31. *Octahedral, Tetrahedral, and Planar Complexes of Nickel*(II) *with Quinoline.*

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The preparation and the magnetic and electronic spectral properties of the compounds Ni(quinoline)$_2$X$_2$ (X = Cl, Br, or I) are described. The chloro-complex exists in a blue and a yellow form. These and the blue bromo-complex are paramagnetic, but the green iodo-complex is diamagnetic. The magnetic and spectral data are used in deducing the structures of the complexes. The bromo- and the blue chloro-complex are considered to be tetrahedral, the yellow chloro-complex to have a distorted octahedral structure, and the iodo-complex to be planar.

IN recent years there have been many studies of nickel(II) complexes, in order to determine the criteria for the three main stereochemical arrangements, octahedral, tetrahedral, and planar, and to identify the factors influencing their adoption. At present, magnetic and electronic spectral data, used in conjunction with ligand field theory, usually enable such structures to be determined with fair certainty and often permit study of deviations from regular geometry. However, much less is known about the reasons for the adoption of a particular structure. We report here the results of a magnetic and electronic spectral study of four closely related complexes of nickel(II) halides with quinoline, which we believe to have interest in this connexion since compounds of all three main stereochemical types are present.

The compounds are Ni(quinoline)$_2$X$_2$ (X = Cl, Br, or I), the chloro-complex existing as a yellow and a blue isomer. These chloro-complexes were first described by Pomilio,[1] and the iodo-complex by Ephraim and Linn.[2] The bromo-complex appears to be new. Although all the complexes were prepared by direct reaction of the nickel halide with an excess of quinoline, only two molecules of the latter are co-ordinated; there seems to be no steric reason why tetrakisquinoline complexes should not be formed, especially since the compound, Ni(quinoline)$_4$(NCS)$_2$, is known.[3]

Bromo-complex.—This dark blue compound is slightly hygroscopic but is otherwise stable in air. It is fairly labile in solution in organic solvents, visible decomposition occurring immediately or on storage. Nitrobenzene solutions are only very weakly conducting (Table 1), indicating that the complex has the formula [Ni(quinoline)$_2$Br$_2$] and

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[1] Pomilio, *Rend. Accad. sci. fis. mat. Napoli*, 911, Ser. 3, **17**, 342; *Chem. Abs.*, 1912, **6**, 1289.

[2] Ephraim and Linn, *Ber.*, 1913, **46**, 3754.

[3] Grossmann and Hünseler, *Z. anorg. Chem.*, 1905, **46**, 386.

excluding ionic species such as [Ni(quinoline)$_4$][NiBr$_4$]; the molar conductance of 3·0 mho may be attributed to slight decomposition.

TABLE 1.

Complex	Colour	Λ_m in PhNO$_2$ (10^{-3}M)	Magnetic results	
			$\mu_{\text{eff.}}$ (B.M.)	Temp. (K)
$Ni(C_9H_7N)_2Cl_2$	Yellow	Insol.	3·41 ± 0·05	292°
$Ni(C_9H_7N)_2Cl_2$	Blue	Dec.	3·54	293
$Ni(C_9H_7N)_2Br_2$	Blue	3·0	3·48	292
$Ni(C_9H_7N)_2I_2$	Olive-green	13·2 *	Diamag.	292

* Red solution, with decomposition of complex; see text.

The electronic absorption spectra of the compound, in the solid state and in solution, are reported in Figs. 1 and 2 and Table 2. They indicate that the compound has essentially a tetrahedral structure, the spectra resembling those of other tetrahedral complexes of the type L_2NiX_2.[4] The strong, multicomponent band at ~16,500 cm.$^{-1}$ may be assigned,[5] in T_d symmetry, as the transition $^3T_1(F) \longrightarrow {}^3T_1(P)$, ν_3, and the band at ~10,000 cm.$^{-1}$ as $^3T_1(F) \longrightarrow {}^3A_2$, ν_2. There is very good agreement between the calculated[5] and the observed energies for both of these transitions when Dq = 500 cm.$^{-1}$. The high values of

