,400 sh, 15,000, 15,600 sh, 16,400 16,700, 17,540, 18,400, 18,700		
	CHCl$_3$	5620 (22), 6850 (51), 9525 (21)	14,815 (590), 16,100 sh, 16,665 (295), 17,545 sh, 18,180 sh, w		
Co(MQN)I$_2$	Mull	5550 sh, 6710, 9090	14,085, 14,700, 15,750, 16,000 sh, 17,700 sh	390	670
	CHCl$_3$	5400 (15), 6495 (66), 8930 (42)	14,165 (630), 14,620 (640), 15,530 (375), 16,395 sh, 17,420 sh, w		
Co(PQN)Cl$_2$	Mull	5830, 7245, 9800	15,150, 15,530 sh, 17,170, 18,020 sh, 18,890 sh, w	425	695
	CHCl$_3$	5750 (24), 7190 (43), 9900 (18)	15,150 (380), 15,625 (345), 17,270 (235), 18,020 sh, 18,725 sh, w		
Co(DQN)Cl$_2$	Mull	5970, 7245, 10,200	15,385, 17,125, 18,020, 18,780 sh	445	680
	CHCl$_3$	5815 (20), 7220 (41), 10,100 (15)	15,130 (350), 15,550 sh, 17,390 (185), 18,020 sh, 18,725 sh, w		
Co(MQN)(NCS)$_2$·C$_2$H$_5$OH	Acetone	6370 (10), 8200 (35), 10,700 (20)	15,450 (450), 16,025 sh, 17,860 (150), 18,520 sh	490	630

[a] Abbreviations: w, weak; sh, shoulder. Molar extinction coefficients are given in parentheses. [b] Spectral data obtained at 280°K. [c] Spectral data obtained at 25°K.

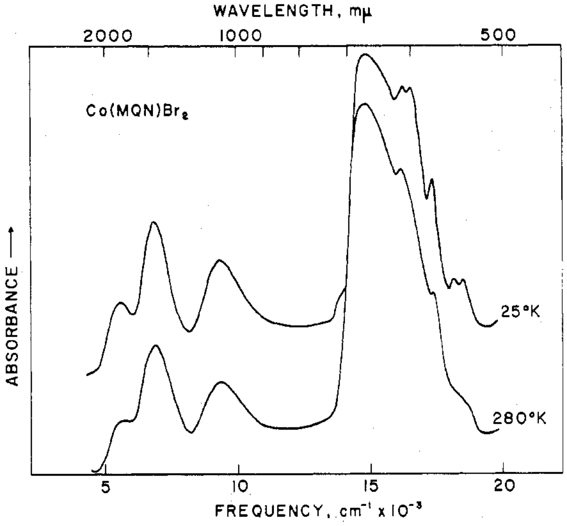

Figure 1. Electronic absorption spectrum of Co(MQN)Br$_2$ in a mull at 280 and 25°K.

for a series of hindered bis(amine)cobalt halides and by Murakami, *et al.*,[22] for a series of dipyrromethene complexes. The low-intensity shoulders between 18,000 and 20,000 cm^{-1} are most likely due to spin-forbidden transitions to components of the ^2G term, which becomes partially allowed by spin-orbit mixing of energy levels. The low-temperature spectrum of Co(MQN)Br$_2$ (Figure 1) lends further support to our assignment of the components of ν_2 to the transitions to the reduced-symmetry terms of the $^4T_1(F)$ state since they do not change appreciably with temperature. In addition, the weak higher energy shoulders on the ν_3 band become well resolved at low temperature as might be expected for spin-forbidden transitions to the components of the ^2G free-ion state.

As is often the case in tetrahedrally coordinated cobalt(II) ions,[19] the ν_1 $^4A_2(F) \rightarrow {}^4T_2(F)$ transition was not identified. It is usually predicted to be in the range between 3000 and 3500 cm^{-1}. This, unfortunately, is the region where one often observes ligand vibrations and absorption bands of water.[23]

With broad structured bands it is often difficult to make unambiguous assignments of band positions. We have chosen to estimate band positions as the center of the curve at half-maximum. The values of the spectral parameters *Dq* and *B* are listed in Table I—their magnitudes are typical of tetrahedral coordination[18] and follow the same order generally found in the spectrochemical series and the nephelauxetic series. By assuming the average ligand field approximation,[24] *Dq* values for MQN, PQN, and DQN were calculated[11] to be 280, 275, and 295 cm^{-1}, respectively. The *Dq* values for the halides were taken from reported spectral parameters for the complexes CoX_4^{2-}.[24] It is apparent that the ligand field strengths of MQN and PQN are essentially identical, and both are somewhat lower in field strength than DQN.