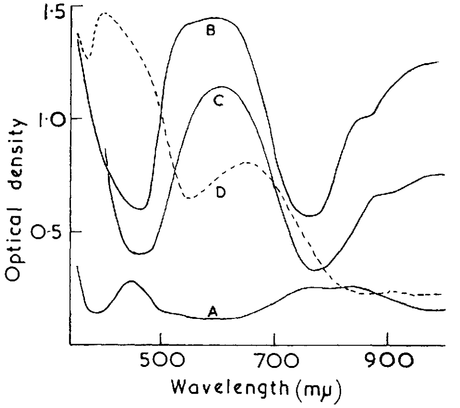

FIG. 1. Reflectance spectra of Ni(quinoline)$_2$X$_2$.
(A) X = Cl, yellow; (B) X = Cl, blue; (C) X = Br; (D) X = I.

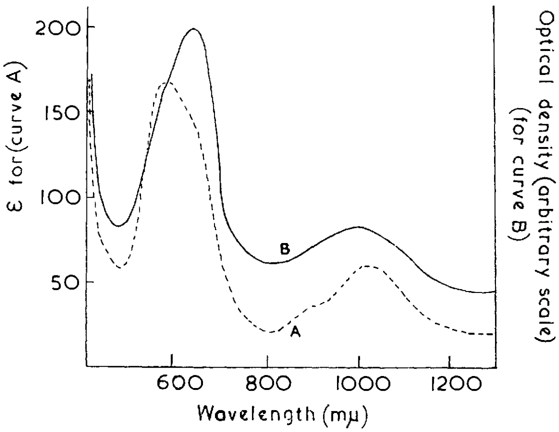

FIG. 2. Spectra of Ni(quinoline)$_2$Br$_2$.
(A) 0·0075M in CH$_2$Cl$_2$; (B) C$_4$Cl$_6$ mull.

TABLE 2.

Electronic absorption spectra of the complexes.

Complex	State	Absorption maxima (cm.$^{-1}$) (ε for solutions)
$Ni(C_9H_7N)_2Cl_2$ (yellow)	Reflectance	22,700, ~19,200(sh), 13,150, 12,000
	C$_4$Cl$_6$ mull *	22,800, ~19,100(sh), 7940, ~6850(sh), ~6062(sh), 5130, 4640
$Ni(C_9H_7N)_2Cl_2$ (blue)	Reflectance	~18,200(sh), 17,100, ~11,750(sh), 10,260
	C$_4$Cl$_6$ mull	18,020, 17,120, ~11,750(sh), 10,220
$Ni(C_9H_7N)_2Br_2$	Reflectance	16,400, ~11,400(sh), ~10,000
	C$_4$Cl$_6$ mull	~17,400(sh), 15,900, 10,100
	CH$_2$Cl$_2$ (0·0075M)	~17,450(169), ~15,750(sh), ~11,400(sh), 9936(60)
$Ni(C_9H_7N)_2I_2$	Reflectance	25,000, ~21,750(sh), 15,430, 11,000
	C$_4$Cl$_6$ mull	24,150, ~21,700(sh), 15,150

* Instrument unreliable for mull spectra at 12,000—14,000 cm.$^{-1}$.

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[4] Cotton and Goodgame, *J. Amer. Chem. Soc.*, 1960, **82**, 5771, 5774.

[5] Liehr and Ballhausen, *Ann. Phys.*, 1959, **6**, 134.

the molar extinction coefficients are also in agreement with those for other tetrahedral nickel(II) complexes.[4,6]

Since the bromide ion lies at the weak end of the spectrochemical series and quinoline is probably near pyridine, well towards the strong end, regular T_d symmetry would not be expected. A strong C_{2v} component to the ligand field should, by perturbing the energy levels due to regular T_d symmetry, cause splittings in the crystal-field absorption bands and, in particular, by its effect on the ground-state multiplet, reduce the magnetic moment from the high values found for nickel(II) complexes of regular, or nearly regular, T_d symmetry. The ν_3 band, although multicomponent, shows no significantly greater splitting than has been observed [4,6] for complexes of nickel(II) which approach T_d symmetry quite closely. However, even in the case of dichlorobis(triphenylphosphine)nickel(II), which has a distorted tetrahedral structure,[7] this band shows no pronounced splitting.[8] The shoulder on the high-energy side of ν_2 in the spectrum of Ni(quinoline)$_2$Br$_2$, is present in the solid state as well as in solution, and therefore is not due to solvolysis of the type reported for the tetrahalogenonickelate(II) ions.[6b] The solution spectrum shows that the band causing the shoulder is much weaker than the ν_2 band at $\sim$10,000 cm.$^{-1}$. From the energy-level diagram for tetrahedral nickel(II),[5] it may be seen that, when $Dq \approx 500$ cm.$^{-1}$, there is appreciable interaction between the levels $^1\Gamma_5(^1D_2)$ and $^3\Gamma_5(^3A_2)$, with the singlet level lying slightly above the triplet level. Thus the shoulder at $\sim$11,400 cm.$^{-1}$ is probably due to the transition $^3T_1(F) \longrightarrow {}^1\Gamma_5(^1D_2)$ which, although formally spin-forbidden, acquires intensity since the upper level has some triplet character due to the interaction mentioned above. Since the $^3A_2$ level is an orbital singlet, it should not be split by low-symmetry components of the ligand field, and the shoulder at $\sim$11,400 cm.$^{-1}$ cannot be attributed to perturbations of this type.

The effect of the low-symmetry component of the ligand field is, however, seen in the value of the magnetic moment at room temperature, namely, 3·48 B.M. This is intermediate between the values (3·8—4·0 B.M.) found for nickel(II) in environments having regular or nearly regular T_d symmetry [4,6a,9] and those (3·2—3·3 B.M.) observed for paramagnetic complexes of nickel bromide with tertiary phosphines.[10]

In the electronic absorption spectrum the relative intensities of ν_3 and ν_2 also merit comment. When deviations from T_d symmetry are small, the intensity of ν_3 is much greater [6b] than that of ν_2, in agreement with the fact that in the strong-field limit ν_3 remains a one-electron transition while ν_2 becomes a two-electron transition. When low-symmetry components of the ligand field are pronounced, as with the paramagnetic complexes of the nickel halides with tertiary phosphines,[8,10] the intensity of ν_2 increases appreciably relatively to ν_3. In this respect, as with the magnetic moments, the quinoline complex shows intermediate behaviour.

From *X*-ray powder photographs, the compound is not isomorphous with its blue cobalt(II) analogue, or with the blue isomer of Ni(quinoline)$_2$Cl$_2$.

Chloro-complexes.—The existence of the two isomers of Ni(quinoline)$_2$Cl$_2$, reported by Pomilio,[1] has been confirmed, and his main conclusions concerning their general chemistry have been substantiated. Physical studies could be carried out only for the solid state as the yellow isomer is practically insoluble in, or is decomposed by, common organic solvents, while the blue isomer is very labile, changing rapidly to the yellow form or decomposing on contact with solvents. The blue isomer is very hygroscopic.

(*a*) *Blue isomer.* The electronic absorption spectrum of the blue isomer (Fig. 1, Table 2) is similar to that of the bromo-complex and, by the same reasoning, indicates an

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[6] (*a*) Gill and Nyholm, *J.*, 1959, 3997; (*b*) Goodgame, Goodgame, and Cotton, *J. Amer. Chem. Soc.*, 1961, **83**, 4161.

[7] Garton, Henn, Powell, and Venanzi, unpublished work, quoted in ref. 10*b*.

[8] Cotton, Faut, and Goodgame, *J. Amer. Chem. Soc.*, 1961, **83**, 344.

[9] Cotton and Francis, *J. Amer. Chem. Soc.*, 1960, **82**, 2986.

[10] (*a*) Coussmaker, Hely Hutchinson, Mellor, Sutton, and Venanzi *J.*, 1961, 2705; Browning *et al.*, *J.*, (*b*) 1961, 4816; (*c*) 1962, 693; (*d*) Hayter and Humiec, *J. Amer. Chem. Soc.*, 1962, **84**, 2004.

essentially tetrahedral structure for this compound. The band energies are slightly greater than are those for the bromo-complex, in accord with the larger Dq value expected on replacement of bromide by chloride.