After an investigation of the near-infrared spectrum of some pseudotetrahedral cobalt(II) and nickel(II) complexes, Goodgame and Goodgame[25] reaffirmed a general conclusion made earlier,[26] namely that the electronic absorption spectrum, especially in the case of the ν_2 transition, is very sensitive to the environment of the central metal ion. They concluded that the degree of splitting of the ν_2 band and the intensity of the ν_1 band in cobalt(II) complexes may be used as a guide to distortion from pure T_d symmetry. In every case, more extensive splitting of the ν_2 band was observed in the compounds reported herein than were found in the spectra of tetrahedral CoX_4^{2-} ions.[24] Splitting of the order of 4000 cm^{-1} occurs in the cobalt chloride complexes as opposed to *ca.* 1500 cm^{-1} in $CoCl_4^{2-}$. This extensive splitting was not observed in the ν_3 bands; the reason that the ν_3 transition is not similarly affected has been discussed by Ferguson.[27] Splittings between the highest and lowest

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(22) Y. Murakami, Y. Matsuda, and K. Sakata, *Inorg. Chem.*, **10**, 1728 (1971).

(23) A recent study has dealt with this problem: M. B. Quinn and D. W. Smith, *J. Chem. Soc. A*, 2496 (1971).

(24) F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *J. Amer. Chem. Soc.*, **83**, 4690 (1961).

(25) D. M. L. Goodgame and M. Goodgame, *Inorg. Chem.*, **4**, 139 (1965).

(26) D. M. L. Goodgame, M. Goodgame, and F. A. Cotton, *J. Amer. Chem. Soc.*, **83**, 4161 (1961).

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

energy components of the ν_2 band for each complex were calculated, and they revealed the following trends: (1) distortion in the coordination geometry of the MQN complexes occurs in the order I < Br < Cl, both in the solid phase and in solution; (2) distortion apparently increases upon solution of the MQN complexes, except for the iodide which remains essentially unchanged; (3) cobalt(II) chloride complexes of MQN, PQN, and DQN are distorted in the order MQN < PQN < DQN in the solid phase and PQN < MQN ~ DQN in solution.

Table II. Magnetic Susceptibility Data[a]

$Co(MQN)Cl_2$ (mol wt 354.1, $\chi^c = 206$ cgsu): 293.0, 4.66; 285.0, 4.64; 247.0, 4.67; 215.0, 4.61; 187.5, 4.60; 134.5, 4.57; 103.0, 4.54; 66.5, 4.51; 39.5, 4.61; 29.7, 4.74; 26.8, 4.83

$Co(MQN)Br_2$ (mol wt 443.0, $\chi^c = 228$ cgsu); 294.5, 4.58; 258.0, 4.57; 232.0, 4.54; 193.0, 4.52; 158.0, 4.49; 122.5, 4.47; 94.5, 4.41; 65.5, 4.42; 48.5, 4.44; 28.5, 4.56; 25.0, 4.48

$Co(MQN)I_2$ (mol wt 537.0, $\chi^c = 258$ cgsu): 296.5, 4.85; 110.5, 4.68

$Co(PQN)Cl_2$ (mol wt 352.18, $\chi^c = 237$ cgsu): 296.5, 4.51; 191.0, 4.41; 96.0, 4.29

$Co(DQN)Cl_2$ (mol wt 312.11, $\chi^c = 183$ cgsu): 297.5, 4.49; 199.0, 4.32; 98.5, 4.26

$Ni(MQN)Cl_2$ (purple form) (mol wt 353.9, $\chi^c = 203$ cgsu): 300.5, 3.35; 267.0, 3.38; 246.0, 3.39; 228.5, 3.34; 191.0, 3.41; 174.0, 3.41; 154.0, 3.41; 112.5, 3.38; 95.5, 3.39; 71.5, 3.41; 55.0, 3.43; 36.5, 3.41; 19.0, 3.44