The magnetic moment, 3·54 B.M., at room temperature is also in agreement with tetrahedral structure, with the presence of a low-symmetry component to the ligand field. This perturbation is evidently smaller for the blue chloride than for the bromide, in accord with the higher position of the former ion in the spectrochemical series.

The compound is not isomorphous with its cobalt(II) analogue.

(*b*) *Yellow isomer.* The electronic absorption spectrum (Fig. 1, Table 2) is similar to those exhibited by nickel(II) complexes of distorted octahedral structure with triplet ground states.[11] The bands are much weaker than are those of the tetrahedral compounds. The magnetic moment, 3·41 B.M., at room temperature is within the range normally found for six-co-ordinate nickel(II) compounds, although rather towards the high end of this range, and is similar to that found for Ni py_2Cl_2 (3·37 B.M.) which is octahedral.[12] In the quinoline complex the nickel(II) ion presumably achieves six co-ordination by polymerisation by means of chloride bridges. A polymeric structure would account for the relative insolubility of the compound. If the structure is similar to that adopted by Co py_2Cl_2 [13] and Ni py_2Cl_2,[12] the symmetry of the ligand field is D_{4h}. However, the electronic energy levels of nickel(II) in this symmetry are very dependent on the values of the various ligand field parameters,[11] and, in the absence of detailed calculations on closely related compounds, assignment of the spectral bands is unreliable.

Iodo-complex.—This green compound was air-stable but solutions in organic solvents were red and visible decomposition occurred, usually fairly rapidly. Thus the value of ~13 mho^{-1} for the molar electrolytic conductance in nitrobenzene is not of great significance, but does suggest that the compound is non-ionic, the conductivity being due to decomposition. Spectral studies were limited to the solid state.

The diamagnetism of the compound shows that it is not tetrahedral, and indicates a planar structure, similar to those of the diamagnetic complexes of the nickel halides with tertiary phosphines.[10a,c] This is further shown by the electronic absorption spectrum (Fig. 1, Table 2).[14] The mull spectrum showed no bands in the range 10,000—4500 cm.^{-1}. If we assume the symmetry of the planar field to be D_{2h} (*trans*-), rather than C_{2v} (*cis*-), then the band assignments[11,14] are: 25,000 cm.^{-1} ${}^1A_g \longrightarrow {}^1A_g$; ~21,700 cm.^{-1} ${}^1A_g \longrightarrow {}^1B_{1g}$; and 15,430 cm.^{-1} ${}^1A_g \longrightarrow {}^1B_{3g}$. The very weak band at 11,000 cm.^{-1} is probably due to either or both of the spin-forbidden transitions ${}^1A_g \longrightarrow {}^3B_{1g}$ and ${}^1A_g \longrightarrow {}^3A_g$ since these triplet levels lie quite close together in this region. It is not considered to be the ν_2 band for a small amount of a tetrahedral isomer, such as those described for the phosphine compounds,[10] since the results for the tetrahedral quinoline complexes show that this band should lie below 10,000 cm.^{-1}.

Discussion.—Thus we have for the structures of $\text{Ni(quinoline)}_2X_2$, octahedral and tetrahedral for $X = \text{Cl}$, tetrahedral for $X = \text{Br}$, and planar for $X = \text{I}$. No evidence has been found during our studies for the existence of isomers for either the bromo- or the iodo-complex. However, we have not searched exhaustively for these. We believe the chloro-complexes to represent the first recognised case of octahedral–tetrahedral isomerism for nickel(II), although such systems are well known for cobalt(II).[12] During this work, Ni py_2I_2 and similar complexes of the nickel halides with α-picoline, all of which appear to be tetrahedral, have been reported.[15] The complex Ni py_2Cl_2 is known to have a bridged octahedral structure,[12] and it seems possible that further examples of octahedral–tetrahedral isomerism might be found with these or related compounds.

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[11] Maki, *J. Chem. Phys.*, 1958, **28**, 651; 1958, **29**, 162.