$Ni(MQN)Cl_2$ (off-white form) (mol wt 353.9, $\chi^c = 203$ cgsu): 298.0, 3.40

$Ni(MQN)Cl_2 \cdot H_2O$ (mol wt 371.0, $\chi^c = 216$ cgsu): 293.0, 3.49; 248.0, 3.45; 201.0, 3.50; 143.0, 3.60; 102.5, 3.68

$Ni(MQN)Br_2$ (mol wt 442.8, $\chi^c = 226$ cgsu): 300.0, 3.37; 293.0, 3.35; 273.0, 3.37; 249.0, 3.36; 233.0, 3.34; 210.5, 3.31; 192.5, 3.32; 188.5, 3.33; 172.5, 3.32; 161.5, 3.30; 154.5, 3.28; 122.0, 3.31; 121.0, 3.30; 112.0, 3.31; 94.5, 3.31; 72.5, 3.29; 53.0, 3.26; 33.5, 3.28; 19.0, 3.20[b]

$Ni(MQN)I_2$ (mol wt 536.8, $\chi^c = 258$ cgsu): 296.0, 3.58; 269.0, 3.59; 253.0, 3.57; 230.0, 3.55; 210.0, 3.59; 190.5, 3.59; 171.0, 3.56; 130.5, 3.55; 112.0, 3.54; 92.5, 3.55; 70.0, 3.69; 52.0, 3.74; 35.5, 4.12;[b] 18.5, 4.34[b]

$Fe(MQN)Cl_2$ (mol wt 351.0, $\chi^c = 233$ cgsu): 294.0, 5.27; 257.0, 5.27; 203.0, 5.27; 143.0, 5.21; 102.0, 5.16

$Co(MQN)_2(ClO_4)_2$ (mol wt 706.4, $\chi^c = 364$ cgsu): 299.5, 4.36; 105.0, 4.18

$Ni(MQN)_2(ClO_4)_2 \cdot 4H_2O$ (mol wt 778.3, $\chi^c = 416$ cgsu): 297.0, 4.02

[a] Temperature in °K followed by μ_{eff} in BM. [b] Magnetic field dependent value; highest field susceptibility used to calculate μ_{eff}.

Magnetic susceptibility data for the cobalt(II) complexes are given in Table II. Values of χ_M' are corrected for diamagnetism but not for temperature-independent paramagnetism. The values of μ_{eff} at room temperature are consistent with those normally found in pseudotetrahedral compounds containing this ion.[5,18] The slight temperature dependence in μ_{eff} may be ascribed to the second-order Zeeman effect and to a small amount of electron delocalization. The small increase in μ_{eff} for $Co(MQN)Br_2$ at low temperature may be the result of traces of ferromagnetic impurities.

The infrared spectra of the cobalt halide complexes are all essentially the same except in the low-energy region where fundamental metal-ligand vibrational modes occur. The $\nu(C{=}O)$ vibrational band observed in the ligand does not shift upon complexation. Energies of metal-halide stretching frequencies are useful in distinguishing tetrahedral complexes from octahedral complexes,[28] and the values of ν(Co-X) reported here are in the ranges found for pseudotetrahedral structures. The assignments are as follows (cm^{-1}): Co-Cl, 355 (sh), 343 (s), 319 (s); Co-Br, 274 (m), 257 (m); Co-I, 245 (sh), 230 (s). For complexes of the same metal, the ratio ν(M-Br)/ν(M-Cl) generally falls in the range between 0.74 and 0.77, and the ratio ν(M-I)/ν(M-Cl) is 0.65.[29] Here, ν(Co-Br)/ν(Co-Cl) is found to be 0.80, and the ratio is the same for the other metal(II) complexes reported herein. The ratio ν(Co-I)/ν(Co-Cl) is 0.67 and, though both ratios are somewhat greater than expected, the results indicate logical ν(Co-X) assignments. In view of the results for the complexes of MQN, it is reasonable to assign ν(Co-Cl) in $Co(PQN)Cl_2$ to bands at 352 and 317 cm^{-1}. In $Co(DQN)Cl_2$, these bands are found at 355 and 320 cm^{-1}.

The pseudohalide complex $Co(MQN)(NCS)_2 \cdot C_2H_5OH$ is briefly discussed below and will be treated in more detail elsewhere.[30] Because this complex is octahedral in the solid state as indicated by the spectral and magnetic results, a dimeric, NCS-bridged structure is proposed. The complex is decomposed in solution; in acetone, the product is distinctly tetrahedral and is most likely $Co(MQN)(NCS)_2$ monomers. The solution absorption spectrum is very similar to those of the cobalt(II) halide complexes; band positions and spectral parameters are given in Table I

Nickel(II) Halide Complexes. These complexes are air stable, soluble in most organic solvents, and decomposable in aqueous solutions; their X-ray powder diffraction patterns are dissimilar. Two complexes corresponding to the formula $Ni(MQN)Cl_2$ were prepared and characterized. One of these, the purple form, is tetrahedral; the other, an off-white form, is octahedral by virtue of bridging chloride ligands.

The electronic absorption spectral data and assignments for the purple chloride, the bromide, and the iodide complexes are listed in Table IIIA. The ligand field parameters presented in this table were calculated by using the methods described by Lever[19] and confirm the pseudotetrahedral coordination proposed for these complexes. The electronic absorption spectrum of $Ni(MQN)Br_2$ in a mull at 25 and 300°K is presented in Figure 2. The solution and mull spectra of the purple chloride and the iodide are very similar to the bromide spectrum. However, for the mull spectrum of the iodide complex, the two small peaks at *ca.* 11,200 cm^{-1} in the chloride and bromide are present only as shoulders. These peaks, on the high-energy side of ν_2 in each complex, are tentatively assigned as spin-forbidden transitions to the states arising from the ^1D free-ion term in agreement with some previous assignments.[26,31]

A study of the effect of low temperature on the intensity of these two peaks was made in an attempt to verify their nature. A band associated with a spin-allowed transition is expected to become sharper at low temperature, while its oscillator strength remains constant. Likewise, a spin-forbidden transition which gains intensity through vibronic coupling should decrease in intensity with decreasing temperature. It is somewhat surprising that the two sharp peaks at *ca.* 11,000 cm^{-1} in the mull spectrum of Ni(MQN)-

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(28) R. J. H. Clark, *Halogen Chem.*, 3, 85 (1968).

(29) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," 2nd ed, Wiley-Interscience, New York, N. Y., 1970, p 214.

(30) R. C. Dickinson and G. J. Long, *J. Inorg. Nucl. Chem*, in press.

(31) F. A. Cotton and D. M. L. Goodgame, *J. Amer. Chem. Soc.*, 82, 5771 (1960).

Table III. Electronic Absorption Spectral Data for Nickel(II) Halide Complexes[a]

A. Tetrahedral Compounds

	Solvent	$^3T_1(F) \rightarrow {}^3T_2(F)$, ν_1, cm^{-1}	$^3T_1(F) \rightarrow {}^3A_2(F)$, ν_2, cm^{-1}	^1D cm^{-1}	$^3T_1(F) \rightarrow {}^3T_1(P)$, ν_3, cm^{-1}	*Dq*, cm^{-1}	*B*, cm^{-1}
$Ni(MQN)Cl_2$ (purple form)	Mull		10,115	11,325, 11,765	19,050	550	1010
	CH_3CN	~7200 sh	10,000 (43)	11,390 (18), 11,810 (14)	16,000 sh, 18,180 sh, 19,370 (90), 22,200 sh		
	CH_3NO_2	~7200 sh	10,000 (45)	11,385 (18), 11,800 (14)	16,000 sh, 18,180 sh, 19,415 (97)		
$Ni(MQN)Br_2$	Mull (300°K)	~7200 sh	9885	10,915, 11,353	17,390 sh, 18,470	530	940
	Mull (25°K)	~6670 sh, 8630	10,000 10,150 sh	10,460, 11,200	14,900 sh, 15,600 sh, 17,900 sh, 18,400, 21,300 sh		
	CH_3CN	~7200 sh	9780 (53)	10,990 (26), 11,395 (19)	15,385 sh, 17,475 sh, 18,570 (122)		
$Ni(MQN)I_2$	Mull	~7200 sh	9660		14,290 sh, 17,000	525	885
	CH_3NO_2	~7200 sh	9400 (53)	10,280 sh, 10,540 sh	14,290 sh, 17,115 (218)		
	Nitrobenzene	~7200 sh	9350 (80)	10,255 sh	14,290 sh, 16,950 (337)		