[12] Gill, Nyholm, Barclay, Christie, and Pauling *J. Inorg. Nuclear Chem.*, 1961, **18**, 88, and refs. therein.

[13] Dunitz, *Acta Cryst.*, 1957, **10**, 307.

[14] Maki, *J. Chem. Phys.*, 1958, **29**, 1129.

[15] Glonek, Curran, and Quagliano, *J. Amer. Chem. Soc.*, 1962, **84**, 2014.

The changes in structure shown by the nickel(II) quinoline complexes demonstrate the comparative reluctance with which nickel(II) adopts tetrahedral structure compared with cobalt(II), where the analogous compounds are all tetrahedral.[16] As with Co py_2X_2, the tetrahedral form of Ni(quinoline)$_2$X$_2$ is favoured on passing from chloride to bromide. However, the planar structure of Ni(quinoline)$_2$I$_2$ contrasts with the tetrahedral structure of Co py_2I_2. The change from tetrahedral to planar structure on passing from bromide to iodide is somewhat analogous to the behaviour of the tertiary phosphine complexes described by Venanzi and his co-workers,[10c] where the existence of tetrahedral and planar isomers reveals the fine balance of factors influencing the adoption of one or other of these structures by a given complex.

With a ligand such as quinoline steric factors probably have little effect, but since the donor nitrogen forms part of a π-electron system it is possible that the structural changes are connected with varying contributions of σ- and π-bonding.

EXPERIMENTAL

Dichlorodiquinolinenickel(II).—(*a*) *Yellow isomer.* Nickel chloride hexahydrate (10 g.) was refluxed with quinoline (100 ml.), with a water-trap beneath the condenser. When no more water distilled over, the dark blue solution was filtered and rapidly cooled. A mixture of blue and yellow crystals separated and was filtered off. When kept in a desiccator over sulphuric acid overnight, the product became completely yellow. It was then washed thoroughly with cold benzene (60 ml.) and dried *in vacuo* (yield, 10·5 g., 64%) (Found: Cl, 18·35; Ni, 14·95. Calc. for $C_{18}H_{14}Cl_2N_2Ni$: Cl, 18·3; Ni, 15·1%).

(*b*) *Blue isomer.* Quinoline (25 ml.) and anhydrous nickel chloride (2 g.) were heated to 180° for 1 hr. Molecular sieves (4 A) were then added to remove any water present. The deep blue solution was filtered, allowed to cool slowly to ~100°, and kept at this temperature until blue crystals were formed. These were filtered off, washed with a small amount of hot (~100°), dry quinoline, and then with cold " AnalaR " carbon tetrachloride, and dried *in vacuo* over sulphuric acid (yield, 1·05 g., 18%). They are very hygroscopic (Found: Cl, 18·6; Ni, 15·1%).

Dibromodiquinolinenickel(II).—Anhydrous nickel bromide (4 g.) was refluxed with quinoline (25 ml.), and the deep blue solution filtered and allowed to cool to room temperature. Dark blue crystals were formed, and were filtered off, washed with ligroin, and dried *in vacuo* over sulphuric acid. The *compound* (5·7 g., 65%) decomposes at ~225° and is slightly hygroscopic (Found: Br, 33·7; Ni, 12·3. $C_{18}H_{14}Br_2N_2Ni$ requires Br, 33·5; Ni, 12·3%).

Di-iododiquinolinenickel(II).—This olive-green compound was prepared, in 52% yield, as described for the bromide. It had m. p. 243° (decomp.) (Found: I, 44·3; Ni, 10·1. Calc. for $C_{18}H_{14}I_2N_2Ni$: I, 44·5; Ni, 10·3%).

Physical Measurements.—Magnetic measurements were made with a standard Gouy balance. Reflectance spectra were obtained with a Unicam S.P. 500 spectrophotometer, equipped with the standard reflectance accessory. A Perkin-Elmer Model 4000 recording spectrophotometer was used for the other spectra. The electrolytic conductances were measured with a Mullard E 7566 Bridge and a conventional cell.

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[16] Cotton, Goodgame, Goodgame, and Haas, *Inorg. Chem.*, 1962, **1**, 565, and unpublished work.