B. Octahedral Compounds[b]

	T, °K	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, ν_1, cm^{-1}	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$, ν_2, cm^{-1}	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$, ν_3, cm^{-1}	*Dq*, cm^{-1}	*B*, cm^{-1}
$Ni(MQN)Cl_2$	300	10,000	12,270 sh, 14,285, 15,625 sh, 16,130 sh	18,520 sh, 19,800 sh, 24,240	1000	570
	25	9660	12,500 sh, 14,985, 15,625 sh, 16,260 sh	18,520 sh, 19,600 24,690	965	715
$Ni(MQN)Cl_2 \cdot 0.25H_2O$	300	9400	12,120 sh, 14,185, 15,625 sh	20,000 sh, 24,270	940	685
	25	9350	12,500 sh, 14,250, 15,600 sh	18,200 sh, 19,900, 24,700	935	725

[a] sh shoulder. Molar extinction coefficients are given in parentheses. [b] Kel-F No. 90 mulls.

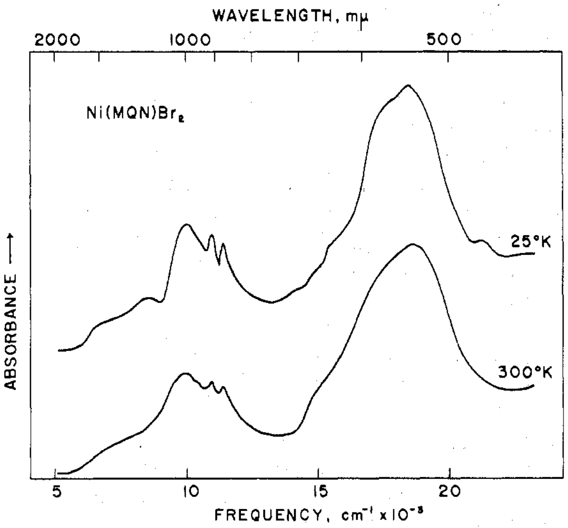

Figure 2. Electronic absorption spectrum of $Ni(MQN)Br_2$ in a mull at 300 and 25°K.

Br_2 become well resolved at low temperature. It should be noted that the ν_1 band is split at low temperature, presumably as a result of the distorted tetrahedral ligand field.

Magnetic susceptibility data are listed in Table II. The values of μ_{eff} for the purple chloride, the bromide, and the iodide complexes are a good deal greater than the spin-only value, a condition which indicates a considerable orbital contribution to μ_{eff}. Even though these values are lower than predicted for regular tetrahedral complexes with an orbital contribution, they are in keeping with those values found in many pseudotetrahedral nickel(II) complexes.[32] This reduction results from the reduced symmetry removal of the orbital degeneracy. The temperature dependence is expected for complexes containing approximately $^3T_1$ ground states. The increase in μ_{eff} values below *ca.* 90°K for the $Ni(MQN)I_2$ may result from traces of a ferromagnetic impurity. The field dependence at these temperatures supports this conclusion. A similar increase at low temperatures has also been observed in other pseudotetrahedral nickel(II) complexes.[33]

The infrared spectra of the purple chloride, the bromide, and the iodide nickel complexes are essentially the same. In the low-energy regions we assign the nickel-halide stretching frequencies as follows: Ni-Cl, 342 (s), 302 (m); Ni-Br, 277 (s); Ni-I, 223 (s). The ratios ν(Ni-Br)/ν(Ni-Cl) = 0.81 and ν(Ni-I)/ν(Ni-Cl) = 0.65 are indicative of reasonable assignments.[28]

Perhaps the most interesting nickel complex reported here is the off-white complex corresponding to the formula $Ni(MQN)Cl_2$. This material possesses properties very different from those of the purple complex of the same empirical formula. The off-white complex is best prepared in noncoordinating solvents which can pick up moisture from the reactants; hot solvents seem to work best. We prepared this complex under a variety of conditions (hot solvents, cold solvents, solvents of various polarities, and inert atmosphere) and have demonstrated its reproducibility.

We have observed that samples of this complex appear off-white when dried over P_4O_{10} *in vacuo* and rapidly change to pale green when exposed to the atmosphere. This color change can be reversed by redrying the compound. Presumably, the color variation is due to the absorption of moisture from the atmosphere. Elemental analyses for C, H, and N and the compounds' infrared spectra also reflect these

(32) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed, Interscience, New York, N. Y., 1972.

(33) P. LaMarche and W. A. Baker, Jr., unpublished results.

changes. Samples of purple Ni(MQN)Cl_2, when dissolved in boiling ethanol—a purple solution results—and quenched in an ice bath, are converted to the off-white compound—pale green, if the solvent is wet. If either some off-white or pale green Ni(MQN)Cl_2 is dissolved—it dissolves slowly—in hot ethanol, it likewise forms a purple solution, but we cannot isolate a purple product; the product isolated is always the initial reactant. When samples of the off-white and the purple isomer are dissolved quantitatively in 0.1 *N* hydrochloric acid, their resulting electronic spectra are essentially identical.

The off-white material is practically insoluble in noncoordinating solvents, such as alcohols, chloroform, and acetone and is decomposed, *i.e.*, solvated, in stronger solvents (for example, CH_3NO_2 and DMF) as judged by a comparison of the solution absorption spectrum and mull spectrum. In nitromethane or acetonitrile, off-white Ni(MQN)Cl_2 dissolves to give a pink solution whose absorption spectrum is the same as that of the purple tetrahedral Ni(MQN)Cl_2 complex. The mull electronic spectrum of off-white Ni(MQN)Cl_2 at 25 and 300°K is presented in Figure 3. Very concentrated mulls were required to obtain the spectrum indicating that the intensities of the bands are low. The appearence of the spectrum is typical of octahedral coordination,[19] and spectral parameters calculated on this basis are consistent with this geometry. Band locations and spectral parameters, calculated by using the methods described by Lever,[19] are given in Table IIIB. The abnormally low value of B at 300°K reflects the difficulty in accurately choosing band locations when the band is not well resolved, as in the case of ν_1. It is worth noting that, if experimental values of ν_2 and ν_3 obtained at 25°K are used to calculate Dq (hence, ν_1), the calculated Dq is about 95% of the value given in Table IIIB. This represents a good internal consistency in the spectral assignments.

Pseudooctahedral coordination in the off-white and pale green Ni(MQN)Cl_2 complexes is thought to be a result of the formation of halide bridges between the metal atoms. It is known[29] that the metal-halogen stretching frequencies in bridging structures are lower than in terminal metal-halogen structures. This frequency lowering is most pronounced where a change in coordination number is involved and has often been used as evidence for a bridging halide.[34] Figure 4 shows the infrared spectra of purple tetrahedral Ni(MQN)Cl_2 and off-white octahedral Ni(MQN)Cl_2 in the region of 700-200 cm^{-1}; band locations are given elsewhere.[11] The bands at 302 and 342 cm^{-1} in the purple Ni(MQN)Cl_2 complex are assigned above to the Ni-Cl stretching bands. These bands are absent from the spectrum of the off-white octahedral Ni(MQN)Cl_2; their absence is further evidence for chlorine bridging.

The proposed polymer-like pseudooctahedral structure for the off-white compound is also supported by its X-ray powder diffraction patterns. These patterns are completely different from those of the tetrahedral Ni(MQN)X_2 complexes and, in general, show three broad lines at 2θ values of *ca.* 8.8, 11.6, and 16.1° indicating an amorphous solid. These angles would correspond to repeat units of *ca.* 5.5, 7.6, and 10.3 Å.

The magnetic susceptibilities listed in Table II for off-white Ni(MQN)Cl_2 and pale green Ni(MQN)$Cl_2 \cdot H_2O$ are total susceptibilities, uncorrected for TIP, and are consistent with an octahedral nickel(II) geometry. Octahedral nickel(II) complexes have a $^3A_{2g}$ ground state; their magnetic moments are expected to be independent of temperature and independent of slight distortions from regular octahedral symmetry.[5] The increase in μ_{eff} with decrease in temperature observed in the off-white complex may indicate a magnetically nondilute system with magnetic exchange. However, lower temperature studies would be required to prove the presence of magnetic exchange.

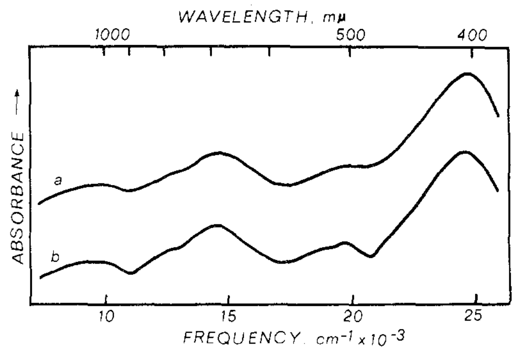

Figure 3. Electronic absorption spectrum of off-white Ni(MQN)Cl_2 in a mull at (a) 300°K and (b) 25°K.

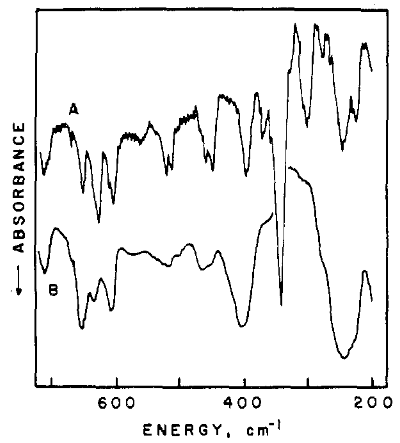

Figure 4. Infrared spectrum of Ni(MQN)Cl_2: (A) purple tetrahedral complex; (B) off-white octahedral complex.

Sacconi, *et al.*,[35] have reported that Ni(Me_4en)Cl_2 and Ni(Me_4pn)Cl_2 in *o*-$Cl_2C_6H_4$ solutions changed color from green to violet as the temperature was raised; the violet form was attributed to the tetrahedral isomer in an octahedral ⇌ tetrahedral equilibrium. At first glance, the behavior of these complexes may appear analogous to that of off-white Ni(MQN)Cl_2. If allowed to stand in dry ethanol at room temperature, this white, polymeric, octahedral complex slowly dissolves to give a light purple solution which has an electronic spectrum the same as that of the purple, tetrahedral Ni(MQN)Cl_2 complex. Heat hastens the solution of the off-white complex and a more deeply colored solution with the same electronic spectrum results; this solution is not thermochromic. Cooling results in the re-formation of the solid off-white polymeric complex. Thus, no octahedral ⇌ tetrahedral equilibrium is observed in solution.

Iron(II) Chloride Complex of MQN. The only complex of a divalent iron halide which was prepared in high purity was Fe(MQN)Cl_2, and this was prepared and handled in a dry, inert atmosphere. Results of the bromide, iodide, and perchlorate preparations were never reproducible, and their preparations were abandoned.

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(34) R. J. H. Clark and C. S. Williams, *Inorg. Chem.*, 4, 350 (1965), and references therein.

(35) L. Sacconi, I. Bertini, and F. Mani, *Inorg. Chem.*, 6, 262 (1967).

The iron(II) ion has a ^5D free-ion ground state which, in the presence of a ligand field of T_d symmetry, is split into ^5E and $^5T_2$ terms. Thus, a single electronic spectral band corresponding to the $^5E \rightarrow {}^5T_2$ transition is expected, and single bands are usually found around 4000 cm^{-1}, although split bands are not uncommon.[36]

The electronic absorption spectrum of $Fe(MQN)Cl_2$ obtained in a mull contains a band at 6700 cm^{-1} accompanied by a shoulder at *ca.* 5300 cm^{-1}. In nitromethane solution, this band is observed at 6500 cm^{-1} (ϵ_M 20) and the shoulder occurs at *ca.* 5550 cm^{-1}. In both cases, the band asymmetry is attributed to the loss of degeneracy of the $^5T_2$ state which results from the actual symmetry being closer to C_{2v} than T_d.[37]

The magnetic behavior of this compound is characteristic of pseudotetrahedral iron(II) compounds.[38] The observed magnetic moments are reported in Table II. Tetrahedral iron(II) complexes are expected to have only a small orbital contribution to the magnetic moment and hence moments close to the spin-only value of 4.90. However, many compounds containing tetrahedrally coordinated iron(II) that have μ_{eff} in the range 5.3–5.4 BM have been reported.[39] These results have been explained by considering the effect of mixing of the first excited state with the ground state through spin-orbit coupling. Thus, the room-temperature value of 5.27 BM for μ_{eff} reported for $Fe(MQN)Cl_2$ is in keeping with a tetrahedral structure, and its slight variation with temperature is in keeping with a ^5E ground state.

Compounds containing the iron(II) nucleus have been extensively studied by using the Mossbauer effect,[36,40] and the interpretation of their properties has undergone critical review and discussion.[41] We have studied the Mossbauer spectrum of $Fe(MQN)Cl_2$ at several temperatures. The spectral parameters are given in Table IV and confirm the pseudotetrahedral nature of the complex when compared to compounds of known structure.[42] The isomer shift in the range of 0.8–0.9 mm/sec has been found to be particularly characteristic of tetrahedral iron(II) coordination.[42]

Metal(II) Perchlorate Complexes. Perchlorate complexes of cobalt and nickel were prepared. In each case, the elemental analyses indicated two MQN ligands per metal ion. The complexes are air stable and rather insoluble in noncoordinating solvents; extensive solvation takes place in coordinating solvents.

The electronic absorption spectrum of a mull of the $Co(MQN)_2(ClO_4)_2$ complex exhibits only shoulders on an intense charge-transfer band; these shoulders are located at 8700 (w), 11,800 (w), 17,200, and 19,000 cm^{-1}. Hence, we cannot rely on calculated ligand field parameters for clues to the stereochemistry in this complex. However, the magnetic data included in Table II are useful in that the value of 4.36 BM for μ_{eff} indicates a tetrahedral ligand field about the cobalt(II) ion.

Table IV. Mossbauer Parameters for $Fe(MQN)Cl_2$

T, °K	Quadrupole splitting, ΔE_Q, mm/sec	Isomer shift,[a] δ, mm/sec
300	2.74	0.91
195	2.67	0.86
78	2.57	0.79

[a] Relative to natural iron foil.

The absorption bands in the electronic spectrum of mulls of $Ni(MQN)(ClO_4)_2 \cdot 4H_2O$ are resolved and are shifted to higher energies than those found in the spectra of the nickel halide complexes. Bands were found at 10,350 (sh), 14,850, 19,800 (sh), and 26,000 (sh) cm^{-1}. The shoulder at *ca.* 10,350 cm^{-1} is assigned to the ν_2 transition, and the band at 14,850 cm^{-1} is assigned to the ν_3 transition in tetrahedral symmetry. From these assignments Dq is calculated to be 520 cm^{-1} and B is 720 cm^{-1}. The value of 4.02 BM for μ_{eff} is rather high for Ni(II) complexes; however, high moments are expected for a Ni(II) ion surrounded by a tetrahedral ligand field composed of four identical coordinating atoms.[32] Thus, the most reasonable structure is, again, two bidentate tetrahedrally coordinated MQN ligands and noncoordinating perchlorate groups.

Sacconi, *et al.*,[35] have discussed in some detail the tendency of substituted ethylenediamine complexes to form tetrahedral as opposed to octahedral or square-planar complexes. The quinuclidinone-containing ligands under study here may be considered to be rather highly C- and N-substituted ethylenediamine ligands. However, in these ligands, the N-substituted ring-containing species produce a more bulky and rigid ligand than those studied by Sacconi. In spite of this difference, essentially the same trends toward pseudotetrahedral complex formation are observed. It is interesting to note that with MQN, tetrahedral cobalt(II) and nickel(II) perchlorate complexes containing two ligands per metal may be isolated. No such bis complexes containing N-substituted alkylenediamines could be prepared.[35] This difference may result from the cyclic nature of the quinuclidine moiety which anchors the ethylene ring groups together providing less steric interaction between ligands in the bis complexes. It would be interesting to determine whether 2-methyl substituents on the quinuclidine rings would prevent the formation of the bis compounds.

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Registry No. $Co(MQN)Cl_2$, 42892-78-4; $Co(MQN)Br_2$, 42892-79-5; $Co(MQN)I_2$, 42892-80-8; $[Co(MQN)(NCS)_2 \cdot C_2H_5OH]_2$, 43021-08-5; $Co(MQN)(NCS)_2$, 42942-73-4; $Co(MQN)_2(ClO_4)_2$, 43021-09-6; $Fe(MQN)Cl_2$, 42892-81-9; $Ni(MQN)Cl_2$, 42892-82-0; $[Ni(MQN)Cl_2]_x$, 42886-08-8; $Ni(MQN)Br_2$, 42892-83-1; $Ni(MQN)I_2$, 42892-84-2; $Ni(MQN)_2(ClO_4)_2$, 42892-85-3; $Co(PQN)Cl_2$, 42892-86-4; $Co(DQN)Cl_2$, 42892-87-5; 3-quinuclidinone, 3731-38-2; morpholine, 110-91-8; formaldehyde, 50-00-0; 2-(*N*-morpholinomethyl)-3-quinuclidinone, 41971-48-6.

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